Production of High Purity of Oxygen by Combination of Membrane and PSA Methods

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황 선 탁

PRODUCTION OF HIGH PURITY OXYGEN BY COMBINATION OF MEMBRANE AND PSA METHODS

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ABSTRACT

There are growing needs to produce relatively high purity (99.0% or higher) oxygen at low cost. For small scale production, both pressure swing adsorption (PSA) and membrane process are competitive and less expensive or more convenient than well known cryogenic fractionation technology. A continuous membrane column (CMC) combined with a PSA oxygen generator can be employed to produce high purity oxygen continuously. The oxygen-enriched gas generated by a PSA unit, with a concentration of 93-94%, is fed to the CMC that consists of three modules of poly(imide) hollow fibers. Several experiments were conducted by varying parameters, such feed flow rate, transmembrane pressure drop, stage cut, and feed location in order to obtain a high oxygen concentration above 99.0%. A two-series unit mode was also employed with CMC operation to optimize the given membrane area.

INTRODUCTION

Conventional methods to produce O_2 of 99.9% or higher purity are based on cryogenic fractionation of air (1). For large O_2 production, this is a very mature, highly developed, competitive technology. There are, however, many applications in industry as well as in medicine where the daily requirements of O_2 are rather small, and a purity of only 40 to 90% O_2 is needed (2,3). For this segment of the O_2 market, competitive pressure swing adsssorption (PSA) processes have been developed (4,5) and membrane permeation (MP) processes have been explored in recent years (6). The advantages of PSA and MP processes for small-scale, lower purity O_2 separation from air are: easy and trouble-free operation, reduced maintenance costs, quick start-up, and relocation of the PSA or MP equipment, if necessary.

It has been shown that by using inorganic zeolites as adsorbents (for example, Linde 5Å molecular sieves), one can design a PSA process to separate up to 95% O_2 from air (7,8). The principle of air separation used by the PSA process is based on the fact that among nonpolar molecules, the one with highest quadrupole moment is preferentially adsorbed on zeolites over others with lower quadrupole moments (9). Since N_2 has a higher quadrupole moment than O_2 when air is contacted with the zeolite, the adsorbed phase will have a higher concentration of N_2, while an O_2-enriched gas stream can be removed from the atmosphere ambient to the zeolite. On the other hand, Ar does not have a quadrupole moment and thus is less absorbed by zeolites. Therefore, a single stage commercial PSA process can separate up to 95% O_2 plus 5% Ar from air.

The principle of O_2 separation from air used by a membrane process is that O_2 permeates faster through polymeric membranes than N_2 or Ar (10). The degree of O_2 separation from air by a membrane process is limited because the polymer membranes shown that in a single-stage membrane process for O_2 separation from air, even the most favorable case (12,13) is not possible to produce more thatn about 65% O_2 - enriched air.

Several permeator configurations have been investigated for high purity gas separations: recycle permeator, two strippers in series (TSS), continuous membrane column (CMC) and so forth (14-17). Figure 1(a) shows a CMC, which has a similar configuration to a distillation column and in which the feed gas is introduced between the enriching and the stripping section. The more permeable gas can concentrate at the top of the column, while the less permeable one concentrates at the bottom of the column. The CMC is shown to concentrate the more permeable component much more than a conventional permeator without recycle. Theoretically greater recycle, less stage cut, longer membrane column, and larger membrane area will result in a higher concentration of oxygen up to 100% regardless of the oxygen selectivity (14). Therefore a CMC could be a method for obtaining high purity oxygen.

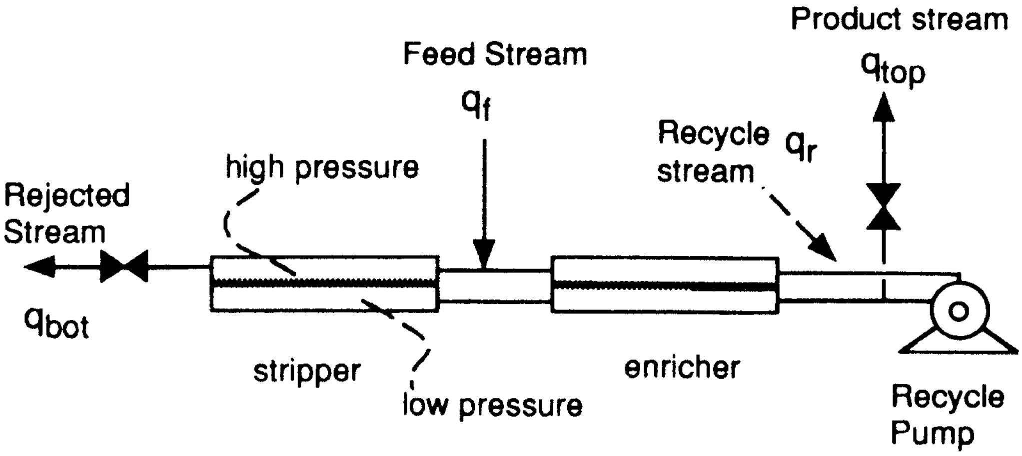
Theoretical studies on permeator configurations with recycle, such as a CMC and TSS, have been extensively investigated to provide optimal separation (13,16-20). However, there has not been sufficient experimental verification in literature. Hwang and Thorman (14) first separated the binary gases: air, CO_2/O_2, and CO_2/N_2 with a CMC. In addition, the separation of methane from binary and ternary mixtures has been demonstrated by Hwang and Ghalchi (21). Also a model study was carried out for ternary gas mixtures using different membrane columns (22).

In this report, we propose a new separation system in which both a CMC and PSA are combined. The basic idea behind this system is that oxygen-enriched gas produced by PSA is fed to the CMC, which further enriches oxygen. The operating conditions of PSA were kept constant and the CMC experimental parameters, such as feed flow rate, transmembrane pressure, stage cut, and feed location, were investigated to obtain high-purity oxygen. The main purpose of this work is to obtain high purity oxygen with a membrane separation, and for these purposes the following objectives were set:

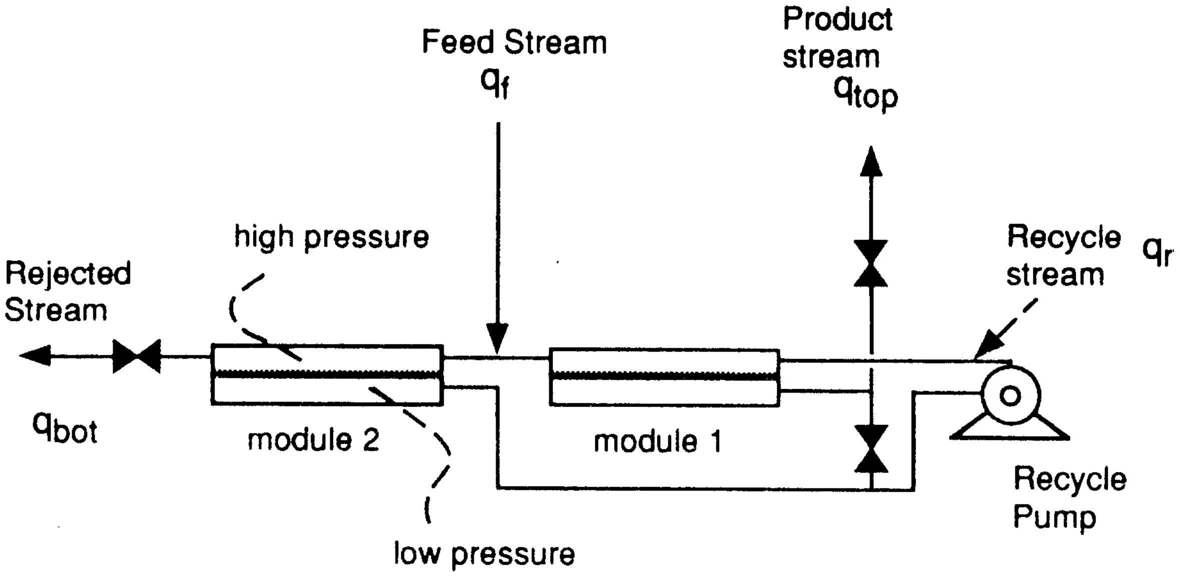
1. The proposal of a new system that consists of both a CMC and PSA.
2. The parametric study of CMC operating factors, such as feed flow rate, transmembrane pressure, and stage cut, were systematically investigated.
3. The experimental data were compared with those calculated from the plug-flow model.

Furthermore, we have proposed a new CMC configuration, which is combined with the conventional CMC and two membranes in series, shown in Fig. 1(b). We call this configuration "CMC in TSS mode." The first module in a CMC in TSS mode is used like a partial condenser of a distillation column. Part of the permeate stream in the first module is removed as a product stream, while the rest is mixed with the permeate stream of the other module and then recycled again. The ratio of the product to the recycle stream can be controlled with the valves.

In a conventional TSS mode, the permeate in the first module is not mixed with the permeate stream of the second module, which is at a lower concentration than the first. The difference between the conventional TSS and the CMC in TSS is that the product flow rate can be controlled at will for the latter configuration, while for the former configuration the product flow rate is determined by the membrane area of the first module and consequently cannot be independently changed. Therefore the CMC in TSS mode is a more flexible configuration for any given module used. This is the reason why this configuration is expected to have a better performance than the conventional CMC configuration.



(a) Continuous membrane column



(b) CMC in TSS mode

Fig. 1 Continuous membrane column(CMC) and CMC in TSS mode

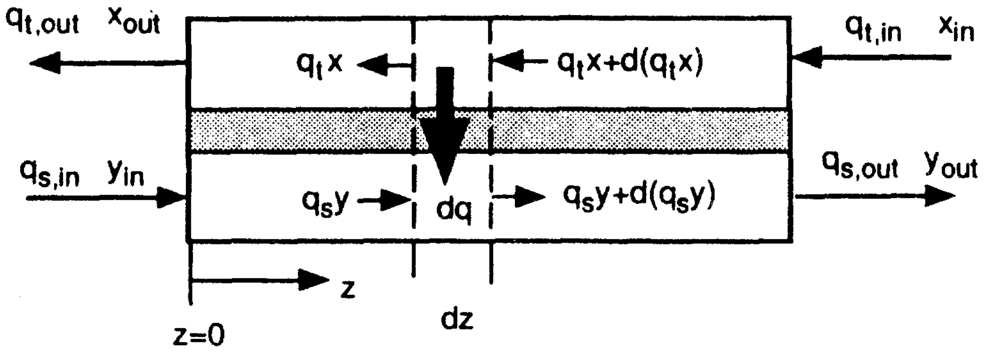


Fig. 1 (c) Material balance for a permeator

THEORY

The plug-flow model (14-19) is used in this study with the following assumptions:

1. Ideal gas behavior for the binary gaseous system
2. Steady state isothermal operation
3. Constant ambient pressure at the shell-side
4. Negligible axial pressure drop.

Governing equations

The basic equation for the plug-flow model is expressed as the following overall and component material balances in the membrane capillary, shown in Fig. 1(c).

$$\frac{dq_t}{dz} = \frac{2\pi N}{\ln(r_o/r_i)} \{Q_1(xP_t - yP_s) + Q_2[(1-x)P_t - (1-y)P_s] \tag{1}$$

$$\frac{d(q_t x)}{dz} = \frac{2\pi Q_1}{\ln(r_o/r_i)}(xP_t - yP_s) \tag{2}$$

The shell-side composition and flow rate can be related by applying the overall and component material balances as follows.

$$q_{t,out} + q_s = q_{s,out} + q_t \tag{3}$$

$$q_{t,out}x_{out} + q_s y = q_{s,in} + q_t x \tag{4}$$

Boundary and junction conditions

The following boundary and junction conditions can be used for Fig. 2(a) and (b).

At the bottom of the shell-side for both CMC and CMC in TSS, the flow rate is zero

$$q_{s,in}^{(3)} = 0 \tag{5}$$

and the composition is obtained through a calculation of the closed-end assumption.

$$\frac{y_{in}^{(3)}}{1 - y_{in}^{(3)}} = \frac{Q_1}{Q_2} \left\{ \frac{x_{out}^{(3)} P_t - y_{in}^{(3)} P_s}{(1 - x_{out}^{(3)}) P_t - (1 - y_{in}^{(3)}) P_s} \right\} \tag{6}$$

The above boundary conditions are applied to the bottom of the stripper for the CMC in TSS mode.

At the feed location, the tube-side flow from the second module is mixed with the feed flow.

$$q_{t,in}^{(3)} = q_{t,out}^{(2)} + q^{(F)} \tag{7}$$

$$q_{t,in}^{(3)} x_{in}^{(3)} = q_{t,in}^{(2)} x_{out}^{(2)} + q^{(F)} x^{(F)} \tag{8}$$

At the recycling pump, the following boundary conditions for the overall and component material balances should be fulfilled.

For the CMC:

$$q_{t,in}^{(1)} = q_{s,out}^{(1)} - \theta q^{(F)} \tag{9}$$

$$x_{in}^{(1)} = y_{out}^{(1)} \tag{10}$$

For the CMC in TSS:

$$q_{t,in}^{(1)} = q_{s,out}^{(2)} + (q_{s,out}^{(1)} - \theta q^{(F)}) \tag{11}$$

$$x_{t,in}^{(1)} q_{t,in}^{(1)} = \{x_{s,out}^{(2)} q_{s,out}^{(2)} + x_{s,out}^{(1)} (q_{s,out}^{(1)} - \theta q^{(F)})\} \tag{12}$$

By solving the four differential equations with the appropriate boundary and junction conditions at a given membrane module condition, we can determine the composition of the product and reject streams from the feed composition at a given operating condition, such as feed flow rate, transmembrane pressure, and overall stage cut, which is the fraction of feed that is taken as the permeate product from the entire membrane unit.

EXPERIMENTAL

Membranes and Modules

Three asymmetric hollow-fiber membranes made of polyimide (23) were used in this work; these were kindly supplied by UBE Industries (Japan). The dense layer of the membranes is on the outer side; the inner and outer diameters of hollow-fibers are approximately 180 and 390 μm, respectively. Each hollow-fiber module, which is made of a stainless steel tubing (O.D. 6 mm, I.D. 4 mm), has 30 fibers (effective length 31 cm). Table I shows the detailed dimensions of the modules used.

Pure Gas Permeability

The pure gas permeabilities of oxygen, nitrogen, and argon were measured at the transmembrane pressure of 10 to 30 psi and at room temperature (20-26°C). High purity gas obtained by Union Carbide Corp. was fed inside of the membrane fibers, while the shell-side of the modules was kept at atmospheric pressure in order to measure the flow rate with a soap

Table I Membrane dimension (UBE 1990)

Module	I.D. [μm]	O.D. [μm]	Membrane area [cm^2]	Effective length [cm]
1	182	393	115	31.1
2	182	393	115	31.1
3	182	393	116	31.2

Table II Pure gas permeability and selectivity

	Q/L[10^{-5}cc(STP)/cm^2/s/cmHg]			Separation factor [-]	
Module	O_2	N_2	Ar	O_2/Ar	O_2/N_2
1	1.52	0.210	0.394	3.85	7.24
2	1.60	0.210	0.410	3.87	7.28
3	1.71	0.240	0.457	3.75	7.18

(measured at 25-26°C, 20 psi)

film flow meter.

Continuous Membrane Column

The experimental apparatus for the CMC is shown in Fig. 2(a). A PSA oxygen generator (Bunn Lite, manufactured by John Bunn Co.) produced the oxygen-enriched air, which was fed into a surge tank to stabilize the pressure, feed flow rate, and composition. Since the oxygen concentration produced by PSA, in principle, depends on flow rate, the operating conditions of PSA were kept constant by adjusting the vent valve in order to feed a constant concentration of oxygen to CMC. The average feed composition was 93.3 ± 0.4% of oxygen, 6.1 ± 0.4% of argon, 0.5 ± 0.4% of nitrogen and 200 ppm of neon. Helium could not be detected because it was used as a carrier gas in the GC.

Three modules were connected in series. Permeate gas, which flowed countercurrently to the high-pressure stream, was recycled with a metal-bellows vacuum pump (Metal Bellows Corp.). The permeate side (shell-side) was kept at 1-2 psig to prevent air leakage, while the pressure on the tube-side was changed from 10 to 30 psi. Product and reject flows were withdrawn continuously from the bottom and the top of the column, respectively. The flow rate of product, reject, recycle, and feed streams were monitored with the mass flow meters (Matheson, NJ).

Figure 2(b) shows the experimental apparatus for the CMC in TSS mode. The product stream is withdrawn as part of the permeate only through the first module and is not mixed with the permeates from the other modules. Stage cut was adjusted by controlling the valve that connects the permeate stream from the first module with the others. The pressure of the permeate stream was kept at 1-2 psig.

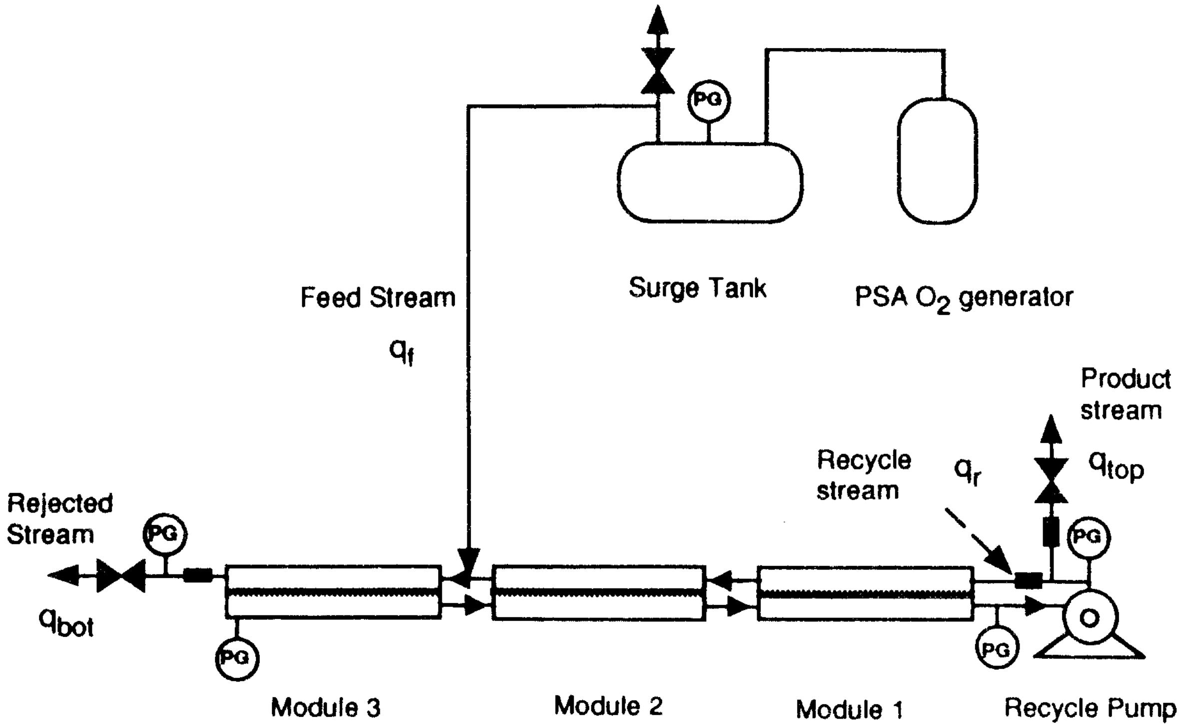


Fig. 2-a Schematic Experimental Apparatus of the CMC

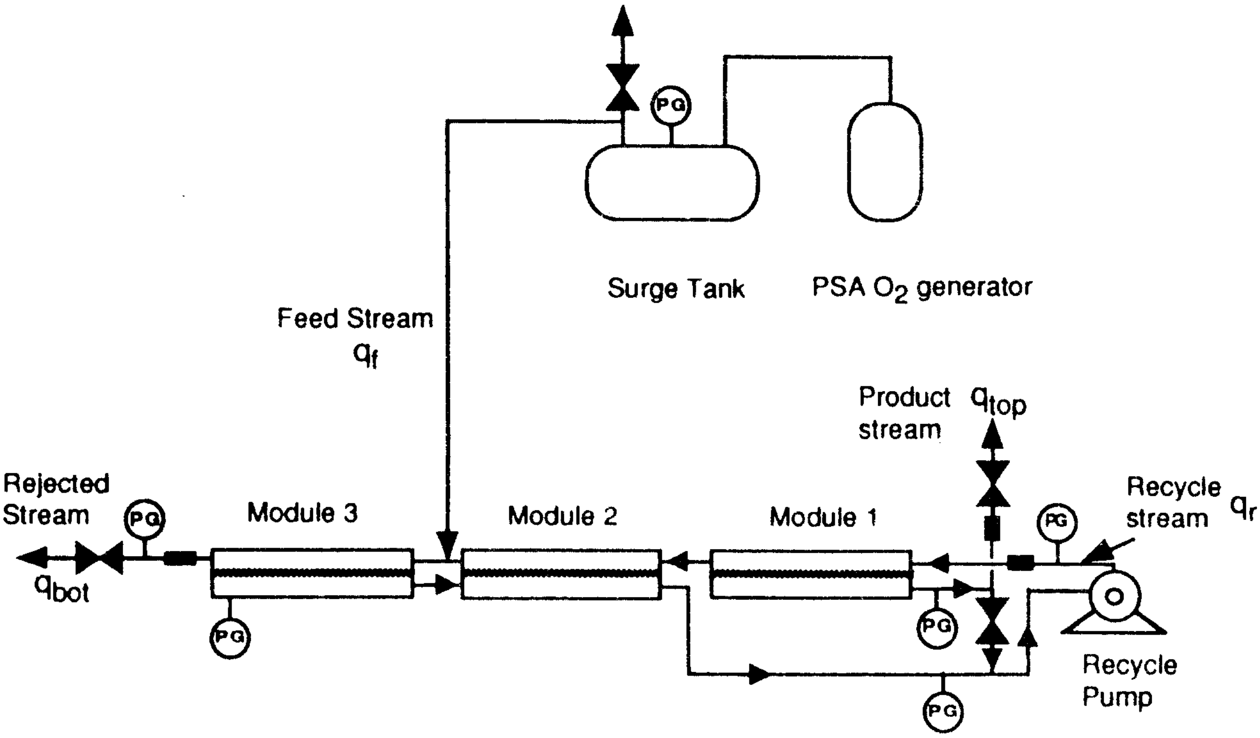


Fig. 2-b Schematic Experimental Apparatus of the CMC in TSS mode

Operating parameters, such as feed flow rate, transmembrane pressure, stage cut, and feed location, were systematically varied. The standard operating conditions of flow rate, transmembrane pressure, and stage cut were 10 cc (STP)/min, 20 psi, and 0.1, respectively. The PSA gas was fed into the tube-side stream between the second and third modules.

The gas composition was determined by gas chromatography, (Hewlett-Packard model 5840A) with a 12 m-long column of HayeSep A Polymer. Helium was used as the carrier gas.

RESULTS AND DISCUSSION

Pure Gas Permeation Experiments

The pure gas permeabilities for oxygen, nitrogen, and argon are summarized in Table II. Although the membranes used have asymmetric structures, the permeabilities are obtained on the assumption that they are symmetric membranes with the inner and outer diameters listed in Table I. The dependence of the permeability on the transmembrane pressure was negligible in the pressure range of 10 to 30 psi. However, the permeability of this polymer membrane was dependent on the temperature. The selectivity was found to be almost constant, since the ratio of the increase in oxygen permeability with temperature was nearly the same as that of argon in this range.

The permeabilities of the three gases in the mixture were measured at a small stage cut (less that 0.1) with PSA gas of 20 psi. These were found to be nearly the same as the permeability of the pure components at the same experimental conditions, although mixing effects on permeability have been reported for glassy polymers (24).

PSA Gas Separation Without Recycle

To check the membrane performance without recycle, the PSA gas was fed to the first module with a constant transmembrane pressure of 20 psi. In this configuration, the stage cut is dependent upon the feed flow rate since all permeating gases through the module are removed as the permeate stream. At low cut (high feed flow rate) the permeate oxygen concentration was the highest, approximately 97.3%. This value coincides with the one calculated by assuming that the feed composition along the module is kept at the same composition as the PSA. This result shows that a single-stage permeator without recycle is not adequate for the production of high purity oxygen.

PSA Gas Separation With A CMC

1. Effect of stage cut on the product oxygen concentration

Decreasing the stage cut results in higher oxygen concentrations in the product stream. In a CMC configuration stage cut is controlled independently of the feed flow rate. At low stage cut, the oxygen was enriched above 99.0% The superiority of the CMC to the configuration without recycle is clearly shown. The composition of reject stream approaches that of the feed stream at lower cut, while the permeate composition approaches the feed stream at higher cut. The oxygen concentration of reject stream decreased to about 50% at higher cut; this means that the argon is enriched above 50%. This result also suggests that this system is suitable for the production of argon, which is currently manufactured as a byproduct of oxygen and nitrogen purification by cryogenic fractionation technology.

The concentration is lower since the recycling rate at this pressure is approximately half that at 20 psi, due to the lower permeate flux.

The feed composition is a ternary mixture of oxygen, argon, and nitrogen, However, the nitrogen concentration was so low (about 0.5%) that the calculation for a binary system was carried out, assuming nitrogen could be considered as argon. The agreement between the experimental and calculated oxygen concentrations is very good.

2. Pressure and flow rate effects

A higher transmembrane pressure causes a higher oxygen concentration since the higher pressure increases the permeate flux and thus increases the recycle rate. The "zero pressure ratio" condition, which is achieved either by making the high pressure side infinite or by pulling a vacuum on the low pressure side, will give the best separation (14).

The oxygen concentration is also dependent on the feed flow rate. The stage cut and transmembrane pressure were kept constant at 0.1 and 20 psi, respectively. Lower feed flow rates give higher oxygen concentrations. Ultimately, the maximum degree of separation will be achieved at a total reflux condition, at which there is no feed or no product flow (14).

3. Error range

The error of oxygen concentration with GC analysis was estimated less than ± 0.3% (probably within 0.2%) from repeated measurements of the same samples. The errors were within ± 5% for flow rate and pressure, since they needed to be adjusted manually.

CMC Used in TSS Mode

The oxygen concentration of the product stream for a CMC in TSS was approximately 0.4% higher than that obtained with CMC at a lower cut. This is because the product stream could avoid mixing with the permeates from the other modules. Since the product was removed from the first module, there was a maximum stage cut at this experimental condition (P = 20 psi, Q_f = 10cc/min). The concentration of oxygen was higher at the lower feed flow rate, which is the same as with an ordinary CMC.

The CMC in TSS mode produced higher purity oxygen at the same condition. This suggests that the CMC in TSS mode is superior to the conventional CMC. The permeate product composition of CMC was O_2 = 99.0%, Ar = 0.8%, Ne = 0.1%, and N_2 = 0.1%; and that of CMC in TSS (cut 0.1) was O_2 = 99.4%, Ar = 0.4%, Ne = 0.1%, and N_2 = trace.

CONCLUSION

In this study, we propose a new hybrid system which combines both a CMC and PSA in order to obtain high purity oxygen.

1. It has been demonstrated that the CMC combined with PSA can produce high purity oxygen (above 99%) from air.
2. The parametric study of CMC operating factors, such as feed flow rate, transmembrane pressure, stage cut, and feed location, showed that higher oxygen concentrations could be produced continuously under the following conditions: lower feed flow rate, higher pressure, smaller cut, and the optimum feed location so that a longer enricher section results.
3. We have proposed a new configuration called "CMC in TSS mode," and verified that this configuration produced higher purity oxygen than the conventional CMC, in the experimental range studied.
4. The model calculations of the CMC and CMC in TSS mode showed good agreement with the experimental data.

NOMENCLATURE

L = membrane thickness [cm]

N = number of fibers [-]

P = pressure [psi]

Q = permeability $[\mathrm{cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg}]$

q = flow rate [cc/min]

r_i= inner radius of the capillary [cm]

r_o= outer radius of the capillary [cm]

x = mole fraction of more permeable component in the tube side [-]

y = mole fraction of more permeable component in the shell side [-]

z = axial length along the permeator [cm]

Z = length fraction from the bottom [-]

θ = stage cut [-]

<superscript>

i = number of the module from the top

f = feed stream

<subscript>

1 = the more permeable component

2 = the less permeable component

out = exit

in = entrance

t = tube-side (high pressure)

s = shell-side (low pressure)

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