R_ψ = regime numbers, equations (15) to (17)
s = (ρ_s/ρ_l), ratio of solid to liquid densities
v = mean slurry velocity, m/s
v_c = critical velocity of slurry, m/s
v_∞ = settling velocity of solid in unbounded quiescent fluid, m/s
v_s = hindered settling velocity of solid, m/s
v_0 = $\sqrt{\tau_0/\rho_l}$, friction velocity in pipe flow, m/s
$\tilde{v}_i$ = root mean of time averaged square of velocity fluctuation in direction i, m/s
x = fraction of eddies with velocities exceeding v_s, Equation (43)

Greek Letters
γ = v_∞/v_c, Equation (43)
μ = carrier liquid viscosity, kg/m − s
ρ_l = liquid density, kg/m^3
ρ_m = slurry density, kg/m^3
ρ_s = solid density, kg/m^3
τ_0 = shear stress at pipe wall, N/m^2
ψ = $[v^2\sqrt{C}]/[gD(s-1)]$, Equation (5)]

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The Continuous Membrane Column

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The continuous membrane column provides a revolutionary separation technique. Both the most and the least permeable components can be separated continuously to any degree without cascading. Experimental data for several binary systems show good agreement with theory.

SCOPE

With the advance of hollow fiber technology, membrane separation processes are becoming economically competitive with conventional separation methods such as cryogenic fractional distillation and gas absorption. However, high cost is still a problem owing to the large membrane area and many interstage compressors required for cascade operations. The continuous membrane column will undoubtedly change this situation.

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The revolutionary development of this new technique has placed membrane separations in a new perspective. Past efforts to utilize membranes have been mainly concerned with permeability and selectivity. While these properties are important in the continuous membrane column concept, they are not considered paramount. In principle, the continuous membrane column can provide nearly complete separation of a binary mixture even if the permeability and selectivity of the membrane employed are relatively low. The large surface area/unit volume available using capillary membranes can offset low permeabilities while increasing the amount of permeation relative to product removal can counter low selectivities. In general, the selection of a membrane for a specific separation can now be based more equally on all qualities of a membrane (that is, mechanical strength, durability, inertness), not just permeability and selectivity. Furthermore, from an engineering standpoint, the continuous membrane column is very flexible. Either porous or nonporous membranes in tube or sheet form can be employed. Capillary membranes can be pressurized on either the tube side or shell side, and the feed stream need not be introduced under pressure, although it is usually advantageous to do so.

The essence of the continuous membrane column is countercurrent plug flow, minimal backmixing and a high amount of internal permeation relative to product flow rates. One of the unique aspects of the unit is probably the enriching section, where gas is recycled around the end of the column through a compressor. This permits unlimited enrichment of the more permeable gas as compared to the limited enrichment experienced in a conventionally operated cell. Throughout the column, the more permeable gas is stripped from the high pressure stream, resulting in a separation of the feed mixture.

Possible commercial applications of the continuous membrane column include hydrogen separation from industrial gases, helium recovery from natural gas, preparation of high purity gases, recovery of hydrocarbons from refinery gases, generating oxygen enriched air for oxygen therapy and high temperature furnaces, providing inert atmosphere for fuel tanks, and controlling carbon dioxide in breathing atmospheres.

CONCLUSIONS AND SIGNIFICANCE

A new unit operation has been developed for membrane separations. This revolutionary separation device is called the continuous membrane column. It can separate both the most and least permeable components from a binary mixture of any composition as highly concentrated products. The continuous membrane column is viewed as a continuous cascade rather than as a single stage permeation cell. Therefore, the degree of enrichment is unlimited in a continuous membrane column, while there exists a maximum limit in a conventional cell.

Experiments are carried out for gaseous binary systems of oxygen-nitrogen (air), carbon dioxide-nitrogen and carbon dioxide-oxygen mixtures using continuous membrane columns made of silicone rubber capillaries. Experimental data are taken for stripper, enricher, and total columns at total reflux as well as with product removal. Also, a numerical simulation of the continuous membrane column is developed based on permeation, pressure drop and deformation equations. The agreement between theory and experiment is excellent.

The performance of a continuous membrane column is characterized by the number of membrane units (NMU) and the height of a membrane unit (HMU). These concepts are very useful in design. Satisfactory correlations are obtained dealing with the above quantities using experimental data.

PREVIOUS WORK

During the past decade, study of gas separation via membranes has advanced considerably. Hollow-fiber and spiral-wound permeators, accommodating large surface areas within small volumes, and new asymmetric membranes have been developed. With regard to capillary permeators, the applicability of either countercurrent or cocurrent separation models has been experimentally verified by Blaisdell and Kammermeyer (1973), Thorman et al. (1975), Ohno et al. (1976) and Stern et al. (1977). Stern and Wang (1978) have shown that respective countercurrent and cocurrent models developed by several investigators are essentially the same. Theoretical and experimental investigations of axial pressure loss within capillary membranes have been conducted by Thorman et al. (1975), Thorman and Hwang (1978), Pan et al. (1978) and Pan and Habgood (1978b). Antonson et al. (1977) have presented a theoretical analysis of gas separation in a commercial scale permeator incorporating the effects of axial pressure loss, process variables, flow patterns and broken fibers. Blaisdell and Kammermeyer (1972) and Stern et al. (1977), along with Thorman and Hwang (1978), have also studied capillary deformation theoretically and experimentally. Especially comprehensive reviews dealing with capillary permeators can be found in books by Hwang and Kammermeyer (1975) and by Meares (1976)

There have been a variety of other contributions. Stern et al. (1969, 1971, 1972) and Fang et al. (1975) have dealt extensively with the pressure dependency of gas permeability coefficients in polymer membranes. Pan and Habgood (1974) have presented a unified analysis of the gas permeation cell for several flow patterns and discussed usage of a purge stream in the permeate. Ohno and coworkers (1976, 1977, 1978*a*, 1978*b*) have developed a permeator comprised of two different membranes to be used in separating radioactive rare gases. Separations with cas-

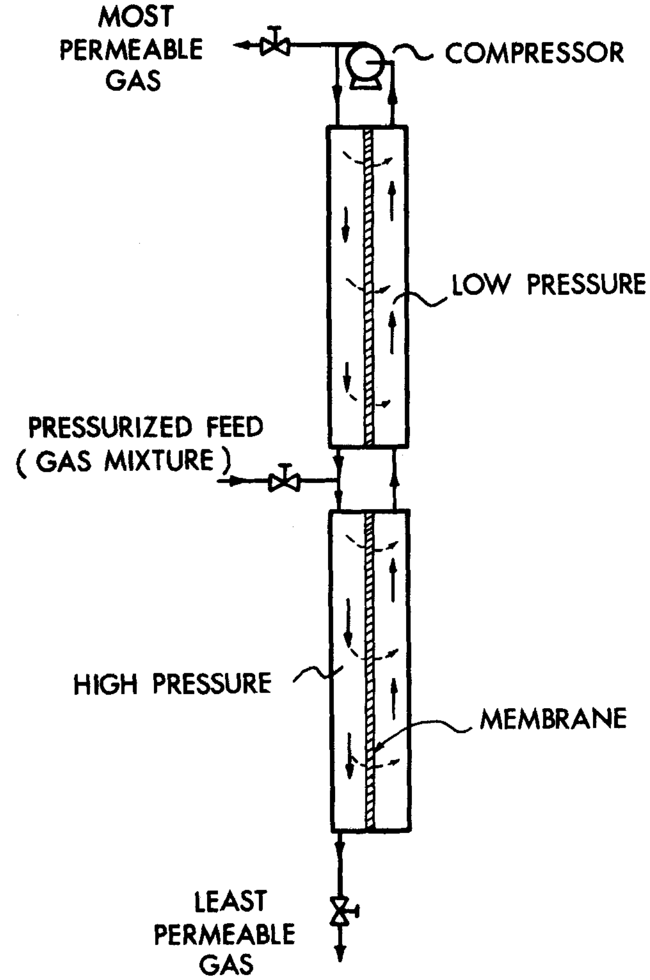

Figure 1. Continuous membrane column.

cades have been studied by Higashi et al. (1970), Rainey et al. (1971), Yamamoto and Kanagawa (1975), Thorman et al. (1975), Higashi and Miyamoto (1976), Ohno et al. (1977, 1978*a*, 1978*b*), Pan and Habgood (1978*a*) and several other Japanese investigators.

DESCRIPTION OF A CONTINUOUS MEMBRANE COLUMN

In a conventional permeation cell, separation takes place across the membrane due to the different permeation rates of constituents. Therefore, the maximum degree of enrichment is always limited by the permeability ratio of constituents for a given membrane. Except for so-called one-step separations, such as hydrogen purification through silver-palladium alloy and helium separation through silica glass, it is necessary to cascade multiple stages in a series to achieve further enrichment. This usually requires cumbersome operation and prohibitive cost. It is important to note that a diffusion cell is considered a single stage in cascade operations.

In the present paper, a recent innovation in membrane separations will be discussed which will revolutionize the entire concept of membrane technology. This new device is proposed to be called the continuous membrane column. The permeation cell is no longer regarded as a single stage but rather as a continuous cascade. The performance of a continuous membrane column is analogous to that of packed columns used in distillation, extraction and gas absorption. When a binary feed mixture is introduced to the membrane column as shown in Figure 1, both components can be separated to any degree of purity on a continuous basis.

As the mixture travels downward on the high pressure side of the membrane, the more permeable component preferentially permeates through the membrane. Thus, the gas stream on the high pressure side is depleted of the more permeable component. This stripping action, coupled with countercurrent reflux provided by the permeate stream, concentrates the less permeable gas at the bottom of the stripper. At the same time, gas from the low pressure side is circulated to the high pressure side by a compressor located at the top of the column. The same stripping action takes place in the enriching section, resulting in a high concentration of the more permeable component near the compressor. At steady state, the more permeable gas congregates at the top of the enricher and the less permeable gas gathers at the bottom of the stripper, thus separating the mixture on a continuous basis.

It is obvious that the absence of backmixing is essential because any axial mixing tends to equalize compositions. Other pertinent features of the continuous membrane column are countercurrent enrichment and reflux action. The degree of separation achieved will depend on product flow rates, separation factor, pressure difference across the membrane and membrane geometry. It is important to note that a high degree of internal reflux action is needed in order to produce a high degree of separation.

When only the more permeable component is to be separated, an enricher alone is sufficient. Likewise, the less permeable component can be separated using a stripper alone. Only if both components need to be separated should a total column be used by connecting an enricher and a stripper as shown in Figure 1.

THEORY

Modeling the Continuous Membrane Column

The total membrane column can be modeled by coupling the models of the stripper and enricher with allowance for an external feed stream. Hence, the essential portion of the numerical simulation for a continuous membrane column is modeling compressible flow of a binary mixture in a bundle of permeable capillaries under deformation. Individual models for gas separation in rigid capillary membranes (Thorman et al., 1975) and the compressible flow of pure gases in deformable capillary membranes (Thorman and Hwang, 1978) have previously been reported. By combining these two approaches, the simulation of a gas permeator can be refined.

The governing equations are the axial pressure loss equation, the gas permeation equation and a differential mass balance over an infinitesimal membrane column segment:

$$\frac{dP}{dz} = \frac{K_1\bar{\mu}qRT}{\pi(r_i)^4P}\left(\frac{1}{K_2} - \frac{4Re_w z}{Re_z r_i}\right) - \frac{4/r_i}{Re_z/(3P) - \pi(r_i)^3 \; P/(2\bar{\mu}qRT)} - \frac{8\bar{\mu}qRT}{\pi(r_i)^4P} \quad (1)$$

$$\frac{dq}{d\dot{z}} = \frac{2\pi N}{\ln(r_o/r_i)}[Q_1(xP - yP_o) + Q_2\{(1-x)P - (1-y)P_o\}) \quad (2)$$

$$\frac{dx}{dz} = \left[\frac{2\pi NQ_1(xP - yP_o)}{\ln(r_o/r_i)} - x\frac{dq}{dz}\right]/q \quad (3)$$

where

$$K_1 = 8(1 + 0.75Re_w - 0.0407Re_w{}^2$$

$$+ 0.0125Re_w^{3} \ldots) \qquad (4)$$

$$K_2 = -1 + 0.056Re_w - 0.0153Re_w^{2} \ldots \qquad (5)$$

Here, the capillary dimensions r_i, r_o and z should be deformed values instead of the original ones. These values are functions of pressure and vary from point to point. Viscosities and permeabilities also change along the axis and should be computed at every location using the local composition and partial pressures (Maitland and Smith, 1972; Wilke, 1950). Temperature of the system is assumed to be constant, as is pressure outside of the capillaries. In addition to the above differential equations, overall and component material balances can be used to relate compositions and flow rates on both sides of the membrane:

$$q - q_B = G - G_B \qquad (6)$$

$$xq - x_B q_B = yG - y_B G_B \qquad (7)$$

Except in the case of a total reflux stripper, the calculation is initiated at the bottom of the column. There are two reasons for this. One is that the numerical integration becomes unstable if the computation begins at the top of a stripping section with product removal. The second is that flow rates of the streams in and out of the compressor are difficult to measure accurately. Therefore, errors in the initial values of an enricher calculation may propagate significantly along the column if computation starts at the top of the enricher.

All boundary values are measured experimentally, except the permeate composition at the very end on the low pressure side of a stripper. However, this composition can be estimated from the permeation equations if plug flow is assumed. The composition will be that of the gas which passes through the endmost increment of the membrane. The flow rate of each component is

$$y_B \frac{dq}{dz} = \frac{2\pi N}{\ln(r_o/r_i)} Q_1 (x_B P - y_B P_o) \qquad (8)$$

$$(1 - y_B)\frac{dq}{dz} = \frac{2\pi N}{\ln(r_o/r_i)} Q_2 [(1 - x_B)P - (1 - y_B)P_o] \qquad (9)$$

Taking the ratio of these expressions, a quadratic equation results with respect to y_B which can be solved easily:

$$\frac{y_B}{1 - y_B} = \frac{Q_1}{Q_2}\left\{\frac{x_B P - y_B P_o}{(1 - x_B)P - (1 - y_B)P_o}\right\} \qquad (10)$$

After all the boundary values are determined, the calculation becomes an initial value problem. The fourth (fifth)-order Runge-Kutta integration routine is employed to solve Equations (1), (2) and (3) simultaneously with global error assessment (Fehlberg, 1970, 1976). The integration is carried out over the measured length of the stripper.

At the junction of the stripper and enricher (feed point), it is necessary to reestablish a new set of boundary conditions in order to commence the enricher computation. Since the permeate stream (shell side) is fed to the enricher, the inlet conditions of the enricher are identical to the outlet conditions of the stripper. The outlet stream from the enricher plus the fresh feed make up the stripper feed stream. Thus, overall and component material balances around the feed point provide new boundary conditions on the high pressure side (tube side). Integration then proceeds upwards over the measured length of the enricher.

The stepwise numerical simulation gives complete information on column behavior. This includes the composition profile, pressure profile and flow rate distribution along the column.

Performance Characterization

Since the continuous membrane column is analogous to the packed column of other unit operations, such as distillation, extraction and gas absorption, it is only logical to employ the same type of performance analysis. The difficulty of separation and the efficiency of a packed column are characterized by the number of transfer units (NTU) and the height of a transfer unit (HTU), respectively. The product of these two quantities becomes the total column height. This concept was originally proposed by Chilton and Colburn (1935) and has been used extensively for design and scale-up purposes. A similar analysis for continuous membrane columns should be feasible, even though membrane separations are based on nonequilibrium rather than equilibrium processes.

The fundamental formula can be obtained by combining the differential permeation and mass balance equations, that is Equations (2) and (3):

$$\frac{dx}{dz} = \frac{2\pi N Q_1 P}{q \ln(r_o/r_i)} [x - yP_r - x\{(1 - Q_r)(x - yP_r) + Q_r(1 - P_r)\}] \qquad (11)$$

where

$$P_r \equiv \frac{P_o}{P} \qquad (12)$$

and

$$Q_r \equiv \frac{Q_2}{Q_1} \qquad (13)$$

It is possible here to regroup the variables into two sets: one involving only the compositions, that gives the degree of separation, and the other consisting of the remaining variables, that expresses the difficulty of separation. When these two groups of quantities are integrated over a section of the continuous membrane column, they yield a result equivalent to the number of transfer units and height of a transfer unit. Therefore, it is proposed here to name them as the number of membrane units (NMU) and the height of a membrane unit (HMU), respectively. The definitions of these dimensionless groups are

$$\mathrm{NMU} \equiv \int_B^T \frac{dx}{x - yP_r - x\{(1 - Q_r)(x - yP_r) + Q_r(1 - P_r)\}} \qquad (14)$$

and

$$\mathrm{HMU} \equiv \frac{Z}{\displaystyle\int_B^T \frac{2\pi N Q_1 P}{q \ln(r_o/r_i)} dz} \qquad (15)$$

Combining these with Equation (11), we get

$$Z = (\mathrm{NMU})\,(\mathrm{HMU}, \qquad (16)$$

which will serve as a design equation for the continuous membrane column.

Thus, a complete analogy has been established between the continuous membrane column and the conventional packed columns of equilibrium processes. However, the evaluations of NMU and HMU are much more difficult than those of NTU and HTU. In general, the pressure and flow rates vary continuously along the column. Therefore, the capillary radii and gas permeabilities change also. There is no simple relationship between x and y. The complete numerical simulation of a column must be carried out first in order to calculate NMU and HMU, which defeats somewhat the purpose of having these formalisms.

However, when axial pressure loss is negligible, then the capillary radii and gas permeabilities will remain relatively constant along the column. In this case, a simplified approximate equation results for the expression of HMU. In Equation (15), the flow rate is the only significant variable over the column height. If the following approximation is introduced

$$\int_B^T \frac{dz}{q} = \int_B^T \frac{dz}{dq}\frac{dq}{q} = \int_B^T \frac{dz}{dq}\, d\ln q$$

$$\simeq \frac{Z}{(q_T - q_B)}(\ln q_T - \ln q_B) \qquad (17)$$

then Equation (15) will be simplified as

$$\text{HMU} \simeq \frac{(q_T - q_B)}{2\pi N Q_1 P}\frac{\ln(r_o/r_i)}{\ln(q_T/q_B)} \qquad (18)$$

If we use this approximate equation, the value of HMU can be estimated with the knowledge of boundary values.

Unfortunately, there is no similar simplification that can be made for the NMU calculation. The main difficulty is the lack of a simple relationship between x and y. However, in special cases the integration can be carried out analytically as shown below.

Zero Pressure Ratio

Since the driving force in a membrane separation process is the pressure difference across the membrane, the efficiency of separation will reach a maximum when the pressure ratio becomes zero. This condition can be obtained experimentally either by making the high pressure infinite or by pulling a vacuum on the low pressure side. All the terms containing y in Equations (2) and (3) will then drop out.

First, the NMU expression in Equation (14) becomes simplified as

$$\text{NMU} = \int_B^T \frac{dx}{(1-Q_r)x(1-x)} = \frac{1}{(1-Q_r)}\ln\left(\frac{x_T}{x_B}\right)\left(\frac{1-x_B}{1-x_T}\right) \qquad (19)$$

which can be utilized knowing only the boundary values at the top and bottom of a continuous membrane column. If we combine Equations (18) and (19) into Equation (16), the length required to achieve a given separation is

$$Z \simeq \frac{(q_T - q_B)\ln(r_o/r_i)\ln[x_T(1-x_B)/x_B(1-x_T)]}{2\pi N Q_1 P(1-Q_r)\ln(q_T/q_B)} \qquad (20)$$

It should be noted that Equation (20) is an approximate expression which can be used in design when the high pressure changes very little.

Second, another useful relationship can be derived between the compositions and flow rates at the top and bottom of a continuous membrane column by combining Equations (2) and (3) after substituting $P_r = 0$ and integrating from the bottom to the top:

$$\int_B^T \frac{Q_r + (1-Q_r)x}{(1-Q_r)x(1-x)}dx = \int_B^T \frac{dq}{q} \qquad (21)$$

This yields

$$\left(\frac{x_T}{x_B}\right)\left(\frac{1-x_B}{1-x_T}\right)^{\left(\frac{1}{Q_r}\right)} = \left(\frac{q_T}{q_B}\right)^{\left(\frac{1}{Q_r}-1\right)} \qquad (22)$$

The last expression is exact and does not involve the column height Z nor the pressure P. Therefore, the composition can be predicted by knowing the ratios of flow rates and permeabilities only. Conversely, the flow rate can be calculated by knowing the end compositions and the ratio of permeabilities.

Total Reflux

In distillation, total reflux gives the minimum number of plates. Or, for a given column, total reflux generates maximum separation, but without any products. Even though it does not have any practical applications, it serves as an example of a special situation in understanding column behavior. In the operation of a continuous membrane column, total reflux may arise when there are no feed and no products.

At total reflux, the streams entering and leaving the stripper or enricher must have identical flow rates and compositions. If we extend this material balance to any intermediate section within the column, it can be easily seen that the high pressure and low pressure streams have identical flow rates and compositions. The entire gas within the column must permeate through the membrane and pass through the compressor. However, owing to the membrane selectivity, the more permeable component will concentrate near the compressor and the less permeable component will congregate at the opposite end of the column. The degree of separation within the column reaches a maximum when the column is operated at total reflux.

Stripper and enricher can be separately operated at total reflux. Because of the peculiar boundary conditions for a total reflux stripper, the numerical model calculation must be initiated at the feed inlet. There is no numerical instability associated with the total reflux calculations.

Since x equals y at every point, the expression in Equation (14) becomes simplified as follows:

$$\text{NMU} = \int_B^T \frac{dx}{(1-Q_r)(1-P_r)x(1-x)}$$

$$= \frac{1}{(1-Q_r)(1-P_r)}\ln\left(\frac{x_T}{x_B}\right)\left(\frac{1-x_B}{1-x_T}\right) \qquad (23)$$

Consequently, the column height for a given separation can be calculated approximately by

$$Z = (\text{NMU})(\text{HMU}) \cong$$

$$\frac{(q_T - q_B)\ln(r_o/r_i)\ln[x_T(1-x_B)/x_B(1-x_T)]}{2\pi N Q_1 P(1-Q_r)(1-P_r)\ln(q_T/q_B)} \qquad (24)$$

when the high pressure remains almost constant. It can also be shown that Equation (22) is valid for the total reflux case. Thus, the degree of separation can be predicted by only knowing the ratio of flow rates when no products are removed, that is, at total reflux. The above equations may be useful in estimating the design pa-

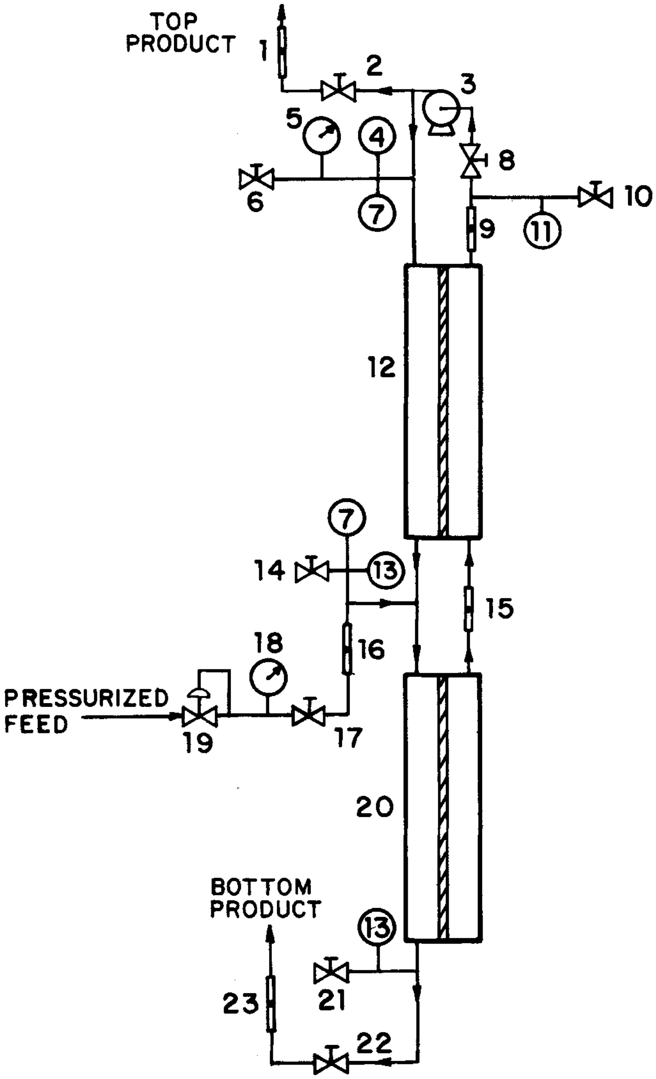

Figure 2. Measurement apparatus for continuous membrane column.

rameters since they do not require a detailed knowledge of the column behavior.

EXPERIMENTAL

The total column apparatus is represented schematically in Figure 2. The feed stream was introduced on the high pressure side of the column, while the low pressure side was maintained at ambient pressure to facilitate composition sampling. Homogeneous silicone rubber capillary membranes were pressurized internally to 200 kPa absolute. Feed mixtures consisted of oxygen-nitrogen (air), carbon dioxide-nitrogen and carbon dioxide-oxygen. All experiments were carried out at room temperature.

Each cell in the apparatus contained thirty-five capillaries (238 μm I.D. × 610 μm O.D.) loosely extended in a Tygon casing (7.94 mm I.D. with a 1.59 mm wall). Cell design resembled that of a shell and tube heat exchanger. Tube manifolds were formed by potting the capillary bundle into pipe nipples with epoxy glue. The casing was securely fastened over the nipples.

The column was brought to steady state over a period of 4 to 6 hr, depending on the relative amount of reflux. Steady state was maintained 2 to 4 hr, mainly to duplicate the shell side composition profile (ten samples). Pressure levels along with product compositions and flow rates were also measured. The composition profile was obtained by withdrawing 0.1 ml samples through pinholes along the Tygon casing using a gas syringe. Composition samples were analyzed with a Hewlett-Packard (model 720) gas chromatograph equipped with a thermal conductivity cell. Molecular sieve and Porapak-S chromatograph columns were employed to separate the oxygen-nitrogen (air) and carbon dioxide based mixtures, respectively. Top and bottom product flow rates were measured using a bubble flow meter. Mercury manometers were read with a cathetometer to determine the pressure at the compressor and pressure losses along the column. A water manometer, referenced to ambient pressure, was used to adjust the pressure outside of the capillaries.

Rotameters were used as flow indicators for the pressurized feed stream, the low pressure streams at the enriching and stripping sections, and the top and bottom product streams. High precision needle valves were used to regulate all flow rates. A schematic diagram of the total column apparatus is shown in Figure 2.

The stripping and enriching sections were similarly operated as individual units (stripper and enricher). Of course, operation of the stripper is the same as that of a conventional permeator.

Pure gas permeabilities were measured using a capillary bundle permeator at various temperatures and pressure levels. The results of these measurements will be reported elsewhere. However, they generally confirm the reported values for silicone rubber membrane by Robb (1967).

The measurement of Young's modulus was reported in our previous publication (Thorman and Hwang, 1978). The determination of inside and outside radii of membrane capillaries is described in detail by Thorman (1979). The undeformed values of inside and outside radii are 0.118 and 0.305 mm, respectively (less than 1% error). Axial pressure losses varied from 3 to 9 kPa. Composition analyses were normally within ±0.5 vol %. The estimated error in the flow rate measurements is less than 1%.

RESULTS AND DISCUSSION

As mentioned earlier, the maximum degree of separation within a continuous membrane column is achieved at total reflux. Both stripper and enricher units may be separately operated at total reflux. When a stripper is operated at total reflux with zero bottom flow rate, the concentra-

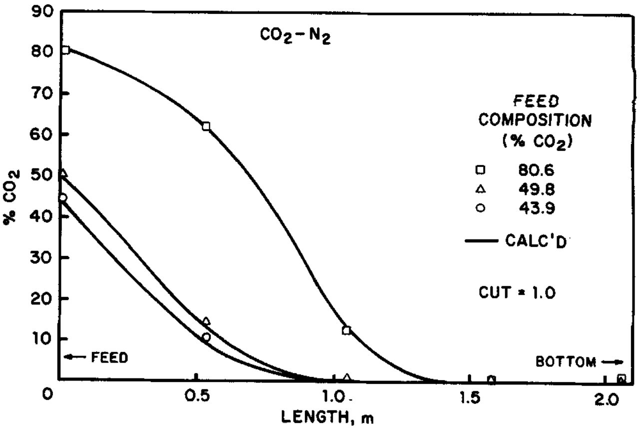

Figure 3. Carbon dioxide profile in shell side of a carbon dioxide-nitrogen stripper at total reflux.

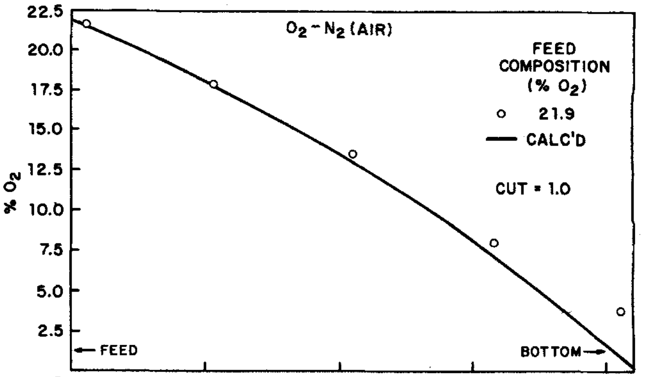

Figure 4. Oxygen profile in shell side of an oxygen-nitrogen stripper at total reflux.

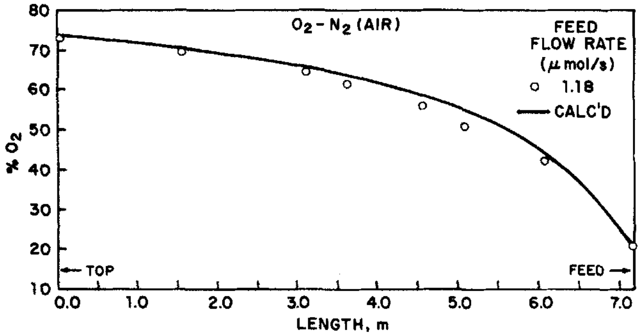

Figure 5. Oxygen profile in shell side of an oxygen-nitrogen enricher at *total reflux*.

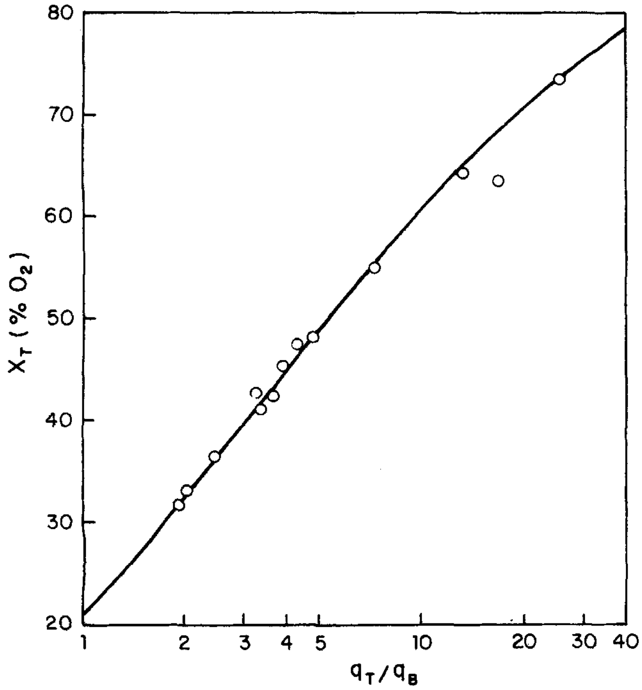

Figure 6. Summary of total reflux oxygen enricher data.

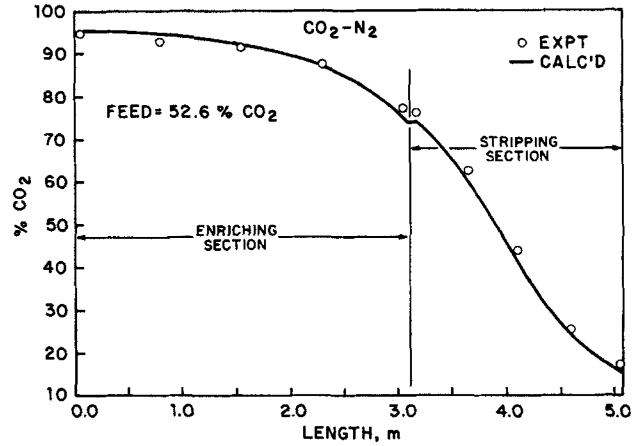

Figure 7. Shell side composition profile of a total continuous membrane column for carbon dioxide-nitrogen.

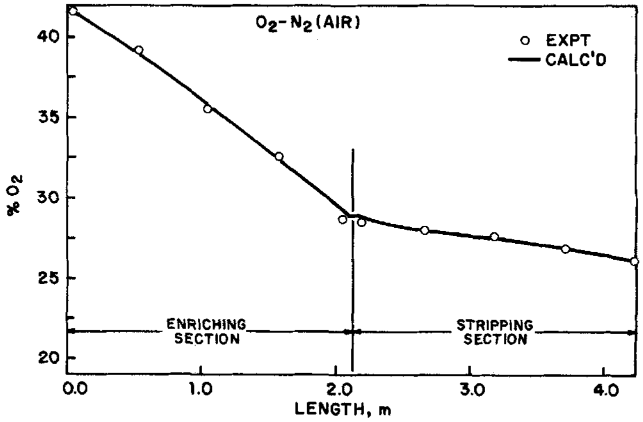

Figure 8. Shell side composition profile of a total continuous membrane *column for oxygen-nitrogen*.

tion of more permeable gas at the bottom must be zero regardless of permeabilities, pressure drop and column length, as shown by Equation (22). This is illustrated in Figure 3 for the carbon dioxide-nitrogen system. Note that the concentration of carbon dioxide approaches zero for all three cases half way along the 2.11 m column. The calculated shell side composition profiles fit the experimental data points very nicely. Stripper data for the same column and oxygen-nitrogen system are shown in Figure 4. The concentration profile is much less steep than that of the carbon dioxide-nitrogen system owing to a lower separation factor.

While the less permeable component can be easily isolated in a total reflux stripper, it is much more difficult to enrich the more permeable component in a total reflux enricher. As seen in Equation (22), the top flow rate must increase indefinitely in order to achieve complete separation. The indefinite increase of top flow rate means infinite membrane area and compressor load. This difficulty is well illustrated in Figure 5 for the oxygen-nitrogen system, where a total cell length of 7.23 m was used to provide a large membrane area. Maximum oxygen enrichment of 73.5% was obtained. This is a significant result because the maximum degree of oxygen enrichment in a conventional permeation cell made from silicone rubber membrane cannot exceed 36% theoretically and is only 28% under similar operating conditions. However, it has been demonstrated experimentally that this limit can be overcome by employing a continuous membrane column.

A number of runs were made for oxygen enrichment from room air at total reflux. Various cell lengths ranging from 2.11 to 7.23 m have been used at many different flow rates. The results are summarized in Figure 6. The solid curve represents Equation (22), and the points are experimental data. It should be noted here that the flow rates at the compressor end, q_T, were not measured experimentally but calculated from the numerical simulation as explained earlier.

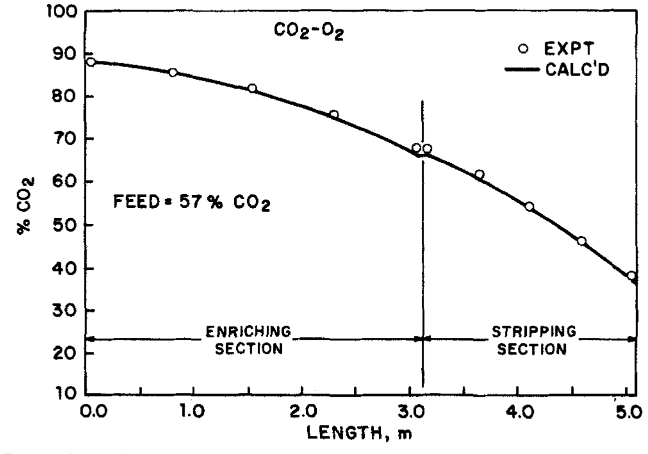

Figure 9. Shell side composition profile of a total continuous membrane column for carbon dioxide-oxygen.

Once steady state, total reflux conditions are established, either in a stripper or an enricher, a concentrated product can be obtained by opening a valve near the bottom of a stripper or the compressor end of an enricher. However, concentration of the product will drop from the value obtained at total reflux, and the continuous membrane column will establish another level of steady state conditions. Therefore, the relative amount of feed withdrawn as product will determine the extent of separation that can be achieved continuously.

Separations with steady product streams were conducted using a stripper, an enricher and a total column for many binary systems. Typical total column data are shown here for carbon dioxide-nitrogen, oxygen-nitrogen and carbon dioxide-oxygen in Figures 7, 8, and 9, respectively. The agreement between the experimental data and the calculated profiles of concentration, pressure and flow rate is excellent. For the carbon dioxide-nitrogen system, 94.6% carbon dioxide was obtained as a top product at a flow rate of 2.37 μ mole/s, while the bottom product contained only 8.2% carbon dioxide at 2.59 μ mole/s out of a feed containing 52.6% carbon dioxide. In the case of air separation, the top product was 41.7% at 0.933 μ mole/s, and the bottom product was 19.6% at 12.92 μ mole/s. Finally, for carbon dioxide-oxygen system, 87.3% carbon dioxide was the top product at a flow rate of 7.90 μ mole/s, and the bottom product contained 20.5% carbon dioxide with a flow rate of 6.75 μ mole/s from a feed containing 57.2% carbon dioxide. The high pressure at the compressor was kept in the range of 223 to 227 *kPa*, and the axial pressure drop along the column varied from 3 to 9 *kPa* on the tube side, keeping the shell side pressure at the atmospheric level.

Although the tube side composition and flow rate profiles could not be measured, an example of calculated profiles is shown for the carbon dioxide-nitrogen system in Figure 10. Other systems showed similar trends.

The complete numerical simulation of a continuous membrane column is very accurate; however, it is tedious and inconvenient for quick design calculations. The concepts of HMU and NMU are very attractive if these values can be evaluated only knowing the boundary values. In the present study, the high pressure changed very little (less than 5%), thus enabling one to use the approximate expression for HMU given by Equation (18).

In order to test how good Equation (18) is, the calculated value of HMU from Equation (15), using a column simulation profile, is plotted against the ratio of log mean flow rate to average permeability of more permeable component in Figure 11. The straight line represents Equation (18). In this correlation, all of the membrane column data are included except those of the total reflux stripper.

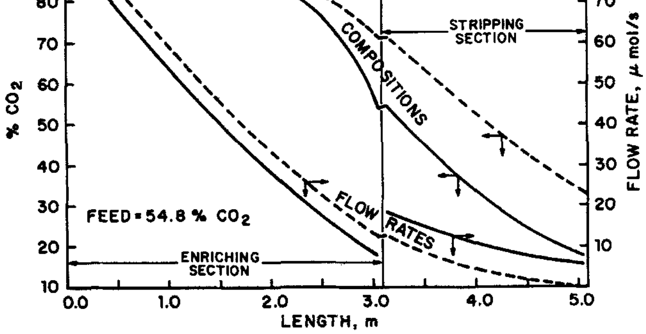

Figure 10. Calculated profiles for compositions and flow rates.

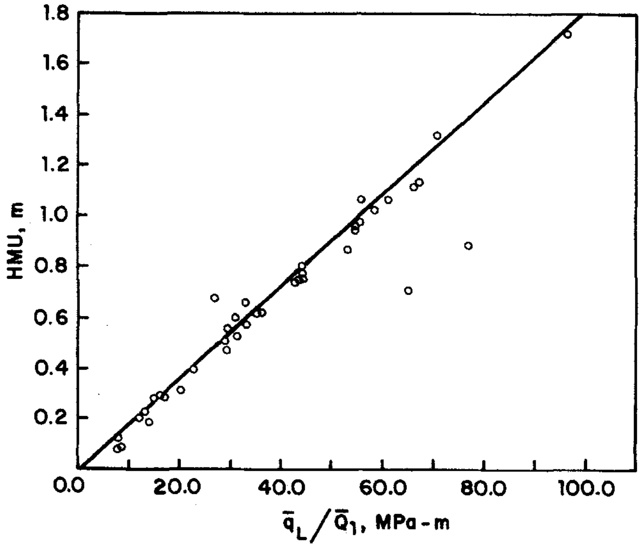

Figure 11. Correlation of *HMU* for all data.

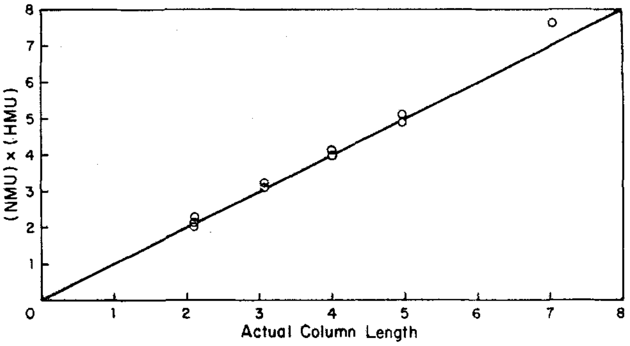

Figure 12. Correlation of *Z* =*(HMU) (NMU)* for total reflux oxygen enricher.

Only three out of almost forty points deviate significantly from the straight line, which is the approximate expression for HMU. Inspection of the data reveals that all three of those points represent the enriching section of a total membrane column. The high sensitivity of the concentration profiles to material balance adjustments made at the feed point is believed to be the primary cause of the discrepancies. Thus, Equation (18) may be used in evaluating HMU for most cases.

At total reflux, the value of NMU can be calculated exactly by knowing only the boundary conditions as given by Equation (23). Therefore, the required column length can be estimated by Equation (24). The previously mentioned total reflux oxygen enrichment data are plotted again in Figure 12. The straight line represents Equation (24). All experimental results agree quite well with Equation (24). Therefore, it can be safely concluded that Equation (24) may be used in the design of a continuous membrane column operated at total reflux.

ACKNOWLEDGMENT

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NOTATION

G = shell side flow rate, μ mole/s
HMU = height of a membrane unit as defined by Equation (15), m
K_1 = function of Re_w as defined by Equation (4)
K_2 = function of Re_w as defined by Equation (5)
N = number of capillaries

NMU = number of membrane units as defined by Equation (14)
P = absolute local tube side pressure, kPa
P_o = atmospheric pressure, kPa
q = tube side flow rate, μ mole/s
Q = permeability coefficient, $\frac{(\text{mole})\ (\text{m})}{(\text{s})\ (\text{m}^2)\ (\text{Pa})}$
r = radius of capillary, m
R = gas constant
Re_w = Reynolds number at the wall defined by $r_i\ V_{rw}\bar{\rho}/\mu$
Re_z = axial Reynolds number
T = absolute temperature, °K
V_{rw} = radial velocity at the wall, m/s
x = mole fraction of the more permeable component in tube side
y = mole fraction of the more permeable component in shell side
z = axial coordinate measured from the bottom of the column, m
Z = total column height, m
μ = viscosity, (Pa) (s)
π = 3.141 592 . . .
ρ = density of gas, kg/m^3

Subscripts

o = outside
z = axial direction
w = at the capillary wall
i = inside
B = at the bottom of a column
T = at the top of a column
1 = more permeable component
2 = less permeable component
r = ratio

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