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(71) Applicant: **PBI PERFORMANCE PRODUCTS, INC.**
[US/US]; 9800-D Southern Pine Boulevard, Charlotte, NC 28273 (US).(72) Inventors: **WANG, Yan**; District D, Shiji Xindu, Dongtang Road, Anhui Province, Chaohu City, 238000 (CN). **GRUENDER, Michael**; 206 N. Brackenbury Lane, Charlotte, NC 28270 (US). **CHUNG, Tai-shung**; 4323 Pine Ridge Court, Ann Arbor, MI 48105 (US).(74) Agents: **HAMMER, Robert, H., III** et al.; Hammer & Associates, P.C., 3125 Springbank Lane, Suite G, Charlotte, NC 28226 (US).(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

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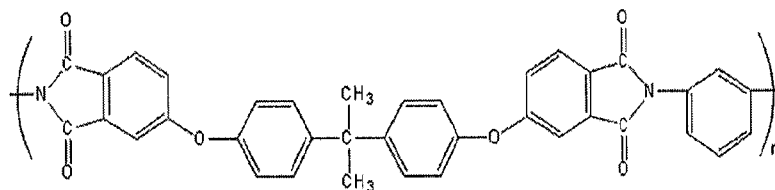
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(54) Title: ACID RESISTANT PBI MEMBRANE FOR PERVAPORATION DEHYDRATION OF ACIDIC SOLVENTS



(57) **Abstract:** A pervaporation membrane may be an acid-resistant polybenzimidazole (PBI) membrane. The acid-resistant PBI membrane may be a PBI membrane chemically modified by a process selected from the group consisting of sulfonation, phosphonation, cross-linking, N-substitution, and/or combinations thereof. The membrane may be thermally stabilized. A method for the dehydration of an acid material may include the steps of: contacting an acidic aqueous solution with a membrane of an acid-resistant polybenzimidazole; taking away a permeate stream rich in water; and taking away a concentrate steam rich in the acid material. The acidic aqueous solution may be acetic acid.

ACID RESISTANT PBI MEMBRANE FOR PERVAPORATION
DEHYDRATION OF ACIDIC SOLVENTS

Field of the Invention

An acid-resistant PBI membrane is used for the dehydration of an acidic solvent, e.g., acetic acid, via membrane-based pervaporation.

Background of the Invention

Pervaporation is a process for the separation of liquid mixtures by partial vaporization through a membrane. The separation process has two steps: first, one component of the mixture permeates away from the mixture through the membrane (the escaping component is called the permeate, and the remaining mixture is called the retentate or concentrate); and second, the permeate evaporates away from the membrane. *Pervaporation*, Wikipedia (3/10/2010).

The efficacy of the pervaporation membrane may be determined by the membrane's selectivity (expressed as separation factor) and productivity (expressed as flux). Flux refers to the rate of flow or transfer of permeate from the mixture to vapor, and denotes a quantity of permeate that crosses a unit of area of a given surface in a unit of time. Separation factor refers to the membrane's ability to selectively remove more of one mixture component than the other component(s) of the mixture.

Productivity and selectivity are membrane-dependent. *Membrane technology*, © 1998-

2009 Lenntech Water Treatment & Purification Holding B.V., Delft, the Netherlands (www.lenntech.com).

US Publication 2011/0266222 discloses a method to dehydrate organic liquid (e.g., ethylene glycol, EG) by pervaporation using a PBI permselective hollow fiber. The PBI permselective layer of the hollow fiber is not chemically modified to make it acid resistant.

The dehydration of acidic solvents is an important commercial operation. One acidic solvent, acetic acid, is among the top 50 chemicals based upon production quantity. Currently, the dehydration of acidic solvents, e.g., acetic acid, is carried out by a binary distillation. This separation method, however, is difficult as acetic acid and water have very close volatilities. As such, more energy is required to achieve acetic acid with purity higher than 95 wt% due to the need for greater reflux and a larger distillation column with many stages. In view of these disadvantages of distillation, research emphasis has been placed on the pervaporation dehydration of acetic acid. More specifically, research has focused on developing a membrane that gives a reasonable flux and has a good separation factor. In pervaporative dehydration, a significant number of pervaporation dehydration membranes are made from cross-linked polyvinyl alcohol (PVA), chitosan, and cellulose acetate.

Accordingly, there is a need for new and better pervaporation membranes, particularly, pervaporation membranes for dehydration, and the dehydration of acidic solvents, such as acetic acid.

Summary of the Invention

A pervaporation membrane may be an acid-resistant polybenzimidazole (PBI) membrane. The acid-resistant PBI membrane may be a PBI membrane chemically modified by a process selected from the group consisting of sulfonation, phosphonation, cross-linking, N-substitution, and/or combinations thereof. The membrane may be thermally stabilized. A method for the dehydration of an acid material may include the steps of: contacting an acidic aqueous solution with a membrane of an acid-resistant polybenzimidazole; taking away a permeate stream rich in water; and taking away a concentrate stream rich in the acid. The acidic aqueous solution may be acetic acid.

Description of the Drawings

For the purpose of illustrating the invention, there is shown in the drawings a form that is presently preferred; it being understood, however, that this invention is not limited to the precise arrangements and instrumentalities shown.

Figure 1 is a schematic illustration of a representative polybenzimidazole (PBI) molecule.

Figure 2 is a chart comparing the separation factor and flux at various temperature of known pervaporation membranes used to dehydrate acetic acid to the present invention.

Description of the Invention

In a membrane separation process, an influent stream is separated into two effluent streams known as the permeate and the concentrate (or retentate). The permeate is the portion of the influent stream passing through the semi-permeable membrane, whereas the concentrate stream contains the constituents that have been rejected by the membrane. This separation may be conducted in a membrane contactor where the influent stream is contacted with the membrane and the permeate and the concentrate are taken away from the contactor. The membrane may be flat membrane, a multi-layer flat membrane (e.g., a dual layer membrane), a hollow fiber membrane, a multi-layer hollow fiber membrane (e.g., a dual layer membrane), or tubular. In the multi-layer hollow fiber and tubular membranes, one layer is the membrane used in the separation and another membrane may be a support membrane.

In the instant membrane separation process, an acid-resistant polybenzimidazole (PBI) membrane may be used to dehydrate an acidic solvent. Acidic solvents (or polar protic solvents) may include, but are not limited to, methanol, ethanol, n-butanol, isopropanol, n-propanol, acetic acid, formic acid, hydrogen fluoride, and ammonia. In one embodiment, the acidic solvent may be acetic acid.

Polybenzimidazole (PBI) may be any PBI. PBI also refers to blends of PBI with other polymers, co-polymers of PBI, and combinations thereof. In one embodiment, the PBI component is the major (*i.e.*, at least 50 wt%) component. A representative (non-limiting) illustration of the PBI molecule is set forth in Figure 1. PBI also refers to, for example, the product of the melt polymerization of an tetraamine (*e.g.*, aromatic and heteroaromatic tetra-amino compounds) and a second monomer being selected from the group consisting of free dicarboxylic acids, alkyl and/or aromatic esters of dicarboxylic acids, alkyl and/or aromatic esters of aromatic or heterocyclic dicarboxylic acid, and/or alkyl and/or aromatic anhydrides of aromatic or heterocyclic dicarboxylic acid. Further details may be obtained from US Patent Nos. Re 26065; 4506068; 4814530; and US Publication No. 2007/0151926, each of which is incorporated herein by reference. PBI is commercially available from PBI Performance Products, Inc. of Charlotte, NC.

The aromatic and heteroaromatic tetra-amino compounds, used in accordance with the invention, are preferably 3,3',4,4'-tetra-aminobiphenyl, 2,3,5,6-tetra-aminopyridine, 1,2,4,5-tetra-aminobenzene, 3,3',4,4'-tetra-aminodiphenylsulfone, 3,3',4,4'-tetra-aminodiphenyl ether, 3,3',4,4'-tetra-aminobenzophenone, 3,3',4,4'-tetra-aminodiphenyl methane, and 3,3',4,4'-tetra-aminodiphenyldimethylmethane, and their salts, in particular, their mono-, di-, tri-, and tetrahydrochloride derivatives.

The aromatic carboxylic acids used, in accordance with the invention, are dicarboxylic acids or its esters, or its anhydrides or its acid chlorides. The term

"aromatic carboxylic acids" equally comprises heteroaromatic carboxylic acids as well. Preferably, the aromatic dicarboxylic acids are isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,6-dihydroxyisophthalic acid, 4,6-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, diphenylsulfone-4,4'-dicarboxylic acid, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid, or their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or their acid chlorides.

The heteroaromatic carboxylic acids used, in accordance with the invention, are heteroaromatic dicarboxylic acids or their esters or their anhydrides. The "heteroaromatic dicarboxylic acids" include aromatic systems that contain at least one nitrogen, oxygen, sulfur, or phosphorus atom in the ring. Preferably, it is pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridine dicarboxylic acid, 3,5-pyrazole dicarboxylic

acid, 2,6-pyrimidine dicarboxylic acid, 2,5-pyrazine dicarboxylic acid, 2,4,6-pyridine tricarboxylic acid, and benzimidazole-5,6-dicarboxylic acid, as well as their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or their acid chlorides.

The aromatic and heteroaromatic diaminocarboxylic acid used in accordance with the invention is preferably diaminobenzoic acid and its mono- and dihydrochloride derivatives.

Preferably, mixtures of at least 2 different aromatic carboxylic acids are used. These mixtures are, in particular, mixtures of N-heteroaromatic dicarboxylic acids and aromatic dicarboxylic acids or their esters. Non-limiting examples are isophthalic acid, terephthalic acid, phthalic acid, 2,5-dihydroxyterephthalic acid, 2,6-dihydroxyisophthalic acid, 4,6-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, diphenylsulfone-4,4'-dicarboxylic acid, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidine dicarboxylic acid, and 2,5-pyrazine dicarboxylic acid. Preferably, it is the diphenyl isophthalate (DPIP) and its ester.

Examples of polybenzimidazoles which may be prepared according to the process as described above include:

poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole;

poly-2,2'-(biphenylene-2"2''')-5,5'-bibenzimidazole;

poly-2,2'-(biphenylene-4"4''')-5,5'-bibenzimidazole;

poly-2,2'-(1",1",3"-trimethylindanylene)-3"5"-p-phenylene-5,5'-bibenzimidazole;

2,2'-(m-phenylene)-5,5'-bibenzimidazole/2,2'-(1",1",3"-trimethylindanylene)-5",3'-(p-phenylene)-5,5'-bibenzimidazole copolymer;

2,2'-(m-phenylene)-5,5'-bibenzimidazole-2,2'-biphenylene-2",2'''-5,5'-bibenzimidazole copolymer;

poly-2,2'-(furylene-2",5'')-5,5'-bibenzimidazole;

poly-2,2'-(naphthalene-1",6'')-5,5'-bibenzimidazole;

poly-2,2'-(naphthalene-2",6'')-5,5'-bibenzimidazole;

poly-2,2'-amylene-5,5'-bibenzimidazole;

poly-2,2'-octamethylene-5,5'-bibenzimidazole;

poly-2,2'-(m-phenylene)-diimidazobenzene;

poly-2,2'-cyclohexenyl-5,5'-bibenzimidazole;

poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole)ether;

poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole)sulfide;

poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole)sulfone;

poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole)methane;

poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole)propane-2,2; and

poly-ethylene-1,2-2,2''-(m-phenylene)-5,5''-dibenzimidazole)ethylene-1,2

where the double bonds of the ethylene groups are intact in the final polymer. Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, a preferred polymer, can be prepared by the reaction of 3,3',4,4'-tetraaminobiphenyl with a combination of isophthalic acid with diphenyl isophthalate or with a dialkyl isophthalate such as dimethyl isophthalate; a combination of diphenyl isophthalate and a dialkyl isophthalate such as dimethyl isophthalate; or at least one dialkyl isophthalate such as dimethyl isophthalate, as the sole dicarboxylic component.

Acid-resistant PBI refers to a chemically modified PBI that is resistant to acids. The acid-resistant PBI has greater resistance to adsorbing (or imbibing) the acidic solvent to be dehydrated than the same non-acid-resistant PBI. In other words, PBI's inherent affinity for acid is decreased so that its separation efficiency is increased. The acid-resistant PBI may be obtained by any modification method. Such modifications methods may include, without limitation, cross-linking, N-substitution, sulfonation, phosphonation, and combinations thereof. This modification may be at the surface (if, for example, the PBI is in the form of a sheet, fiber, hollow fiber, or tube) or may be throughout the shaped PBI (if, for example, the PBI is made acid-resistant prior to being shaped). There may be several routes for each of the foregoing modifications. For example, there are at least three ways to sulfonate (*i.e.*, add a sulfate group to the PBI polymer backbone). They include, without limitation, i) direct sulfonation of the PBI structure, ii) chemical grafting of the monomers with sulfate group, and iii) sulfonation following radiation grafting of monomer groups. Hereinafter, the invention will be

described with reference to a PBI film where the surface of the film is directly sulfonated, it being understood that the invention is not so limited.

In general, the PBI film may be made in any fashion. In one embodiment, the PBI film is a solid film without pores or micropores. For example, the film may be cast from a PBI solution. Solvents for the PBI polymer may include, without limit, DMAc, N-methyl pyrrolidinone (NMP), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and combinations thereof. The PBI solution, in one embodiment, may contain 10-45 wt% PBI, and in others, 12-30 wt% PBI, and 14-28 wt% PBI. In one embodiment, the casting solution is degassed, cast onto a substrate, then the solvent is driven from the cast film, and the solvent-free cast film is vacuum-dried and cooled.

The cast PBI film may then be chemically modified to be acid-resistant. In one embodiment, the film may be sulfonated. The film may be immersed in a sulfuric acid (e.g., concentration up to 20 wt% or 1-20 wt%, or 2-15 wt%, or 2-10 wt% or 2-6 wt%) at a given temperature (e.g., from 30-80°C, or 40-70°C, or 45-55°C) for given time (e.g., 1-4 hours, or 1.5-3.5 hours or 1.75-2.5 hours). Thereafter, excess acid may be removed from the surface of the film.

Optionally, the sulfonated film may be thermally stabilized. During this thermal stabilization, the sulfonated film is heated to a given temperature (e.g., 300-500°C, or 350-450°C, or 400-450°C) for a given time (e.g., up to 5 minutes, or 0.3-4.5 minutes, or 0.5-1.5 minutes).

Thereafter, the sulfonated film may be freed of trace sulfonate groups. This may be accomplished by immersing the sulfonated film in boiling water for a give time (e.g., 1-5 hours, or 2-4 hours, or 2.5-3.5 hours). Then, this film may be dried to remove any adsorbed water molecules by placing the film in a vacuum oven.

A contactor may be used to house the foregoing membranes. Contactors are known and may include: plate-and-frame modules, tubular modules, hollow fiber modules, and spiral wound modules. See for example: "Membrane technology," *Wikipedia, The Free Encyclopedia* (2012); Kesting, R. E., *Synthetic Polymeric Membranes, 2nd Edition*, John Wiley & Sons, NYC, NY (1985), pages 10-14; Cheryan, M., *Ultrafiltration Handbook*, Technomic Publishing Co., Lancaster PA (1986), pages 127-168; and *Chemical Engineering Handbook, 5th Edition*, McGraw-Hill Book Company, NYC, NY (1973), Figure 17-38, US Patent Nos. 5264171 and 5352361, each of which is incorporated herein by reference.

A dehydration system may comprise one or more of the foregoing contactors or other equipment containing the foregoing membranes that are used to dehydrate the aqueous acidic solvent. For example, a plurality of contactors, arranged in series or parallel or a combination of both, and associated equipment (e.g., pumps, control/monitoring equipment, and vacuum pumps) are assembled for the purpose of dehydrating the aqueous acidic solvent.

The aqueous acidic solvent may be dehydrated by contacting an acidic aqueous solution with a membrane comprising an acid-resistant polybenzimidazole; taking away a permeate stream rich in water; and taking away a concentrate stream rich in the acid. In one embodiment, the permeate stream is coupled to a vacuum. The feed concentration of the acidic aqueous solution may be, in one embodiment, any concentration. In other embodiments, the feed concentration may range from 50-95 wt%, or 75-95 wt%, or 78-92 wt%. The operating temperature during the dehydration may be, in one embodiment, any temperature. In other embodiments, the temperature may range from 20-85°C, or 25-75°C.

In Figure 2, there is a comparison of separation factor and flux at various temperatures between the acid-resistant PBI disclosed herein and other known membranes for acidic solvents (*e.g.*, acetic acid).

While the examples below are directed to the pervaporative dehydration of the acidic solvent, acetic acid, the invention is not so limited. The acid-resistant membrane may be used in other pervaporation processes or dehydration processes.

The invention will be further illustrated in the following non-limiting examples.

Examples

Materials

Polybenzimidazole (PBI) was used in the fabrication of the membranes. PBI polymer solution was provided by PBI Performance Products, Inc. with the composition of PBI 26.2 wt%, dimethylacetamide (DMAc) 72.3 wt%, and lithium chloride (LiCl) 1.5 wt%.

Concentrated sulfuric acid (H_2SO_4) of analytical grade, obtained from Merck was used to mix with de-ionized water to prepare the sulfonation solution with varied concentration.

Membrane preparation procedures

A dense flat-sheet PBI membrane with sulfonation modification on the membrane surface was prepared. The flat-sheet PBI dense membrane is cast from a 15 wt% PBI polymer solution in DMAc. The polymer dope solution of PBI/DMAc/LiCl (15/84.1/0.9 wt%) is prepared by diluting the supplied PBI solution. The diluted solution is allowed to degas overnight prior to casting onto a glass plate with a casting knife at a thickness of about 70-100 μm . The as-cast membrane is then placed on a hot plate preset at 75 °C for 15 hours, to allow the solvent evaporated slowly. The resultant film is carefully peeled off from the glass plate and then dried in a vacuum oven between two wire meshes, with temperature gradually increased to 250°C at a rate of 0.6°C/min and held there for 24 hours to remove the residual solvents before cooling down naturally. The wire meshes not only prevent the membrane from sticking to the glass

plate but also help uniformly dry the membrane from both surfaces. With this drying protocol, the LiCl remains in the as-fabricated PBI membrane.

Modification of the PBI membrane is a combination of sulfonation and thermal treatment. PBI membranes were immersed in a sulfuric acid aqueous solution of a fixed concentration at 50°C for 2 hours. They were subsequently dried using filter paper to remove the excess sulfuric acid on their surface. The PBI membranes were then thermally treated by placing them in a furnace pre-set at 450°C for a fixed time in air (without vacuum). Thereafter, the samples were immersed in boiling water for 3 hours to remove traces of sulfate groups and dried between two wire meshes at 100°C in the Binder programmable vacuum oven to remove adsorbed water molecules. A Mitutoyo micrometer was then employed to measure the final membrane thickness, which was about 15-20 μm .

Pervaporation experiments

A static pervaporation cell was used to test flat-sheet dense membrane performance at room temperature. Also see: Y. Wang, M. Gruender, T. S. Chung, Pervaporation dehydration of ethylene glycol through polybenzimidazole (PBI)-based membranes. 1. Membrane fabrication, *J. Membr. Sci.* 363 (2010) 149-159, incorporated herein by reference. A testing membrane was placed in the stainless steel permeation cell with an effective surface area of 15.2 cm^2 . The system was stabilized for 2 hours before the collection of samples. Thereafter, permeate samples were collected by a cold trap immersed in liquid nitrogen. The samples were weighted. The sample

compositions were analyzed with three parallel injections by a Hewlett-Packard GC 7890 A with a HP-INNOWAX column (packed with cross-linked polyethylene glycol) and a TCD detector. Finally, the data of flux and composition were averaged. The feed content varied less than 0.5 wt% during the entire experiment and can be therefore considered as constant during the experiment because of the large quantity of feed solution comparing to the permeate sample. The feed flow rate was maintained at 1.38 l/min. The operating temperature was room temperature ($22\pm 2^\circ\text{C}$) unless stated otherwise. The permeate pressure was maintained at less than 3 mbar by a vacuum pump, unless it is stated. Flux and separation factors were calculated by the following equations:

$$J = \frac{Q}{At} \quad (1)$$

$$\alpha_{2/1} = \frac{y_2 / y_1}{x_2 / x_1} \quad (2)$$

where, J is the flux, Q is the total mass transferred over time t (hour), A the membrane area (m^2), subscripts 1 and 2 refer to acetic acid and water, respectively; y_w and x_w are the weight fractions of components in the permeate and feed, respectively, and were analyzed through a Hewlett-Packard GC 7890 A with a HP-INNOWAX column (packed with cross-linked polyethylene glycol) and a TCD detector.

Pervaporation Examples

The present examples in pervaporation application are intended to help illustrate the process of the present invention. The flux of permeate in all examples for acetic acid (AA) dehydration through the flat-sheet dense membranes is given in unit of $\text{g}\cdot\mu\text{m}/\text{m}^2\cdot\text{hr}$, which is normalized by the membrane thickness.

Examples 1-4 demonstrate the pervaporation performance of the sulfonated PBI dense membranes with the effect of varying sulfuric acid concentration for the feed composition of AA/H₂O (50/50 wt%). The post thermal treatment is carried at 450 °C for 30 seconds.

Examples 1-4

Sulfuric acid concentration (wt%)	Permeate (AA wt%)	Flux (g/m ² hr)	Separation factor (water/AA)
original	13.60	100	7
0	14.91	49	7
2.5	0.015	168	6631
5	0.014	138	7156
10	27.06	99	27

The results show the pervaporation performance of the dense PBI membranes in its neat form is quite poor. The separation factor is less than 10 and the total flux is about 100 g/m²hr. With sulfonation of the PBI membrane, both the flux and separation factor are significantly improved.

Examples 5-10 demonstrate the pervaporation performance with the effect of varying post thermal treatment duration after sulfonation, for pervaporation dehydration of acetic acid with the feed composition of AA/H₂O (50/50 wt%). All PBI membranes were sulfonated in 2.5 wt% sulfuric acid solution for 2 hours before thermal treatment. The thermal treatment after the sulfonation stabilizes the sulfonated structure.

Examples 5-10

Thermal treatment duration (seconds)	Permeate (AA wt%)	Flux (g/m ² hr)	Separation factor (water/AA)
0	3.247	96	30
10	6.309	110	46
20	0.016	124	6348
30	0.015	168	6631
60	0.019	201	5341
120	1.15	114	86

In Examples 11-16, the effect of feed composition on the normalized total flux and separation factor of the sulfonated PBI membranes is demonstrated with the pervaporation operation at room temperature. All PBI membranes were sulfonated with 2.5 wt% sulfuric acid solution for 2 hours and thermal treated at 450 °C for 30 seconds.

Examples 11-16

Feed composition (AA wt%)	Permeate (AA wt%)	Flux (g/m ² hr)	Separation factor (water/AA)
50	0.015	168	6631
60	0.022	151	6692
70	0.027	142	8825
80	0.030	121	13,000
90	0.036	98	24,000
95	0.040	86	39,000

The separation factor for feeds with 80 and 90 wt% of acetic acid are assigned an arbitrarily value of greater than 10,000 as the permeate contains less than 0.05 wt% of acetic acid. From the results, the separation factor generally increases with the increase in acetic acid concentration in the feed up to 90 wt% of acetic acid and then

decreases slightly. On the other hand, the flux generally decreases for feed containing between 50 and 95 wt% of acetic acid.

In Examples 17-20, the effect of operating temperature on the normalized total flux and separation factor of the sulfonated PBI membranes is demonstrated with the feed composition of AA/water (50/50 wt%). All PBI membranes were sulfonated with 2.5 wt% sulfuric acid solution for 2 hours and thermal treated at 450°C for 30 seconds. The total flux increases while separation factor decreases with the operational temperature.

Examples 17-20

Operation temperature (°C)	Permeate (AA wt%)	Flux (g/m ² hr)	Separation factor (water/AA)
25	0.0151	168	6631
40	0.0164	203	6215
60	0.0183	207	5461
80	0.0195	276	5110

The present invention may be embodied in other forms without departing from the spirit and the essential attributes thereof, and, accordingly, reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.

We claim:

1. A pervaporation membrane comprising:
an acid-resistant polybenzimidazole (PBI) membrane.
2. The pervaporation membrane according to claim 1 wherein said acid-resistant PBI membrane being a PBI membrane chemically modified by a process selected from the group consisting of sulfonation, phosphonation, cross-linking, N-substitution, and/or combinations thereof.
3. The pervaporation membrane according to claim 1 wherein said membrane being: a flat membrane, a multi-layer flat membrane, a hollow fiber membrane, or a multi-layer hollow fiber membrane.
4. The pervaporation membrane according to claim 3 wherein said multi-layer flat membrane having one layer being the acid-resistant PBI membrane and another layer being a microporous support layer.
5. The pervaporation membrane according to claim 3 wherein said multi-layer hollow fiber membrane having one layer being the acid-resistant PBI membrane and another layer being a microporous support layer, the PBI layer being either the inner or outer layer.

6. The pervaporation membrane according to claim 1 wherein said membrane being thermally stabilized.
7. A membrane contactor comprising the membrane of claim 1.
8. A dehydration system comprising the membrane of claim 1.
9. A method for the dehydration of an acid material comprising the steps of:
contacting an acidic aqueous solution with a membrane comprising an acid-resistant polybenzimidazole;
taking away a permeate stream rich in water; and
taking away a concentrate stream rich in the acid material.
10. The method of claim 9 wherein the membrane being contained in a membrane contactor.
11. The method of claim 9 wherein the membrane being acid-resistant PBI membrane being a PBI membrane chemically modified by a process selected from the group consisting of sulfonation, phosphonation, cross-linking, N-substitution, and/or combinations thereof.
12. The method of claim 9 wherein the acidic aqueous solution comprising an organic acid.

13. The method of claim 9 wherein the acidic aqueous solution comprising acetic acid.

14. A method of making an acid-resistant polybenzimidazole (PBI) membrane comprising the steps of:

forming a PBI film from a solution of PBI polymer; and

chemically modifying the PBI film by a process selected from the group consisting of sulfonation, phosphonation, cross-linking, N-substitution, and/or combinations thereof.

15. The method of making an acid-resistant polybenzimidazole (PBI) membrane according to claim X further comprising the step of:

thermally stabilizing the modified PBI film.

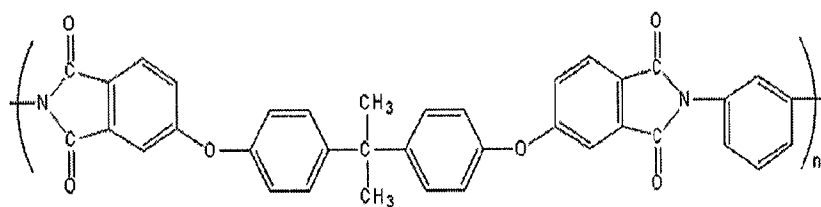


Figure 1

Feed (AA wt%)	Membrane	Separation factor (water/AA)	Flux (g/m ² h)	T (°C)
50	SPEK-C/PVA blend membrane	40	850	50
50	GA cross-linked STA filled SPEK-C/PVA blend membrane on PEK-C substrate	60	675	50
50	PVA membrane grafted with AN & HEMA	4	550	30
50	Acid-resistant PBI membrane*	6631	168	22
50	Acid-resistant PBI membrane *	5461	207	60
70	SPEK-C membrane	144	421	30
70	SPEK-C membrane	56	590	50
70	PVA membrane grafted with AN & HEMA	4	300	30
70	Acid-resistant PBI membrane*	8825	142	22
80	SPEK-C membrane	69	310	50
80	PS hollow fiber membrane	63.5	511	70
80	PVC/PAN composite membrane with porous PAN support layer	182-274	560-740	80
80	PVC/PAN bi-layer membrane with dense PAN support layer	5027	35	80
80	Acid-resistant PBI membrane *	13,000	121	22
90	poly(4-methyl-1-pentene) membrane modified with 4-vinylpyridine	807	68	25
90	PVA membrane grafted with AN	14.6	90	30
90	PVA-silicone hybrid membrane cross-linked by TEOS using sol-gel method	1116	33.3	30
90	PVA cross-linked by malic acid	670	48	40
90	SPEK-C/PVA blend membrane	59.3	492	50
90	GA cross-linked STA filled SPEK-C/PVA blend membrane on PEK-C substrate	91.2	592	50
90	PVA cross-linked by PAA	795	5.6	30
90	PVA membrane cross-linked by amic acid based on m-phenylene diamine	176	12	30
90	Acid-resistant PBI membrane *	24,000	98	22
95	Acid-resistant PBI membrane *	39,000	86	22

*Present Invention (e.g., sulfonated PBI, SPBI)

Figure 2

A. CLASSIFICATION OF SUBJECT MATTER**B01D 71/62(2006.01)i, B01D 61/36(2006.01)i, B01D 69/00(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D 71/62; B01D 69/08; B01D 61/14; C25B 13/08; H01M 8/10; C08K 5/5353; C08J 5/22; B01D 61/36; B01D 69/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & keywords: pervatpration membranem, acid-resistant polybenzimidazole (PBI) membrane, chemically modified, contactor, dehydration system**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0266222 A1 (WANG, YAN et al.) 03 November 2011 See paragraph [0071]; claims 1, 7 and 14-16.	1,3-10,12-13
Y		2,11,14-15
Y	US 2008-0308491 A1 (HARING, THOMAS) 18 December 2008 See claims 1-2.	2,11,14-15
A	US 2006-0257705 A1 (NAKATO, KUNIHIRO et al.) 16 November 2006 See claim 1.	1-15
A	KR 10-0684730 B1 (SAMSUNG SDI CO., LTD.) 20 February 2007 See claim 1.	1-15
A	US 2002-0045085 A1 (FORMATO, RICHARD M. et al.) 18 April 2002 See claims 1 and 11-12.	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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Name and mailing address of the ISA/KR

Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City,
302-701, Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

LEE Dong Wook

Telephone No. +82-42-481-8163



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/037901

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