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Hybrid Air Separation Processes for Production of Oxygen and Nitrogen

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Novel hybrid air separation processes for oxygen production are developed that use an unusual adsorption unit, Cycling-Zone Pressure-Swing Adsorption (CZPSA) [also known as feed purge pressure swing adsorption], to increase the oxygen concentration of the feed to the cryogenic distillation plant. Four cases are studied: 1. CZPSA before the main air compressor increases oxygen concentrations to 23.5% or less. 2. CZPSA after the main air compressor increases oxygen concentrations to significantly higher values. 3. CZPSA in between the stages of the main air compressor increases oxygen concentration to intermediate values. 4. CZPSA before the main air compressor to increase oxygen concentrations to 23.5% or less plus CZPSA after the main air compressor to increase oxygen concentrations to higher values. All cases can be applied either to new designs, or for retrofitting and debottlenecking existing plants. The reason for a 23.5% limit on oxygen in cases 1 and 4 is that above this concentration more expensive materials of construction are required. Although 23.5% is a low concentration, it represents a more than 11% reduction in gas flow rate. This reduction in flow rate results in reduced power requirements for compression, and reduced sizes of the downstream equipment.

Keywords adsorption; cryogenic distillation; hybrid; oxygen

INTRODUCTION

Separation processes are essential for many commercial applications, and can account for as much as 40% to 70% of chemical plant capital and operating costs (1). Gas separations are of importance because of their prevalence in many industries, and in light of contemporary issues, such as alternative energy and environmental "green" efforts. For example, coal gasification usually requires oxygen instead of air as a feedstock (2). If it is found to be economically viable as coal gasification processes will significantly increase the demand for oxygen worldwide (3).

Current Technology for Air Separation

The state-of-the-art in air separation is comprised of three alternatives: cryogenic distillation, adsorption-based processes, and membrane technologies. Process economics, required purity, and production scale, ultimately determine which of these processes is most practical for a given specification. Cryogenic distillation is the most economical process at large scale, and can produce very pure gas and liquid products. For small-scale nitrogen units, membrane technologies are most economical, except when very high purities are required. Pressure Swing Adsorption (PSA) is used for air separation at unit capacities that lie between cryogenic distillation and membranes.

Cryogenic distillation of air is a mature, large-scale process. A typical plant (Fig. 1) has several key unit operations: the two or three stage main air compressors (MAC), the air pre-cooler and pre-purification unit, the heat exchanger, the turbo-expander for the generation of refrigeration, and the dual-pressure "double" cryogenic distillation column (4,5). Air is purified in a TSA adsorption unit, containing layers of activated alumina and zeolite (6) to reduce moisture and carbon dioxide impurity concentrations to the acceptable levels of 0.1 ppm and 1.0 ppm, respectively (7).

The dry carbon dioxide- and impurity-free air is cooled to liquefaction temperature in heat exchangers, using cold gaseous nitrogen and oxygen product streams. It is then sent to the double cryogenic column, where it is separated into nitrogen and oxygen, and in many cases, argon is produced in an additional column. A fraction of the high pressure nitrogen leaving the cryogenic column, is typically expanded to generate refrigeration, or turbo-expanded, to generate power for the process. Liquid oxygen and nitrogen products can be produced. Most ASU plants are sized based on oxygen demand and produce excess nitrogen.

The cryogenic air separation process is robust, but capital costs are relatively high, and plants are only economical at relatively large sizes that take advantage of economies of scale. Table 1 shows the approximate capital cost and capacity data for a number of cryogenic air separation

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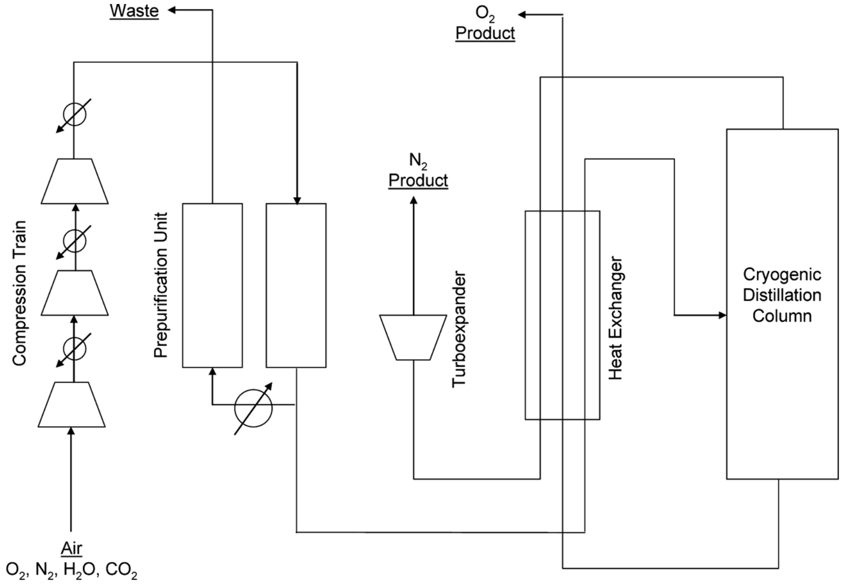

FIG. 1. Schematic of a conventional cryogenic air separation plant.

plants built within the last decade. Table 2 shows estimates of the relative costs of each unit in a cryogenic ASU. Based on the numbers in Tables 1 and 2, one can see that any reductions in size of the cryogenic distillation unit, prepurification unit, and/or MAC can potentially yield large capital cost savings.

PSA, invented by C. W. Skarstrom (8–10), is used extensively for air separation, albeit on a smaller-scale and often with lower purity requirements. For oxygen production, the beds are typically packed with zeolite with equilibrium-based adsorptive selectivity for nitrogen. To produce nitrogen, a carbon molecular sieve with kinetic-based selectivity for oxygen is used. Several other PSA processes, such as vacuum-swing adsorption (VSA), and dual-reflux pressure-swing adsorption (DR-PSA) have been developed (11–13). Due to the use of pure product gas for purge, PSA has a purity versus recovery trade-off, and at high purities, significant amounts of pure product gas are required to regenerate the adsorbent. Compression costs make low recoveries expensive for PSA systems (14). Because of the resulting low recovery, the power requirements for PSA oxygen are greater than for cryogenic distillation although, typically at moderate scales, PSA systems have lower costs because the equipment is less expensive. Ultimately the scale of operation and the degree of separation required will determine whether cryogenic distillation, adsorption, or membranes are the technology of choice. Another factor to consider is process complexity.

TABLE 1
Conventional air separation plant capital costs. Currency is 2008 U.S. Gulf Coast dollars

Plant capacity (mtpd)	Plant capital cost[*] ($ MM)	Reference
250	26	Chemical & Engineering News, 12/5/05, p. 36
1000	50	Chemical & Engineering News, 8/31/1998, p. 10
2800	120	Chemical & Engineering News, 1/19/04, p. 18
3000	131	Chemical & Engineering News, 6/3/02, p. 11

[*] Plant capital cost has been adjusted for location and year using recommended factors (27).

TABLE 2
Relative capital costs assumed for conventional air separation plant

Unit operation or cost factor	Relative capital cost (%)
Cryogenic Distillation Column	30
Air Prepurification Unit[*]	10
Main Air Compressor	15
Heat Exchangers	15
Piping, Tanking, & Instrumentation	15
Foundation & Construction	15

[*] 3.33% is associated with furnace and 6.67% is associated with packed adsorbent beds.

For oxygen production, Gunardson has suggested that although vacuum-swing adsorption (VSA) may be less expensive than cryogenic distillation, its complexity makes it difficult to practice at large scale (15).

One alternative for increasing oxygen recovery is Cycling-Zone Pressure-Swing Adsorption (CZPSA). Originally developed by Skarstrom in 1966, CZPSA (Skarstrom did not use this name), uses a purge of feed (dry low pressure air) instead of product, thereby allowing most of the pressurized oxygen to be collected as product (10). Because the purities obtained with the feed purge were significantly lower than with a product purge, Skarstrom did not develop this process further. A schematic of the CZPSA process used in the current study is shown in Fig. 2. Similar to conventional PSA, CZPSA for oxygen production uses two beds and six steps:

1. dry air is fed to the process at high pressure; nitrogen is adsorbed and oxygen is produced,
2. co-current depressurization to moderate pressure (gas is used to pressurize a parallel bed),
3. counter-current blowdown to low pressure,
4. counter-current regeneration with low pressure dry air,
5. counter-current pressurization to moderate pressure (with gas from parallel bed), and
6. co-current repressurization to high pressure with feed. Zeolite 13X, which preferentially adsorbs nitrogen, was used.

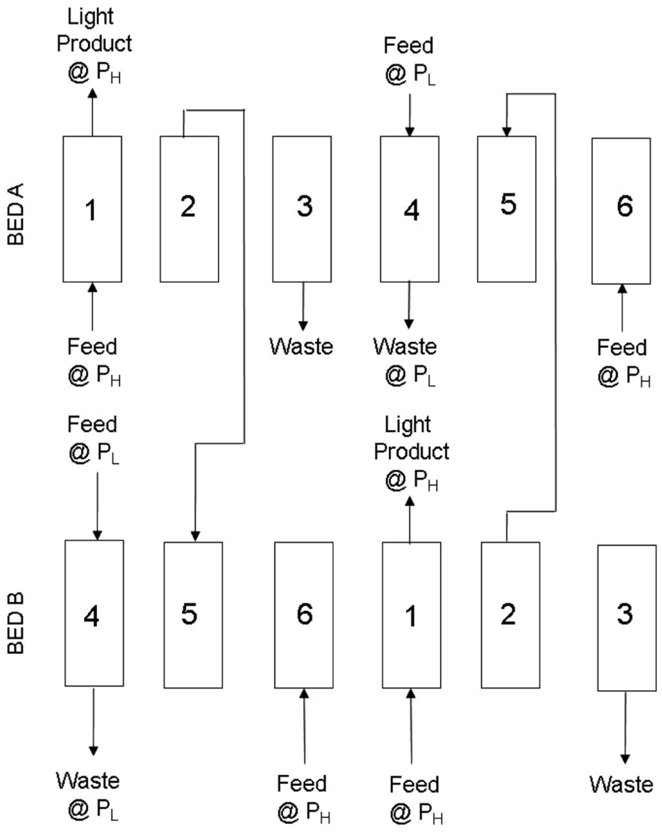

FIG. 2. Step-wise schematic of CZPSA cycle for air separation.

The key feature of CZPSA is its use of low pressure air for the purge step. This results in a higher recovery of pressurized oxygen but with a lower oxygen purity as a result of incomplete clean-out during the purge step. Previous work showed that CZPSA recovers more high pressure oxygen product than conventional PSA, when relatively low oxygen product purities are acceptable (16,17). For example, under base operating conditions with a high pressure of 5 bar and a low pressure of 1 bar, the conventional PSA (modified Skarstrom cycle) produced ~88% oxygen with a pressurized oxygen recovery of ~44%; CZPSA produced ~72% oxygen with a pressurized oxygen recovery of 75%. Thus, the increase in recovery achieved by CZPSA (compared to normal PSA) is significantly greater than the reduction in purity. The utility of this feature will be made evident in our design of a hybrid ASU.

From a process standpoint, it is important to consider that CZPSA requires an additional blower and prepurification unit for the low pressure air used during the purge step. Although this additional hardware is required, the benefit of recovering all of the high pressure oxygen likely surpasses the associated costs, especially at high feed pressures. The capital and operating costs of the blower are relatively small because it needs to be sized only to overcome the pressure drop associated with the prepurification and CZPSA beds. Because the low pressure air used for purge is considerably less expensive than the high pressure air (only a blower and a drier are required), recovery of oxygen from it is not accounted for. In terms of the prepurification unit, the capital and operating costs can be kept relatively small by designing the unit as a PSA/TSA hybrid to reduce its size. Several novel PSA/TSA process designs are discussed in this work and elsewhere (18).

A few hybrid adsorption/cryogenic distillation systems have been patented. For example, Howard et al. developed a hybrid adsorption/cryogenic distillation process for production of low and high purity oxygen in 1997 (19). A front-end adsorbent system operating under unspecified conditions was used to produce oxygen, in the range from 50 to 98.5 mole percent, from a feed stream of wet air. The oxygen product from the adsorber was then compressed to the pressure required by the cryogenic distillation, and a fraction was collected as the "low purity" oxygen product. The remaining fraction was either expanded for refrigeration (or power) purposes, or sent to the cryogenic distillation column after heat exchange. The column produced a high purity (>98.5 mole percent) oxygen product. Alternatives for energy integration were presented. Also in 1997, Howard et al. developed a hybrid adsorption/cryogenic distillation process for the production of low purity oxygen and high purity nitrogen (20). Reddy developed a hybrid process for the separation and coproduction of hydrogen and carbon dioxide (21). Feed gas comprised of H_2 and CO_2 is fed to a CO_2 scrubber in combination with a flash unit. The CO_2-rich product is fed to the downstream liquefaction unit. The gaseous H_2-rich product is fed to a standard PSA or membrane separator, which produces a 99 mole percent H_2 product stream, and a "waste" stream that is fed to the liquefaction unit. A CO_2 product with purity greater than 98% is produced as product by the liquefaction unit.

HYBRID PROCESSES

In this work, CZPSA is used with cryogenic distillation to form a hybrid air separation process. CZPSA has very high recoveries of the pressurized oxygen in the oxygen-enriched product. Although stand-alone CZPSA cannot economically produce high purity oxygen, when coupled with cryogenic distillation in a hybrid ASU the hybrid process requires less power and downstream equipment becomes significantly smaller than in a conventional cryogenic ASU. Four cases were studied, and two will be discussed in detail. Case 1 places the CZPSA before the MAC and Case 2 places the CZPSA after the MAC. Installing the CZPSA between stages in the MAC (Case 3) was also studied, but because of construction difficulties involved in interrupting the MAC, case 3 did not appear to be economically viable and design details are reported elsewhere (18). Case 4, which places a CZPSA before the MAC and a CZPSA after the MAC, was not studied in detail, but results were estimated from the Case 1 and Case 2 results.

Figure 3 (Case 1) shows a hybrid CZPSA/cryogenic distillation process with the CZPSA placed before the MAC. The CZPSA is fed dry air (21% oxygen) at a moderate pressure and produces oxygen-enriched air with a high recovery of the pressurized oxygen. A low pressure PSA/TSA prepurification unit to remove carbon dioxide and water is shown in Fig. 3. Use of a low pressure TSA prepurification unit was also studied. As noted previously, most ASU plants produce excess nitrogen. Clearly, enrichment of the oxygen concentration by the CZPSA unit removes nitrogen and reduces the flow rate. This reduction in flow rate reduces the size of all downstream equipment (e.g., the MAC, heat exchangers, and cryogenic distillation column), and reduces the MAC power requirements in a fixed capacity plant.

Figure 4 (Case 2) shows the hybrid plant with the CZPSA unit after the MAC. In this case, energy usage in the MAC always increases, because the capacity of the MAC must be increased to accommodate the recovery losses in the CZPSA unit. However, this configuration produces much more concentrated oxygen from the CZPSA, which then reduces the sizes of the heat exchangers and the cryogenic distillation.

In terms of process design, there are several trade-offs to consider when comparing Case 1 vs. Case 2 (i.e., Fig. 3 vs. Fig. 4) qualitatively. One advantage of Case 2 is that the air prepurification and CZPSA units operate at high pressure

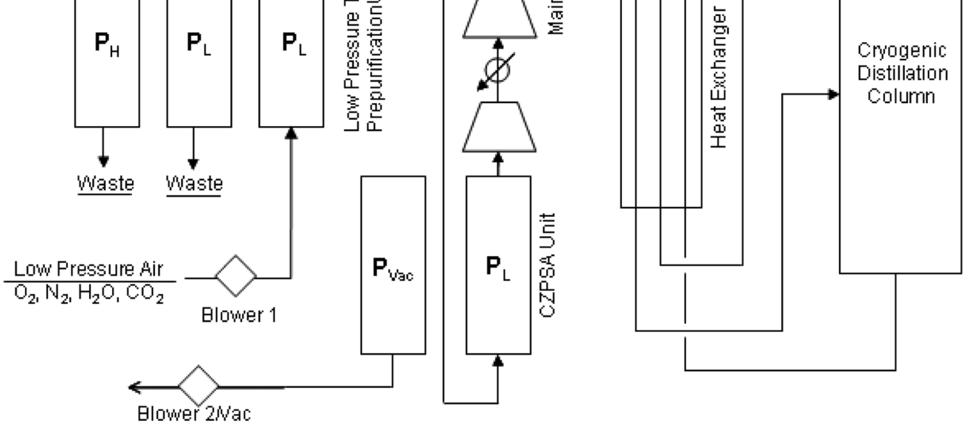

FIG. 3. Case 1. Hybrid ASU with CZPSA before the main air compressors (configuration E1) and the PSA/TSA air prepurification process. In this case, CZPSA unit produces 23.5% oxygen. Note: tanks and particle filter not shown.

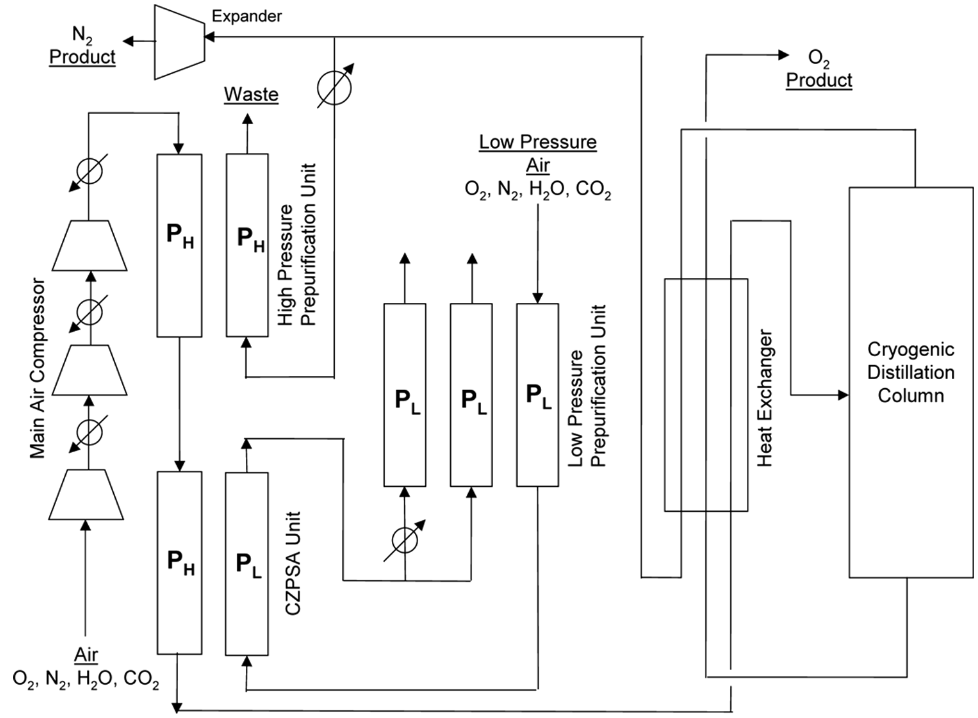

FIG. 4. Case 2. Hybrid ASU process with CZPSA after the main air compressors and the two-TSA air prepurification process. Note: tanks and particle filter not shown.

and are thus smaller than their counterparts in Case 1 which operate at low pressure. On the other hand, an advantage of Case 1 is that less total beds are required and the overall flowsheet is less complex than Case 2. A quantitative comparison of the performances of Cases 1 and 2 will be presented later.

One additional factor significantly affects the design of the hybrid systems. Above a 23.5% limit on oxygen, more expensive materials of construction are required (22,23). Thus, enriching the oxygen concentration beyond 23.5% will affect construction of the CZPSA unit, heat exchanges, all associated piping, and all downstream equipment; obviously, this will increase capital costs. Because of the need for expensive materials of construction, the oxygen concentration from the pre-MAC CZPSA unit in Cases 1 and 4 is limited to 23.5%. Although 23.5% is a low concentration, it represents a more than 11% reduction in gas flow rate compared to a feed that is 21% oxygen. If a higher limit is allowed without requiring a change in materials, that higher limit on concentration would be used. Because downstream units are already designed for high oxygen concentrations, the high pressure CZPSAs in Cases 2 and 4 do not have an oxygen limitation.

DESIGN OF CZPSA AND AIR PREPURIFICATION SYSTEMS

The oxygen-concentrating CZPSA unit in the hybrid air separation process is generally similar to the CZPSA process developed earlier and shown in Fig. 2 (17). In addition to the question of where to place the CZPSA unit, three other issues to consider when integrating CZPSA into a cryogenic air separation plant revolve around its use of low pressure feed gas as purge. When the CZPSA unit is before the MAC, a blower (a relatively inexpensive item), is required to overcome the pressure drop in the CZPSA unit during purge. Second, for all configurations, the feed streams must be moisture- and carbon dioxide-free to prevent these impurities from getting into the adsorbers. Thus, a low pressure air prepurification unit is necessary for the purge air, and a moderate or high pressure prepurification unit is needed for the feed to the CZPSA. In case 2 (Fig. 4) a two-bed TSA, very similar to the unit in a standard cryogenic distillation ASU, can be used for the high pressure feed air. For cases 1 (Fig. 3), 3, and 4, the CZPSA feed will be at lower pressures which will result in a larger dryer. Thus, the hybrid cryogenic distillation/CZPSA process requires the design of a novel, low pressure air prepurification unit. Finally, buffer tanks are required between the CZPSA, and downstream units to prevent pressure surges from reaching the compressors, heat exchangers, and the cryogenic distillation column.

A single-stage prepurification/CZPSA unit can also be conceived which utilizes different adsorbent layers for water/carbon dioxide removal and air separation. However, this design has several issues that make its implementation difficult. The first issue concerns timing and penetration distance. For water/carbon dioxide removal, a relatively long feed step and penetration distance can be used due to the strong adsorption of these materials and the dilute nature of the feed. In contrast, for air separation, the feed is concentrated and the adsorption strength is relatively moderate (and somewhat competitive between oxygen and nitrogen), making the feed step and penetration distance short. A second issue is regeneration timing. Because of the strong adsorption of water, a relatively long regeneration step is required to purge a highly loaded bed; in contrast, the regeneration step for air separation is relatively short due to the moderate adsorption strength of nitrogen and the relatively short penetration distance. The third issue is the choice of adsorbent material. Many adsorbents, such as Zeolite 13X which is used herein, adsorb water so strongly that other adsorbing species are displaced. In the case of a layered design, any water breaking through the prepurification layer would displace adsorbed nitrogen in the CZPSA layer and degrade the overall air separation performance. This issue is most easily mitigated by adjusting the timing properly which is most easily accomplished by using separate beds for air prepurification and CZPSA.

Design of the Air Prepurification Unit

Drying and removing carbon dioxide from the air at low pressure is uncommon in a cryogenic ASU, because the adsorbent capacity is lower and the column diameter is higher than at high pressure. However, for the unique circumstance of the hybrid air separation process, a high pressure TSA air prepurification unit is uneconomical, because a significant part of its dry, carbon dioxide-free air product is needed at low pressure. Figure 5 shows a schematic of the TSA/PSA air prepurification process. The process uses three beds in parallel and five steps:

1. air containing water and carbon dioxide is fed at low pressure and dry, carbon dioxide-free air is produced at low pressure,
2. counter-current pressurization with hot nitrogen product from cryogenic distillation column,
3. high pressure counter-current purge with hot nitrogen product from cryogenic distillation column,
4. counter-current depressurization,
5. low pressure counter-current purge with cold, dry, carbon dioxide-free nitrogen-rich waste stream (the purge gas) from CZPSA unit.

Three beds are required to produce low pressure dry air without interruption and to have purge gas available for the last step in the cycle. Zeolite 13X, which adsorbs water strongly and carbon dioxide to a weaker extent is used as the adsorbent material. The utility of operating prepurification units with thermal regeneration has been proven and is concisely discussed by Basmadjian (24). However, the hybrid PSA/TSA air prepurification unit designed herein has other advantages.

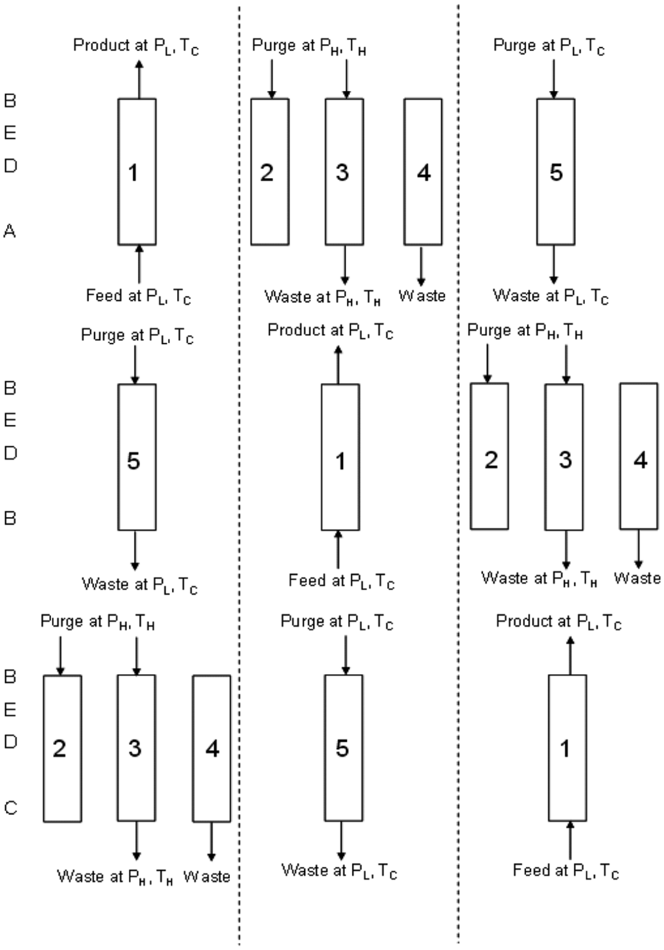

FIG. 5. Step-wise schematic of TSA/PSA cycle for air prepurification.

Since excess high pressure nitrogen product is available from the distillation, it is heated and used as hot purge gas. High pressure hot purge has a shorter regeneration time than low pressure hot purge. A second advantage is that the dry, carbon dioxide-free, nitrogen-rich waste stream from the CZPSA unit is conveniently available for the cold purge step. Third, to reduce energy consumption, the high pressure hot gas is stopped before thermal breakthrough. The thermal wave is pushed towards the end of the bed during depressurization and is pushed out of the bed as a wide pulse during the cold low pressure purge. Thus, the cold purge step is used to simultaneously complete thermal breakthrough, purge the bed at low pressure, and cool the bed.

The feed stream to the PSA/TSA prepurification unit needed to contain concentrations of water and carbon dioxide representative of air: typical values of 2.8 mole percent water and 0.035 mole percent (350 ppm) carbon dioxide were taken from the literature (6,7). This very humid stream (~90% relative humidity), was purposely chosen to test the capability of the prepurification system. The oxygen and nitrogen concentrations were set at 20 mole percent and

76 mole percent, respectively, with an inert Argon concentration of 1.165 mole percent being calculated by difference. The inlet gas pressure, temperature, and superficial velocity were specified as 1.1 bar and 298 K, and 30 cm/s, respectively. For the regeneration step, hot nitrogen temperatures (T_{hot}) of 573 K, 673 K, and 773 K were examined and the required hot nitrogen flow rates ($Q_{N2,hot}$) required for adequate separation were determined. The results, presented later, show that the unit performed as required.

Design of CZPSA

The critical novel technology in Cases 1 and 2 of the hybrid air separation process, shown in Figs. 3 and 4, is the CZPSA unit. Detailed simulations of the adsorption processes at a small-scale, followed by scale-up, were completed to show proof of concept. For the simulation calculations, the feed stream delivered to the CZPSA bed was 21 mole percent oxygen, 1 mole percent argon, and 78 mole percent nitrogen at 298 K. No moisture or carbon dioxide was present in the feed to the CZPSA unit because the air prepurification unit reduced water and carbon dioxide concentrations to below 0.1 ppm and 1.0 ppm, respectively. The remaining unit operations (heat exchangers, cryogenic distillation column, etc.), are well-established and are used in the same roles as in a standard air separation plant. Optimization of the overall hybrid ASU plant requires the context of a particular location including plant size, the cost of power, itemized equipment costs, and the desired interest rate for economic calculations; thus, this optimization is beyond the scope of this work.

THEORY AND SIMULATION FOR CZPSA AND AIR PREPURIFICATION UNITS

Non-isothermal bed adsorption is modeled by simultaneous solution; the well-known equilibrium equations, standard mass and energy balance equations, and mass and energy transfer equations (25). For oxygen-nitrogen separation with zeolite 13X, the equilibrium isotherm is (26):

$$q_i = \frac{q_{m_i} B_i P_i^{n_i}}{1 + \sum_{j=1}^{n} B_j P_j^{n_j}} \tag{1}$$

$$q_{m_i} = k_{1_i} + k_{2_i} T \tag{2}$$

$$B_i = k_{3_i} \exp\left(\frac{k_{4_i}}{T}\right) \tag{3}$$

$$n_i = k_{5_i} + \frac{k_{6_i}}{T} \tag{4}$$

For water and carbon dioxide adsorption on zeolite 13X, the equilibrium isotherm is (6):

$$q_i = \frac{q_{m_i} b_i P_i^{n_i}}{1 + b_i P_i^{n_i}} \tag{5}$$

$$b_i = b_{0_i} \exp\left(-\Delta \frac{H_{ads_i}}{RT}\right) \tag{6}$$

Experimental data from the literature is provided in Table 3 (6,26), and operating conditions are listed in Table 4.

TABLE 3
Simulation parameters from experimental literature

Parameter	Zeolite 13X – prepurification unit (7,28)	Zeolite 13X – CZPSA unit (28)
Bed Length	50 cm	50 cm
Bed Diameter	5 cm	5 cm
External Porosity	0.39	0.39
Internal Porosity	0.21	0.21
Bed Density	0.713 g/cm^3	0.713 g/cm^3
Particle Radius	0.07 cm, 0.035 cm (intensified processes)	0.07 cm, 0.035 cm (intensified processes)
$k_{MTC,solid}$	Carbon Dioxide: 0.1 s^{-1}; Water: 0.1 s^{-1}	Nitrogen: 0.197 s^{-1}; Oxygen: 0.62 s^{-1}
Isotherm parameters	Carbon Dioxide, Water $q_m = 5.24, 20.93$	Nitrogen, Oxygen $k_1 \times 10^3 = 12.52, 6.705$ mol/g
	$b = 19.43, 18.93$	$k_2 \times 10^5 = -1.785, -1.435$ mol/(g-K)
	$n = 0.7, 0.43$	$k_3 \times 10^5 = 2.154, 3.253$ atm^{-1}
	$T_0 = 293$ K	$k_4 = 2{,}333, 1{,}428$ K
		$k_5 = 1.666, -0.3169$
		$k_6 = -245.2, 387.8$ K
$C_{p,solid}$		0.32 cal/(g-K)
ΔH_{ads}	Carbon Dioxide: −8.2 kcal/mol	Nitrogen: −4,390 cal/mol Oxygen: −3,060 cal/mol
	Water: −12.3 kcal/mol	
h_p	Estimated with $k_{ez} = 0.026$ W/(m-K)	Estimated with $k_{ez} = 0.026$ W/(m-K)

TABLE 4
Operating conditions for small-scale simulation of CZPSA and air prepurification units

Variable	Air prepurification unit: PSA-TSA	Air prepurification unit: 2-TSA/Intensified 2-TSA
Feed pressure (bar)	1.0	1.0/1.0
Purge pressure (bar)	6.0 (hot purge)/1.0 (cold purge)	1.0/1.0
Feed temperature (K)	298	298/298
Purge temperature (K)	573/673/773	573/573
Feed flowrate (kmol/s)	2.43e-5/2.23e-5/2.09e-6	1.97e-6/1.97e-6
Purge flowrate (kmol/s)	See Table 5	Both: 3.4e-6 (hot), 3.4e-6 (cold)
Cycle time (s)	12,600	3600/831
Feed time (s)	4200	1200/277
Purge time (s)	8380 (4180 hot, 4200 cold)	2400/554 ($\frac{1}{2}$ hot, $\frac{1}{2}$ cold)
Repressurization time (s)	10	N/A
Depressurization time (s)	10	N/A
Variable	CZPSA Unit: Pre-MAC Case 1-1/1-2/1-3/1-1i/1-2i/1-3i	CZPSA Unit: Post-MAC Case 2-1/2-2/2-1i/2-2i
Feed pressure (bar)	6.0 (all cases)	1.82 (all cases)
Purge pressure (bar)	1.0 (all cases)	1.0 (all cases)
Feed temperature (K)	298 (all cases)	298 (all cases)
Purge temperature (K)	298 (all cases)	298 (all cases)
Feed flowrate (kmol/s)	1e-5 (all cases)	1e-5 (all cases)
Purge flowrate (kmol/s)	1.67e-6 (all cases)	5.5e-6 (all cases)
Cycle time (s)	60/240/240/21/66/66	28/20/14/10
Feed time (s)	26/116/116/6.5/29/29	10/7/5/3
Pressure equalization time* (s)	4 (all cases)	4 (all cases)
Purge time (s)	26/116/116/6.5/29/29	10/7/5/3
Repressurization time (s)	2 (all cases)	2 (all cases)
Depressurization time (s)	2 (all cases)	2 (all cases)
Bed length-Bed Diameter (cm)	50-5/50-5/50-5/12.5-5/12.5-5/12.5-5	50-5/50-5/12.5-5/12.5-5

*Denotes sum of depressurization equalization time + pressurization equalization time.

ADSIM, a product of Aspen Technology, Inc., was used to numerically solve the governing equations, via the method of lines. The following assumptions were made: radial gradients and axial dispersion are negligible, adsorption beds are adiabatic, no chemical reactions (other than adsorption) take place, and the linear driving force kinetic models are valid. Although the adsorption of the components of interest on zeolite 13X is predominately equilibrium-controlled, finite mass and heat transfer were accounted for based on kinetic parameters reported in the literature (6,26). The necessary heat transfer coefficients were estimated by use of the Colburn j-factor (27). The pressure-drop was calculated with the Karman-Kozeny equation, and ideal gas behavior was assumed. Changes in gas density and velocity, as a result of adsorption, were accounted for, and the processes were simulated dynamically, until cyclic steady-state was reached. Additional information on simulation methodology is provided elsewhere (17,18).

RESULTS AND DISCUSSION FOR ADSORPTION SYSTEMS

Air Prepurification Unit

Results of simulations for a small-scale prepurification unit are summarized in Table 5. For case 1 (Fig. 3), the product from this unit is used both as the feed for the CZPSA, and as the low pressure feed purge. For case 2, the product is needed only for the low pressure feed purge. For all cases, the product effluent concentration of water is ~25% below the target levels of 0.1 ppm, and carbon dioxide product effluent is ~3% below its target level of 1.0 ppm. This agrees with the literature that carbon dioxide breakthrough controls (7). The observed trade-off between $T_{N2,hot}$ and $Q_{N2,hot}$ – as hot regeneration temperature increases, its required flow rate decreases – is expected (7).

The air prepurification process for case 2 (bottom two rows in Table 5), is a two-unit TSA process. The high pressure TSA unit, which is essentially identical to the TSA unit in a conventional ASU, removes the moisture

TABLE 5
Simulation results for various feasible air prepurification processes

Air prepurification unit	CZPSA Config.	Feed pressure (bar)	Purge pressure (bar)	Purge temperature (K)	Purge flowrate (kmol/s)	$Q_{N2,hot}$/ $Q_{N2,total}$ (%)	y_{H_2O} (ppm)	y_{CO_2} (ppm)
PSA/TSA Hybrid	1-1	1.0	6.0/1.0	573/298	3.45e-6	82	0.073	0.973
		1.0	6.0/1.0	673/298	2.70e-6	64	0.071	0.970
		1.0	6.0/1.0	773/298	1.95e-6	46	0.074	0.975
Intensified PSA/TSA Hybrid	1-1i	1.0	6.0/1.0	573/298	3.45e-6	82	0.044	0.904
		1.0	6.0/1.0	673/298	2.70e-6	64	0.056	0.888
		1.0	6.0/1.0	773/298	1.95e-6	46	0.071	0.876
TSA @ P_L (Two-TSA)	1-2, 1-3, 2-1, 2-2	1.0	1.0	573/298	3.48e-6	0	5e-4	0.44
Intensified TSA @ P_L (Two-TSA)	1-2i, 1-3i, 2-1i, 2-2i	1.0	1.0	573/298	3.48e-6	0	9e-5	0.38

and carbon dioxide from the air feed stream to the CZPSA unit; however, it is slightly larger due to the recovery losses associated with the CZPSA unit. This unit was not simulated because very similar TSA dryers are used in a conventional cryogenic ASU. The low pressure (1 bar) TSA unit removes water and carbon dioxide from the low pressure CZPSA purge gas. All three steps in this three bed TSA unit are at low pressure:

1. feed of wet air containing carbon dioxide and production of dry, carbon dioxide-free air,
2. counter-current purge with hot, dry, carbon-dioxide free, nitrogen-enriched waste gas from the CZPSA unit, and
3. counter-current purge with cold, dry, carbon dioxide-free, nitrogen-enriched waste gas from the CZPSA unit.

Because the low pressure TSA solely uses the low pressure waste effluent from the CZPSA unit for regeneration purposes, it does not require nitrogen product from the cryogenic distillation column. The low pressure TSA unit used layered beds with a 2:1 adsorbent ratio of activated alumina to zeolite 13X. The effect of the adsorbent ratio has been investigated, and the 2:1 value used is reasonable (7,24,26). The regeneration temperature was 573 K. With the 6/1 pressure ratio used for the CZPSA for case 2, γ_{CZPSA} was set at 1.0. Although less gas was available for purging the low pressure TSA unit, moisture and carbon dioxide removal met the specifications (Table 5).

The small-scale simulation results were scaled up to the commercial sizes needed for different size ASU plants. White and Barkley recommend adhering to two practical design constraints (28). First, they suggest that the velocity should be no more than 80% of the entrainment velocity (28). For the air prepurification unit, this translates to velocities of 1.69 and 0.80 ft/s during the low pressure and high pressure steps, respectively. In commercial practice, lower velocities may be required to conform to safety requirements, prevent adsorbent attrition and churning, and enhance mass transfer. Second, the pressure drop in the adsorbent bed should remain reasonable. The maximum pressure drop (~0.2 bar), occurs during the feed step for the air prepurification unit. The scaled up results are presented in Table 6. Because the separation is relatively easy, but the flow rates are quite large, horizontal beds are used. This is the same geometry often used for solvent recovery with activated carbon (29).

As a result of process intensification by reducing particle diameter and scaling column height and diameter appropriately to retain the desired purities (25,30), the height (and therefore the overall size) of the air prepurification unit was reduced significantly. The same design heuristics used previously were applied to the intensified cases: gas velocity was set to no more than 80% of entrainment and a maximum pressure drop of 0.2 bar was deemed permissible. The intensified cases are denoted by "i" in Table 6. It was assumed that the size (and thus cost) of the intensified high pressure TSA was reduced by the same amount as the intensified low pressure TSA. The total size of the low and high pressure TSA units is smaller than the PSA/TSA process because one of the units in the two-TSA process operates at high pressure, while the PSA/TSA process operates at low pressure.

CZPSA Unit

For case 1 (Fig. 3), the feed to the CZPSA unit enters at 1 atm and regeneration occurs under vacuum. Case 1-1 upgrades all of the low pressure feed air to 23.5% oxygen with $P_L = 0.8$ bar. Cases 1-2 and 1-3 alternatively upgrade only a portion of the low pressure feed air but to above 23.5% oxygen, and remix it with the remainder of the low pressure feed air. After mixing, the low pressure air has an oxygen concentration of 23.5%. Case 1-2 undergoes

TABLE 6

Scaled-up design scenarios for cases 1 and 2 air prepurification processes. All beds use a horizontal orientation

Prepurification unit	CZPSA Config.	CZPSA feed pressure (bar)	Capacity (mtpd)	Bed length −1 unit in parallel (ft)	Bed diameter (ft)	Packed height (ft)
PSA/TSA	1-1	1.0	1000	63	16	3
Two-TSA	1-2	1.0	1000	13	4	3
Two-TSA	1-3	1.0	1000	17	3	3
PSA/TSA	1-1	1.0	500	31	16	3
Two-TSA	1-2	1.0	500	7	4	3
Two-TSA	1-3	1.0	500	9	3	3
PSA/TSA	1-1	1.0	250	16	16	3
Two-TSA	1-2	1.0	250	3	4	3
Two-TSA	1-3	1.0	250	4	3	3
PSA/TSA	1-1i	1.0	1000	41	16	1
Two-TSA	1-2i	1.0	1000	13	3	1
Two-TSA	1-3i	1.0	1000	9	2	1
PSA/TSA	1-1i	1.0	500	21	16	1
Two-TSA	1-2i	1.0	500	7	3	1
Two-TSA	1-3i	1.0	500	5	2	1
PSA/TSA	1-1i	1.0	250	10	16	1
Two-TSA	1-2i	1.0	250	3	3	1
Two-TSA	1-3i	1.0	250	2	2	1
Two-TSA	2-1	6.0	1000	23	8	3
Two-TSA	2-2	6.0	1000	27	8	3
Two-TSA	2-1	6.0	500	11	8	3
Two-TSA	2-2	6.0	500	14	8	3
Two-TSA	2-1	6.0	250	6	8	3
Two-TSA	2-2	6.0	250	7	8	3
Two-TSA	2-1i	6.0	1000	16	6	1
Two-TSA	2-2i	6.0	1000	24	6	1
Two-TSA	2-1i	6.0	500	8	6	1
Two-TSA	2-2i	6.0	500	12	6	1
Two-TSA	2-1i	6.0	250	4	6	1
Two-TSA	2-2i	6.0	250	6	6	1

Note. Bed dimensions refer to PSA unit and low pressure TSA unit in the PSA/TSA and Two-TSA prepurification processes, respectively; conventional high pressure TSA beds for both processes were assumed to be a well-known technology and were not sized in this work

purge at 0.8 bar, while case 1-3 uses a vacuum pressure of 0.6 bar for purge. Case 1-1 is coupled with the PSA/TSA air prepurification unit (shown in Fig. 3); cases 1-2 and 1-3 are coupled with the two-TSA air prepurification process. Because of its higher pressure ratio (P_H/P_L), case 1-3 upgrades the oxygen concentration more; therefore, the CZPSA and prepurification units in case 1-3 process less feed compared to cases 1-1 and 1-2. Cases 1-2 and 1-3 require that the CZPSA unit and the piping from its outlet to the mixing point be upgraded for oxygen service.

The small-scale simulation results for CZPSA in Table 7 show that low purities, but high recoveries can be attained by using modest pressure ratios. In case 1-1, ~23% oxygen is produced with ~86% recovery of pressurized oxygen: in this case, the product is below the materials change threshold of 23.5% oxygen, and product gas can be delivered directly to the MAC. Cases 1-2 and 1-3, respectively produce ~26% oxygen and ~33% oxygen with pressurized oxygen recoveries of ~94% and 91%. These gases are mixed with fresh feed air to produce the 23.5% oxygen stream that is fed to the MAC. Although the degree to which the oxygen concentration is upgraded by CZPSA in these configurations is small, the economic prospects are attractive because the approximately 11% reduction in flow rate decreases costs of the MAC, heat exchangers, distillation column and cold box.

Table 8 shows the scaled-up designs for these CZPSA cases. The scale-up procedure was identical to that used

TABLE 7

Small scale simulation results for case 1 (Figure 3) and case 2 (Figure 4) CZPSA configurations. Systems labeled with i are intensified by using smaller diameter adsorbent and adjusting the column length and cycle times

CZPSA configuration	CZPSA feed pressure (bar)	CZPSA Purge pressure (bar)	γ_{CZPSA}	O_2 product purity	High pressure O_2 recovery
1-1	1.0	0.8	0.0	23.4%	86.0%
1-2	1.0	0.8	1.0	26.4%	93.6%
1-3	1.0	0.6	1.0	32.9%	91.3%
1-1i	1.0	0.8	0.0	23.6%	86.2%
2-1	6.0	1.0	1.0	35.3%	94.1%
2-2	6.0	1.0	1.0	67.9%	87.4%
2-1i	6.0	1.0	1.0	35.0%	93.2%
2-2i	6.0	1.0	1.0	68.6%	88.3%

TABLE 8

Scaled-up design scenarios for case 1 and case 2 CZPSA configurations. Bed orientation: V – vertical, H – horizontal. For cases 1-1i through 1-3i, packed height is 4.1 feet

CZPSA Config.	CZPSA Feed pressure (bar)	Capacity (mtpd)	Bed orientation	Bed length (ft)	Bed diameter (ft)	ΔP during feed (bar)
1-1	1.0	1000	V	13	43	0.19
1-2	1.0	1000	V	13	24	0.19
1-3	1.0	1000	V	13	16	0.19
1-1	1.0	500	V	13	30	0.19
1-2	1.0	500	V	13	17	0.19
1-3	1.0	500	V	13	12	0.19
1-1	1.0	250	V	13	21	0.19
1-2	1.0	250	V	13	12	0.19
1-3	1.0	250	V	13	8	0.19
1-1i	1.0	1000	H	90	16	0.19
1-2i	1.0	1000	H	63	8	0.19
1-3i	1.0	1000	H	21	8	0.19
1-1i	1.0	500	H	45	16	0.19
1-2i	1.0	500	H	32	8	0.19
1-3i	1.0	500	H	14	8	0.19
1-1i	1.0	250	H	23	16	0.19
1-2i	1.0	250	H	16	8	0.19
1-3i	1.0	250	H	7	8	0.19
2-1	6.0	1000	V	22	35	0.20
2-2	6.0	1000	V	22	38	0.20
2-1	6.0	500	V	22	24	0.20
2-2	6.0	500	V	22	27	0.20
2-1	6.0	250	V	22	17	0.20
2-2	6.0	250	V	22	19	0.20
2-1i	6.0	1000	H	44	16	0.06
2-2i	6.0	1000	H	66	16	0.06
2-1i	6.0	500	H	22	16	0.06
2-2i	6.0	500	H	33	16	0.06
2-1i	6.0	250	H	11	16	0.06
2-2i	6.0	250	H	17	16	0.06

for the prepurification units, but with limiting gas velocities during the feed and purge steps, of 1.34 and 1.69 ft/s, respectively, and a highest pressure drop on the order of 0.2 bar or less. Because case 1-1 processes all of the incoming low pressure air while cases 1-2 and 1-3 do not, the case 1-1 CZPSA and air prepurification units are larger than those of cases 1-2 and 1-3. In this case bypassing and blending are advantageous because the 23.5% limit on oxygen is artificial as far as the separation devices are concerned. Table 8 also shows that, as expected, intensification of the CZPSA process greatly decreases bed size.

Compressor power requirements for adiabatic compressors and blowers were determined with an assumed efficiency of 80% (31).

$$\dot{P} = \frac{0.371 T_a \gamma q_0}{\eta(\gamma - 1)} \left[\left(\frac{P_b}{P_a} \right)^{1-\frac{1}{\gamma}} - 1 \right] \tag{7}$$

Table 9 shows that cases 1-1 and 1-1i have slightly negative net compression power savings while cases 1-2, 1-2i, 1-3, and 1-3i all have net compression power savings above 5%. From an overall economic perspective, configurations 1-2i and 1-3i are the most interesting, because they appear to save on both capital and operating costs simultaneously.

In case 2, where the CZPSA unit is placed after a MAC (Fig. 4), there will always be more energy usage in the MAC, regardless of the oxygen concentration of the CZPSA product stream (Table 9). The results in Table 7 for cases 2-1 and 2-2 show the expected trade-off between oxygen purity and recovery: case 2-1 produces ~35% oxygen with ~94% recovery of pressurized oxygen, while case 2-2 produces ~68% oxygen with ~87% recovery of pressurized oxygen. Cases 2-1 and 2-1i both have net power increases (% of conventional) of ~8%, and cases 2-2 and 2-2i both have net power increases of ~16%.

The scaled-up designs for the CZPSA are shown in Table 8 for cases 2-1 and 2-2. As shown, the CZPSA unit is designed with a vertical orientation, while the prepurification unit (Table 6), was designed with a horizontal orientation and the use of parallel units is examined. Compared to the pre-MAC cases, the post-MAC bed sizes are relatively small, and thus less expensive. Further size savings were realized after process intensification, and the intensified CZPSA was reoriented as a horizontal bed (Table 8). Case 2-2i with the highest oxygen concentration will have the smallest downstream units. It is interesting to note that even at the highest oxygen concentration (68.6%), no "cold spot" was observed in the CZPSA unit.

DISCUSSION

Other Equipment

All of the existing equipment in a conventional cryogenic ASU downstream from the CZPSA unit will be smaller and will need to be redesigned. Fortunately, this redesign is straightforward for case 1, since it involves scaling-down for a reduction in flow rate. For example, in a conventional cryogenic air separation plant, the air feed stream to the cryogenic distillation column is ~21% oxygen. Increases of the oxygen concentration to 23.5%, results in a 11% decrease in flow rates for the downstream units at constant oxygen capacity. If capacity is increased by 11%, the current designs are probably adequate. For cases 2 and 4, the large increase in oxygen concentration will require a more radical redesign of the distillation column with the possibility of additional savings.

The hybrid ASU also requires the addition of blowers, surge tanks, and perhaps additional particulate filters. All blowers are relatively small compared to the compressors, since they only overcome the pressure drops in the beds they service. Surge tanks are required to serve as a buffer between discontinuous adsorption units, and the continuous compressors and distillation column. Conventional cryogenic air separation plants typically have a particulate filter already in place, after the air prepurification unit. The additional particulates and dust created by the addition of the adsorbers may require additional filters. Equipment costs for the auxiliary equipment are probably minimal.

TABLE 9
Compression power savings for hybrid ASU

CZPSA config.	Prepurification process	CZPSA Feed pressure (bar)	Conventional process power requirement (kJ/mol O_2 produced)	Hybrid process power requirement (kJ/mol O_2 produced)	Net operating cost savings (% of conventional)
1-1/1-1i	PSA/TSA	1.0	29.23	29.72	−1.67
1-2/1-2i	Two-TSA	1.0	29.23	27.55	+5.75
1-3/1-3i	Two-TSA	1.0	29.23	27.23	+6.83
2-1/2-1i	Two-TSA	6.00	29.23	31.50	−7.76
2-2/2-2i	Two-TSA	6.00	29.23	33.98	−16.26

Note. (+) indicates positive operating savings while (−) indicates operating expenditure.

Alternative Process Designs

Several variations of this hybrid ASU are possible. One variation for case 2 is to replace the normal thermal dryer with a layer of activated alumina inside the CZPSA unit. As conceived, regeneration of this air prepurification layer would be accomplished by a pressure-swing, since thermal regeneration is not used in the CZPSA cycle. This design would require either a larger purge-to-feed ratio, or the use of excess nitrogen from the distillation column for purge to obtain proper regeneration. The potential advantage is fairly significant capital cost reductions.

If there is a market for the nitrogen produced by the distillation column, the nitrogen production can be increased by heating a fraction of the purge gas from the CZPSA unit, and using it for hot purge at low pressure. If not enough purge gas is available from the CZPSA unit to adequately complete both hot and cold purge steps in the air prepurification unit, some nitrogen from the distillation column will still be required.

This process was originally conceived for the production of oxygen; serendipitously, a limited amount of nitrogen can be produced. By attaching an argon column to the existing cryogenic column, a purified argon product stream can also be produced. Compared to its conventional counterpart, the argon-producing column in the hybrid ASU will be smaller, particularly for cases 2 and 5, since the argon feed to the columns is more concentrated.

Case 4 involves combining Case 1: CZPSA before the MAC producing oxygen enriched air with 23.5% oxygen or less, and Case 2: CZPSA after MAC. This case is conceptual since exact simulations were not run. However, by combining the results of cases 1 and 2, we can predict the performance of case 4. If we assume the same recovery of compressed oxygen as in the case 2 scenarios (this is conservative since a higher feed concentration to the post-MAC CZPSA should result in a slightly higher recovery), the power use for case 2-2i (Table 9) can be multiplied by the reduction in flow rate, because of the higher feed gas concentration, (20.9%/23.5% = 0.889). Then the power use for the MAC becomes 33.98 × 0.889 = 30.21 kJ/mol. Adding to this the power required by the Case 1 CZPSA unit, 2.93 kJ/mol, the total compression power for case 4 is 33.14 kJ/mol, which is 13.4% greater than the standard ASU. Although there is still an energy penalty, it is smaller than for case 2. The reduction in the sizes of the heat exchangers and distillation column would be based on the flow rate after the CZPSA unit, which is 30.5% of the flow rate of the standard ASU for the same oxygen production rate.

A process with a different purpose could be developed for the production of nitrogen, and presumably produce a limited amount of oxygen. Such a process would essentially be the same as the hybrid ASU for oxygen production, except the adsorbent in the CZPSA unit would be a carbon molecular sieve. The stream fed to the cryogenic distillation column would be nitrogen-enriched; however, because air is naturally nitrogen-enriched, the advantages of this hybrid air separation process is not expected to be as great as the oxygen-enriching process presented in this work.

Future Process Optimization

The goal of this work was to establish proof of concept for several hybrid air separation processes. Based on our findings, the key variables for optimization are:

1. Adsorbent in CZPSA unit. Although zeolite 13X works reasonably well in the CZPSA, it may not be the optimal choice. Other adsorbents such as LiX should be explored.
2. Adsorbent in Air Prepurification unit. Layered adsorbent beds are used for air prepurification (7); in this case, the addition of an activated alumina layer should be explored.
3. CZPSA volumetric purge-to-feed ratio (γ_{CZPSA}). Increasing γ_{CZPSA} will provide better clean-out of the CZPSA unit, resulting in higher purity, lower recovery, and a larger air prepurification unit; decreasing γ_{CZPSA} will result in a lower purity oxygen product, higher recovery, and a decrease in the size of the air prepurification unit. These competing effects of γ_{CZPSA} should be explored to find the optimum values.
4. Air Prepurification unit regeneration step. The optimum regeneration temperature needs to be determined.
5. Cryogenic distillation column. As the concentration of the feed stream to the cryogenic distillation column changes, so does the optimal feed stage within the column. For major changes in the oxygen feed concentration, the entire arrangement of the distillation system is likely to change. Thus, the cryogenic distillation column will need to be optimized for the higher oxygen concentrations.
6. Energy integration scheme. It was assumed that the same energy integration used in a normal ASU could be used. This may not be optimum.
7. CZPSA unit operating conditions. Further optimization should be done of bed length, bed diameter, gas velocity, and cycle timing.
8. Air prepurification operating conditions. Further optimization of bed length, bed diameter, gas velocity, and cycle timing is also likely necessary.
9. Simulate and optimize the case 4 process.

Retrofitting Existing Plants

It may be desirable to retrofit an existing conventional plant to convert it to a hybrid-type operation with a significantly higher oxygen production capacity. An existing conventional air separation plant has a preset plant capacity and thereby predetermined sizes for the cryogenic distillation column, the heat exchanger, and compression stage. Thus, economically converting the existing flowsheet into a hybrid air separation process, will require that most of the equipment remain intact at its current size. Case 1 will increase capacity by approximately 11%, and this is done with a decrease in power costs per unit of oxygen product. Because oxygen concentration is kept at or below 23.5%, the existing equipment can be used after the air is concentrated. Also, because the plant capacity is fixed, the total gas flowrate after the CZPSA unit is based on the limiting downstream system (compressors, heat exchangers or distillation column) for the new oxygen purity. With the product flow rate from the CZPSA unit set, the required feed flow rate and blower size to the CZPSA can be calculated. A low pressure air prepurification unit will be required. The optimal feed stage in the cryogenic distillation column, and the energy integration scheme, may need to be modified in light of the increased oxygen concentration in the feed to the cryogenic distillation column. These modifications will be small or negligible for case 1 but could be significant for cases 2 and 4.

SUMMARY AND CONCLUSIONS

Hybrid air separation processes that combine adsorption with cryogenic distillation technologies have been developed for production of oxygen and limited production of nitrogen. The adsorption hybrid processes make use of CZPSA, an unconventional PSA process that produces moderate oxygen purity, but has high recovery of pressurized oxygen, to enrich the oxygen concentration of air before it is further compressed and fed to the heat exchangers and the cryogenic distillation column. The high recovery of pressurized oxygen characteristic of CZPSA is realized by its use of low pressure, dry, carbon dioxide-free air as purge; this is in contrast with conventional PSA, which uses a portion of product for purge. A novel, hybrid PSA/TSA air prepurification unit was designed to deliver impurity-free low pressure air to purge the CZPSA unit. Simulation results from small-scale air prepurification and CZPSA units were used to scale-up to a full-scale commercial hybrid ASU. For a specified oxygen production capacity, the oxygen-enriched product effluent from the CZPSA unit makes all of the unit operations downstream of the CZPSA unit considerably smaller and cheaper.

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NOMENCLATURE

English Symbols

b_i	Langmuir-Freundlich isotherm parameter, atm^{-n}
$b_{0,i}$	Langmuir-Freundlich isotherm parameter at reference temperature, atm^{-n}
B_i	Extended Langmuir-Freundlich isotherm parameter, atm^{-1}
ΔH_{ads}	heat of adsorption, kJ/kmol
k_j	Extended Langmuir-Freundlich isotherm parameters
$n_{feed,CZPSA}$	amount of feed gas processed by CZPSA unit, moles
n_i	exponent in Langmuir-Freundlich isotherms, dimensionless
$n_{purge,CZPSA}$	amount of purge gas processed by CZPSA unit, moles
$\dot{P}$	compressor power, kW
P_a	compressor inlet gas pressure, bar
P_b	compressor outlet gas pressure, bar
$P_{feed,CZPSA}$	pressure of CZPSA unit during feed step, atm
P_H	high pressure, bar
P_i	partial pressure of species i, atm
P_L	low pressure, bar
$P_{purge,CZPSA}$	pressure of CZPSA unit during purge step, atm
q_i	amount of solute i adsorbed, kmol/kg
$q_{m,i}$	isotherm parameter in Langmuir-Freundlich isotherms, mmol/kg
q_0	volumetric flowrate of gas for compression, standard m^3/s
R	universal gas constant
T	temperature, K
T_a	compressor inlet gas temperature, K
$V_{feed,CZPSA}$	volume of feed gas processed by CZPSA unit, m^3
$V_{purge,CZPSA}$	volume of purge gas processed by CZPSA unit, m^3

Greek Symbols

γ	ratio of specific heats (C_p/C_v), dimensionless
γ_{CZPSA}	volumetric purge-to-feed ratio for CZPSA unit, dimensionless
η	compressor efficiency, dimensionless

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