US 20040000513A1

(19) United States

(12) Patent Application Publication (10) Pub. No.: US 2004/0000513 A1

Colling et al. (43) Pub. Date: Jan. 1, 2004

(54) APPARATUS USING SOLID PERM-SELECTIVE MEMBRANES IN MULTIPLE GROUPS FOR SIMULTANEOUS RECOVERY OF SPECIFIED PRODUCTS FROM A FLUID MIXTURE

(76) Inventors: **Craig W. Colling**, Warrenville, IL (US); **George A. Huff JR.**, Naperville, IL (US)

Correspondence Address:
CAROL WILSON
BP AMERICA INC.
MAIL CODE 5 EAST
4101 WINFIELD ROAD
WARRENVILLE, IL 60555 (US)

(21) Appl. No.: **10/183,793**

(22) Filed: **Jun. 27, 2002**

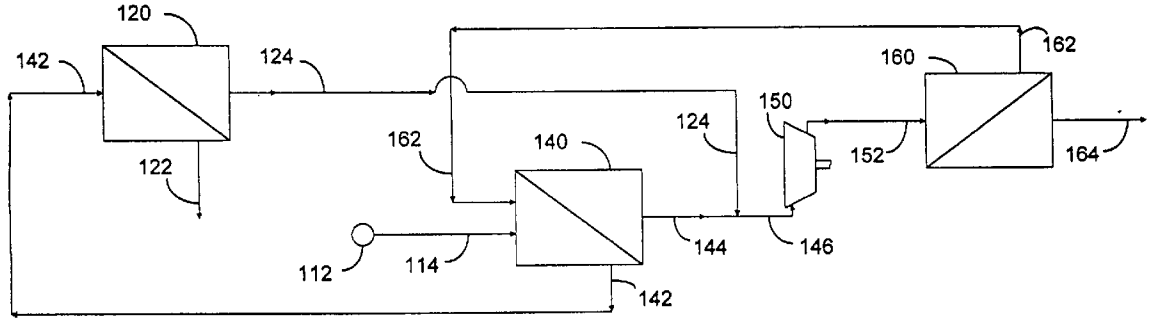
Publication Classification

(51) **Int. Cl.**[7] **B01D 63/00**

(52) **U.S. Cl.** **210/323.1**; 210/321.6

(57) **ABSTRACT**

Apparatus is disclosed for economical separation of fluid mixtures. Broadly, apparatus of the invention comprises modules using solid perm-selective membranes. More particularly, the invention relates to a plurality of membrane modules disposed in a first product group, a second product group, and optionally one or more intermediate group. Apparatus of the invention with the membrane modules in multiple groups is beneficially useful for simultaneous recovery of a very pure permeate product and a desired non-permeate product from a mixture containing organic compounds.



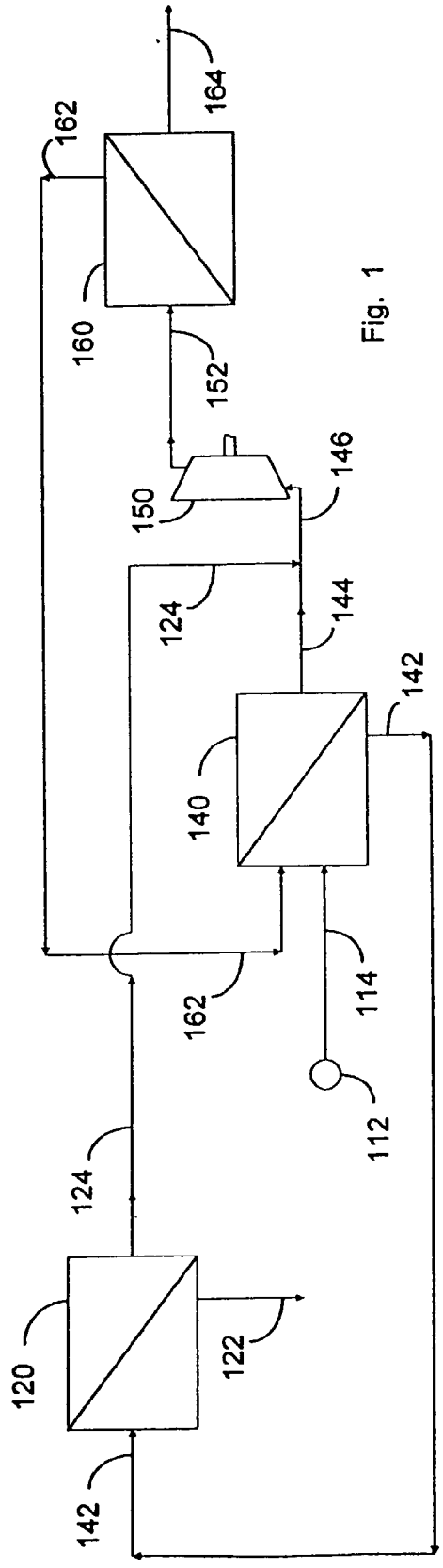

164
162
160
152
146
150
124
144
142
140
162
114
112
124
120
122
142

Fig. 1

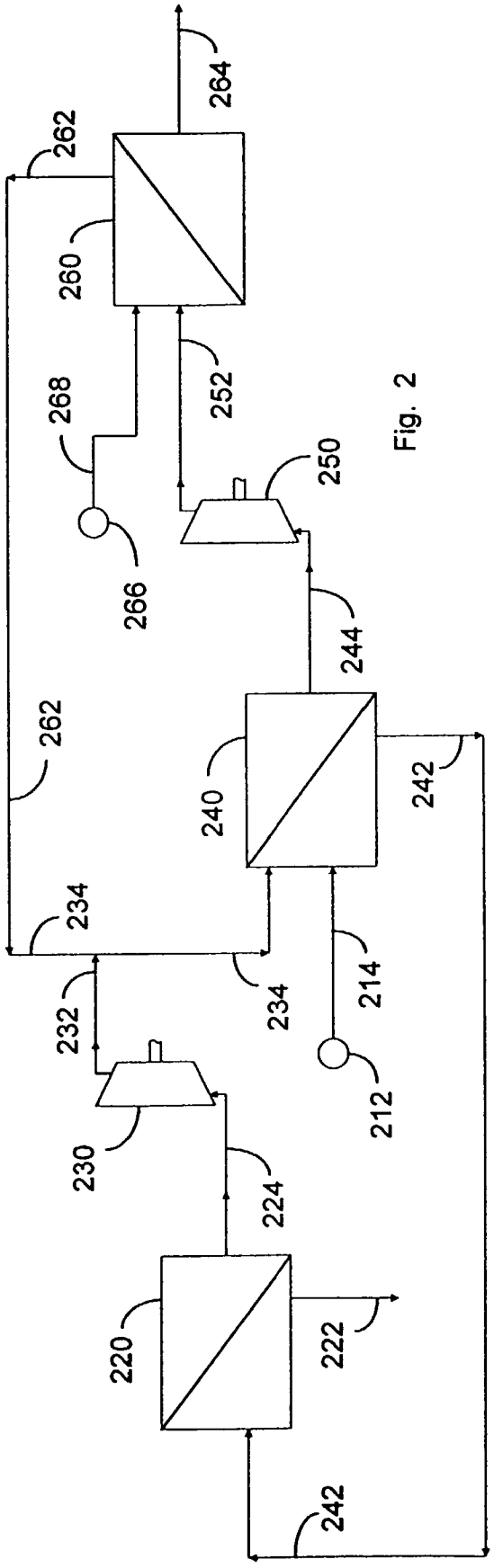

264
262
260
252
268
250
266
244
262
240
242
234
234
214
232
212
230
224
220
222
242

Fig. 2

APPARATUS USING SOLID PERM-SELECTIVE MEMBRANES IN MULTIPLE GROUPS FOR SIMULTANEOUS RECOVERY OF SPECIFIED PRODUCTS FROM A FLUID MIXTURE

TECHNICAL FIELD

[0001] The present invention relates to novel apparatus for separation of fluid mixtures. Broadly, apparatus of the invention comprises modules using solid perm-selective membranes. More particularly, the invention relates to a plurality of membrane modules disposed in a first product group, a second product group, and optionally one or more intermediate groups. Apparatus of the invention with the membrane modules in multiple groups is beneficially useful for simultaneous recovery of a very pure permeate product and a desired non-permeate product from a mixture containing organic compounds.

BACKGROUND OF THE INVENTION

[0002] Membranes useful for the separation of gaseous mixtures are of two very different types: one is microporous while the other is nonporous. Discovery of the basic laws governing the selectivity for gases effusing through a microporous membrane is credited to T. Graham. When the pore size of a microporous membrane is small compared to the mean-free-path of non-condensable gas molecules in the mixture, the permeate is enriched in the gas of the lower molecular weight. Practical and theoretical enrichments achievable by this technique are very small because the molecular weight ratios of most gases are not very large and the concomitant selectivities are proportional to the square roots of these ratios. Therefore, a large number of separation stages is needed to effect an efficient separation of a given gas from a gaseous mixture. However, because this method of separation relies solely on mass ratios and not chemical differences among the effusing species, it is the only membrane based method capable of separating isotopes of a given element. For this reason, this method was chosen to enrich uranium in the fissionable isotope 235 for development of the atomic bomb during World War II. However, this method of separation is inherently expensive due to the large amount of capital investment needed for processing a necessary large amount of gas, stringent membrane specifications requiring high porosity and small pore size, and high energy requirements for operation.

[0003] In nonporous membrane systems, molecules permeate through the membrane. During permeation across the nonporous membrane, different molecules are separated due to the differences of their diffusivity and solubility within the membrane matrix. Not only does molecular size influence the transport rate of each species through the matrix but also the chemical nature of both the permeating molecules and the polymer matrix itself. Thus, conceptually useful separations should be attainable.

[0004] The art is replete with processes said to fabricate membranes possessing both high selectivity and high fluxes. Without sufficiently high fluxes the required membrane areas required would be so large as to make the technique uneconomical. It is now well known that numerous polymers are much more permeable to polar gases (examples include H_2O, CO_2, H_2S, and SO_2) than to nonpolar gases (N_2, O_2, and CH_4), and that gases of small molecular size (He, H_2) permeate more readily through polymers than large molecules (CO, C_2H_4).

[0005] Another aspect of the art is related to two-stage and/or multi-stage membrane separation processes and apparatus for removing a component from a fluid stream. Such systems may be considered when a desired separation cannot be completed using avaiable membrane materials in a single stage. Several membrane permeator processes have been described, for example, S. Weller and W. Steiner published one of the first articles to address aspects of multi-stage membrane apparatus in "Engineering Aspects of Gases Fractional Permeation Through Membranes" in Chem. Eng. Prog. 46, 585-590 (1950).

[0006] More recently, U.S. Pat. Nos. 5,256,295 and 5,256,296 in the name of Richard W. Baker and Johannes G. Wijmans relate to membrane separation systems having an auxiliary membrane module installed across the pump that drives the main membrane unit, so that the permeate streams from the main and auxiliary membrane units are mixed and pass together through a common driving pump. The concentration of the mixed permeate stream is said to build up by circulating the stream through the auxiliary unit, and where the concentration reaches a desired level, the mixed stream can be tapped and the product stream drawn off. An auxiliary membrane module is also described as being installed across the second stage of the two-stage membrane separation system. The driving force for the auxiliary module is provided by the pump or other driving unit for the first membrane stage. The auxiliary module provides additional treatment of the residue stream from the second membrane stage, but is driven by the first stage driving unit. Baker and Wijmans did not discover that the efficiency of this design can be dramatically improved by choosing a different feed position. Location of the feed position for multi-stage systems becomes critical to the recovery of two products.

[0007] U.S. Pat. Nos. 5,102,432 and 5,709,732 in the name of Ravi Prasad relate to three-stage membrane gas separation systems for air. U.S. Pat. No. 5,102,432 is directed to production of very high purity nitrogen by separation of air in a three stage membrane system in which the permeate from the product stage is recycled to the intermediate second stage and permeate from this second stage is recycled to the feed stage with the membrane surface area being distributed between the stages to recovery a single purified product. U.S. Pat. No. 5,709,732 is directed to production of purified oxygen gas (60-90% purity) from ambient air in systems of at least three permeator stages which together use less than one compressor per stage. In this three-stage system the permeate from the product stage is the purified oxygen gas, the non-permeate from the product stage is recycled to the intermediate stage (identified as stage 1), non-permeate from this intermediate stage is recycled to the feed stage (identified as stage 2), and the non-permeate effluent of the feed stage is the oxygen depleted waste stream. Only a single purified product is recovered.

[0008] More recently U.S. Pat. No. 5,873,928 in the name of Richard A. Callahan describes a membrane process for the production of a desired very high purity permeate gas by use of a two-stage membrane process. A process feed gas mixture is provided to a primary unit comprising a membrane having a relatively high intrinsic permeability to provide an intermediate permeate gas and a retentate by-product, and the intermediate permeate gas is provided to a secondary membrane unit comprising a membrane having a

relatively low intrinsic permeability to produce therefrom a very high purity permeate gas product. The non-permeate from the secondary membrane unit is recycled with the feed gas mixture to the primary unit.

[0009] Although Callahan claimed reduced membrane area as the advantage of the process, the required recycle rate increased significantly. Considering that increased recycle requires higher compression and operating costs, little, if any, overall benefit is suggested for this process.

[0010] An article by T. Peterson and K. Lien entitled "Design Studies of Membrane Permeator Processes for Gas Separations" in Gas Sep. Purif. 9, 151-169 (1995) examined the effect of using different membrane materials at each state of a multi-stag membrane process, for the separation of CO_2 and CH_4. They concluded that the total costs of a multiple permeability membrane system are not significantly different than those of a single permeability membrane system.

[0011] Neither U.S. Pat. No. 5,873,928 nor the article by T. Peterson and K. Lien considered any possibility of purity specifications on both permeate and non-permeate products.

[0012] There is, therefore, a present need for processes and apparatus using perm-selective membranes for simultaneous recovery of a very pure permeate product and a desired non-permeate product, in contrast to by-product, waste streams, in particular, processes which do not have the above disadvantages. A further object of the invention is to provide inexpensive processes and apparatus for the efficient separation of chemical compounds from mixtures which are difficult to separate, e.g., separation of propane-propylene by fractional distillation.

[0013] Improved apparatus should provide for an integrated sequence, carried out with streams in gas and/or liquid state, using a suitable perm-selective membrane, preferably a solid perm-selective membrane which under a suitable differential of a driving force exhibits selective permeability of a desired product. Advantageously, apparatus using perm-selective membranes for simultaneous recovery of a very pure permeate product and a desired non-permeate product shall avoid or minimize formation of unwanted by-products, waste streams. Beneficially, an improved separation apparatus shall efficiently employ perm-selective membranes having the same or different pre-selected permeabilities, and with optimum distribution between stages so as to efficiently produce very high purity product.

SUMMARY OF THE INVENTION

[0014] In broad aspect, the present invention is directed to apparatus using solid perm-selective membranes for economical separation of fluid mixtures. More particularly, this invention relates to apparatus comprising a plurality of membrane modules disposed in a first product group, a second product group, and optionally one or more intermediate groups. Advantageously apparatus of the invention with the membrane modules in multiple groups is employed for simultaneous recovery of a very pure permeate product and a desired non-permeate product from a mixture containing organic compounds.

[0015] This invention contemplates the treatment of a fluid feedstock, e.g. various type organic materials, especially a fluid mixture of compounds of petroleum origin. In general, the fluid feedstock is a gaseous mixture comprising a more selectively permeable component and a less permeable component. Apparatus of the invention are particularly useful in processes for treatment of a gaseous mixture comprised of a more selectively permeable alkene component and a corresponding alkane component, e.g. the separation of propylene from propane.

[0016] In one aspect, the invention provides apparatus using perm-selective membranes in multiple groups for simultaneous recovery of a very pure permeate product and a desired non-permeate product from a fluid mixture of compounds. The apparatus comprises: a plurality of membrane modules disposed in a first product group, one or more intermediate groups, and a second product group, each module comprising a solid perm-selective membrane which under a suitable differential of a driving force exhibits a permeability of at least 0.1 Barrer, a channel having at least one inlet and one outlet for flow of fluid in contact with one side of a membrane, and contiguous with the opposite side thereof a permeate chamber having at least one outlet for flow of permeate; means for distribution of a fluid feedstock into the channel inlets of at least a portion of the intermediate group of modules; means for collection of permeate effluent from the chamber outlets of at least a portion of the intermediate group of modules and distribution of this intermediate permeate into the channel inlets of the first product group modules; means for collection of a permeate product effluent from the chamber outlets of the first product group of modules; means for collection of non-permeate effluent from the channel outlets of the first product modules and distribution thereof into the channel inlets of at least a portion of the intermediate group of modules; means for collection of non-permeate from the channel outlets of the intermediate group of modules and distribution of this intermediate non-permeate into the channel inlets of the second product group modules; means for collection of a non-permeate product effluent from the channel outlets of the second product group of modules; and means for collection of permeate effluent from the chamber outlets of the second product modules and distribution thereof into the channel inlets of the first product of modules.

[0017] The means for collection and distribution of permeate into the channel inlets of the first product group modules, advantageously comprises a compressor and/or pump, preferably a compressor.

[0018] Depending on the separation required to simultaneously recover a very pure permeate product and a desired non-permeate product from feed streams in a particular application, preferred embodiments of the invention further comprises means for distribution of another fluid feedstock into the channel inlets of the first and/or second product of modules. In another preferred embodiment of the invention, the apparatus further comprises means for distribution of another feedstock into the channel inlets of the first product of modules. Optionally, the apparatus may further comprises means for distribution of a "sweep" stream into the permeate chambers of one or more of the modules.

[0019] In another aspect, this invention provides apparatus using perm-selective membranes in multiple groups for simultaneous recovery of a very pure permeate product and a desired non-permeate product from a fluid mixture of compounds in which the apparatus comprises: a plurality of

membrane modules disposed in a first product group, one or more intermediate group, and a second product group, each module comprising a solid perm-selective membrane which under a suitable differential of a driving force exhibits a permeability of at least 0.1 Barrer, a channel having at least one inlet and one outlet for flow of fluid in contact with one side of a membrane, and contiguous with the opposite side thereof a permeate chamber having at least one outlet for flow of permeate; means for distribution of a first fluid feedstock into the channel inlets of at least a portion of the intermediate group of modules; means for collection of permeate effluent from the chamber outlets of at least a portion of the intermediate group of modules and distribution of this intermediate permeate into the channel inlets of the first product group modules; means for distribution of a second fluid feedstock into the channel inlets of the first product group of modules; means for collection of a permeate product effluent from the chamber outlets of the first product group of modules; means for collection of non-permeate effluent from the channel outlets of the first product modules and distribution thereof into the channel inlets of at least a portion of the intermediate group of modules; means for collection of non-permeate from the channel outlets of the intermediate group of modules and distribution of the non-permeate into the channel inlets of the second product group modules; means for collection of a non-permeate product effluent from the channel outlets of the second product group of modules; and means for collection of permeate effluent from the chamber outlets of the second product modules and distribution thereof into at least a portion of the channel inlets of the intermediate group of modules.

[0020] Depending on the separation required to simultaneously recover a very pure permeate product and a desired non-permeate product from feed streams in a particular application, preferred embodiments of the invention further comprises means for distribution of another fluid feedstock into the channel inlets of the second product of modules. In another preferred embodiment of the invention, the means for collection and distribution of permeate into the channel inlets of the first product group modules comprises a compressor, and/or the means for collection and distribution of permeate into at least a portion the channel inlets of the intermediate group modules comprises a compressor.

[0021] According to the invention, the membrane modules in a group having membranes of about the same selectivity which selectivity is about the same or may be critically different from that of the other group or groups. In one aspect of the invention the membrane modules in the second product group have membranes of lower selectivity than membranes in at least one of other group. Preferably, the membrane modules in the second product group have membranes of lower selectivity than membranes in the other groups.

[0022] In another aspect of the invention the membrane modules in at least a portion of the intermediate group have membranes of higher selectivity than membranes in at least one of the other groups. Advantageously, the membrane modules in the intermediate group have membranes of a selectivity which is about 35 percent or more higher than membranes another group, preferably at least about 50 percent higher, and more preferably at least about 100 percent higher. Preferably, the membrane modules in at least a portion of the intermediate group have membranes of higher selectivity than membranes in the other groups.

[0023] In other preferred embodiments, the membrane modules in the first product group have membranes of higher selectivity than membranes in at least one of the other groups. More preferably the membrane modules in the first product group have membranes of higher selectivity than membranes in the other groups.

[0024] This invention is particularly useful towards separations involving organic compounds, in particular compounds which are difficult to separate by conventional means such as fractional distillation. Typically, these include organic compounds are chemically related as for example alkanes and alkenes of similar carbon number.

[0025] For a more complete understanding of the present invention, reference should now be made to the embodiments illustrated in greater detail in the accompanying drawing and described below by way of examples of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] The invention is hereinafter described in detail with reference to the accompanying drawings in which are schematic flow diagrams depicting preferred aspects of the multi-stage membrane separation processes and apparatus of the present invention for simultaneous recover of a very pure permeate product and a desired non-permeate product from a fluid mixture of compounds.

[0027] **FIG. 1** is schematic drawing showing an embodiment of the present invention which includes three groups of perm-selective membrane modules, one feedstream location and a compressor.

[0028] **FIG. 2** is schematic drawing showing an embodiment of the present invention which includes three groups of perm-selective membrane modules, one and/or two feedstream locations and two compressors.

GENERAL DESCRIPTION

[0029] Any solid perm-selective membrane which under a suitable differential of a driving force exhibits a permeability and other characteristics suitable for the desired separations may be used according to the invention. Suitable membranes may take the form of a homogeneous membrane, a composite membrane or an asymmetric membrane which, for example may incorporate a gel, a solid, or a liquid layer. Widely used polymers include silicone and natural rubbers, cellulose acetate, polysulfones and polyimides.

[0030] Preferred membranes for use in vapor separation embodiments of the invention are generally of two types. The first is a composite membrane comprising a microporous support, onto which the perm-selective layer is deposited as an ultra-thin coating. Composite membranes are preferred when a rubbery polymer is used as the perm-selective material. The second is an asymmetric membrane in which the thin, dense skin of the asymmetric membrane is the perm-selective layer. Both composite and asymmetric membranes are known in the art. The form in which the membranes are used in the invention is not critical. They may be used, for example, as flat sheets or discs, coated hollow fibers, spiral-wound modules, or any other convenient form.

[0031] The driving forces for separation of vapor components by membrane permeation include, predominately their partial pressure difference between the first and second sides of the membrane. The pressure drop across the membrane can be achieved by pressurizing the first zone, by evacuating the second zone, introducing a sweep stream, or any combination thereof.

[0032] The membranes used in each group of modules may be of the same type or different. Although both units may contain membranes selective to the desired component to be separated, the selectivities of the membranes may be different. For example, where intermediate modules process the bulk of the fluid feedstock, these modules may contain membranes of high flux and moderate selectivity. The module group which deals with smaller streams, may contain membranes of high selectivity but lower flux. Likewise the intermediate modules may contain one type of membrane, and product modules may contain another type, or all three groups may contain different types. Useful embodiments are also possible using membranes of unlike selectivities in the intermediate modules and product modules.

[0033] Suitable types of membrane modules include the hollow-fine fibers, capillary fibers, spiral-wound, plate-and-frame, and tubular types. The choice of the most suitable membrane module type for a particular membrane separation must balance a number of factors. The principal module design parameters that enter into the decision are limitation to specific types of membrane material, suitability for high-pressure operation, permeate-side pressure drop, concentration polarization fouling control, permeability of an otional sweep stream, and last but not least costs of manufacture.

[0034] Hollow-fiber membrane modules are used in two basic geometries. One type is the shell-side feed design, which has been used in hydrogen separation systems and in reverse osmosis systems. In such a module, a loop or a closed bundle of fibers is contained in a pressure vessel. The system is pressurized from the shell side; permeate passes through the fiber wall and exits through the open fiber ends. This design is easy to make and allows very large membrane areas to be contained in an economical system. Because the fiber wall must support considerable hydrostatic pressure, the fibers usually have small diameters and thick walls, e.g. 100 μm to 200 μm outer diameter, and typically an inner diameter of about one-half the outer diameter.

[0035] A second type of hollow-fiber module is the bore-side feed type. The fibers in this type of unit are open at both ends, and the feed fluid is circulated through the bore of the fibers. To minimize pressure drop inside the fibers, the diameters are usually larger than those of the fine fibers used in the shell-side feed system and are generally made by solution spinning. These so-called capillary fibers are used in ultra-filtration, pervaporation, and some low- to medium-pressure gas applications.

[0036] Concentration polarization is well controlled in bore-side feed modules. The feed solution passes directly across the active surface of the membrane, and no stagnant dead spaces are produced. This is far from the case in shell-side feed modules in which flow channeling and stagnant areas between fibers, which cause significant concentration polarization problems, are difficult to avoid. Any suspended particulate matter in the feed solution is easily trapped in these stagnant areas, leading to irreversible fouling of the membrane. Baffles to direct the feed flow have been tried, but are not widely used. A more common method of minimizing concentration polarization is to direct the feed flow normal to the direction of the hollow fibers. This produces a cross-flow module with relatively good flow distribution across the fiber surface. Several membrane modules may be connected in series, so high feed solution velocities can be used. A number of variants on this basic design have been described, for example U.S. Pat. Nos. 3,536,611 in the name of Filipp et al., 5,169,530 in the name of Schucker et al., 5,352,361 in the name of Prasad et al., and 5,470,469 in the name of Eckman which are incorporated herein by reference each in its entirety. The greatest single advantage of hollow-fiber modules is the ability to pack a very large membrane area into a single module.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0037] In order to better communicate the present invention, several preferred aspects of the multi-stage membrane separation process and apparatus of the present invention for simultaneous recovery of a very pure permeate product and a desired non-permeate product from a fluid mixture of compounds are depicted schematically in **FIG. 1** and **FIG. 2**. In these preferred embodiments of the invention, the fluid feedstock is a gaseous mixture comprising a more selectively permeable alkene component and a corresponding alkane component, for example propane and propene (propylene). Other examples of light hydrocarbon compounds which are difficult to separate by traditional separtion methods, such as fractional distillation, are shown in Table I.

TABLE I

NORMAL BOILING POINT TEMPERATURES OF LIGHT HYDROCARBON COMPOUNDS

HEAVY HYDROCARBON	B.P. ° C.	LIGHT HYDROCARBON	B.P. ° C.
Ethane	−88.5	Ethene (ethylene)	−102.4
Propane	−42.2	Propene (propylene)	−47.7
Propadiene	−34.5	Propane	−42.2
Butane	−0.6	Methylpropene (isobutylene)	−6.6
Butane	−0.6	1-Butene (α-butylene)	−6.47
Butane	−0.6	1,3-Butadiene	−4.75
2-Butene (β-butylene)	3.73	Butane	−0.6
n-Butane	−0.6	iso-Butane	−12
1-Butene (α-butylene)	−6.47	Methylpropene (isobutylene	−6.6
2-Butene (β-butylene)	3.73	Methylpropene (isobutylene	−6.6

[0038] The membrane staging configuration for a particular separation depends on many factors. These factors include (1) the concentration of the desired component in the feed stream; (2) the physical and chemical properties of the components being separated; (3) the required purity of the product streams; (4) the relative values of the products, which determines acceptable recovery; (5) the tradeoff between membrane capital cost and the cost of pumping or compression; and (6) how the membrane is integrated with other processing steps. In the separation of mixtures using

membranes, the required product recoveries and product purity must be achieved at acceptable capital and operating costs. For multi-staged systems, the stage configuration and operating conditions of the individual stages must be balanced to meet the purity, recovery, and cost requirements.

[0039] Referring now to **FIG. 1**, membrane modules are disposed according to a preferred aspect of the invention in three groups represented in the drawing by modules **120**, **140** and **160**. A feedstock from a source **112** is passed through conduit **114**, and, depending on the operating conditions employed in a particular application, an optional compressor or pump and vaporizer (not shown), into a first zone of intermediate membrane module **140**.

[0040] Permeate, comprising the more selectively permeable component of the feedstock, e.g. alkene, is withdrawn from the second zone of membrane module **140** and transferred to compressor **150** through conduit **144** and manifold **146**. Effluent from compressor **150** is transferred into the first zone of a first product module **160** through conduit **152**. Very pure permeate product is recovered from the second zone of the first product module **160** through conduit **164**.

[0041] Non-permeate effluent, comprising the less permeable component of the feedstock, e.g. alkane, is withdrawn from the first zone of the first product module **160** is recycled through conduit **162** into the first zone of intermediate membrane module **140**. Non-permeate effluent, comprising the less permeable component of the feedstock, e.g. alkane, is withdrawn from the first zone of intermediate module **140** and transferred through conduit **142** into a first zone of second product module **120**.

[0042] A second product, the non-permeate effluent enriched in the less permeable component of the feedstock, e.g. alkane, is withdrawn from the first zone of second module **120** through conduit **122**. A permeate gas is withdrawn from the second zone of second product module **120** and transferred to the suction side of compressor **150** through conduit **124** and manifold **146**. Permeate from the second product module **120** and permeate from the intermediate module **140** are thereby mixed as they pass through the compressor, and a single stream is transferred into the first zone of a first product module **160** through **152**.

[0043] Referring now to **FIG. 2**, the membrane modules are disposed according to the invention in three groups represented in the drawing by modules **220**, **240** and **260**. A first feedstock which typically includes hydrocarbon compounds, such as a gaseous mixture of light hydrocarbons having from 1 to about 4 carbon atoms, from source **212**, such as a steam-cracker, light-olefins upgrading unit or another refinery operation, is passed through conduit **214** and, depending on the operating conditions employed in a particular application, an optional compressor and/or pump and vaporizer (not shown), into a first zone of intermediate membrane module **240**.

[0044] Permeate, comprising the more selectively permeable alkene component of the feedstock, is withdrawn from the second zone of membrane module **240** and transferred to the suction side of compressor **250** through conduit **244** and, depending on the operating conditions employed in a particular application, an optional heat exchanger (not shown). Effluent from compressor **250** is transferred into the first zone of a first product module **260** through conduit **252**. An additional feedstock which typically has a higher concentration of the alkene component than the first feedstock, from a source **266** is passed through conduit **268** and, depending on the operating conditions employed in a particular application, an optional compressor or pump and vaporizer (not shown), and into a first zone of the first product module **260**. Very pure permeate product is recovered from the second zone of the first product module **260** through conduit **264**.

[0045] Non-permeate effluent, comprising the less permeable alkane component of the feedstock, is withdrawn from the first zone of the first product module **260** is recycled through conduit **262** and manifold **234** into the first zone of intermediate membrane module **240**. Non-permeate effluent, comprising the less permeable alkane component of the feedstock, is withdrawn from the first zone of intermediate module **240** and transferred through conduit **242** into a first zone of second product module **220**.

[0046] A second product, the non-permeate effluent rich in the less permeable alkane component of the feedstock, is withdrawn from the first zone of second module **220** through conduit **222**. A permeate gas is withdrawn from the second zone of second product module **220** and transferred to the suction side of compressor **230** through conduit **224** and, depending on the operating conditions employed in a particular application, an optional heat exchanger (not shown). Effluent from compressor **230** is transferred into the first zone of a intermediate module **240** through conduit **232** and manifold **234**.

[0047] In other preferred embodiments of the invention, another fluid feedstock which advantageously has a concentration of the alkene component of less than the first feedstock, e.g. a steam-cracker, light-olefins upgrading unit or another refinery operation, is passed into the first zone of the second product module **220** thereby replacing or supplementing feedstock from source **212** and/or source **266**.

EXAMPLES OF THE INVENTION

[0048] The following Examples will serve to illustrate certain specific embodiments of the herein disclosed invention. These Examples should not, however, be construed as limiting the scope of the novel invention as there are many variations which may be made thereon without departing from the spirit of the disclosed invention, as those of skill in the art will recognize.

[0049] General

[0050] These Examples demonstrate effects of different processing configurations and membrane selectivities on overall process performance for simultaneous recovery of a very pure permeate product and a desired non-permeate product from a propane-propylene feedstock. The examples include the results of computer calculations, performed using commercially available chemical process modeling programs (e.g. Aspen Plus from Aspen Technology, Inc.) where models of membranes have been incorporated with standard chemical process equipment models. The models of membranes were developed by BP and based on generally accepted gas permeation equations. (See Shindo et al., "Calculation Methods for Multicomponent Gas Separation by Permeation,"*Sep. Sci. Technol.* 20, 445-459 (1985), Kovvali et al., "Models and Analyses of Membrane Gas Perme-

ators,"*J. Memb. Sci.* 73, 1-23 (1992), and Coker et al., "Modeling Multicomponent Gas Separation Using Hollow-Fiber Membrane Contactors,"*AIChE J.* 44, 1289-1302 (1998).)

[0051] For the purposes of the present invention, the permeability of gases through membranes is measured in "Barrer", which is defined as 10^{-10} [cm^3 (STP) $cm/(cm^2 \cdot sec \cdot cmHg)$] and named after R. M. Barrer. Membrane permeability is a measure of the ability of a membrane to permeate a gas. The term "membrane selectivity" is defined as the ratio of the permeabilities of two gases and is a measure of the ability of a membrane to separate the two gases. (For example, see Baker, Richard W., "Membrane Technology and Applications", pp 290-291, McGraw-Hill, New York, 2000)

[0052] The feedstock compositions represent an industry average composition of catalytic or pyrolysis cracker effluents. The liquid feed was pressurized with a pump to the operating level and vaporized before introduction into the apparatus. The permeate from the non-permeate product and intermediate stages was compressed from the permeate pressure to the feed pressure before introduction to the next stage. Calculations suggested that three stage compressors with two interstage coolers (to limit compressor temperatures to 200-250° F.) were sufficient between each membrane stage. A cooler was used after each compressor to keep the feed to each membrane stage at 200° F. The final non-permeate product was condensed with 100° F. water after exiting the process. The final permeate product was compressed after exiting the process to a pressure where it could be condensed with 100° F. water (approximately 250 psia). For feedstock and other stream compositions of the present invention, the term "percent" is defined liquid percent by volume.

[0053] Calculations for these examples were performed using the following parameters:

Feedstock Composition	
Propylene	70 percent
Propane	30 percent
Feedstock Flow Rate	10,000 BPD†
Membrane Temperature	200° F.
Module Feed Pressure	580 psia
Module Permeate Pressure	40 psia

†BPD is barrels per day

Example 1

[0054] This example documents an aspect of the preferred embodiment of the invention depicted in **FIG. 1**. Feed was supplied to modules **140** from source **112**. Membrane propylene selectivity of 35 and a propylene permeability of 1 Barrer in each of membrane modules were used for these calculations.

[0055] Membrane area for the non-permeate product modules and the permeate product modules were adjusted so that the final permeate product stream **164** met Polymer-Grade Propylene (PGP) specifications and, at the same time, the final non-permeate product steam **122** met Liquified Petroleum Gas (LPG) specifications. Also the membrane area for the intermediate modules **140** was adjusted to minimize the total required compression work, which is a major cost driver. The results of these calculations are shown in Table II. When the membrane selectivity dropped below about 25, the flow of material in stream **124** increased and the concentration of propylene in stream **152** decreased so much that it was no longer possible to make a final permeate product which met PGP specifications. At these lower membrane selectivities, an appratus similar to that shown in **FIG. 2**, where the permeate from the non-permate product stage is directed to an intemediate stage, is required.

TABLE II

TOTAL COMPRESSION 0.051 kWh/lb of Permeate Product†

MODULE	MEMBRANE AREA, $ft^2 \times 10^{-3}$	PROPYLENE CONCENTRATION, Percent
Final Non-Permeate Product	120	5.0
Intermediate	410	
Final Permeate Product	160	99.5

†Total is for the interstage compressor and the Permeate Product compressor.

Example 2

[0056] This example documents an aspect of the preferred embodiment of the invention depicted in **FIG. 2** where only the feed stream from source **212** was introduced into the apparatus, and the membrane modules had different membrane properties. In particular, two propylene permeability-selectivity pairs were used in these calculations: propylene permeability of 2 Barrer with 15 propylene selectivity and propylene permeability of 1 Barrer with 35 propylene selectivity.

[0057] The membrane area for the permeate product module was adjusted so that the final permeate product met Polymer-Grade Propylene (PGP) specifications. At the same time, the membrane area for the final non-permeate product module was adjusted so that the final non-permeate product met Liquefied Petroleum Gas (LPG) specifications. Also the membrane area for the intermediate module was adjusted to minimize the total required compression work.

TABLE III

SEPARATIONS USING MEMBRANES HAVING TWO LEVELS OF SELECTIVITY ACCORDING TO WHICH THE MODULES ARE DISPOSED INTO THREE GROUPS

DISPOSITION OF MEMBRANE SELECTIVITY†	TOTAL COMPRESSION‡	MEMBRANE AREA, $ft^2 \times 10^{-3}$	EDUCTION OF ENERGY REQUIRED Percent
15 - 15 - 15	0.084	510	0.0
35 - 35 - 35	0.050	675	40.5
15 - 35 - 35	0.051	607	39.3
35 - 15 - 35	0.058	684	31.0
35 - 35 - 15	0.056	701	33.3

TABLE III-continued

SEPARATIONS USING MEMBRANES HAVING TWO LEVELS OF SELECTIVITY ACCORDING TO WHICH THE MODULES ARE DISPOSED INTO THREE GROUPS

DISPOSITION OF MEMBRANE SELECTIVITY†	TOTAL COMPRESSION‡	MEMBRANE AREA, $ft^2 \times 10^{-3}$	EDUCTION OF ENERGY REQUIRED Percent
35 - 15 - 15	0.078	978	7.1
15 - 35 - 15	0.059	537	29.8
15 - 15 - 35	0.061	528	27.4

†Disposition in order of Non-Permeate Product Module - Intermediate Module - Permeate Product Module.
‡Total is for both interstage compressors and the final permeate product compressor, k Wh/lb permeate product.

[0058] The results of these calculations are shown in Table III. These results show that less energy and more membrane area are required when higher selectivity membranes are used. However these results show the unexpected result that exactly how much less energy is required depends on the stage in which the higher selectivity membrane is employed. Note that using the membranes with a propylene selectivity of 35 in the intermediate or permeate product modules stages reduces the energy required to about 30 percent of the energy required using membranes with a propylene selectivity of 15 in each stage while requiring an increase in membrane area of only approximately 5 percent. Using membranes with propylene selectivities of 35 in the intermediate and permeate product modules requires about the same amount of energy as using membranes with propylene selectivities of 35 in all three stages while using approximately 10 percent less membrane area. These results suggest that the energy and membrane area requirements can be adjusted by using different selectivities in each stage.

Example 3

[0059] This example documents an aspect of the preferred embodiment of the invention depicted in **FIG. 2** where different feed streams supplied from source **212** and source **266** were introduced into the apparatus at two different locations. For clarity, membranes with the same permeability-selectivity have been employed in each stage of the apparatus in this example: propylene permeability of 1 Barrer with a 35 propylene selectivity. To ease comparison to the previous examples, the same total feed rate (10,000 BPD) has been used for these calculations and has been split evenly between source **212** and source **266** (5,000 BPD each). As before, the membrane area for the permeate product and non-permeate product modules were adjusted so that the propylene and propane products met the PGP and LPG specifications, respectively, and the membrane area for the entermediate module was adjusted to minimize the total required compression work. This example illustrates the effect of the composition of the streams from sources **212** and **266** on the total required compression work and membrane area needed to meet the PGP and LPG specifications. The specific compositions used in this example were selected to keep the total amount of propylene constant (70 percent) and the same as that employed in previous examples.

[0060] Table IV shows the results of these calculations. Recall that in the previous example where a propylene permeability of 1 Barrer and 35 propylene selectivity was employed in each stage and feed with 70 percent propylene was introduced only from source **212** the total required compression work was 0.050 kWh/lb of propylene product and the total required membrane area was 675,000 ft^2. Table V shows that the required work and membrane area increases when feed containing 70 percent propylene is introduced form sources **212** and **266**. However, Table V shows that the total work and membrane requirements are dependent on the propylene content of the streams from sources **212** and **266**. When the propylene content from source **266** rose above about 83 percent and the propylene content from source **212** fell below about 57 percent, the total work and membrane area requirements fell below those levels that would have been needed if these streams had been mixed and introduced only to the Intermediate stage. This example shows that depending on the propylene content of the feed sources it may be possible to lower the total work and membrane area required to make PGP and LPG by introducing the feeds at more than one location.

Comparative Example A

[0061] This example is based upon the preferred embodiment of the invention depicted in **FIG. 2**, except that feed streams supplied from source **212** and source **266** were replaced with a single feed (not shown) which was introduced into the apparatus at a different location, i.e., into the first zone of the second product module **220**. Membranes with the same permeability-selectivity have been employed in each stage of the apparatus in this example: propylene permeability of 1 Barrer with a 35 propylene selectivity. As before, the membrane area for the permeate and non-permeate modules were adjusted so that the propylene and propane products met the PGP and LPG specifications, respectively, and the membrane area for the intermediate module was adjusted to minimize the total required compression work.

[0062] Table V shows that the position where the feed is introduced greatly influences the compression and membrane area requirements needed to meet the PGP and LPG specifications.

TABLE IV

SEPARATIONS USING TWO FEED LOCATIONS WITH MODULES DISPOSED INTO THREE GROUPS†

PROPYLENE CONTENT OF SOURCE212, percent	PROPYLENE CONTENT OF SOURCE266, percent	TOTAL COMPRESSION†\	MEMBRANE AREA, $ft^2 \times 10^{-3}$
70	70	0.069	813
65	75	0.062	770
60	80	0.055	718
55	85	0.047	656
50	90	0.040	597

†The feed rate from source 212 is 5,000 BPD and the feed rate from source 266 is 5,000 BPD in every case.
††Total is for both interstage compressors and the final permeate product compressor, k Wh/lb permeate product.

[0063]

TABLE V

SEPARATIONS USING ONE FEED LOCATION WITH MODULES DISPOSED INTO THREE GROUPS AND TOTAL COMPRESSION 0.088 kWh/lb of Permeate Product†

MODULE	MEMBRANE AREA, $ft^2 \times 10^{-3}$	Propylene Concentration, Percent
Final Non-Permeate	1930	5.0
Intermediate	338	
Final Permeate	147	99.6

†Total is for both interstage compressors and the final permeate product compressor, k Wh/lb permeate product.

[0064] For the purposes of the present invention, "predominantly" is defined as more than about fifty percent. "Substantially" is defined as occurring with sufficient frequency or being present in such proportions as to measurably affect macroscopic properties of an associated compound or system. Where the frequency or proportion for such impact is not clear, substantially is to be regarded as about twenty percent or more. The term "a feedstock consisting essentially of" is defined as at least **95** percent of the feedstock by volume. The term "essentially free of" is defined as absolutely except that small variations which have no more than a negligible effect on macroscopic qualities and final outcome are permitted, typically up to about one percent.

That which is claimed is:

1. Apparatus using perm-selective membranes in multiple groups for simultaneous recovery of a very pure permeate product and a desired non-permeate product from a fluid mixture of compounds, which apparatus comprises

(1-A) a plurality of membrane modules disposed in a first product group, one or more intermediate group, and a second product group, each module comprising a solid perm-selective membrane which under a suitable differential of a driving force exhibits a permeability of at least 0.1 Barrer, a channel having at least one inlet and one outlet for flow of fluid in contact with one side of a membrane, and contiguous with the opposite side thereof a permeate chamber having at least one outlet for flow of permeate,

(1-B) means for distribution of a fluid feedstock into the channel inlets of at least a portion of the intermediate group of modules,

(1-C) means for collection of permeate effluent from the chamber outlets of at least a portion of the intermediate group of modules and distribution of this intermediate permeate into the channel inlets of the first product group modules,

(1-D) means for collection of a permeate product effluent from the chamber outlets of the first product group of modules,

(1-E) means for collection of non-permeate effluent from the channel outlets of the first product modules and distribution thereof into the channel inlets of at least a portion of the intermediate group of modules,

(1-F) means for collection of non-permeate from the channel outlets of the intermediate group of modules and distribution of this intermediate non-permeate into the channel inlets of the second product group modules, and

(1-G) means for collection of a non-permeate product effluent from the channel outlets of the second product group of modules.

2. Apparatus using perm-selective membranes in multiple groups for simultaneous recovery of a very pure permeate product and a desired non-permeate product from a fluid mixture of compounds, which apparatus comprises

(2-A) a plurality of membrane modules disposed in a first product group, one or more intermediate group, and a second product group, each module comprising a solid perm-selective membrane which under a suitable differential of a driving force exhibits a permeability of at least 0.1 Barrer, a channel having at least one inlet and one outlet for flow of fluid in contact with one side of a membrane, and contiguous with the opposite side thereof a permeate chamber having at least one outlet for flow of permeate,

(2-B) means for distribution of a fluid feedstock into the channel inlets of at least a portion of the intermediate group of modules,

(2-C) means for collection of permeate effluent from the chamber outlets of at least a portion of the intermediate group of modules and distribution of this intermediate permeate into the channel inlets of the first product group modules,

(2-D) means for collection of a permeate product effluent from the chamber outlets of the first product group of modules,

(2-E) means for collection of non-permeate effluent from the channel outlets of the first product modules and distribution thereof into the channel inlets of at least a portion of the intermediate group of modules,

(2-F) means for collection of non-permeate from the channel outlets of the intermediate group of modules and distribution of this intermediate non-permeate into the channel inlets of the second product group modules,

(2-G) means for collection of a non-permeate product effluent from the channel outlets of the second product group of modules, and

(2-H) means for collection of permeate effluent from the chamber outlets of the second product modules and distribution thereof into the channel inlets of the first product of modules.

3. The apparatus according to claim 1 wherein the membrane modules in the second product group have membranes of lower selectivity than membranes in at least one of the other groups.

4. The apparatus according to claim 1 wherein the membrane modules in the second product group have membranes of lower selectivity than membranes in the other groups.

5. The apparatus according to claim 1 wherein the membrane modules in at least a portion of the intermediate group have membranes of higher selectivity than membranes in at least one of the other groups.

6. The apparatus according to claim 1 wherein the membrane modules in at least a portion of the intermediate group have membranes of higher selectivity than membranes in the other groups.

7. The apparatus according to claim 1 wherein the membrane modules in the first product group have membranes of higher selectivity than membranes in at least one of the other groups.

8. The apparatus according to claim 1 wherein the membrane modules in the first product group have membranes of higher selectivity than membranes in the other groups.

9. The apparatus according to claim 1 wherein the (1-C) means for collection and distribution of permeate into the channel inlets of the first product group modules comprises a compressor.

10. The apparatus according to claim 1 further comprising means for distribution of another feedstock into the channel inlets of the first product of modules.

11. Apparatus using perm-selective membranes in multiple groups for simultaneous recovery of a very pure permeate product and a desired non-permeate product from a fluid mixture of compounds, which apparatus comprises

(11-A) a plurality of membrane modules disposed in a first product group, one or more intermediate group, and a second product group, each module comprising a solid perm-selective membrane which under a suitable differential of a driving force exhibits a permeability of at least 0.1 Barrer, a channel having at least one inlet and one outlet for flow of fluid in contact with one side of a membrane, and contiguous with the opposite side thereof a permeate chamber having at least one outlet for flow of permeate,

(11-B) means for distribution of a first fluid feedstock into the channel inlets of at least a portion of the intermediate group of modules,

(11-C) means for collection of permeate effluent from the chamber outlets of at least a portion of the intermediate group of modules and distribution of this intermediate permeate into the channel inlets of the first product group modules,

(11-D) means for distribution of a second fluid feedstock into the channel inlets of the first product group of modules,

(11-E) means for collection of a permeate product effluent from the chamber outlets of the first product group of modules,

(11-F) means for collection of non-permeate effluent from the channel outlets of the first product modules and distribution thereof into the channel inlets of at least a portion of the intermediate group of modules,

(11-G) means for collection of non-permeate from the channel outlets of the intermediate group of modules and distribution of the non-permeate into the channel inlets of the second product group modules,

(11-H) means for collection of a non-permeate product effluent from the channel outlets of the second product group of modules, and

(11-I) means for collection of permeate effluent from the chamber outlets of the second product modules and distribution thereof into at least a portion of the channel inlets of the intermediate group of modules.

12. The apparatus according to claim 11 further comprising means for distribution of another fluid feedstock into the channel inlets of the second product of modules.

13. The apparatus according to claim 11 wherein the membrane modules in the second product group have membranes of lower selectivity than membranes in at least one of the other groups.

14. The apparatus according to claim 11 wherein the membrane modules in the second product group have membranes of lower selectivity than membranes in the other groups.

15. The apparatus according to claim 11 wherein the membrane modules in at least a portion of the intermediate group have membranes of higher selectivity than membranes in at least one of the other groups.

16. The apparatus according to claim 11 wherein the membrane modules in at least a portion of the intermediate group have membranes of higher selectivity than membranes in the other groups.

17. The apparatus according to claim 11 wherein the membrane modules in the first product group have membranes of higher selectivity than membranes in at least one of the other groups.

18. The apparatus according to claim 11 wherein the membrane modules in the first product group have membranes of higher selectivity than membranes in the other groups.

19. The apparatus according to claim 11 wherein the (11-C) means for collection and distribution of permeate into the channel inlets of the first product group modules comprises a compressor.

20. The apparatus according to claim 11 wherein the (11-I) means for collection and distribution of permeate into at least a portion the channel inlets of the intermediate group modules comprises a compressor.

* * * * *