Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Peng, Ping , Shi, Baoli and Lan, Yongqiang(2011) 'A Review of Membrane Materials for Ethanol Recovery by Pervaporation', Separation Science and Technology, 46: 2, 234 — 246
To link to this Article: DOI: 10.1080/01496395.2010.504681
URL: http://dx.doi.org/10.1080/01496395.2010.504681

Separation Science and Technology, 46: 234–246, 2011
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.504681

A Review of Membrane Materials for Ethanol Recovery by Pervaporation

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Due to an emerging scarcity of oil resources and an associated increase of oil prices, biofuels (e.g., ethanol) play an important role in the energy crisis. Fermentation is a common process for producing ethanol from renewable biomass. Pervaporation is an attractive technique for the recovery of ethanol from the fermentation systems. Separation membrane is the key element in the pervaporation separation equipments. In this article, the pervaporation performances of ethanol-permselective membranes presented in the recovery of ethanol from dilute ethanol aqueous solution are reviewed. An analytical overview on the challenges and opportunities, and the prospect of ethanol-permselective membranes by pervaporation is also discussed.

Keywords ethanol recovery; membrane materials; PDMS; pervaporation

INTRODUCTION

Due to an emerging scarcity of the oil resources and an associated increase of the oil prices, it is generally accepted that the fossil sources for our energy supply have to be gradually replaced by renewable substrates. It will complement solar, wind, and other intermittent energy sources. One of the most immediate and important application of biomass energy systems could be in the fermentation of ethanol from biomass (1).

Biomass has been taken as an interesting energy source for several reasons. The main reason is that bioenergy can contribute to sustainable development. Moreover, biomass energy can play an important role in reducing the emission of greenhouse gas. Since produced and utilized in a sustainable way, the use of biomass for energy will offset the emission of greenhouse gas from the fossil fuel. Because biomass plantations may create new employment opportunities in rural areas in the development countries, it also contributes to the social aspect of sustainability (2,3). Ethanol represents one of the more important resources of renewable energies.

Fermentation is an attractive process for producing ethanol from renewable biomass (4). One approach to improving the productivity of ethanol fermentations is to continuously remove ethanol from the fermentation broth as it is produced, thus reducing the inhibitory effect of high ethanol concentration. This approach would also allow a continuous fermentation to be conducted. The proposed techniques for ethanol recovery from fermentation broths include vacuum distillation (5), solvent extraction (6), gas stripping by CO_2 (7), and membrane pervaporation (8,9). Since pervaporation has many advantages such as energy saving, cost effectivenecs, and the protection of the enviroment, coupling the pervaporation to fermentation is a significant technique for the continuous conversion of biomass into ethanol.

Pervaporation is a membrane process for liquid separation. It is a unit operation in which two components are separated with a nonporous polymeric or inorganic membrane through the combination of different permeation rates of the components. Commonly, vacuum operation is applied to the downstream side of the membrane because an evaporative phase change usually happens (10). According to the vapor–liquid equilibrium curve of ethanol–water, the mass fraction of ethanol in vapor is much higher than its mass fraction in liquid when the ethanol concentration in liquid is between 0 to 20%. Consequently, pervaporation has an inherent selectivity for ethanol at low ethanol concentration. The separation membrane is the key element in pervaporation equipments. The pervaporation performances of the membrane are generally characterized with flux and selectivity. Flux is defined by the following equation:

$$J = \frac{Q}{At} \tag{1}$$

where J, Q, A, t are permeation flux ($g \cdot m^{-2} \cdot h^{-1}$), total amount of permeation (g), membrane area (m^2), and operating time (h), respectively. The selectivity is expressed in terms of the separation factor α which is defined as follows:

$$\alpha = \frac{Y_A X_B}{X_A Y_B} \tag{2}$$

Received 1 April 2010; accepted 24 June 2010.

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where X_A and X_B represent the weight fractions of ethanol and water concentrations (wt%) in the feed solution, respectively. And Y_A and Y_B represent the weight fractions of ethanol and water concentrations (wt%) in the permeation.

Although many membrane materials have been studied for the purpose of recovering ethanol from dilute fermentation broths by pervaporation, the materials with good ethanol-permselective properties are few and their pervaporation performances do not meet the demands of industrialization at this stage. In this paper, the pervaporation performances of the ethanol-permselective membranes presented in the recovery of ethanol from dilute ethanol aqueous solution is reviewed. An analytical overview on the challenges and opportunities, and the prospect of ethanol-permselective membranes by pervaporation is also discussed.

POLYMERIC MEMBRANE MATERIALS FOR ETHANOL RECOVERY

Polydimethylsiloxane (PDMS)

PDMS, often referred to as "silicone rubber", has been known as the most representative alcohol-permselective membrane material for the removal of alcohol from aqueous solutions at low alcohol concentrations, thanks to its hydrophobic nature. The high diffusivity of ethanol in the PDMS membrane, resulting from free rotation of Si-O bond, also contributes to the excellent ethanol selectivity. Several companies have manufactured PDMS membranes, such as SolSep BV (Apeldoorn, Netherlands), Pervatech BV (Enter, Netherlands), Sulzer Chemtech (Neunkirchen, Germany), and Celanese Corp. (NC, United States). A comprehensive review paper reported by Beaumelle et al. (11) indicated that the fluxes of unmodified PDMS membranes ranged from 1 to 1000 $\mathrm{g \cdot m^{-2} \cdot h^{-1}}$ and the separation factors were less than 10 for the removal of ethanol by the pervaporation process (12–25). O'Brien et al. (26), after analyzing the fermentation-pervaporation processes of a commercial-scale fuel ethanol plant, concluded that a coupling system would be cost-competitive if the performances of pervaporation membranes could be improved modestly so as to exhibit the flux of 150 $\mathrm{g \cdot m^{-2} \cdot h^{-1}}$ and separation factor of 10.3 for ethanol to water. Moreover, PDMS has poor film-forming ability and relative low permselectivity due to its low mechanical properties and high swelling capacity of PDMS vulcanizate.

In order to enhance the pervaporation performances, attempts have been made to modify PDMS in different ways. Literature data of PDMS membranes on different supports are included in Table 1. On the other hand, the reported modifications on PDMS mainly focused on PDMS block or graft copolymers with other polymers. Miyata et al. (35) prepared PDMS/polystyrene (PSt) interpenetrating polymer network (IPN) membranes by the bulk copolymerization of styrene and divinylbenzene in the PDMS networks. The mechanical properties of PDMS were improved. The PDMS/PSt IPN membrane with a PDMS content of 40 mol% had stronger mechanical properties. When an aqueous ethanol solution permeated through the PDMS/PSt IPN membranes by pervaporation, the PDMS/PSt IPN membranes exhibited ethanol selectivity, regardless of the PDMS content. For the PDMS/PSt IPN membrane having a PDMS content of 40 mol%, in an aqueous solution with 10 wt% ethanol at 40°C, the ethanol concentration in the permeate was about 50 wt%, and the normalized flux was approximately $2 \times 10^9\ \mathrm{g \cdot m \cdot m^{-2} \cdot h^{-1}}$. PDMS membranes containing polyurethaneurea were prepared by Takegami et al. (17). It was found that the ethanol separation factor was 8.6 which was similar to the unmodified PDMS membranes. Zhe et al. (36) synthesized a novel silicone copolymer consisting of PDMS segments and ladder-like phenylsilsesquioxane segments. High separation factor was obtained at

TABLE 1

Ethanol–water separation performance of PDMS membranes with different support

Support	Feed concentration (wt%)	Temperature (°C)	Thickness (μm)	Separation factor	Flux ($\mathrm{g\ m^{-2}\ h^{-1}}$)	Reference
PTFE	2	30	50	10	~102	27
CA	5	40	1–2[a]	9.3	1140	28
PA	4	45	5[a]	8.5	1850	29
CA	5	40	8[a]	8.5	1300	30
PS	5	42	1[a]	6.7	1440	31
PS	8	50	–	6.4	265	32
PS	4	45	1[a]	5	1600	29
PVDF	10	–	–	2.2	8000	33
CA	3	50	8[a]	1	2800	34

[a] Supported on porous material.

low ethanol concentrations. The flux of ethanol increased but the flux of water kept constant as the concentrations of ethanol in feed increased. The reason was that because the copolymer consisted of rubbery PDMS segments and glassy ladder-like phenylsilsesquioxane segments, a microphase separated structure existed in the copolymer. In addition, the non-polar phenyl groups bonded to silicon atoms along the ladder-like chain had a regular outward arrangement which restricted the swelling of the membrane. Chang and Chang (37) reported a modified PDMS membrane, which was prepared through modifying PDMS solution with hexamethyldisiloxane, curing the solution with phenyltriethoxysilane, and coating on PDMS-g-PVDF support. The experimental results showed that the flux and separation factor were near $1300\,g \cdot m^{-2} \cdot h^{-1}$ and 5.1, respectively. Aroujalian and Raisi (38) compared the pervaporation performances of PDMS with POMS (polyoctylmethylsiloxane) membranes. They found that the total flux for both the PDMS and POMS membranes were close to $380\,g \cdot m^{-2} \cdot h^{-1}$ for a 2 wt% ethanol aqueous solution at 50°C. However, the separation factor of the PDMS membrane was near 9, while the separation factor of the POMS membrane was more than 5. Poly(1-phenyl-1-propyne) (PPP)/PDMS graft copolymer membranes also significantly showed preferential permeation ability to ethanol (39). Block copolymers of PDMS/PS/poly(4-hydroxystyrene) (PHS) having PDMS weight fraction of 0.6–0.7 showed a little lower separation factor ($\alpha = 6.8$) in comparison with the pure PDMS ($\alpha = 8.8$–9.4), and a preferential flux ($4500\,g \cdot m^{-2} \cdot h^{-1}$) in 8 wt% dilute ethanol solution (40). A blend membrane consisting of PDMS and 5.3 wt% copoly(N-isopropylacrylamide/1H,1H,2H,2H-perfluorododecyl acrylate) showed a high ethanol separation factor ($\alpha = 19.7$) in 2.5 wt% aqueous ethanol solution at 24°C (41).

Furthermore, much effort has been expended on searching for other effective means. Matsuyama et al. (42) prepared PDMS membranes by plasma polymerization of octamethyltrisiloxane on porous cellulose ester support. The maximum separation factor of 5.1 was obtained at the flux of $6200\,g \cdot m^{-2} \cdot h^{-1}$ for the separation of 5% (v/v) ethanol/water solution. Kashiwagi et al. (43) prepared highly ethanol-permselective membranes by surface treatment to thin PDMS membranes with silane compounds containing octadecyl groups. A separation factor of 18.0 and a flux of $150\,g \cdot m^{-2} \cdot h^{-1}$ was obtained with the membranes of plasma polymerization with hexamethyltrisiloxane treated by octadecyldiethoxymethylsilane. Preparing multi-layer PDMS/PVDF composite membrane with an alternative PDMS/PVDF/non-woven-fiber/PVDF/PDMS configuration was a novel method for producing ethanol-permselective membranes. Separation performances of the multi-layer composite membrane were enhanced compared with one side PDMS/PVDF composite membranes, especially in the low ethanol concentration range. The composite membrane gave the best pervaporation performances with a separation factor of 15 and a flux of $450\,g \cdot m^{-2} \cdot h^{-1}$ in 5 wt% ethanol solution at 60°C (44). Chang and Chang (33) also produced ethanol-permselective membranes with an alternative PDMS/PVDF/PDMS multi-layer structure. The membrane with four silicone layers showed superb pervaporation performances. When the separation factor was 31, the flux was $900\,g \cdot m^{-2} \cdot h^{-1}$, and when the separation factor was 2.2, the flux was $8000\,g \cdot m^{-2} \cdot h^{-1}$, comparing with the traditional membranes having only one active permseletive layer. Microporous polytetrafluoroethylene (PTFE) membrane, the pores of which were impregnated with silicone rubber, was chosen by Mori (45) for its large flux of $760\,g \cdot m^{-2} \cdot h^{-1}$, high ethanol separation factor of 8.3, and high stability.

Feed ingredients, as an important factor to influence the performances of pervaporation membranes, have received extensive attention (46). The PDMS/PAN membrane applied in the pervaporation system combining with a semi-continuous ethanol fermentation of lactose mash proved to possess a high separation factor ($\alpha > 8$) and very advantageous flux (2600–$3500\,g \cdot m^{-2} \cdot h^{-1}$) (47). PDMS membranes supplied by Celanese Corp. (Charlotte, NC) produced a separation factor of 8 and a flux of $135\,g \cdot m^{-2} \cdot h^{-1}$ when coupled to a fed-batch fermentation (48). The composite PDMS membrane offered superior separation for the recovery of ethanol from fermentation broth by pervaporation. The separation factor was 7.7 with the flux of $406\,g \cdot m^{-2} \cdot h^{-1}$ for a fermentation broth (49). When aroma compounds were presented, the separation factor generally decreased in comparison to the pure ethanol solution, while the flux was affected little (50). The average ethanol concentration in the permeation was about 77% (v/v) corresponding to a decrease of ethanol concentration in the retentate from 50 to 30% (v/v) for PDMS membranes, but the overall flux reached $3539\,g \cdot m^{-2} \cdot h^{-1}$ at 40°C (51).

Poly(1-trimethylsilyl-1-propyne) (PTMSP)

PTMSP, a glassy polymer with a large free volume, is another material that exhibits good characteristics for the separation of ethanol from diluted mixtures. The reported separation factor of PTMSP ranged from 9 to 26, which was higher than that of PDMS (45,52–59). The research work by Schmidt et al. (59) showed that PTMSP membranes exhibited a distinct advantage over the conventional poly(dimethyl siloxane) (PDMS) membranes for the removal of ethanol by pervaporation. The flux with PTMSP was about threefold higher and the separation factor was about twofold higher than the corresponding performances achieved with PDMS under similar conditions.

However, it seemed that PTMSP had no practical application as a pervaporation membrane material because of its tendency to physical and/or chemical aging, which caused deterioration of the membrane properties over time. Lopez-Dehesa et al. (60) observed that the initial value of the separation factor was approximately 4.5 and the flux was $1200\,g \cdot m^{-2} \cdot h^{-1}$ when using PTMSP membranes to separate a 50 wt% ethanol/water mixture at 50°C by pervaporation. However, the pervaporation performances of the PTMSP membranes decreased with the operating time because of the relaxation processes of the polymeric chains, which affected the free volume of the polymer.

In order to improve the prospects for this polymer, PTMSP has been modified to yield a more physically stable material. Masuda and Higashimura (61) showed that the properties of PTMSP were affected by the polymerization conditions. A series of PTMPS samples were prepared by varying synthesis conditions to evaluate the relationship between the polymerization conditions and the properties of the polymer membranes (52). It was found that the membrane properties of PTMSPs synthesized with using niobium pentachloride ($NbCl_5$) and tantalium pentachloride/triisobutylaluminum ($TaCl_5/Al(i\text{-}Bu)_3$) as catalysts did not deteriorate over time, even when acetic acid was present in the feed. A combination of high flux with a high separation factor (not less than 15) was observed for all PTMSP samples. In A.G. Fadeev's study (53), they investigated the pervaporation properties of PTMSP synthesized with using $TaCl_5/Al(i\text{-}Bu)_3$ as catalyst. The flux and separation factor of the PTMSP membrane were $330\,g \cdot m^{-2} \cdot h^{-1}$ and 19.9, respectively.

Nagase et al. reported the pervaporation characteristics of modified PTMSP membranes which were grafted by PDMS (57), alkylsilyl groups (54), and fluoroalkyl groups (62). It was found that the separation factor of each PTMSP/PDMS graft copolymer membrane was higher than that of the PTMSP membrane. The separation factor and flux reached the maximum values when the PDMS content was 12 mol%. At the maximum point, 7 wt% ethanol aqueous solution was concentrated to about 70 wt%. The separation factor and flux were 28.3 and $61\,g \cdot m^{-2} \cdot h^{-1}$, respectively (57). Kang et al. (63) studied the selectivity of PTMSP membrane containing dimethylsiloxane oligomer. The above researchers noticed that the PTMSP membranes had high separation factors for ethanol aqueous solutions in pervaporation. However, the fluxes of the modified PTMSP membranes were low. In order to improve the separation factor and keep the flux, Uragami et al. (64) focused on surface modification of PTMSP membranes by adding a small amount of polymer additive in casting solution, PFA-*g*-PDMS, which was a graft copolymer consisting of poly(fluoroacrylate) (PFA) and poly(dimethylsiloxane) (PDMS). It was predictable that the surface properties of the polymer membrane were closely correlated with the modification material. The flux of the surface-modified PTMSP membrane was about $600\,g \cdot m^{-2} \cdot h^{-1}$ and the separation factor was up to 20 when concentrating a 10 wt% ethanol aqueous solution by pervaporation. Introducing alkyl groups (methyl, ethyl, propyl, butyl, hexyl, octyl, and decyl groups) with appropriate length into PTMSP could effectively improve the separation factor (54). A separation factor of 17.8 was achieved for a substituted PTMSP membrane with *n*-Decane, which was similar to the trimethylsilyl substituted PTMSP membrane. To the knowledge of these authors, the membranes constructed from these materials are not commercially available at this time.

Other Polymeric Membrane Materials

Much effort has been expended on searching for other polymeric materials with better ethanol–water separation performance than PDMS and PTMSP. Unfortunately, materials are Seldom reported in the literatures. Polydimethylsiloxane-imide (PSI) copolymers were synthesized from α, ω-(bisaminopropyl) dimethylsiloxane oligomers (ODMS), aromatic dianhydrides (PMDA), and 1,3-bis(3-aminopropyl) tetramethyldisolxane (MDMS). For having a high amount of siloxane blocks, PSI gave the best pervaporation results. The optimum pervaporation performances of PSI were obtained in 10 wt% ethanol solution. The separation factor was 10.6 and the flux was $560\,g \cdot m^{-2} \cdot h^{-1}$ (65). Liu et al. (66) used poly(ether block amide) (PEBA 2533) membranes to separate ethanol/water mixtures. The experimental results showed that the pervaporation performances were not well. The flux was $118\,g \cdot m^{-2} \cdot h^{-1}$, while the separation factor was merely 2.5. Similar results were obtained by Garcia et al. (67) when using a hydrophobic POMS (polyoctylmethyl siloxane) membrane. For 11 wt% ethanol aqueous solution at 53°C, the total flux of the POMS membrane was around $1200\,g \cdot m^{-2} \cdot h^{-1}$ with a separation factor of 8. Ishihara and Matsui (14,68) prepared composite membranes composed of styrene-fluoroalkyl acrylate graft copolymers. The separation factor was up to 45.9, but the flux was only $5\,g \cdot m^{-2} \cdot h^{-1}$. Masuoka et al. (69) prepared the plasma-polymerized perfluoropropane (PFP) thin films on porous polysulfone (PSf) support. The pervaperation result was not very good. SolSep 3360 is a hydrophobic nanofiltration membrane manufactured by SolSep BV (Apeldoorn, Netherlands). Although the flux was up to $3500\,g \cdot m^{-2} \cdot h^{-1}$, the separation factor of the SolSep 3360 membrane was very low (70). Polyphenylmethylsiloxane (PPMS)/CA membranes showed the similar pervaporation performances compared with PDMS/CA for concentrating ethanol/water mixture. The total flux increased from 1140 to $1433\,g \cdot m^{-2} \cdot h^{-1}$ in 5 wt% feed concentration at 40°C, but the separation factor decreased from 9.3 to 6.2. It was attributed to the introduction of more hydrophobic and rigid phenyl groups to the molecular chains (28). Krea et al. (71) reported the synthesis of polysiloxane-imide (PSI) materials based on block copolymerization of two aromatic di-anhydrides: pyromellitic dianhydride (PMDA) and 5,5′-[2,2,2-trifluoro-l-(trifluoromethyl) ethylidene] bis-1,3- isobenzenefurandione (6FDA) with α, ω-diamino oligosiloxanes. When the PDMS content in the copolymer was up to 90%, the flux and separation factor of the fluorinated PSI were $2500\,g \cdot m^{-2} \cdot h^{-1}$ and 6, respectively. Huang et al. (72) synthesized a series of phosphazene heteropolymers (NP $(OC_6H_4C_3H_5)_x(OC_6H_5)_y(OR)_z)_n$ containing different pendant groups ($-OC_2H_5$, $-OCH_2CF_3$ and $-OCH_2CF_2CF_2CF_2CF_2H$) to enhance the hydrophobic property. Pervaporation results showed that the polyorganophosphazene material with $-OCH_2CF_3$ group had the best membrane separation performances for ethanol/water mixture under the same content of hydrophobic group. The separation factor was around 6.1 with a flux up to $260\,g \cdot m^{-2} \cdot h^{-1}$. The authors suggested that this result could be attributed to the highest affinity to ethanol and the highest diffusivity selectivity.

Liquid membrane (LM)-based pervaporation is also one of the potential techniques for the effective separating of dilute ethanol aqueous solution. The common method for preparing liquid membrane is immobilizing a liquid with high boiling point in the pores of a hydrophobic hollow fiber substrate so as to form a nanoporous coating on the hollow fiber surface when contacting the broth. The liquid membranes generally had higher separation factors. Thongsukmak and Sirkar (73) chose trioctylamine (TOA) as the fixed liquid and studied the pervaporation performances of the liquid membrane for the removal of ethanol. The results demonstrated that the TOA-LM had a high separation factor. The achieved separation factor was up to 80 at 54°C, but the flux was too low. To improve the separation performance of the TOA-LM, they (74) added a small amount of *n*-butanol to the solution fibers. As a result, when 2.5 wt% *n*-butanol was added to the feed, the separation factor increased considerably to as much as 113, and the flux was up to $16.2\,g \cdot m^{-2} \cdot h^{-1}$ for the feed containing 10 wt% ethanol at 54°C. Reducing the thickness of the TOA layer in the porous substrate wall of the coated fibers could change the pervaporation performances. It was found that the flux and separation factor were around $59.8\,g \cdot m^{-2} \cdot h^{-1}$ and 100 for a mixture containing about 10 wt% ethanol and 2 wt% *n*-butanol at 54°C, respectively. In addition, Christen et al. (75) developed a liquid membrane which consisted of a porous Teflon sheet support and isotridecanol as the fixed liquid to extract ethanol during semicontinuous fermentation of *Saccharomyces bayanus*. The membrane supplied an ordinary separation factor 7.2 and a lower flux $39\,g \cdot m^{-2} \cdot h^{-1}$. Thus, liquid membranes are of significant interest for the recovery of ethanol aqueous solutions.

Aroujalian and Raisi (38) tested the pervaporation performances of porous polytetrafluoroethylene (PTFE) membrane (0.2 mm pore diameter). It produced the total flux of $12000\,g \cdot m^{-2} \cdot h^{-1}$ with a separation factor near 2 for a 2 wt% ethanol aqueous feed at 60°C. When using a microporous hydrophobic PTFE membrane, Nakao et al. (76) found a separation factor of 8 and a high flux of $4000\,g \cdot m^{-2} \cdot h^{-1}$ in 5 wt% ethanol feed solution at 30°C. Although excellent high flux of ethanol was observed using microporous PTFE membranes, they generally did not exhibit a high separation factor. In contrast to the nonporous membranes, the porous membranes rarely governed the separation in pervaporation.

INORGANIC MEMBRANES FOR ETHANOL RECOVERY

While no organic membrane has yet to challenge PDMS membranes as the benchmark hydrophobic pervaporation membrane material, inorganic membranes based on hydrophobic zeolites have shown both higher ethanol separation factors and fluxes than PDMS membranes (77). An extensive review on zeolite materials and the fundamentals of using zeolites for pervaporation applications was written by Bowen et al. in 2004 (78).

Zeolites are hydrated aluminosilicates with uniform crystalline structures and molecular-sized pores. Small molecules can adsorb in these pores and diffuse through them. Because of the small pore size, the diffusion rates of some molecules with different sizes and adsorption strengths inside the zeolite crystals differ. Zeolites have been prepared as membranes by depositing polycrystalline layers on porous supports (79–81). These membranes took the advantages of differences in adsorption and diffusion to separate mixtures. Compared with the polymeric membranes, zeolite membranes show higher flux and a higher separation factor. Furthermore, the zeolite membranes have other predominances such as low swelling, high chemical resistance, and thermal stability. In recent years, zeolite membranes have been paid great attention to as the candidates for molecular sieving separation membranes and membrane reactors.

MFI membranes (silicalite-1 and ZSM-5) are the main subject for zeolite membranes. MFI type zeolites consist of straight and zig-zag pores with a pore opening of nearly 0.55 nm. Soydas et al. (82) synthesized the MFI type zeolite membranes in a recirculating flow system where the synthesis solution was flown over a tubular α -alumina supports. The pervaporation separation factors were 43 and 23 with the fluxes of 200 and $1900\,g \cdot m^{-2} \cdot h^{-1}$ in 5 wt% ethanol/water mixture at 25 and 85°C, respectively. Kuhn et al. (83) tested two multi-channel defect-free high-silica MFI membranes for the removal of ethanol from 7 mol% and 3 mol% aqueous solutions. One membrane was detemplated by calcination, and the other was ozonicated. The ethanol separation factors of both of the membranes were similar which ranged from about 20 at 100°C to 40 at 75°C. After a second calcination step at 550°C, both of the membranes showed almost a doubling of the fluxes to 2700 and 3300 $g \cdot m^{-2} \cdot h^{-1}$, while no effect on the membrane separation factor was observed.

Silicalite-1 (0.56 nm pore diameter), one of zeolite, is more hydrophobic than any other zeolites. It has been reported that the silicalite was the best hydrophobic zeolite and that the polycrystalline silicalite membrane showed the high pervaporation performances for the separation of ethanol/water mixture. For 20 wt% ethanol broth at 30°C, the separation factor of silicalite zeolite membrane was even up to 218. This high separation factor was due to the salts that were contained in the fermentation broth. What is more, the flux with a value of around 600 $g \cdot m^{-2} \cdot h^{-1}$ was not low, but the high ethanol separation factor was only maintained for 48 h (84).

In order to improve further the separation performances of silicalite-1 zeolite membrane, many efforts have been made, such as improving the membrane preparation technologies (85–93), choosing suitable support (94–98), support pretreatment, membrane post-treatment, etc. Ikegami et al. (85,86) and Sano et al. (87) prepared polycrystalline silicalite membrane by the hydrothermal synthesis. The silicalite membrane exhibited a very high ethanol separation factor in ethanol aqueous solution at 170°C for 48 h. The high ethanol separation factor of more than 60 was achieved in 5 vol% ethanol aqueous solution at 30°C. The flux reached a maximum of 680 $g \cdot m^{-2} \cdot h^{-1}$. In the adsorption experiments of ethanol and water on silicalite, it was found that the high separation factor could be attributed to the selective sorption of ethanol into the silicalite membrane. Sano et al. (87) and Nomura et al. (88) arrived at the same conclusion. They found that the ethanol concentration in the permeate was higher than vapor-liquid equilibrium in all feed compositions. The maximum separation factor and total flux were 64 and 600 $g \cdot m^{-2} \cdot h^{-1}$ in 4.65 wt% feed ethanol concentration at 30°C. Later, Negishi et al. (89) prepared silicalite membrane with a seed technique. The best performances of the membrane showed a separation factor of 35.1 and total flux of 220 $g \cdot m^{-2} \cdot h^{-1}$. Sano et al. (90) prepared polycrystalline silicalite membranes. The pervaporation result showed a high ethanol-permselectivity. The separation factor was 50 and the flux was 720 $g \cdot m^{-2} \cdot h^{-1}$ at 60°C. Chen et al. (91) have shown that the silicalite membrane obtained by only one step in situ hydrothermal synthesis possessed the separation factor of 81 and total flux of 390 $g \cdot m^{-2} \cdot h^{-1}$ in 3 wt% ethanol solution at 60°C. In order to improve the separation performances of silicalite membranes, a two-step synthesis was used to prepare membranes on silica tubes. Although the membrane thickness with the two-step synthesis was much higher than that obtained by the one-step synthesis, the former had higher flux than that of the latter, and the membrane with an ethanol separation factor of 95 and flux of 580 $g \cdot m^{-2} \cdot h^{-1}$ was achieved. Subsequently, Chen and co-workers (92,93) successfully synthesized high-performance silicalite-1 membranes on novel porous silica tubes by a two-step in-situ hydrothermal synthesis by filling with the mixed solution containing water and glycerol. The results showed that the formation of zeolite crystals in the pores of the supports was restrained with the filling solution, which decreased the diffusion resistance of silicalite-1 membranes. It showed higher separation performances with the flux and the separation factors were 560 $g \cdot m^{-2} \cdot h^{-1}$ and 84, respectively. In their work, it suggested that silica supports were more suitable for preparing high-performance silicalite-1 membranes, and the potential advantages of in situ hydrothermal synthesis were that the nuclei was firmly attached to the silica tubes and the preparation of the tubular membrane was easier to be carried out, which may be more suitable for preparation in large scale.

For different supports, Lin et al. (94) reported that a silicalite-1 membrane supported by mullite porous was the best membrane so far for the separation of ethanol/water mixture. Their membrane had a flux of 900 $g \cdot m^{-2} \cdot h^{-1}$ and ethanol separation factor of 106 in a 5 wt% ethanol/water feed at 60°C. When the support was substituted by alumina, the high separation factor of 89 with a high flux of 1800 $g \cdot m^{-2} \cdot h^{-1}$ was also obtained at the same conditions (95). Even when the ethanol feed concentration became 10 wt%, excellent pervaperation performance with 72 and 2550 $g \cdot m^{-2} \cdot h^{-1}$ was still seen for the membrane supported by mullite porous (96). Liu et al. (97) reported that the zeolite membranes on alumina support preferentially permeated alcohols with separation factor of 11.5 and total flux of 100 $g \cdot m^{-2} \cdot h^{-1}$ in 9.7 wt% aqueous solution. A hydrophobic zeolite membrane was prepared which consisted of a multilayered ceramic supporting membrane (support +three intermediate layers) made of titania and a ZSM-5 zeolite layer. At a feed temperature of 40°C, high fluxes up to 1000 $g \cdot m^{-2} \cdot h^{-1}$ and initial ethanol permeate concentration up to 87 wt% were achieved in batch experiments (98).

In another study by Chen et al. (99), high-reproducibility silicalite-1 membranes were synthesized on silica tubes by *in-situ* hydrothermal synthesis. By using an effective method called "solution-filling (SF)", silica tubes were filled with viscous mixed solution containing water and glycerol. The average flux of the membranes prepared with the SF method was improved by about 49% compared to the membranes prepared without the SF method, and the highest flux of the membrane prepared with the SF method towards the ethanol mixture at 80°C was 1490 $g \cdot m^{-2} \cdot h^{-1}$. Pervaporation experiments showed that the fluxes of silicalite-1 membranes was 870 $g \cdot m^{-2} \cdot h^{-1}$ at 60°C, and the corresponding separation factor was 69.

For the research on membrane post-treatment, polycrystalline silicalite membranes prepared on porous stainless-steel supports were modified with silane coupling reagents. The ethanol separation factor of the modified silicalite membrane was markedly increased from 13 to 45. However, the flux exhibited reverse direction (100).

In addition, introducing some hybrid elements (Al, B, Ti, Ge, Fe, Zi, etc.) into the pure silica MFI structure was also an effective method. For example, it was reported that Ti-substituted silicalite-1 (TS-1) zeolite membrane exhibited much higher ethanol-permselectivity than the silicalite-1 zeolite membrane prepared at the similar synthesis condition (101). The separation factor and total flux of this TS-1 membrane were 127 and $770\,g\cdot m^{-2}\cdot h^{-1}$ in 5 wt% ethanol feed concentration at 60°C, respectively. Similar to titanium, zirconium Silicalite-1 zeolite membrane has been used to concentrate an ethanol/water mixture by pervaporation (102). The results showed that a high ethanol separation factor of 73 accompanied with a flux of $1010\,g\cdot m^{-2}\cdot h^{-1}$ was obtained for 5 wt% ethanol/water system at 60°C. Bowen et al. (103) reported separating the ethanol/water mixture with high-quality boron-substituted ZSM-5 zeolite membranes on Al_2O_3-coated SiC multi-channel monolith supports. They observed a flux of $160\,g\cdot m^{-2}\cdot h^{-1}$ and a separation factor of 31 when the feed ethanol concentration was 5 wt% and the temperature was 30°C. The highest separation factor of 47 and the total flux of $223\,g\cdot m^{-2}\cdot h^{-1}$ were obtained for Germanium-substituted ZSM-5 zeolite membrane with a Si/Ge ratio of 41 (104).

Other inorganic membranes were also described in the literature. For example, Song et al. (105) prepared the boehmite (γ-AlOOH)-sol-coated membrane. It was expected that the boehmite-sol-coated membrane had a somewhat higher separation factor. However, it did not show so much of a high separation factor for the 5 times or 10 times coated-membrane. In a 10 wt% ethanol solution at 40°C, the flux and separation factor were merely $31.5\,g\cdot m^{-2}\cdot h^{-1}$ and 1.14, respectively.

However, inorganic membranes are about 10–50 times more expensive than the equivalent polymeric ones (106) and the defect-free commercial-scale silicalite-1 membranes are difficult to manufacture, which cause the termination of their commercial fermentation (107).

MIXED MATRIX MEMBRANES

To overcome the disadvantages of the two types of membranes, several groups have investigated the potential of mixed matrix membranes consisting of an inorganic filler like silica dispersed in polymer. Dispersing silicalite-1 particles in PDMS is a typical method. Preparation of zeolite-filled composite membrane was first seen on the Te Hennepe's report published in 1987 (18). The results presented in the paper indicated that adding the hydrophobic porous zeolite to PDMS could improve the ethanol-permselective. The separation factor increased from 7.6 to 43.1. Since then, zeolite-filled PDMS membranes have gained increasing attention in the literature. Table 2 lists the ethanol–water separation performances reported in the literature for inorganic filler-PDMS mixed matrix membranes. The range of ethanol separation factors reported in the literature, 2.3–59, overlaps the ranges reported for both PDMS and silicalite-1 alone. In fact, PV 1070 is a dense pervaporation membrane of PDMS-Silicalite-1 mixed matrix membranes, which is commercially available from Sulzer Chemtech (Neunkirchen, Germany).

In addition to the above methods, other research works were also reported in the literature. For instance, high flux composite PTMSP-silica nanohybrid membranes were successfully prepared for the first time and applied to separate ethanol/water mixtures. For the composite membrane with PVDF support, an average flux of $3500\,g\cdot m^{-2}\cdot h^{-1}$ was measured, while a flux of $2700\,g\cdot m^{-2}\cdot h^{-1}$ was obtained for the PTMSP-silica/PAN membrane. Both of the composite membranes showed similar ethanol separation factors around 12 (114). Gu et al. (115) found that adding silicalite to PEBA membranes could improve the pervaporation performances. When the silicalite content was 2.0 wt%, both the flux and the separation factor reached the maximum values, which were $833\,g\cdot m^{-2}\cdot h^{-1}$ and 3.6, respectively. For a 65 wt% ZSM-5 zeolite-filled PDMS membrane with a pure PDMS top coat, twice fluxes and separation factors were observed when comparing with pure PDMS membrane, which were up to $521\,g\cdot m^{-2}\cdot h^{-1}$ and 18 (116). With these types of membranes, it was found that the pervaporation performances were effected by the membrane formulation conditions and the preparation parameters, such as siloxane chain length, crosslinking agent concentration, density of the reactive groups, catalyst level, solvent type, zeolite type and loading, mixing method, and the presence of a porous support membrane (108). The following materials and methods potentially important to the performances of mixed matrix membranes are identified:

1. Nano particles are the best choice to be added into the membranes, especially silicalite-1, and particles should be well-dispersed. Sonication is the most useful method (112);
2. The surface chemistry of particles need to be altered. Acid and/or steam treatment and/or silylation should be considered (20); and
3. In the best result there always exist a certain amount of particle loadings, which depend on the thickness of the membranes.

Zeolite particle loading as high as 77 wt% is possible, but some systems may be limited to a maximum of 30 wt% or

TABLE 2
Ethanol–water separation performance of PDMS membranes with different fillers

Fillers	Content (%)	Feed concentration (wt%)	Temperature (°C)	Separation factor	Flux ($g\ m^{-2}\ h^{-1}$)	Reference
Silicalite-1	77	7	22	59	–	19
Silicalite-1	65	5	50	43.1	–	108
Silicalite-1	77	5	22	37	150	19
Silicalite-1	50	5	50	29.3	–	20
Zeolite	60	5	22.5	16.5	51	18
USY	50	–	30	16.1	$610\ L\ m^{-2} h^{-1}$	109
Nano-sized silicalite-1	30	6	35	15.7	–	16
ZSM-5	50	–	30	14	$460\ L\ m^{-2} h^{-1}$	109
Silicate	30	–	35	10	350	21
Polyphosphazene nanotubes (PZSNTs)	10	10	40	10	$11.9 \times 10^{-3}\ g \cdot m \cdot m^{-2} \cdot h^{-1}$	110
Carbon black	10	–	35	9	–	111
Fumed silica	20	5	40	7.0	–	112
Commercially available silicalite zeolite fillers (CBV 3002)	30	3	41	5.5	151	24
ALPO-5	50	–	30	5.2	$200\ L\ m^{-2}\ h^{-1}$	109
ZSM-5	30	–	35	5	250	21
Silicalite-1	15	3	41	4.8	170	24
Zeolite Y	30	–	35	4.5	750	21
$[Cu_2^{II}(bza)_4(pyz)]_n$	3	5	25	2.3	23	113

even lower due to the particle agglomeration and defect formation (19,24). Other particle loadings are usually no more than 10 wt% (113,110).

In order to improve the practicality of zeolite membrane for the concentration of bioethanol, however, the deterioration in pervaporation performances caused by accumulation of by-products during fermentation must be resolved. Ikegami et al. (117,118) have combined PDMS and silicalite-1 in another manner to alter properties. They coated the top layer of a silicalite membrane with silicone rubber for counteracting this deterioration in pervaporation. For this coated membrane, the total recovered ethanol concentration in the permeation was 67 wt%, and the amount of recovered ethanol from the broth was more than 10 times higher than that using a non-coated membrane. For example, a membrane coated with 3 wt% KE108 hexane solution showed a separation factor of 125 with a total flux of $140\,g \cdot m^{-2} \cdot h^{-1}$ (119). Although Ikegami et al. (120) also reported that stable pervaporation performances was obtained by entirely covering the silicalite membrane with a silicone rubber sheet, the flux was strongly limited by the thickness of the silicone rubber. Thus, only a small amount of concentrated bioethanol was recovered. In the latter publication, Ikegami et al. (121–124) coated with two types of silicone rubber during the separation of ethanol/water mixtures or fermentation broths by *Zymomonas mobilis* or *Candida krusei*. Silicalite membrane double-coated with the two types of silicone rubber showed the high pervaporation performance: $350\,g \cdot m^{-2} \cdot h^{-1}$ of flux and 64 of the separation factor. Overall, the separation factors of PDMS-coated silicalite-1 membranes ranged from 47 to 125.

Recently, Xiangli et al. (125) used response surface methodology (RSM) to optimize the preparation conditions for preparing PDMS/ceramic composite membranes. In 4.2 wt% ethanol solution at 60°C, a maximum flux of $12950\,g \cdot m^{-2} \cdot h^{-1}$ was obtained with the maximization separation factor of 9.02.

Due to combinating the advantages of polymeric with inorganic membranes, mixed matrix membranes are easy to fabricate. The cost per unit area is less, and the pervaporation performances are good. Therefore, mixed matrix membranes would be one of the best ways fot the recovery of ethanol from the dilute solution.

FUTURE TRENDS IN PERVAPORATION MEMBRANES

The models used to explain the transport mechanism of ethanol/water mixtures are generally based on the solution–diffusion mechanism (50,126), the Flory–Huggins theory (127), the hydrophobic sorption distillation (HSD) model (128), and the Maxwell-Stefan theory (35,129). Most discussions on the transport mechanism in pervaporation are based on the solution–diffusion mechanism. However, the existing guidance of the theories is still immature and cannot very well describe the separation system. Up to date, the available theory for predicting the pervaperation performances of membrane materials is lack, which greatly restricts the research and development of high performance membranes. Therefore, a great deal of research should be carried out to exploit and design excellent pervaporation membrane materials.

There are also more needed informations on the molecular level. During the last 15 years, detailed molecular dynamics (MD) simulations have become a widely used method for the investigation of the molecular structure of amorphous polymers and the prediction of diffusion and solubility of small molecules through silicone rubber materials (130–132). However, many of these simulations only dealt with gas diffusion (133). In addition, there are also a few of MD simulations papers on exploring the pervaporation separation behavior in the bulk. Tamai (134) and Fritz (135) reported on the MD simulations of the diffusion process of water and ethanol in PDMS. They calculated the excess chemical potential of these systems. There is no doubt that MD simulations will play a greater role in getting much direct experimental information about what is happening in molecular dimensions during pervaporation.

Three basic approaches are known for the development of new pervaporation membranes: (1) the modification of polymers or membranes; (2) the incorporation of adsorber agents such as zeolites into polymer material; and (3) the development of complete new polymers. According to the discussion above, despite many unique and outstanding properties, PTMSP is still not found a commercial application as a membrane material because of its tendency toward physical and/or chemical aging (136,137). This aging results in significant decline of flux and separation factor over time (55,45). On the other hand, blending of general polymers to produce effective membranes is difficult because there are few combinations of miscible polymers, since phase separation generally takes place in the blending of immiscible polymers. Thus, major work should be still carried out basing on PDMS in the future. However, most of the time, the simultaneous increase of both the flux and separation factor is very rare. Since so far only a few membrane materials are available, a great continuous efforts need to be made to synthesis new film-forming materials or to modify available ones to obtain improved membranes with both higher flux and separation factor for the removal of ethanol from aqueous solutions.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support by the Fundamental Research Funds for the Central Universities of China (DL09DBQ02).

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