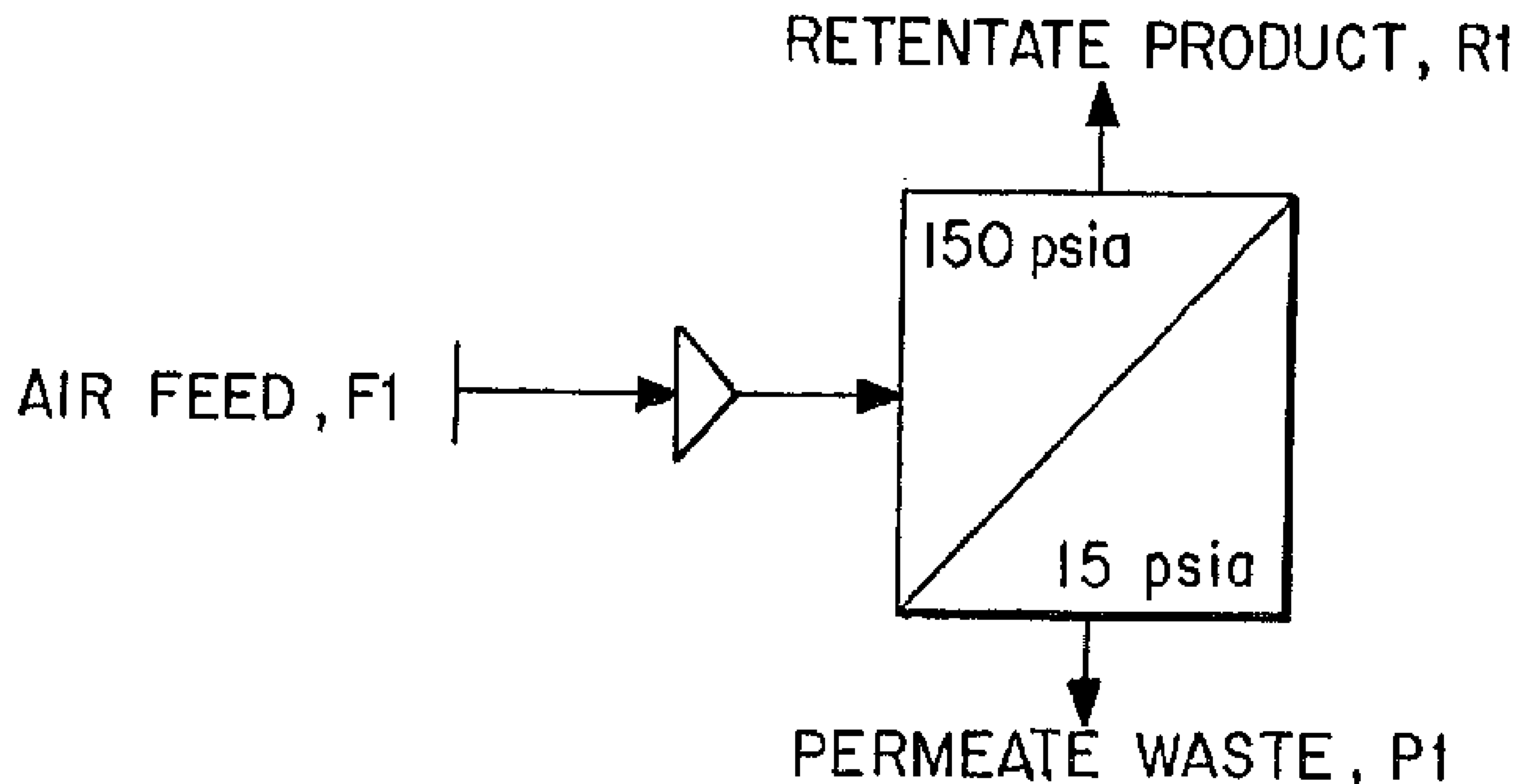




(86) Date de dépôt PCT/PCT Filing Date: 1995/10/10
(87) Date publication PCT/PCT Publication Date: 1996/04/18
(45) Date de délivrance/Issue Date: 2006/03/07
(85) Entrée phase nationale/National Entry: 1997/04/08
(86) N° demande PCT/PCT Application No.: US 1995/012364
(87) N° publication PCT/PCT Publication No.: 1996/011048
(30) Priorité/Priority: 1994/10/11 (08/320,273) US

(51) Cl.Int./Int.Cl. *B01D 53/22* (2006.01)
(72) Inventeur/Inventor:
CALLAHAN, RICHARD A., US
(73) Propriétaire/Owner:
ENERFEX, INC., US
(74) Agent: G. RONALD BELL & ASSOCIATES

(54) Titre : PROCÉDE A PLUSIEURS ETAPES DE SEPARATION DE GAZ PAR MEMBRANES SEMI-PERMEABLES
(54) Title: MULTIPLE STAGE SEMI-PERMEABLE MEMBRANE GAS SEPARATION PROCESS



(57) **Abrégé/Abstract:**

A membrane process and apparatus are described for the production of a desired very high purity permeate gas by use of a multiple stage membrane process wherein in a primary stage a process feed gas mixture is provided to a primary membrane separator unit comprising a membrane having a relatively high intrinsic permeability to provide an intermediate permeate gas and a retentate gas, and providing the intermediate permeate gas in a secondary stage to a secondary membrane separator unit comprising a membrane having a relatively low intrinsic permeability, to produce therefrom a very high purity permeate gas product.



PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01D 53/22	A1	(11) International Publication Number: WO 96/11048 (43) International Publication Date: 18 April 1996 (18.04.96)
(21) International Application Number: PCT/US95/12364 (22) International Filing Date: 10 October 1995 (10.10.95) (30) Priority Data: 08/320,273 11 October 1994 (11.10.94) US (71) Applicant: ENERFEX, INC. [US/US]; 30 Commerce Street, Williston, VT 05495 (US). (72) Inventor: CALLAHAN, Richard, A.; 67 Union Street #2F, Winooski, VT 05404-1948 (US). (74) Agents: RUCH, Joseph, J. et al.; Sughrue, Mion, Zinn, Macpeak & Seas, Suite 800, 2100 Pennsylvania Avenue, N.W., Washington, DC 20037-3202 (US).		(81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: MULTIPLE STAGE SEMI-PERMEABLE MEMBRANE GAS SEPARATION PROCESS (57) Abstract A membrane process and apparatus are described for the production of a desired very high purity permeate gas by use of a multiple stage membrane process wherein in a primary stage a process feed gas mixture is provided to a primary membrane separator unit comprising a membrane having a relatively high intrinsic permeability to provide an intermediate permeate gas and a retentate gas, and providing the intermediate permeate gas in a secondary stage to a secondary membrane separator unit comprising a membrane having a relatively low intrinsic permeability, to produce therefrom a very high purity permeate gas product.		

MULTIPLE STAGE SEMI-PERMEABLE MEMBRANE GAS SEPARATION PROCESSFIELD OF THE INVENTION

5 The present invention relates to a process and
apparatus for the production of a high purity gas
which in general is more permeable in polymeric
membranes relative to other gases with which it is
10 mixed. The more permeable gas, e.g., carbon dioxide,
is separated and concentrated by permeating through
specific membrane stages to a high purity.

BACKGROUND OF THE INVENTION

15 U.S. Patent 4,990,168 to Sauer et al describes a
two or more stage membrane and distillation process to
separate and concentrate carbon dioxide from a
destination tail gas mixture containing it in a high
concentration of about 75% CO₂. The nature and
composition of the membrane material is described in
20 detail, and polyimide, polyarimid, polyester,
polyamide and cellulose acetate are noted as examples.
The use of different membrane materials with different
properties for application in different stages is not
described.

25 Furthermore, although a process such as that
described in the Sauer '168 patent may be useful in
limited localities where gas mixtures containing
carbon dioxide in a high concentration are available,
such as the tail gas of a typical CO₂ liquefier, such
30 a process is of little value in the more numerous
localities where gas containing carbon dioxide in a

high concentration is not readily available, such as a fossil fuel combustion exhaust or limekiln vent gas. Therefore, the Sauer '168 patent does not address adequately the problem of providing high purity carbon dioxide in localities in which a source containing carbon dioxide in a relatively high concentration is not readily available.

U.S. Patent 5,102,432 to Prasad describes a two or more stage membrane process to separate and concentrate high purity nitrogen from ambient air. This process relates to concentrating the less permeable component of a gas mixture to high purity by refining it by passing it through successive stages as a high pressure non-permeate phase. The Prasad '432 patent describes that a permeate stream of a downstream membrane is recycled to the initial feed and/or to the non-permeate phase of an upstream membrane. Also, the Prasad '432 patent specifies a range of membrane selectivities.

A need has continued to exist for improved processes and apparatus for providing high purity gases in an economical and efficient manner; in particular, an improved process and apparatus for providing local production of high purity carbon dioxide starting from abundantly available low concentration sources as mentioned above has been strongly desired.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a membrane process for the production of very high purity permeate gas a desired product from a feed gas mixture containing less than 40 mol% of the desired permeate gas, which process comprises providing in a primary stage the process feed gas mixture to a primary membrane separator unit comprising a membrane having a relatively high intrinsic permeability to provide an intermediate permeate gas and a retentate gas, and providing the intermediate permeate gas in a secondary stage to a secondary membrane separator unit comprising a membrane having a relatively high selectivity, to produce therefrom a very high purity permeate gas product. Preferably, the membrane of the primary membrane separator unit has an intrinsic permeability of more than 250 Barrer/cm x 10⁴. Also preferably, the membrane of the secondary membrane separator unit has an intrinsic permeability of 250 Barrer/cm x 10⁴ or less.

In another aspect, the present invention relates to an apparatus for carrying out the process of the invention, i.e., an apparatus comprising a means for providing a process feed gas mixture to a primary stage membrane separator unit, which unit comprises a membrane having a relatively high intrinsic permeability, and a means for providing an

intermediate permeate gas produced from said primary stage membrane separator unit to a secondary stage membrane separator unit, which unit comprises a membrane having a relatively low intrinsic permeability.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a conventional one stage membrane separation process wherein a highly purified retentate N₂ product is obtained by subjecting air to a separator unit comprising a conventional polymer membrane.

Figure 2 illustrates a two stage process wherein N₂ gas is produced as a highly purified retentate gas in a two stage membrane process, with recycling of the N₂-enriched permeate from the second stage to the initial air feed.

Figure 3 illustrates processes wherein a permeate product is purified in two stages, with recycling of the retentate from the second stage to the process feed, including embodiments of the present invention as described below.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has been found that for some gas separations it is generally beneficial to use more than one membrane stage, comprising using membranes in succeeding stages having lower intrinsic permeability. Specifically, for gas mixture separations where it is desirable to

WO 96/11048

PCT/US95/12364

separate and concentrate the more permeable component to a purity of about 96.0+% (by volume), it has been found that lesser total membrane area is required when a two or more stage membrane system is employed wherein a primary stage utilizes a membrane having a relatively high intrinsic permeability in a primary membrane separator unit, and a secondary stage or succeeding stages utilize a membrane having a relatively low intrinsic permeability. Examples of common gases that exhibit relatively high intrinsic permeability when so treated are carbon dioxide and hydrogen.

A membrane having a relatively high intrinsic permeability needs a smaller area for a given gas flow, however, it also generally shows less selectivity between gases. By comparison, a membrane having relatively high selectivity generally has lower intrinsic permeability for constituent gases of a mixture. However the low intrinsic permeability in the second or succeeding membrane separator stages is not a limitation, because of the reduced flow in the concentrated product permeate feed from the previous membrane separator stage or stages. In the second membrane separator stage, the higher selectivity ensures the highest final permeate product purity. Therefore, in accordance with the present invention, it has now been found that by combining successively higher selectivity membrane separator stages into a

multiple stage membrane process, it is possible to achieve both high permeability and high selectivity in a unitary membrane process, and thus use smaller membranes with higher efficiency. More specifically, in an ideal multiple stage membrane process in accordance with the present invention, the initial primary stage utilizes a high intrinsic permeability membrane whereby intermediate concentration levels (40 to 80 vol%) of the desired very high purity permeate gas product in the intermediate permeate gas are achieved with minimal membrane area. In accordance with the present invention, the secondary or succeeding stages utilized low intrinsic permeability membranes, whereby high levels of about 96.0+% of permeate concentration are achieved with minimal membrane area. Concentrated and reduced permeate flow from the initial stages accommodates the successive or second membrane's lower intrinsic permeability.

The generally accepted unit of permeability is known as the Barrer, and is usually expressed in the following units: $P = (\text{cm}^3 \cdot \text{cm}) / (\text{cm}^2 \cdot \text{sec} \cdot \text{cm Hg}) \cdot 10^{-10}$. The intrinsic permeability is permeability divided by the membrane perma-selective barrier thickness, and is usually expressed in the following units: $P/L = (\text{cm}^3) / (\text{cm}^2 \times \text{sec} \times \text{cm Hg}) \times 10^{-10}$, wherein L is the barrier thickness (in cm).

The selectivity of a more permeable gas over a less permeable gas is defined as the ratio of their

WO 96/11048

PCT/US95/12364

permeabilities. Intrinsic permeabilities in Barrers/cm $\times 10^4$ of typical membrane materials are given below for four common gases, as well as the CO_2/N_2 and O_2/N_2 selectivities.

Gas	silicone/ polycarbonate <u>L=0.0001cm</u>	cellulose acetate <u>L=0.00001cm</u>	poly- carbonate <u>L=0.00001cm</u>
CO ₂	970.0	110	35
H ₂	210.0	84	140
O ₂	160.0	33.0	5.25
N ₂	70.0	5.5	0.875
<u>Selectivity Ratios</u>			
CO ₂ /N ₂	13.86	20.0	40.0
O ₂ /N ₂	2.29	6.0	6.0

From Fick's Law of diffusion combined with Henry's Law of sorption, it is seen that the gas permeation flux (V) (flow volume per unit area per unit time) across a membrane for any component is equal to its intrinsic permeability (P/L) times its partial pressure difference ($p_1 - p_2$) across the membrane barrier where p is the partial pressure in the higher pressure retentate side and P_2 is the partial pressure in the lower pressure permeate side:

$$V = P/L (p_1 - p_2).$$

A desirable component of a gas mixture may be either more permeable or less permeable than the other components of the mixture. If the desired component is the less permeable species, then the membrane is

said to be retentate selective and the feed stream is refined to a high purity in the retained or less permeable (retentate) component. The feed-retentate phase is present on the high pressure upstream side of the membrane and is referred to hereinafter as the retentate phase. On the downstream side of the membrane there is provided a permeate phase at a much lower pressure, usually slightly above one atmosphere. Almost all commercial membrane processes currently operate to refine a retentate to high purity, usually with a single stage membrane. An example is the separation of oxygen from air, or more aptly the production of nitrogen enriched air. For instance, a feed stream of ambient air containing about 79 vol% nitrogen and 21 vol% oxygen is pressurized and passed over the upstream side of a polycarbonate membrane. As this happens, the more permeable oxygen permeates the membrane much more rapidly than nitrogen, leaving behind about a 99% pure nitrogen retentate product phase and generating about a 31.5 vol% oxygen (68.5 vol% nitrogen) permeate waste phase, which is typically dumped back to the atmosphere.

Another commercial example is the separation of carbon dioxide from wellhead natural gas, or more aptly, the production of methane enriched or pipeline quality gas. A feed stream of wellhead gas at 93 vol% methane and 7 vol% carbon dioxide at pressure is passed over the upstream side of a cellulose acetate

WO 96/11048

PCT/US95/12364

membrane. The more permeable carbon dioxide permeates more quickly, yielding a 98% pure methane retentate product phase, and generating about a 37% pure carbon dioxide permeate waste phase, which is typically flared to the atmosphere at the production site. Normally a single stage membrane like those mentioned above is best suited to bring the retentate phase to its asymptotic purity concentration, 99.0+%, in a single pressurized retentate phase. Optimum performance of a single stage retentate membrane is achieved by matching feed flux (flow volume per unit area per unit time) and membrane surface area.

A flow diagram for a typical single stage membrane of polycarbonate to produce a nitrogen enriched retentate is shown in Figure 1. In all cases the feed gas is pressurized ambient air. The asymptotic retentate product phase concentration can be increased to 99.5 vol%, and even 99.95 vol%, by feeding the pressurized retentate stream to subsequent membrane stages to further refine the nitrogen enriched stream. The ultimate purity of the retentate product phase is a function of the feed flow rate and total membrane area. In the case of multiple stages, all stages utilize the same low intrinsic permeability membrane because of its relatively high oxygen over nitrogen selectivity and the relatively high initial nitrogen feed purity of 79%.

Figure 2 is an example of a two stage process to produce nitrogen of up to 99.5 vol% purity. A multiple stage membrane process according to the present invention would not benefit such an air separation where a high purity nitrogen retentate product phase is desired, because the relatively high intrinsic permeability of the primary membrane separator stage plus the relatively high initial feed concentration of nitrogen in air would allow excessive amounts of nitrogen to permeate through the membrane, thereby reducing the recovery of nitrogen in the retentate.

The multiple stage membrane process in accordance with the present invention is optimally utilized when the object is to concentrate by a membrane process a desired gas as a permeate from a relatively low initial level of 40% or lower to a level of about 96.0 vol% or higher purity.

Figure 3 shows a two stage membrane process according to this invention, capable of separating carbon dioxide to a level of about 96.0+ vol% purity with process flows as noted in Table 3 below. Table 1 below shows an example of flow rates, material balances, and membrane areas for a process as shown in Figure 3 in a comparative case wherein both membranes are of a single composition, viz., polycarbonate. The process feed gas mixture, F1, is 11.7% carbon dioxide and 88.3% nitrogen, which is the composition of a

WO 96/11048

PCT/US95/12364

natural gas combustion exhaust after the water of combustion is removed.

Table 1 shows that the first stage requires about 70,713 square feet of membrane and the second stage requires about 4,600 square feet of membrane, or a total area of 75,313 square feet of membrane, to achieve 96.0 vol% carbon dioxide purity in P2 with about 76.5 vol% of the carbon dioxide initially present in the process feed gas mixture being recovered. That is, 23.5 vol% of the carbon dioxide in the feed F1 is dumped as waste in the first stage retentate stream, R1.

TABLE 1

	AREA, FT ²	STREAM	FLOW, SCFH	CONC., VOL%	PRESS., PSIA
STAGE 1 POLYCARBONATE INTRINSIC PERMEABILITIES (BARRER/CM X 10000) CO ₂ : 35 N ₂ : 0.875 SELECTIVITY CO ₂ /N ₂ : 40	70,713	FRESH FEED, F1 RETENTATE, R1 PERMEATE, P1	37,973 34,443 7,336	11.7 3.1 58.9	90 80 15
STAGE 2 POLYCARBONATE INTRINSIC PERMEABILITIES (BARRER/CM X 10000) CO ₂ : 35 N ₂ : 0.875 SELECTIVITY CO ₂ /N ₂ : 40	4,600	FEED, F2 RETENTATE, R2 PERMEATE, P2	7,336 3,793 3,542	58.9 24.3 96.0	100 90 15

WO 96/11048

PCT/US95/12364

Referring to Figure 3 again, Table 2 shows a similar process and similar flows as in Table 1, except, in accordance with the present invention, the first stage utilizes a cellulose acetate membrane instead of polycarbonate.

TABLE 2

	AREA, FT ²	STREAM	FLOW, SCFH	CONC., VOL%	PRESS., PSIA
STAGE 1 CELLULOSE TRIACETATE INTRINSIC PERMEABILITIES (BARRER/CM X 10000) CO ₂ : 110 N ₂ : 5.5 SELECTIVITY CO ₂ /N ₂ : 20	20,255	FRESH FEED, F1 RETENTATE, R1 PERMEATE, P1	37,540 33,999 11,013	11.7 3.0 52.1	90 80 15
STAGE 2 POLYCARBONATE INTRINSIC PERMEABILITIES (BARRER/CM X 10000) CO ₂ : 35 N ₂ : 0.875 SELECTIVITY CO ₂ /N ₂ : 40	4,593	FEED, F2 RETENTATE, R2 PERMEATE, P2	11,013 7,473 3,542	52.1 31.3 96.0	100 90 15

Quite significantly, in this case it has been found that the first stage requires only about 20,055 square feet of membrane, and the combined stages require only a total area of only about 24,648 square feet, to achieve the same results.

Referring to Figure 3 again, Table 3 shows a similar process and flows as in Table 1 and Table 2, except that in accordance with another embodiment of the present invention, the first stage utilizes a silicone polycarbonate copolymer membrane instead of either pure cellulose acetate or polycarbonate.

TABLE 3

	AREA, FT ²	STREAM	FLOW, SCFH	CONC., VOL%	PRESS., PSIA
STAGE 1 SILICONE POLYCARBONATE INTRINSIC PERMEABILITIES (BARRER/CM X 10000) CO ₂ : 970 N ₂ : 70 SELECTIVITY CO ₂ /N ₂ : 14	2,261	FRESH FEED, F1 RETENTATE, R1 PERMEATE, P1	39,621 36,095 14,665	11.7 3.4 49.1	90 80 15
STAGE 2 POLYCARBONATE INTRINSIC PERMEABILITIES (BARRER/CM X 10000) CO ₂ : 35 N ₂ : 0.875 SELECTIVITY CO ₂ /N ₂ : 40	4,598	FEED, F2 RETENTATE, R2 PERMEATE, P2	14,664 11,121 3,543	49.1 34.2 96.0	100 90 15

Note that in this case the first stage requires even less area, about 2,261 square feet of membrane, and the combined stages a total area of only about 6,859 square feet of membrane, to achieve the same results, i.e., ≥ 96.0 vol% CO₂. The process in Table 3 represents a preferred embodiment of the present invention.

For any user of the process and apparatus of the present invention, a major benefit is a substantial reduction in the total membrane area required to accomplish a particular desired gas separation. For any given total membrane area, this invention provides substantially higher productivity. For example, comparing Tables 1 and 3, there is shown an 90.0% reduction in membrane area for a feed stream of about 37,973 to 39,621 standard cubic feet per hour (scfh). For any given area the present invention as described

in Table 3 can process 11.3 (feed flux ratio) times the feed flow compared with the homogeneous membrane process shown in Table 1.

5 The general process steps of the present invention are further described below, together with further explanation with respect to Figure 3 and the data given in Table 3 as a specific preferred example of the present invention. Herein, all parts and percentages (%) are by volume, also equivalent to mole
10 fraction, unless otherwise indicated.

The present invention is further discussed particularly in terms of a preferred embodiment of the present invention wherein the membrane feed stream is the product of the combustion of any hydrocarbon fuel,
15 such as fossil fuel, in air. However, if a process stream is available which comprises 40 vol% or less CO₂, the balance typically air or nitrogen or any other less permeable gas or gases, the same can be processed in accordance with the present invention. The process
20 of the present invention is even more preferred in the case of using a process gas stream containing 25 vol% or less CO₂, and is especially preferred in the case of using a process gas stream containing 11.7 vol% or less CO₂.

25 A typical exhaust of a natural gas or methane combustion device has a composition of about 11.7% carbon dioxide and 88.3% N₂ based on stoichiometric composition after cleaning and dehydrating steps. The

PCT/US 95/12364
IPEA/US 29 JUL 1996

pre-treated feed stream is then compressed to about 90
pounds per square inch absolute (psia) (465 cm Hg) and
cooled to the recommended membrane operating
temperature range of about 25°C (77°F) to 50°C
5 (122°F). The compressed feed gas mixture then enters
the first stage membrane of a two stage membrane
process according to this invention. The first stage
membrane is composed of a silicone/polycarbonate
copolymer with a perma-selective layer of about
10 0.0001cm (1 mm or 10,000 Angstrom). Under these
conditions of feed gas composition, pressure, and
flux, the permeate gas recovered contains about 85% of
the incoming carbon dioxide at about 40 vol% purity.
The calculated permeate flux gives a membrane area
15 factor of about 256 square feet per 100 pounds of
carbon dioxide in the first stage permeate. The fresh
feed, F1, as shown in Table 3 is about 39,621 scfh.
The fresh feed F1 combined with the retentate recycle
R2 from the second stage is about 50,748 scfh, and the
20 area factor calculated above determines a required net
membrane area of about 2,261 square feet in the first
stage. The resultant first stage permeate flow P1 of
about 14,666 scfh is compressed to about 100 psia (517
cm Hg) and cooled to the required membrane temperature
25 as above to become F2, the second stage feed gas.

The second stage feed gas F2 then enters the
secondary and final stage membrane which is composed
of a polycarbonate polymer with a perma-selective

WO 96/11048

PCT/US95/12364

layer of about 0.00001cm (0.1 mm or 1,000 Angstrom).

Under these conditions of feed composition, pressure and flux, the second stage permeate has a purity of about 96.0 vol%. The calculated permeate flux gives a membrane area factor of about 1,103 square feet per 100 pounds of carbon dioxide in the secondary stage permeate. The secondary stage feed gas F2, from Table 3, is about 14,666 scfh, and the area factor above determines a required membrane area of about 4,598 square feet in the secondary stage.

The total membrane area of both stages in the preferred embodiment is about 6,859 square feet, in which the first relatively high intrinsic permeability membrane separator, or silicone polycarbonate copolymer stage, comprises about 33.0% of the total membrane area and the second relatively low intrinsic permeability membrane separator, or polycarbonate stage, comprises stage the balance. By comparison, if both membrane stages are composed of the relatively low intrinsic permeability polycarbonate membrane as shown in Table 1, the total membrane area required for the same separation and process flow is about 75,313 square feet, with about 93.9% of the total, or 70,713 square feet, comprising the first stage. Thus a major benefit of the present invention is a very large reduction in membrane area. Conversely, for a specified size membrane system, the present invention

provides very large increases (e.g., 1130%) in process capacity.

5 This preferred embodiment of the present invention also provides as a by-product a first stage retentate stream with relatively high nitrogen purity of about 97%, the balance carbon dioxide. Though this nitrogen purity may be considered medium in a scale of low to high purity, the stream can be used as a general purpose inert gas because carbon dioxide is
10 also inert. The by-product retentate of this composition may be used or further purified to yield high purity nitrogen as desired.

The very high purity permeate product stream P2 in the preferred embodiment described above is
15 subsequently desirably compressed to about 260 psia and sub-cooled to about -14_F, which is the dew point of a 99.95 vol% carbon dioxide gas mixture. The liquid carbon dioxide so produced may either be stored or used for any useful purpose.

20 Also with respect to the preferred embodiment described above, means for pre-treating, cooling, transporting, and compressing the various process streams in the present invention includes but is not limited to those described in U.S. Patent 5,233,837 to
25 Callahan.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that

WO 96/11048

PCT/US95/12364

various changes and modifications can be made therein
without departing from the spirit and scope thereof.

Enerflex, Inc.
PO Box 1408
237 Commerce Street
Williston, VT 05495

ANNEX 1

September 9, 2004

TABLE 1 (Homogeneous Membrane Process)

	area m ²	scfh	scmh	CO ₂ %	CO ₂ scmh	Press. kPa	feed flux (V)	$P_{CO_2}/L \times 10^4 =$	$P_{N_2}/L \times 10^4 =$	Q _{CO₂N₂}	CO ₂ scmh	Stage CO ₂ % recovery
PC	6569.45						(F ₁)/total area	$V_{CO_2}/(P_{1CO_2} - P_{2CO_2})$	$V_{N_2}/(P_{1N_2} - P_{2N_2})$			
F ₁		37973	1076	11.7%	126	620.528					125.9	
F ₁ +R ₂		41766	1183	12.8%	152						152.0	
R ₁		34443	976	3.1%	30	551.581					30.2	
P ₁		7336	208	58.9%	122	103.421		35.208	0.875	40.2	122.4	80.5%
PC	427.35											
F ₂		7336	208	58.9%	122	689.476					122.4	
R ₂		3793	107	24.3%	26	620.528					26.1	
P ₂		3542	100	96.0%	96	103.421		35.030	0.868	40.4	96.3	78.7%
total	6996.8						0.154					

TABLE 2 (non-Homogeneous Membrane Process)

	area m ²	scfh	scmh	CO ₂ %	CO ₂ scmh	Press. kPa	feed flux (V)	$P_{CO_2}/L \times 10^4 =$	$P_{N_2}/L \times 10^4 =$	Q _{CO₂N₂}	CO ₂ scmh	Stage CO ₂ % recovery
CA	1863.17						(F ₁)/total area	$V_{CO_2}/(P_{1CO_2} - P_{2CO_2})$	$V_{N_2}/(P_{1N_2} - P_{2N_2})$			
F ₁		37540	1063	11.7%	124	620.528					124.4	
F ₁ +R ₂		45013	1275	15.0%	191						190.7	
R ₁		33999	963	3.0%	29	551.581					28.9	
P ₁		11013	312	52.1%	163	103.421		110.338	5.500	20.1	162.5	85.2%
PC	426.7											
F ₂		11013	312	52.1%	163	689.476					162.5	
R ₂		7473	212	31.3%	66	620.528					66.3	
P ₂		3542	100	96.0%	96	103.421		35.009	0.871	40.2	96.3	59.3%
total	2289.87						0.464					

TABLE 3 (non-Homogeneous Membrane Process)

	area m ²	scfh	scmh	CO ₂ %	CO ₂ scmh	Press. kPa	feed flux (V)	$P_{CO_2}/L \times 10^4 =$	$P_{N_2}/L \times 10^4 =$	Q _{CO₂N₂}	CO ₂ scmh	Stage CO ₂ % recovery
SIL/PC	210.05						(F ₁)/total area	$V_{CO_2}/(P_{1CO_2} - P_{2CO_2})$	$V_{N_2}/(P_{1N_2} - P_{2N_2})$			
F ₁		39621	1122	11.7%	131	620.528					131.3	
F ₁ +R ₂		50742	1437	16.6%	239						239.1	
R ₁		36095	1023	3.4%	35	551.581					34.8	
P ₁		14665	415	49.1%	204	103.421		965.557	70.013	13.8	204.0	85.3%
PC	427.17											
F ₂		14665	415	49.1%	204	689.476					204.0	
R ₂		11121	315	34.2%	108	620.528					107.7	
P ₂		3543	100	96.0%	96	103.421		35.031	0.870	40.3	96.4	47.2%
total	637.22						1.761					

WHAT IS CLAIMED IS:

1. A membrane process for the production of a desired very high purity permeate gas product from a feed gas mixture containing less than 40 vol% of the desired permeate gas, which process comprises providing in a primary stage a process feed gas mixture to a primary membrane separator unit comprising a membrane having a relatively high intrinsic permeability, to provide an intermediate permeate gas and a retentate gas, and providing the intermediate permeate gas in a secondary stage to a secondary membrane separator unit comprising a membrane having a relatively high selectivity, to produce therefrom the very high purity permeate gas product.

2. A membrane process as in claim 1, wherein the primary membrane separator unit comprises a membrane with an intrinsic permeability of more than $250 \text{ Barrer/cm} \times 10^4$.

3. A membrane process as in claim 1, wherein the secondary membrane separator unit comprises a membrane with an intrinsic permeability of $250 \text{ Barrer/cm} \times 10^4$ or less.

4. A membrane process as in claim 1, wherein the primary membrane separator unit comprises a membrane with an intrinsic permeability of more than $250 \text{ Barrer/cm} \times 10^4$ and the secondary membrane

separator unit comprises a membrane with an intrinsic permeability of less than 250 Barrer/cm x 10⁴.

5 5. A membrane process as in claim 1 wherein the intermediate permeate gas comprises from 40 vol% to 80 vol% of the gas to be provided as the very high purity permeate gas product.

6. A membrane process as in claim 1 which further comprises using products of fossil fuel combustion as the process feed gas mixture.

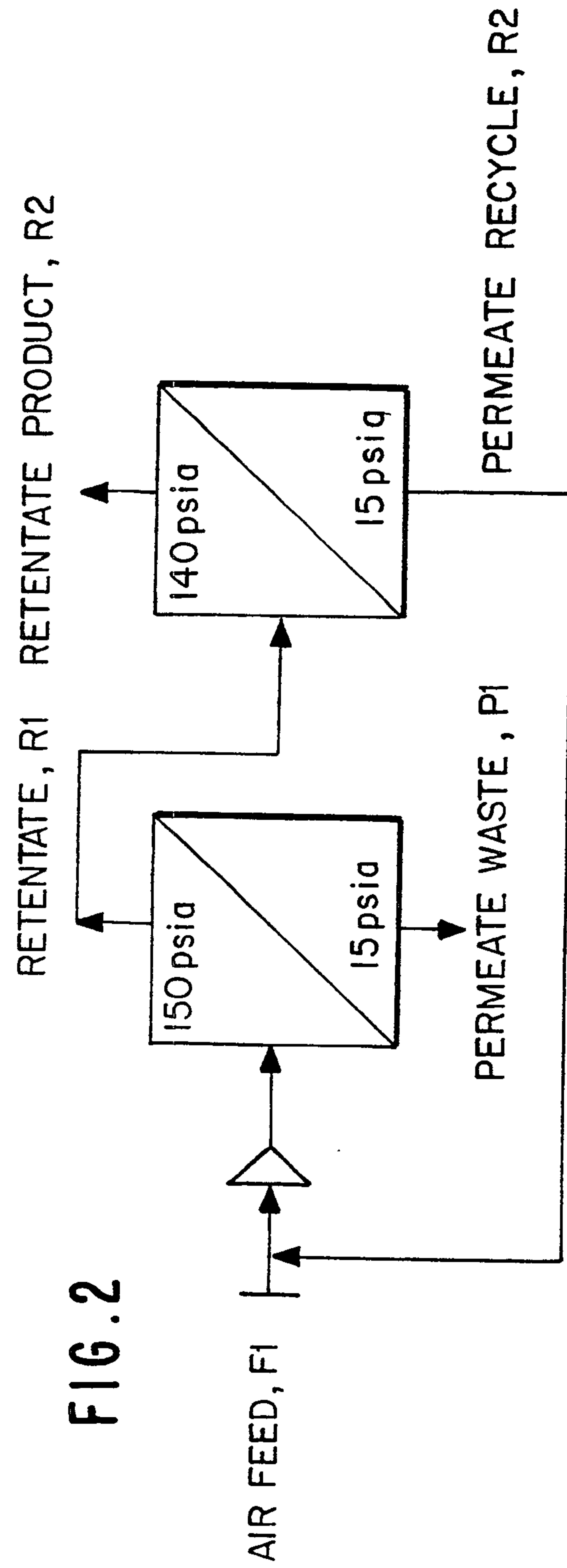
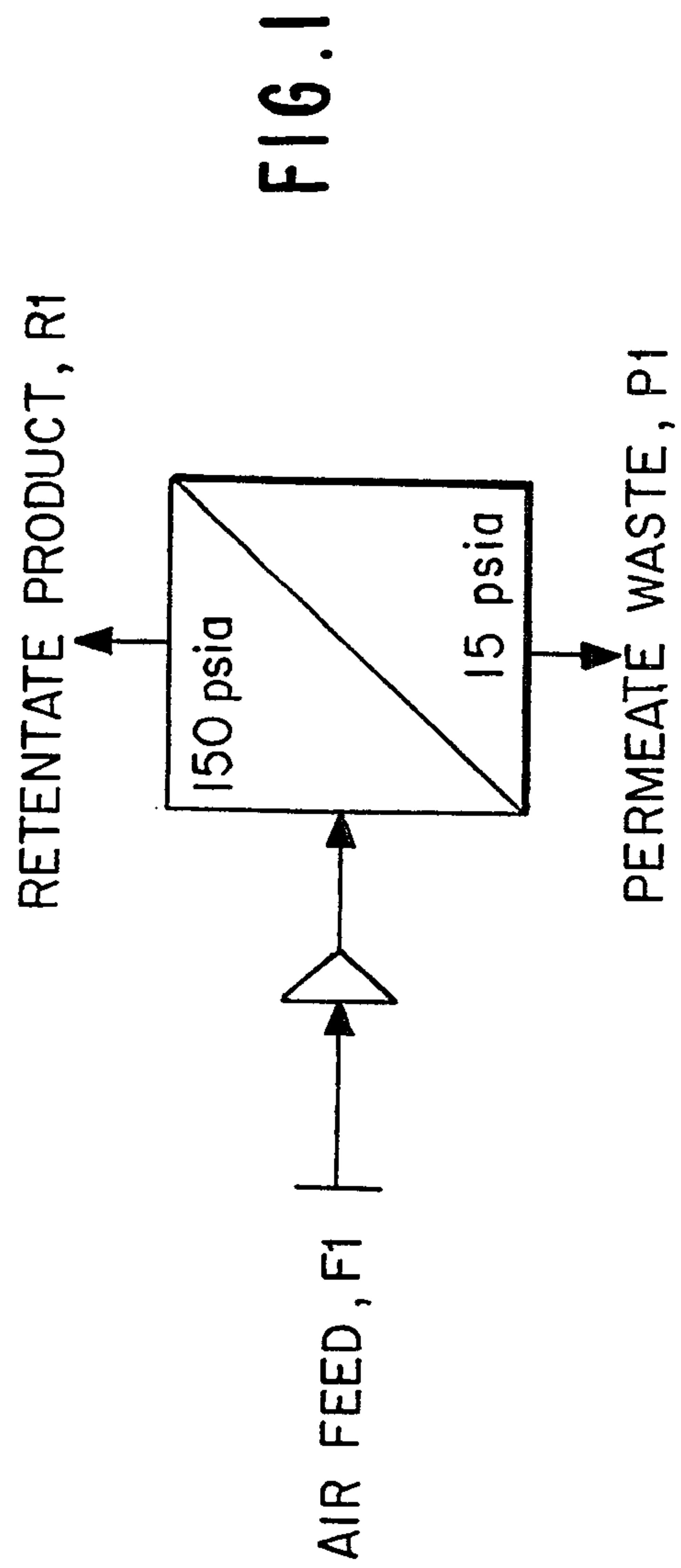
10 7. A membrane process as in claim 1 which further comprises using products of hydrocarbon combustion in air as the process feed gas mixture.

15 8. A membrane process as in claim 1 which further comprises using products of fossil fuel combustion in a limekiln as the process feed gas mixture.

9. A membrane process as in claim 1, wherein the process feed gas mixture is a process gas stream containing 25 vol% or less of carbon dioxide.

20 10. A membrane process as in claim 1, wherein the process feed gas mixture is a process gas stream containing 11.7 vol% or less of carbon dioxide.

25 11. A membrane process as in claim 1, wherein the process feed gas mixture contains carbon dioxide and carbon dioxide is recovered as the very high purity permeate gas product at a purity of more than 96.0 vol%.



2/2

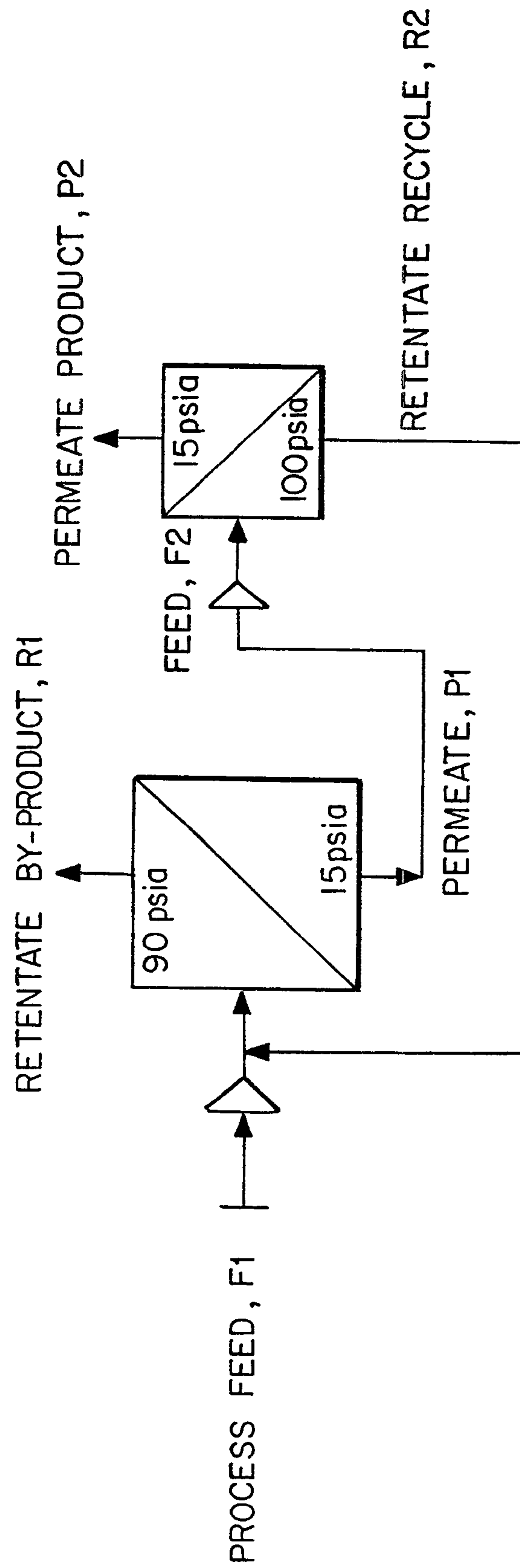


FIG. 3

