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(54) **MULTIPLE STAGE SEMI-PERMEABLE MEMBRANE GAS SEPARATION PROCESS**

MEHRSTUFIGES TRENNVERFAHREN MIT SEMIPERMEABLEN MEMBRANEN

PROCEDE A PLUSIEURS ETAPES DE SEPARATION DE GAZ PAR MEMBRANES SEMI-PERMEABLES

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Description

FIELD OF THE INVENTION

[0001] 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 mixed. The more permeable gas, carbon dioxide, is separated and concentrated by permeating through specific membrane stages to a high purity.

BACKGROUND OF THE INVENTION

[0002] 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% CO_2. The nature and composition of the membrane material is described in 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.

[0003] 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 CO_2 liquefier, such 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 it not readily available.

[0004] U.S. Patent 5,102,432 to Prasad describes 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.

[0005] From WO-A-19/358 a fractionation process is known, for treating a gas stream containing organic vapor in a concentration technically or economically difficult to treat by standard waste control methods. Typically this concentration will be about 0.1-10 % organic vapor. The process involves running the stream through a membrane system containing one or more membranes selectively permeable to the organic vapor component of the gas stream. The fractionation produces two streams: a product residue stream containing the organic vapor in a concentration less than about 0.5 % and a product permeate stream highly enriched in organic vapor content Both residue and permeate streams are then suitable for treatment by conventional separations or waste control technologies. The low concentration residue stream might be passed to carbon adsorption beds, for example, and the high concentration permeate stream might be subjected to condensation or incineration.

[0006] 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

[0007] In accordance with the present invention, there is provided a membrane process according to claim 1. Preferably, the membrane of the primary membrane separator unit has an intrinsic permeability of more than 250 Barrer/cm x 10^4. Also preferably, the membrane of the secondary membrane separator unit has an intrinsic permeability of 250 Barrer/cm x 10^4 or less.

[0008] 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

[0009]

Figure 1 illustrates a conventional one stage membrane separation process wherein a highly purified retentate N_2

product is obtained by subjecting air to a separator unit comprising a conventional polymer membrane.

Figure 2 illustrates a two stage process wherein N_2 gas is produced as a highly purified retentate gas in a two stage membrane process, with recycling of the N_2-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

[0010] 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 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.

[0011] 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.

[0012] The generally accepted unit of permeability is known as the Barrer, and is usually expressed in the following units: $P=(cm^3*cm)\_(cm^{2*}sec*cm\ Hg)*10^{-10}$. The intrinsic permeability is permeability divided by the membrane permaselective barrier thickness, and is usually expressed in the following units: $P/L = (cm^3)\ \_(cm^2 \times sec \times cm\ Hg) \times 10^{-10}$, wherein L is the barrier thickness (in cm).

[0013] The selectivity of a more permeable gas over a less permeable gas is defined as the ratio of their permeabilities. Intrinsic permeabilities in Barrers/cm x 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 L=0.0001 cm	cellulose acetate L=0.00001cm	polycarbonate L=0.00001cm
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
Selectivity Ratios			
CO_2/N_2	13.86	20.0	40.0
O_2/N_2	2.29	6.0	6.0

[0014] 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 (p1 - p2) 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 (p1 - p2).

[0015] 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.

[0016] 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 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.

[0017] 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%.

[0018] 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.

[0019] 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.

[0020] 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 natural gas combustion exhaust after the water of combustion is removed.

[0021] Table 1 shows that the first stage requires about 6 569.45 square metres (70 713 square feet) of membrane and the second stage requires about 427.35 square metres (4 600 square feet) of membrane, or a total area of 6 996.80 square metres (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	*STREAM*	*FLOW*	*CONC., VOL%*	*PRESS.*
STAGE 1 POLYCARBONATE INSTRINSIC PERMEABILITIES	**6 569.45 m^2**	FRESH FEED, F1	**1 075.28 scmh** *(37 973 scfh)*	**11.7**	**620 528.13 Pa** *(90 psia)*
(BARRER/CM*10000) CO2:35 N2: 0,875 SELECTIVITY CO2/N2:40	*(70 713 ft^2)*	RETENTATE, R1	**975.32** scmh *(34 443 scfh)*	**3.1**	**551 580.56 Pa** *(80 psia)*
		PERMEATE, P_1	**207.73 scmh** *(7 336 scfh)*	**58.9**	**103 421.36 Pa** *(15 psia)*

(continued)

	AREA	STREAM	FLOW	CONC., VOL%	PRESS.
STAGE 2 POLYCARBONATE INSTRINSIC PERMEABILITIES (BARRER/CM*10000) CO2: 35 N2: 0,875 SELECTIVITY CO2/N2:40	**427.35 m^2** *(4 600 ft^2)*	FEED, F2	**207.73 scmh** *(7 336 scfh)*	**58.9**	**689 475.70 Pa** *(100 psia)*
		RETENTATE, R2	**107.41 scmh** *(3 793 scfh)*	**24.3**	**620 528.13 Pa** *(90 psia)*
		PERMEATE, P2	**100.30 scmh** *(3 542 scfh)*	**96.0**	**103 421.36 Pa** *(15 psia)*

[0022] 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	STREAM	FLOW	CONC., VOL%	PRESS.
STAGE 1 CELLULOSE TRIACETATE INSTRINSIC PERMEABILITIES (BARRER/CM*10000) CO2: 110 N2: 5,5 SELECTIVITY CO2/N2:20	**1 863.17 m^2** *(20 055 ft^2)*	FRESH FEED, F1	**1063.01 scmh** *(37540 scfh)*	**11.7**	**620 528.13 Pa** *(90 psia)*
		RETENTATE, R1	**962.74 scmh** *(33 999 scfh)*	**3.0**	**551 580.56 Pa** *(80 psia)*
		PERMEATE, P1	**311.85 scmh** *(11 013 scfh)*	**52.1**	**103 421.36 Pa** *(15 psia)*
STAGE 2 POLYCARBONATE INSTRINSIC PERMEABILITIES (BARRER/CM*10000) CO2: 35 N2: 0,875 SELECTIVITY CO2/N2:40	**426.70** m^2 *(4 593 ft^2)*	FEED, F2	**311.85 scmh** *(11013 scfh)*	**52.1**	**689 475.70 Pa** *(100 psia)*
		RETENTATE, R2	**211.61 scmh** *(7 473 scfh)*	**31.3**	**620 528.13 Pa** *(90 psia)*
		PERMEATE, P2	**100.30 scmh** *(3 542 scfh)*	**96.0**	**103 421.36 Pa** *(15 psia)*

[0023] Quite significantly, in this case it has been found that the first stage requires only about 1 863.17 square metres (20 055 square feet) of membrane, and the combined stages require only a total area of only about 2 289.87 square metres (24 648 square feet), to achieve the same results.

[0024] 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	STREAM	FLOW	CONC., VOL %	PRESS.
STAGE 1 SILICONE POLYCARBONATE INSTRINSIC PERMEABILITIES	**210.05 m^2**	FRESH FEED, F1	**1 121.94 scmh** *(39621 scfh)*	**11.7**	**620 528.13 Pa** *(90 psia)*

(continued)

	AREA	*STREAM*	*FLOW*	*CONC., VOL %*	*PRESS.*
(BARRER/CM*10000) CO2: 970 N2: 70 SELECTIVITY CO2/N2: 14	*(2 261 ft^2)*	RETENTATE, R1 PERMEATE, P1	**1022.10 scmh** *(36 095 scfh)* **415.27 scmh** *(14 665 scfh)*	**3.4** **49.1**	**551 580.56 Pa** *(80 psia)* **103 421.36 Pa** *(15 psia)*
STAGE 2 POLYCARBONATE INSTRINSIC PERMEABILITIES (BARRER/CM*10000) CO2:35 N2: 0,875 SELECTIVITY CO2/N 40	**427.17 m^2** *(4 598 ft^2)*	FEED, F2 RETENTATE, R2 PERMEATE, P2	**415.24 scmh** *(14 664 scfh)* **314.91 scmh** *(11 121scfh)* **100.33 scmh** *(3 543 scfh)*	**49.1** **34.2** **96.0**	**689 475.70 Pa** *(100 psia)* **620 528.13 Pa** *(90 psia)* **103 421.36 Pa** *(15 psia)*

[0025] Note that in this case the first stage requires even less area, about 210.05 square metres (2 261 square feet) of membrane, and the combined stages a total area of only about 637.22 square metres (6 859 square feet) of membrane, to achieve the same results, i.e., ≥ 96.0 vol% CO_2. The process in Table 3 represents a preferred embodiment of the present invention.

[0026] 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 1 075.28 to 1 121.94 standard cubic metres per hour "scmh" (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.

[0027] 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 fraction, unless otherwise indicated.

[0028] 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, such as fossil fuel, in air. However, if a process stream is available which comprises 40 vol% or less CO_2, 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 of the present invention is even more preferred in the case of using a process gas stream containing 25 vol% or less CO_2 and is especially preferred in the case of using a process gas stream containing 11.7 vol% or less CO_2.

[0029] A typical exhaust of a natural gas or methane combustion device has a composition of about 11.7% carbon dioxide and 88.3% N_2 based on stoichiometric composition after cleaning and dehydrating steps. The pre-treated feed stream is then compressed to about 620 528.13 pascal "Pa" - (90 pounds per square inch absolute "psia" or 465 cm Hg) and cooled to the recommended membrane operating temperature range of about 25°C (77°F) to 50°C (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 0.0001 cm (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 factor of about 23.78 square metres per 45.36 kilogram (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 1 121.94 scmh (39 621 scfh). The fresh feed F1 combined with the retentate recycle R2 from the second stage is about 1 437.02 scmh (50 748 scfh), and the area factor calculated above determines a required net membrane area of about 210.05 square metres (2261 square feet) in the first stage. The resultant first stage permeate flow P1 of about 415.29 scmh (14 666 scfh) is compressed to about 689 475.7 Pa (100 psia or 517 cm Hg) and cooled to the required membrane temperature as above to become F2, the second stage feed gas.

[0030] 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 layer of about 0.00001 cm (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 102.47 square metres (1 103 square feet) per 45.36 kilograms (100 pounds) of carbon dioxide in the secondary stage permeate. The secondary stage feed gas F2, from Table 3, is about 415.29 scmh (14 666 scfh), and the area factor above determines a required membrane area of about 427.17 square metres (4 598 square feet) in the secondary stage.

[0031] The total membrane area of both stages in the preferred embodiment is about 637.22 square metres (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 6 996.80 square metres (75 313 square feet), with about 93.9% of the total, or 6 569.45 square metres (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.

[0032] 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 also inert. The by-product retentate of this composition may be used or further purified to yield high purity nitrogen as desired.

[0033] The very high purity permeate product stream P2 in the preferred embodiment described above is subsequently desirably compressed to about 1 792 636.82 Pa (260 psia) and sub-cooled to about -25.56°C (-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.

[0034] 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 Callahan, hereby incorporated by reference.

Claims

1. A membrane process for the production of a desired very high purity permeate gas product from a feed gas mixture containing less than 40vol% 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, 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. A membrane process as in claim 1, wherein the primary membrane separator unit comprises a membrane with an intrinsic permeability of more than 250 Barrer/cm x 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 Barrer/cm x 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 Barrer/cm x 10^4 and the secondary membrane separator unit comprises a membrane with an intrinsic permeability of less than 250 Barrer/cm x 10^4.

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.

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

8. A membrane process as in claim 1 which further comprises using products of fossil fuel combustion in a lime kiln 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.

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.

Patentansprüche

1. Membranverfahren für die Herstellung eines gewünschten hochreinen Permeationsgasprodukts aus einer Speisegasmischung, die weniger als 40 Vol.-% des gewünschten Permeationsgases enthält, umfassend in einer primären Stufe die Zuführung einer Prozess-Speisegasmischung in eine primäre Membrantrenneinheit, die eine Membran mit relativ hoher Eigenpermeabilität umfasst, um ein intermediäres Permeationsgas und ein Retentionsgas zu ergeben, und die Zuführung des intermediären Permeationsgases in einer sekundären Stufe in eine sekundäre Membrantrenneinheit, die eine Membran mit relativ hoher Selektivität umfasst, um daraus das hochreine Permeationsgasprodukt herzustellen, wobei die Prozess-Speisegasmischung Kohlendioxid enthält und Kohlendioxid als das hochreine Permeationsgasprodukt mit einer Reinheit von mehr als 96,0 Vol.-% gewonnen wird.

2. Membranverfahren nach Anspruch 1, wobei die primäre Membrantrenneinheit eine Membran mit einer Eigenpermeabilität von mehr als 250 Barrer/cm·10^4 umfasst.

3. Membranverfahren nach Anspruch 1, wobei die sekundäre Membrantrenneinheit eine Membran mit einer Eigenpermeabilität von 250 Barrer/cm·10^4 oder weniger umfasst.

4. Membranverfahren nach Anspruch 1, wobei die primäre Membrantrenneinheit eine Membran mit einer Eigenpermeabilität von mehr als 250 Barrer/cm·10^4 und die sekundäre Membrantrenneinheit eine Membran mit einer Eigenpermeabilität von weniger als 250 Barrer/cm·10^4 umfasst.

5. Membranverfahren nach Anspruch 1, wobei das intermediäre Permeationsgas 40 Vol.-% bis 80 Vol.-% des Gases umfasst, das als hochreines Permeationsgasprodukt zur Verfügung gestellt werden soll.

6. Membranverfahren nach Anspruch 1, des Weiteren umfassend die Verwendung von Produkten der fossilen Brennstoffverbrennung als Prozess-Speisegasmischung.

7. Membranverfahren nach Anspruch 1, des Weiteren umfassend die Verwendung von Produkten der Kohlenwasserstoff-Verbrennung an Luft als Prozess-Speisegasmischung.

8. Membranverfahren nach Anspruch 1, des Weiteren umfassend die Verwendung von Produkten der fossilen Brennstoffverbrennung in einem Kalkofen als Prozess-Speisegasmischung.

9. Membranverfahren nach Anspruch 1, wobei die Prozess-Speisegasmischung ein Prozessgasstrom ist, der 25 Vol.-% oder weniger Kohlendioxid enthält.

10. Membranverfahren nach Anspruch 1, wobei die Prozess-Speisegasmischung ein Prozessgasstrom ist, der 11,7 Vol.-% oder weniger Kohlendioxid enthält.

Revendications

1. Procédé à membrane pour produire un perméat gazeux de très grande pureté voulu à partir d'un mélange gazeux d'alimentation contenant moins de 40% en volume dudit perméat gazeux voulu, le procédé comprenant l'alimentation, dans un étage primaire, d'un mélange gazeux de procédé dans une unité de séparation à membrane primaire comprenant une membrane ayant une perméabilité intrinsèque relativement élevée, afin d'obtenir un perméat gazeux intermédiaire et un rétentat gazeux et, dans un étage secondaire, l'alimentation du perméat gazeux intermédiaire dans une unité de séparation à membrane secondaire comprenant une membrane ayant une sélectivité relativement

élevée, afin de produire à partir de là le perméat gazeux de très grande pureté, dans lequel le mélange gazeux d'alimentation de procédé contient du' dioxyde de carbone et du dioxyde de carbone est récupéré en tant que perméat gazeux de très grande pureté avec une pureté supérieure à 96,0% en volume.

2. Procédé à membrane selon la revendication 1, dans lequel l'unité de séparation à membrane primaire comprend une membrane ayant une perméabilité intrinsèque de plus de 250 barrers/cm x 10^4.

3. Procédé à membrane selon la revendication 1, dans lequel l'unité de séparation à membrane secondaire comprend une membrane ayant une perméabilité intrinsèque de 250 barrers/cm x 10^4 ou moins.

4. Procédé à membrane selon la revendication 1, dans lequel l'unité de séparation à membrane primaire comprend une membrane ayant une perméabilité intrinsèque de plus de 250 barrers/cm x 10^4 et l'unité de séparation à membrane secondaire comprend une membrane ayant une perméabilité intrinsèque de moins de 250 barrers/cm x 10^4.

5. Procédé à membrane selon la revendication 1, dans lequel le perméat gazeux intermédiaire comprend de 40% en volume à 80% en volume du gaz à alimenter, en tant que perméat gazeux de très grande pureté produit.

6. Procédé à membrane selon la revendication 1, qui comprend en plus l'utilisation de produits de la combustion de combustibles fossiles, en tant que mélange gazeux d'alimentation de procédé.

7. Procédé à membrane selon la revendication 1, qui comprend en plus l'utilisation de produits de la combustion d'hydrocarbures dans l'air, en tant que mélange gazeux d'alimentation de procédé.

8. Procédé à membrane selon la revendication 1, qui comprend en plus l'utilisation de produits de la combustion de combustibles fossiles dans un four à chaux, en tant que mélange gazeux d'alimentation de procédé.

9. Procédé à membrane selon la revendication 1, dans lequel le mélange gazeux d'alimentation de procédé est un flux de gaz de procédé contenant 25% en volume ou moins de dioxyde de carbone.

10. Procédé à membrane selon la revendication 1, dans lequel le mélange gazeux d'alimentation de procédé est un flux de gaz de procédé contenant 11,7% en volume ou moins de dioxyde de carbone.

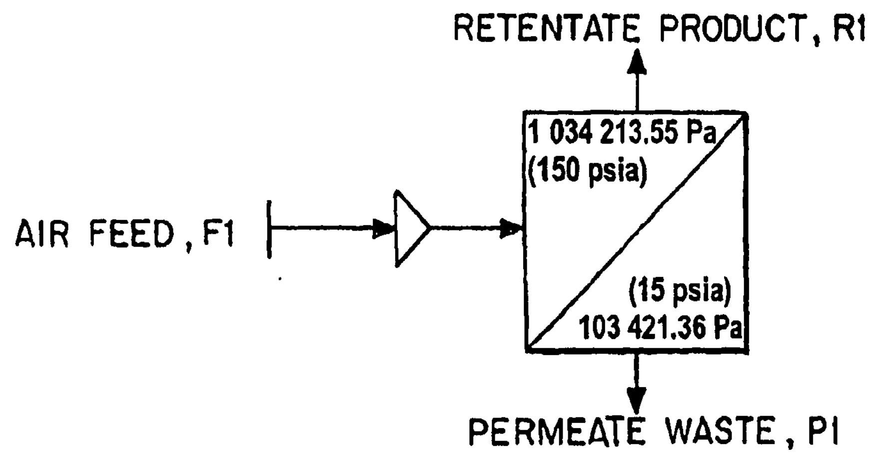
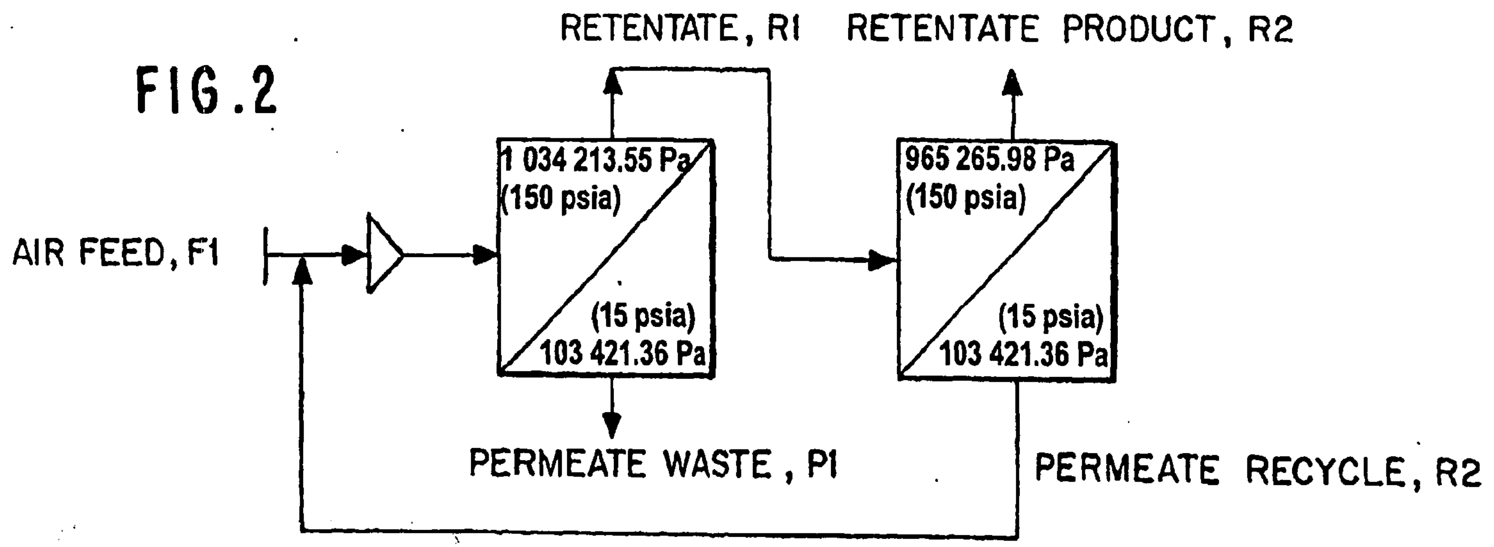

RETENTATE PRODUCT, R1
AIR FEED, F1
1 034 213.55 Pa
(150 psia)
(15 psia)
103 421.36 Pa
PERMEATE WASTE, P1

FIG.1

FIG.2


RETENTATE, R1
RETENTATE PRODUCT, R2
AIR FEED, F1
1 034 213.55 Pa
(150 psia)
(15 psia)
103 421.36 Pa
965 265.98 Pa
(150 psia)
(15 psia)
103 421.36 Pa
PERMEATE WASTE, P1
PERMEATE RECYCLE, R2

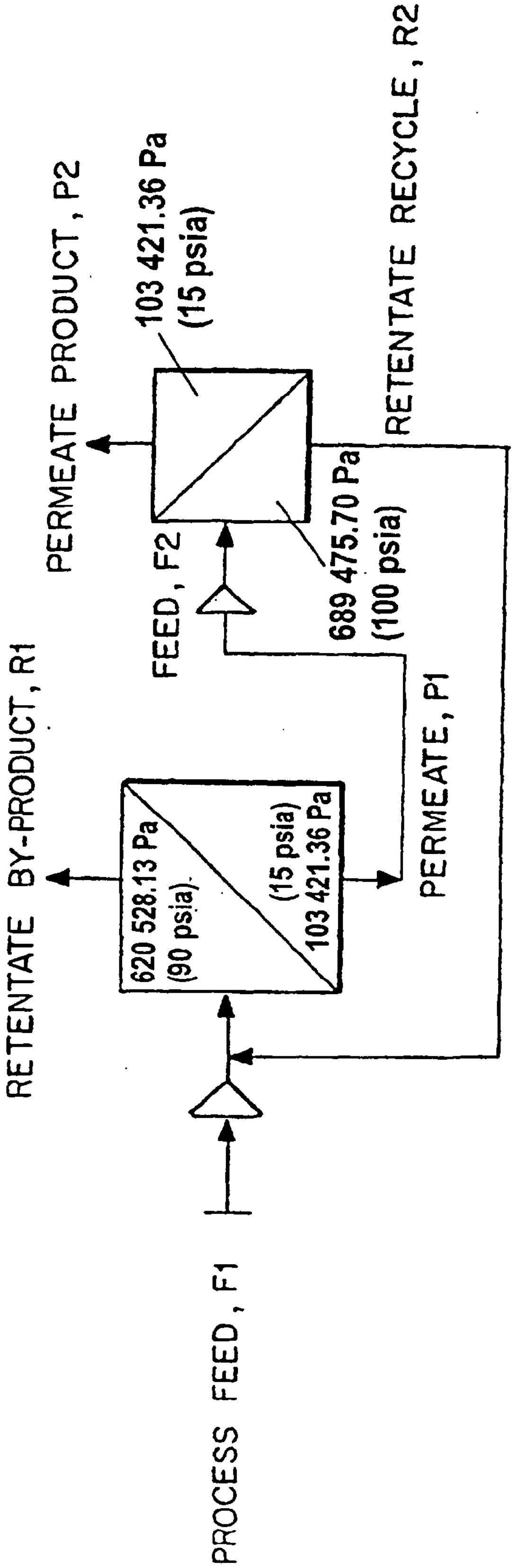

PROCESS FEED, F1
RETENTATE BY-PRODUCT, R1
620 528.13 Pa
(90 psia)
(15 psia)
103 421.36 Pa
PERMEATE, P1
FEED, F2
689 475.70 Pa
(100 psia)
103 421.36 Pa
(15 psia)
PERMEATE PRODUCT, P2
RETENTATE RECYCLE, R2

FIG. 3

REFERENCES CITED IN THE DESCRIPTION

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