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ANNULAR HOLLOW FIBER MEMBRANES FOR GAS SEPARATION**Field of the Invention**

GMM2

This invention relates to annular hollow fiber membranes which are prepared by extrusion of two homogeneous polymer solutions with a triple orifice spinneret. This invention further relates to a novel procedure for fabricating an unified two-membrane permeator from the prepared annular hollow fiber. The permeator is capable of providing two internal separation stages for gas enrichment.

Background of the Invention

Membrane-based gas separation is now widely practiced in chemical, gas and petrochemical industries for a variety of gas-gas and gas-vapour separations processes. One of the problems encountered in membrane separation processes, however, is that the extent of separation achieved is often not high enough because for some gas pairs, the permeability coefficients are not widely separated in magnitude, resulting in poor selectivity. In order to achieve a desired degree of separation, an energy intensive operation such as a multi-stage or cascade process with or without permeate recycling is usually employed, which will result in an increase in operation costs.

Sidhoum et al., "Experimental Behavior of Asymmetric CA Membranes and Its Use in Novel Separation Schemes" *New Membrane Materials and Processes for Separation*. K. K. Sirkar, D. R. Lloyd, eds., *AIChE Symp. Ser.* 84 (261), 102 (1988), discloses a gas permeator which is capable of achieving a higher degree of separation without extra energy consumption. As illustrated in Figure 3 in the above cited Sidhoum et al. reference, the permeator splits the pressure difference between the feed and permeate side into two steps with two membranes of the same type. The permeate, V_s enriched in a more permeable component

emerging from the first membrane at an intermediate pressure would then be applied as feed to the second membrane for the second permeation step. Since the pressure arrangement follows $p_f > p_s > p_p$, the permeator can be operated without interstage recompression to achieve a higher degree of separation compared to that achieved in a conventional single stage permeator.

An article by Sidhoum et al. in *AIChE J.* 35, 764 (1989) discloses a technique for fabricating a new permeator. Two bundles of conventional hollow fibers were housed in a permeator shell which has four openings as shown in Figure 5 of the Sidhoum et al. (1989) reference.

The present invention provides better flow distribution and maximizes the packing densities of the membrane permeator as compared with conventional systems. To date, no such hollow fiber membranes are available. The inventors have made an annular hollow fiber membrane and devised procedures for fabricating an unified two-membrane permeator that has a high degree of gas enrichment, and avoids problems of the prior art noted above.

Summary Of The Invention

The two polymer solutions are useful for preparing an annular hollow fiber membrane using a phase inversion technique. The prepared annular hollow fiber has both internal and external skins appearing at the hollow fiber lumen and the external wall, respectively. Between these two skins, finger-like and sponge-like type of structures are formed with a clear discontinuity which turns the hollow fiber into the annular hollow fiber. A cross-sectional view of the hollow fiber (SEM photograph) is shown in Figure 1.

In another aspect, the present invention is directed to a novel process for preparing an unified two-membrane permeator using the aforementioned annular hollow fiber membranes. The membrane permeator is first assembled using conventional techniques. Thereafter, the hollow fiber

annuluses at one end and the hollow fiber lumen at the other end of the permeator are properly sealed with epoxy resin so that the membrane permeator is capable of providing two separation stages internally for gas enrichment.

The invention is directed to a method for producing an annular hollow fiber membrane suitable for further preparation of an unified two-membrane permeator for gas separation. The method comprises the following steps:

- (a) selecting two polymers;
- (b) selecting a solvent for each polymer;
- (c) selecting a nonsolvent-additive;
- (d) determining an appropriate mass ratio of nonsolvent-additive to solvent in a polymer dope;
- (e) forming two polymer dopes by mixing the polymers, the solvent and/or nonsolvent-additive;
- (f) spinning the two polymer dopes through an outer orifice and an inner orifice of a spinneret while simultaneously injecting coagulant through a tube of the spinneret to form the nascent hollow fibers;
- (g) passing said nascent fiber through an air-gap;
- (h) solidifying the nascent hollow fiber in a coagulation medium and forming solid membrane;
- (i) further removing the solvent mixture from the formed hollow fibers in the coagulating medium;

(j) drying the hollow fibers at ambient condition; and

(k) coating an inner side and an outer side of the dried annular hollow fibers using a coating solution containing silicone elastomer and n-pentane.

The invention is further directed to a method of making an unified two-membrane permeator by properly sealing a lumen at one end of a permeator and annular gap at the other.

The invention is also directed to a method of separating permanent gas pairs by applying gas pairs to a unified two membrane permeator containing an annular hollow fiber membrane; and obtaining separation of the gas pairs to individual gases.

Brief Description Of The Drawings

Figure 1(a) and Figure 1(b) are SEM photographs of cross-sectional views of an annular hollow fiber membrane that has been prepared by the method of the present invention.

Figure 2 illustrates a triple orifice spinneret and an apparatus for the fabrication of an annular hollow fiber membrane.

Figure 3 is a schematic representation of an unified two-membrane permeator.

Figure 4 is a gas separation apparatus.

Figure 5 is a SEM photograph of a cross-sectional view of an annular hollow fiber with very narrow annulus.

Figure 6 is the Permeate concentration vs. throughput (overall stage cut), 1. Conventional hollow fiber permeator, 2. Unified two-membrane permeator.

Detailed Description Of The Invention

The invention, in one aspect, is a novel process of making annular hollow fiber membranes using two polymer solutions, comprising a mixture of:

1. at least one polymer having a membrane forming and good gas separation properties, as well as thermal and mechanical stability. The polymers used include glass polymers, preferably polysulfone, polyethersulfone, polyetherimide, or cellulose,
2. at least one solvent selected from N-methyl-2-pyrrolidene (NMP), N,N-dimethylacetamide (DMAc) or dimethylformamide (DMF), in an amount sufficient to solubilize the polymer(s) at the hollow fiber formation temperature, and
3. optionally, a nonsolvent, preferably an alcohol, or water, more preferably a polar organic alcohol such as methanol, ethanol, 1-propanol, 1-butanol or 1-pentanol.

In accordance with the present invention, annular hollow fiber membranes are prepared using a phase inversion process. The prepared annular hollow fiber membranes are then used to prepare an unified two-membrane permeator for gas separations. Gases such as, but not limited to, CO₂, O₂, N₂ or CH₄ can be effectively separated from gas mixtures using the membrane permeator.

The annular hollow fiber membrane of the present invention is preferably produced by a dry/wet phase inversion process. Polymers that can be used for preparation of the spinning dopes include, but are not limited to, polysulfone, polyethersulfone, polyetherimide and cellulose. Solvents useful in the present invention include, but are not limited to, DMAc, NMP and DMF. In order to produce the annular hollow fibers with the ultrathin skin layers, nonsolvent additives such as alcohols are used in the preparation of fiber spinning dopes.

The concentration of the components in the spinning dopes may vary. For the polymer dopes, the concentration of the polymer is preferably greater than about 15% (weight), usually not more than 40%, preferably 20% to 35%, more preferably about 25% to 35% (weight). The polymer dopes are tailored to be much closer to the phase separation point by addition of a nonsolvent additive.

The amount of the solvent used in the invention is 30% to 80%; preferably 40% to 70%, more preferably 45% to 70%, depending on the properties of the solvent and non-solvent additives and polymer concentration.

The amount of non-solvent additive optionally used in the invention is 2% to 40%, preferably 3% to 35%, more preferably 3% to 25%.

The hollow fibers of this invention may be spun using a spinning apparatus shown schematically in Figure 2. Two polymer spinning dopes preformulated according to the aforementioned composition are filtered and are poured into their solution tanks **201** and **202**, respectively. The two solutions are kept in their solution tanks for 48 hr to ensure proper degassing prior to spinning. During the membrane spinning process, the dopes are fed under nitrogen pressure and by the gear pump through a spinneret **203** into the coagulation bath **204** at ambient conditions, preferably $25 \pm 1^\circ\text{C}$ and $\text{RH} = 60\text{--}65\%$. The spinneret is a triple orifice type, a diagram of which is shown in the insert of Figure 2. The polymer dope 1 is fed into the inner orifice and the polymer dope 2 is fed into the outer orifice; while the internal coagulant is introduced into the inner tube of the spinneret. The extrusion rates of both of the spinning dopes are controlled. Tap water at room temperature is used as both internal and external coagulant. The internal water injection rate is controlled to between 1 and 3 ml/min. Different spinning conditions are selected according to the specific polymer dopes. The spinneret is arranged such that the nascent fiber is extruded vertically downwards into the

coagulation bath. The temperature of the bath is kept at ambient conditions, preferably at $25\pm 1^{\circ}\text{C}$. The nascent fiber emerging from the tip of the spinneret passes through an air gap before entering the coagulation bath.

5 After coagulation, the fibers are guided through the wash bath **205**, and then coiled into the storage tank. The nascent hollow fibers are not forcibly drawn out of the apparatus. In other words, the take-up velocity of the hollow fiber is nearly the same as its free falling
10 velocity in the coagulation bath. The hollow fiber is kept in a storage tank for two days to stabilize the structure.

After the annular hollow fiber membrane is prepared, an unified two-membrane permeator of the present invention
15 is fabricated by assembling the hollow fibers as a bundle and then housing the bundle in a stainless steel pipe acting as the permeator shell. The procedure for fabricating the membrane permeator for gas separation is best understood by reference to Figure 3 which is a
20 representative drawing of the annular hollow fiber membrane and the unified two-membrane permeator.

Referring to Figure 3, the bundle of hollow fibers **301** is first carefully pulled through two tees **302a** and **302b** connected at both ends of the stainless steel pipe **303** acting as the permeator shell. Fiber potting is done
25 by pouring epoxy resin **304** into the two openings of the tees, separately. Before the epoxy resin is set, the fibers are carefully arranged to ensure the filling of epoxy resin liquid in the interstices among the fibers.

30 To fabricate the unified two-membrane permeator, the hollow fiber annuluses **305** at one end and the hollow fiber lumen **306** at the other must be plugged with the epoxy resin. The hollow fiber annuluses are plugged by applying a dilute epoxy resin on the one end of the permeator and
35 at the same time, introducing compressed air into the hollow fiber lumen from the other end to blow away the epoxy resin which may flow into the hollow fiber lumen.

Thus, the hollow fiber lumen remains open, while the hollow fiber annuluses are plugged as the epoxy resin is cured. The plugging of the hollow fiber lumen at the other end of the permeator is carried out in a similar manner. This is done by applying an epoxy resin on the end of the permeator and then applying vacuum in the fiber lumen so that a small portion of the fiber lumen near the potting end is filled with epoxy resin. The annuluses at the end of the permeator are also plugged during the potting process. However, the epoxy resin filled into the annuluses is not as deep as that in the lumen, therefore it can be re-opened by cutting off the plugged portion of the annuluses.

Before the unified two-membrane permeator is employed for actual gas separation, coating of both internal and external separation layers with silicone elastomer (SYLGARD 184, Dow Corning Corporation of Midland, USA) to repair the surface defects should be carried out *in situ*. A coating solution containing about 3-6wt% polydimethylsiloxane in a balance of n-pentane is fed into both the hollow fiber lumen and the shell side. The solution remains in the permeator for about 5 min before it is removed and allowed to cure at room temperature for about 24 hours. During the coating process, vacuum is maintained in the fiber annulus so that the coating solution can fill the pores and repair the defects on both surfaces.

Turning now to Figure 4, a gas separation apparatus includes the unified two-membrane permeator **404**. In operation, the feed gas cylinder **401** provides a feed gas mixture at a substantially constant rate into the shell side of the permeator via the opening **403**. A more permeable gas in the gas mixture is permeated through the outer layer into the hollow fiber annuluses, and the flow rate of the permeated gas in the annuluses is controlled by a mass flow controller **407**. A fraction of the permeated gas in the hollow fiber annuluses is further

permeated through the inner layer into the hollow fiber lumen, and the flow rate of the permeated gas in the hollow fiber lumen is measured by a mass flow meter 406. In Figure 4, 408 is a gas chromatography employed to measure the composition of the gases from 405, 406 or 407.

Examples

Example 1

Two polymer dopes of 1 and 2 were prepared. The polymer dope 1 was formulated by dissolving polyethersulfone in NMP solvent according to the weight ratio of polymer/solvent of 32/68. The dope has a coagulation value of 15.4 and viscosity of 15800 cp at 25°C. The polymer dope 2 was formulated by dissolving polysulfone in DMAc solvent according to the weight ratio of polymer/solvent of 30/70. The dope 2 has a coagulation value of 4.4 and viscosity of 8200 cp at 25°C. The annular hollow fiber was prepared by extruding the two polymer dopes into a triple orifice spinneret with an air-gap (between the tip of the spinneret and coagulation bath) length of 5 cm. Internal water injection rate was controlled at 1.2 ml/min. The cross sectional view of the prepared hollow fiber is given in Figure 5. It can be seen that two distinct layers are formed with the polymer dopes formulated, however, the two layers are interconnected resulting in a considerable resistance for gases flowing through.

Example 2

Again, two polymer dopes of 1 and 2 were prepared. The polymer dope 1 was formulated by dissolving polyethersulfone in a solvent mixture of NMP and ethanol according to the weight ratio of polymer/NMP/ethanol of 30/48.7/21.3. The dope has a coagulation value of 1.5 and viscosity of 6109 cp at 25°C. The polymer dope 2 formulated is the same as that prepared in Example 1. The

annular hollow fiber was formed with an air-gap length of 5 cm. Internal water injection rate was controlled at 1 ml/min. The cross sectional view of the prepared hollow fiber is given in Figure 1b. It can be seen that two distinct layers with a clear discontinuity were formed. The prepared annular hollow fibers can be easily used for the further preparation of an unified two-membrane permeator. The dimensions of the permeator prepared is given in the following example.

Example 3

An unified two-membrane permeator shown in Figure 3 was prepared. A permeator containing 123 annular hollow fibers with the effective length of 125 mm was prepared according to the procedures mentioned in the preceding section under **DETAILED DESCRIPTION OF THE INVENTION**. The shell side diameter of the permeator is 3/4" of side diameter.

Example 4

The unified two-membrane permeator prepared in the previous example was used in a gas separation test. A gas mixture containing 54% CO₂ in a balance of N₂ was employed as a feed gas and was fed into the permeator shell at 7 atm. The gas mixture was permeated into the hollow fiber annuluses where the pressure was controlled at 1.7 atm. The permeated gas in the hollow fiber annuluses was further permeated into the hollow fiber lumen as the pressure in the fiber lumen was maintained at 1 atm. The permeated CO₂ composition from the fiber lumen was enriched to 96 v/v%. Figure 6 further illustrates gas separation performance of the newly prepared permeator. It can be seen that at a given throughput (overall stage cut), the unified two-membrane permeator offers a considerably higher gas enriching performance compared to the conventional single stage permeator at an identical energy consumption.

CLAIMS

- 1 1. A method for producing an annular hollow fiber
2 membrane suitable for further preparation of an
3 unified two-membrane permeator for gas separation,
4 comprising the following steps:
- 5 (a) selecting two polymers;
- 6 (b) selecting a solvent for each polymer;
- 7 (c) optionally selecting a nonsolvent-additive
8 for each polymer;
- 9 (d) determining an appropriate mass ratio of
10 nonsolvent-additives to solvent;
- 11 (e) forming two polymer dopes by mixing the
12 polymers and the solvent and optionally the
13 nonsolvent-additive;
- 14 (f) spinning the two polymer dopes through an
15 outer orifice and an inner orifice,
16 respectively, of a spinneret while
17 simultaneously injecting coagulant through a
18 tube of the spinneret to form nascent hollow
19 fibers;
- 20 (g) passing said nascent fibers through an air-
21 gap;
- 22 (h) solidifying the nascent hollow fibers in a
23 coagulation medium and forming solid
24 membranes;
- 25 (i) further removing the solvent from the formed
26 hollow fibers in the coagulating medium;
- 27 (j) drying the hollow fibers at ambient
28 condition; and

29 (k) coating an inner side and an outer side of
30 the dried annular hollow fibers using a
31 coating solution containing silicone
32 elastomer and n-pentane.

1 2. The process according to claim 1, wherein the
2 nonsolvent-additives are C₁-C₃ aliphatic alcohol,
3 water or mixtures of water and the aliphatic
4 alcohol.

1 3. The process according to claim 1, wherein the
2 polymers are polyethersulfone, polysulfone,
3 polyetherimide or cellulose.

1 4. The process according to claim 1, wherein the
2 solvent is N-methyl-2-pyrrolidone or N,N-
3 dimethylacetamide.

1 5. The process according to claim 1, wherein the
2 coagulant and coagulation medium are tap water.

1 6. The process according to claim 1, wherein the
2 polymer dopes have coagulation values of 1 to 3 g
3 for water by the addition of the nonsolvent-
4 additives.

1 7. The process according to claim 1, wherein the
2 polymer dopes have a polymer concentration of
3 20wt% -35wt%.

1 8. The process according to claim 1, wherein the
2 polymer dope is spun subsequently into a dry air
3 gap and then into the coagulation medium.

1 9. The process according to claim 1, wherein the
2 polymer dopes are degassed and filtered prior to
3 spinning.

1 10. The process according to claim 1, wherein the
2 desolation and washing of the hollow fibers take
3 place in a water bath at room temperature.

- 1 11. The process according to claim 1, wherein the
2 drying of hollow fibers occurs in ambient
3 condition.
- 1 12. The process according to claim 8, wherein the air-
2 gap is within 2-15 cm.
- 1 13. The process according to claim 1, wherein the
2 annular hollow fibers are coated using a coating
3 solution containing 3wt%-6wt% polydimethylsiloxane
4 in a balance of n-pentane.
- 1 14. A method of making an unified two-membrane
2 permeator comprising:
3 bundling annular hollow fibers;
4 encasing the annular hollow fibers in a shell; and
5 sealing lumen in the annular hollow fiber at one
6 end of the permeator and annular gap at the other
7 end.
- 1 15. The method according to claim 14, wherein air or N₂
2 is supplied into the lumen while sealing the
3 annular gap.
- 1 16. The method according to claim 14, wherein vacuum
2 is applied into the lumen while applying an epoxy
3 resin in one end of the permeator.
- 1 17. The method according to claim 14, wherein
2 annuluses, which are sealed while sealing the
3 lumen, are re-opened by cutting off the plugged
4 portion of the annuluses.
- 1 18. The method according to claim 14, wherein two
2 separation stages are provided internally for gas
3 enrichment.

- 1 19. A method of separating permanent gas pairs
2 comprising applying said gas pairs to a unified
3 two membrane permeator containing an annular
4 hollow fiber membrane; and obtaining separation of
5 the gas pairs to individual gases.
- 1 20. The method according to claim 19, wherein said gas
2 pairs are selected from the group consisting of
3 CO₂-CH₄, O₂-H₂ and H₂-N₂.