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Pervaporation Membranes for Biobutanol Production

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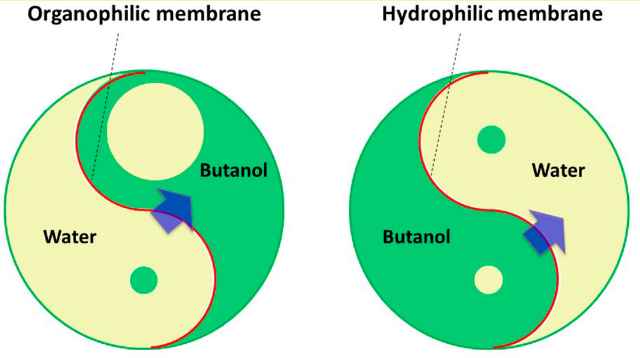
ABSTRACT: Because of the emerging scarcity of oil resources and the demand for environmental protection, as a typical biofuel, biobutanol produced by biomass fermentation is critical for the development of renewable energy. Pervaporation is considered to be an attractive separation technology for both the recovery of butanol from fermentation broth and the dehydration of butanol from low-water content solutions. Thus, as the core of the pervaporation process, pervaporation membranes, including organophilic membranes and hydrophilic membranes, are employed for the separation purpose. This article aims at reviewing the recent research progress in pervaporation membranes involved in biobutanol production. Both polymeric and inorganic membranes are discussed in terms of their design, fabrication, modification, morphology, structure, pervaporation performance, process, etc. A summary of the current state and perspectives of future development of pervaporation membranes for producing biobutanol is also made.



KEYWORDS: *Pervaporation, Butanol, Organophilic membrane, Hydrophilic membrane, Recovery, Dehydration*

INTRODUCTION

During the last two decades, with the increasing concerns of global warming and climatic change, as well as the shortage of fossil energy, there has been a growing interest in the production of chemicals and biofuels by fermentation from renewable resources.[1−3] As a good solvent and important chemical feedstock, butanol has been widely used in the chemical, plastic, cosmetic, paint industries, etc. It is also a new kind of advanced biofuel, which has the advantages of being less volatile and flammable, having a higher energy content, having water insensitivity, and being less hazardous to handle compared with ethanol.[2] Nowadays, butanol is mainly produced by chemical synthesis. As for sustainable development, biomass acetone−butanol−ethanol (ABE) fermentation is considered a more attractive route for producing butanol, which is also called biobutanol.[4]

The economics of biobutanol production are largely dependent on bioconversion efficiency and product purity in the fermentation broth. Because the produced butanol has an inhibition effect on microbial growth, the content of butanol and ABE is lower than 13 and 20 g/L, respectively, in the traditional ABE fermentation process, resulting in a high energy cost to recover butanol from the dilute fermentation broth by distillation.[2] One promising approach to improve the productivity of ABE fermentation is to integrate separation technologies with the fermentation process in order to continuously remove butanol from the fermentation broth as it is produced. Thus, the inhibitory effect would be relieved, and continuous fermentation could be conducted, making a cost-effective biobutanol production.[3]

The existing separation technologies for butanol recovery from fermentation broth include adsorption,[5] liquid−liquid extraction,[6] gas stripping,[7] pervaporation,[8−10] perstraction[6] and reverse osmosis.[11] Among them, pervaporation (PV) is considered to be the greatest potential separation technology because of its energy-saving and efficiency, as well as no harmful effects on the microorganisms. In addition, pervaporation is also an advanced and economic technique for subsequent separation of butanol/water azeotrope in contrast to distillation.[2]

Pervaporation is a membrane process that could realize molecular separation for liquid mixtures in which a feed solution is passed over a membrane surface and some of the components are able to preferentially pass through the membrane and be concentrated as vapors in the permeate.[12] The vapor pressure difference between feed solution and permeate vapor provides the driving force of the pervaporation process, which is usually maintained by applying a vacuum on the downstream side. The core of the pervaporation process is the separation membrane. When selecting a pervaporation membrane for a specific mixture, there are two main parameters that need to be considered: permeate flux (the mass flow rate per unit membrane area) and separation factor (the ratio of two components on the permeate side divided by the ratio of two components on the feed side of the membrane).

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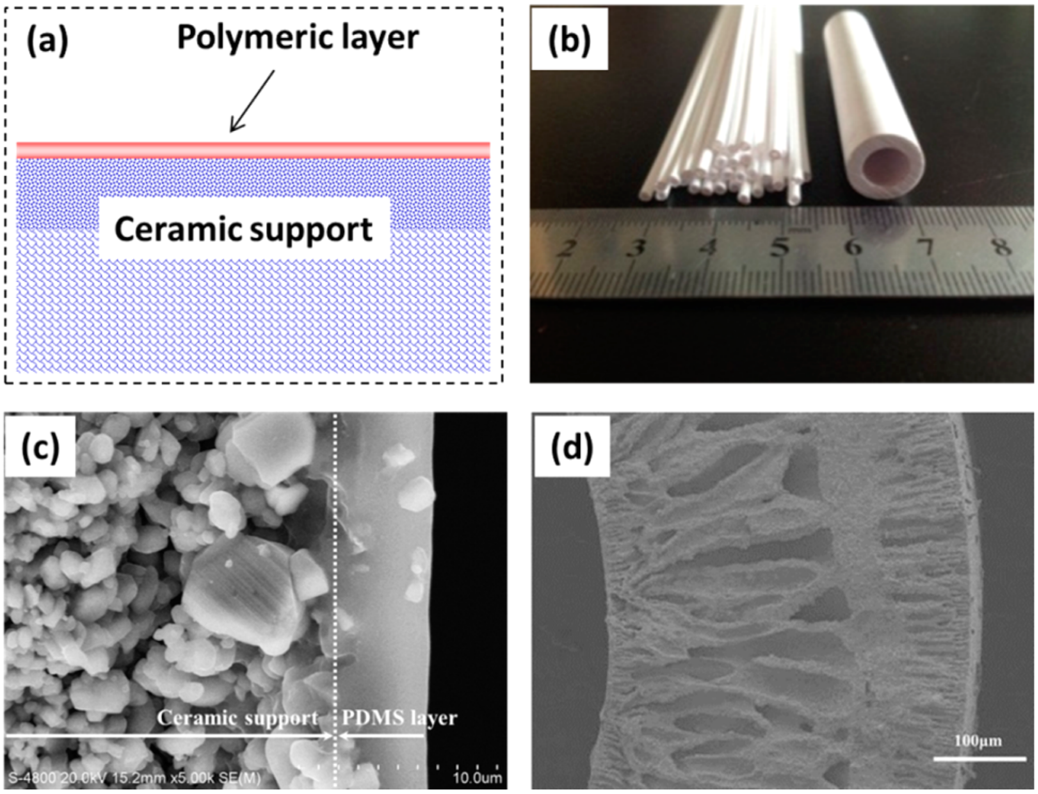

Figure 1. Designing and morphologies of polymer/ceramic composite membranes: (a) schematic diagram of membrane structure, (b) digital photos of tubular and hollow fiber composite membranes, (c) typical SEM cross-section image of tubular membranes, and (d) SEM cross-section image of hollow fiber membranes. Reproduced from ref 8 and 21. Copyright Elsevier.

There are a large number of different types of pervaporation membranes for various applications depending on the individual characteristics of the membrane, for instance, the organophilic and hydrophilic membranes. When applying pervaporation process for biobutanol production, two cases are generally involved. First is the butanol recovery from fermentation broth with low solvent content, in which organophilic membranes can be used that could allow the solvents to pass through while leaving water in retentate.[13] The second is dehydration of butanol–water mixtures containing low water content, which demands for the hydrophilic membranes to preferentially remove water from the solution while dehydrating the solvent in the retentate.[14]

In the past decades, many efforts have been taken to design and fabricate smart membrane materials with the aim of improving the separation performance and long-term stability for pervaporation separation of butanol. Also, some of the researchers have constructed different kinds of fermentation–pervaporation integration processes for producing biobutanol. Therefore, the main purpose of this paper is to review the recent progresses of preparation and application of pervaporation membranes for biobutanol production.

■ ORGANOPHILIC MEMBRANES FOR BUTANOL RECOVERY

The pervaporation membranes for recovering butanol from ABE model solutions or fermentation broths are typically organophilic membranes, including polydimethylsiloxane (PDMS) membranes,[8,9,15−21] poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membranes,[22−24] poly(ether block amide) (PEBA) membranes,[25−28] polypropylene (PP) membranes,[29] polytetrafluoroethylene (PTFE) membranes,[30] liquid membranes,[31−36] zeolite membranes,[37−40] and mixed matrix membranes (MMMs).[16−18,28,41−43]

PDMS Membranes. PDMS (also called silicone rubber) has been known as the most representative organophilic membrane materials for the application of solvent enrichment or recovery from dilute aqueous solution, VOC removal, organic–organic mixture separation, etc.[13] PDMS membranes are also the most commonly used pervaporation membranes for butanol recovery due to their excellent comprehensive performance in permselectivity, stability, and production cost.[44] At present, the commercial PDMS membrane (PERVAP 1060, Sulzer) shows a total flux of 300 g/m^2 h with a separation factor of 27 with the feed of 1 wt % n-butanol/water at 40 °C.[15] Various attempts have been made in different ways to improve the separation performance of the PDMS membrane.

For practical applications, usually a composite membrane with a thin active layer on top of the porous substrate was developed. Our group has designed a new kind of organic/inorganic composite membrane with the deposition of a thin dense polymeric active layer on a porous ceramic support via a dip-coating method (Figure 1).[45] As for butanol recovery, the PDMS layer was uniformly dip-coated on the surface of a porous ceramic tubular support to fabricate PDMS/ceramic composite membranes (typical photo and SEM cross-section image are shown in Figure 1b and c). By controlling the cross-linking of the PDMS casting solution as well as the pretreatment of ceramic support, a defect-free PDMS layer with a thickness of 5−10 μm could be formed on a macroporous ceramic microfiltration membrane with an average pore size of 200 nm via a dip-coating method within one-step.[46,47] As for pervaporation separation of 1 wt % n-butanol/water mixtures at 40 °C, the PDMS/ceramic composite membrane exhibited a total flux of 460−1100 g/m^2 h and a separation factor of 19−26.[48] Ideally, support for the pervaporation composite membrane should only enhance the membrane mechanical strength without adding transport resistance. However, recent studies have illustrated the nonignorable effects of support on microstructures and performance of composite membranes.[21,49] The permeation flux of pervaporation composite membranes might be strongly determined by the transport resistance of support. Recent works indicated that the configuration of the support could play an important role in improving the pervaporation performance of composite membranes.[21,50]

The hollow fiber (HF) membranes with superiorities of low transport resistance, high-packing density, cost-effectiveness, and a self-support structure have been used as support for fabricating high-flux pervaporation composite membranes.[51,52] Recently, we developed macroporous HF ceramic-supported PDMS composite membranes (typical photo and SEM cross-section image are shown in Figure 1b and d).[21] Owing to the integrated PDMS layer and low transport resistance of HF, the PDMS/ceramic composite membrane using HF support showed much a higher pervaporation performance than the PDMS composite membranes using tubular ceramic support; total flux was 1282 g/m^2 h with a separation factor of 43 for 1 wt % n-butanol−water mixtures at 40 °C. To obtain an inner skin hollow fiber PDMS composite membrane, a dynamic cross-flow coating method was developed by dynamically coating PDMS on the inner surface of polysulfone (PS) hollow fiber under a pressure-driven process.[53] Moreover, the selectivity of the composite membrane could also be affected by the supports. Li et al. designed a trilayer PDMS composite membrane and found that both the separation factor and total flux can be enhanced by the addition of a porous hydrophobic polyethylene layer between the PDMS and rigid substrate.[49]

PTMSP Membranes. PTMSP is more permeable than silicon rubber for organics recovery, and as a glassy polymer, it has excellent mechanical and film-forming properties. Owing to the unique molecular structure and large free volumes, the PTMSP membranes showed at least a 4-fold higher flux than a commercial PDMS membrane at the same selectivity after 30 h of operation time in ABE fermentation broth.[24] However, many studies demonstrated that the PTMSP membrane would undergo physical and/or chemical aging during the pervaporation process, leading to the decline of separation performance or even the deterioration of membrane properties over time.[23,24,54] Fadeev et al. found that blocking of PTMSP nanopores by high adsorption of organic molecules controlled the pervaporation of butanol from dilute aqueous solution.[24] A compaction behavior in the PTMSP membrane under the pervaporation condition was observed due to a pressure gradient across the membrane, resulting in a thinner membrane and decline of flux.[23] Membrane compaction occurred faster at higher feed concentrations due to the plasticizing action of adsorbed organics, making PTMSP polymer chains more mobile. Additionally, the aging and fouling behavior of the PTMSP membranes could be monitored by using X-ray photoelectron spectroscopy and infrared spectroscopy.[55]

PEBA Membranes. PEBA is a group of copolymers comprising flexible polyether segments and rigid polyamide segments. By adjusting the functional groups and relative content of the soft/hard segments, PEBA membranes with optimal properties can be used for specific applications in pervaporation and gas separation. PEBA membranes have been found to be effective for the removal of aroma compounds such as esters and phenol from wastewater by pervaporation. Boddeker et al.[56] studied the pervaporation of four isomeric butanols through the PEBA 40 membrane and found that the PEBA membrane was more permeable than PDMS and polyether-based polyurethane membranes tested. The first investigation of PEBA membranes for ABE extraction from dilute aqueous solutions was carried out by Feng's group.[27,57] They chose PEBA 2533 with 80 wt % organophilic poly(tetramethylene glycol) soft segments and 20 wt % nylon 12 hard segments for membrane fabrication, which has a considerably high affinity to butanol. The permselectivity of the PEBA membrane for ABE/water separation was found to follow the order of n-butanol > acetone > ethanol. As for pervaporation of 0.62 wt % acetone/1.91 wt % n-butanol/0.64 wt % ethanol at 23 °C, the total flux of the PEBA membrane was 33.78 g/m^2 h with a separation factor of acetone, n-butanol, and ethanol of 6.5, 13.2, and 4.4, respectively. This performance is relative lower compared with the PDMS membranes.

Liquid Membranes. Liquid membranes are of significant interest for the recovery of dilute amounts of butanol or ABE from their aqueous solutions because of their higher selectivity compared with polymeric membranes and inorganic membranes. Earlier liquid membranes for butanol recovery were reported by Matsumura et al.[31] By putting oleyl alcohol (OA) in porous PP membranes, a high butanol selectivity of 180 was obtained. However, the fermentation broth was contaminated by the OA that is toxic to the organism, and meanwhile, the life of the liquid membrane was reduced. Hence, permanent liquid immobilization is crucial for the technical application of supported liquid membranes (SLMs).

To improve membrane stability and prevent contamination, Thongsukmak and Sirkar[32] developed a new liquid membrane by immobilizing trioctylamine (TOA) in the pores of a hydrophobic hollow fiber substrate with a nanoporous coating on the broth side. The thin TOA-based liquid membrane achieved butanol flux and a separation factor of 53 g/m^2 h and 240, respectively (feed: 1.5 wt % butanol at 54 °C). It was also reported that a blended SLM composed of OA and poly(octylmethylsiloxane) together in microporous PP could further improve the butanol selectivity.[36] Recently, novel extraction solvents such as ionic liquids (ILs) began to be involved in SLMs development due to the negligible vapor pressure and adjustable functional groups of ILs.[33−35,58] For instance, Heitmann et al.[33] prepared supported IL membranes (SILMs) by immobilizing tetracyanoborate and tris(pentafluoroethyl)trifluorophosphate in two ways: inclusion between silicone layers and dissolution in PEBA. Cascon et al.[35] investigated that the gelling of alkylphosphonium dicyanamide IL with a PVDF-co-HFP copolymer could significantly improve the lifetime of SILMs without greatly comprising its favorable transport characteristics. Some other ILs such as hydrophobic ammonium- and phosphonium-based ILs were used also to prepare SILMs for butanol recovery.[34] It was found that butanol flux was highly positively correlated with the ILs' partition coefficient for butanol and inversely correlated with the membrane's hydrophobicity and viscosity.

Zeolite Membranes. Over the past decades, the development of inorganic membranes, particularly zeolite membranes, has gained an increasing interest, due to their higher mechanical strength, thermal and chemical stability than polymeric

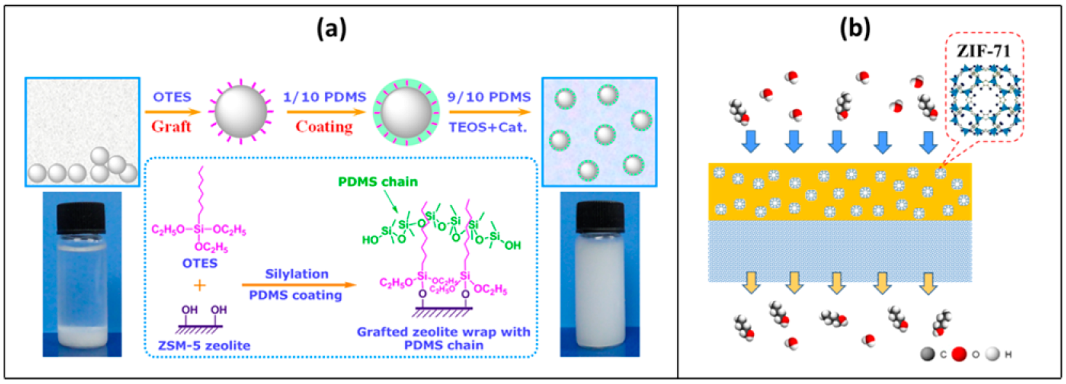

Figure 2. Schematic diagrams of(a) surface graft/coating approach for highly dispersed MMMs preparation and (b) development of ZIF-71/PEBA MMMs for butanol recovery. Reproduced from refs 64 and 28. Copyright Elsevier.

membranes. MFI-type zeolite membranes (e.g., silicalite-1), have been studied most extensively because of its well-defined pore structure (ca. 0.5 nm) and high hydrophobicity, which is suitable for pervaporation of butanol from aqueous solution.[37−40,59,60] Zeolite membranes for industrial-scale application depend on reliable manufacturing that can generate large membrane area and achieve essential membrane characteristics: high hydrophobicity and integrity, appropriate out-of-plane orientation and thin membrane thickness.[38]

The hydrophobicity plays an important role in developing high-selective silicalite-1 membranes. Shen et al.[39] prepared silicalite-1 membranes on macroporous alumina tubes by introducing ethyl triethoxysilane to improve the membrane hydrophobicity. As a result, the silicalite-1 membranes showed a high separation factor of 150 with flux of 0.1 kg/m^{2}h for pervaporation of 2 wt % n-butanol/water mixtures at 70 °C. Furthermore, Tsapatsis' group[38] reported a simple and reliable method (sonication assistance) for the deposition of silicalite-1 seeds on porous stainless steel tubes and rapid thermal processing treatment with further conventional calcination for the synthesis of a continuous and preferentially *c-/h0h*-oriented silicalite-1 membrane.

The development of ultrathin membrane has been a critical approach to obtain high-flux silicalite-1 membranes. When the thickness of silicalite-1 membrane was reduced to 0.5 μm, the flux could be improved by at least 1 order of magnitude, 4 kg/m^{2}h for pervaporation of 3 wt % n-butanol/water mixtures at 60 °C.[37] But the separation factor was just 10, probably due to the formation of nonselective defects. To avoid interspaces among the zeolite nanocrystals, Liu et al.[40] proposed a "packing−filling" method using PDMS as the filling polymer, thus an ultrathin (300 nm) homogeneous silicalite-PDMS nanocomposite membrane was fabricated. The membrane possesses very high flux of 7.1 kg/m^{2}h and good separation factor of 32 for the pervaporation recovery of 1 wt % isobutanol at 80 °C.

Organophilic mixed matrix membranes. Up to now, traditional organophilic membranes for butanol recovery consist of polymeric membranes and inorganic membranes. However, both of their industrial applications are limited by the contradictory relation between performance and cost of membranes. The performance of polymeric membranes is currently not so high to meet the requirement of industrial application of pervaporation for butanol recovery, while the cost of inorganic membranes is too high to make the process of pervaporation recovery of butanol profitable. In recent years, new kinds of membrane materials come up in the membrane field, so-called mixed matrix membranes (MMMs).[61] MMMs are generally fabricated by homogeneously incorporating inorganic fillers into a polymer matrix, which could take advantage of easy preparation and the low-cost of polymeric membranes, as well as the high performance and stable structure of inorganic membranes. Thus, development of MMMs should be a promising and cost-effective approach to break the trade-off between permeability and selectivity in polymeric membranes, obtaining high-performance membranes. Different types of inorganic fillers with high-selective adsorption and/or diffusion for butanol molecules, such as MFI zeolite,[16−18,25,62,63] hydrophobic silica,[22] metal organic frameworks (MOFs),[28,42] and carbon nanotubes (CNTs),[43] have been incorporated into the polymer matrix for MMMs fabrication.

The butanol separation factor of the PDMS membrane was increased over 2 times by preparing silicalite-1/PDMS MMMs,[63] and high-flux PDMS MMMs could be obtained when nanosized zeolite particles were used to further reduce the membrane thickness.[16] Additionally, Claes et al.[22] claimed their 25 wt %-loaded hydrophobic silica-filled PTMSP membrane with a membrane thickness of 2.4 μm could perform an initial flux of 9.5 kg/m^2 h with a separation factor of 104 for 5 wt % butanol/water mixture separation at 50 °C. One of the key issues for manufacturing high-quality MMMs is homogeneous dispersion of inorganic fillers. Silylation was commonly adopted to create chemical bonding between inorganic fillers and polymer chains, so as to make uniformly dispersed MMMs.[18,41] An alternative strategy for homogeneous MMMs could be the enhancement of molecular interactions and compatibility between fillers and polymer. A representative example was the surface graft/coating approach proposed in our previous work to prepare ZSM-5/PDMS MMMs.[64] Zeolite surface was first grafted with n-octyl chains and then coated with a thin PDMS polymer layer (approach schematic is shown in Figure 2a). As a result, PDMS chains could entangle with n-octyl chains to form a stable thin PDMS coating on a zeolite surface, offering considerable interactions between the zeolite particles and PDMS matrix to achieve homogeneous dispersion.

In contrast to the structures and synthesis of zeolite, MOFs have the prominent advantages of abundant functional groups and versatile architectures, as well as easy and low-cost preparation. Thus, they have been able to develop MMMs for recovering butanol very recently. Among various types of MOFs, zeolitic imidazolate frameworks (ZIFs) received

Table 1. PV Performance of Organophilic Membranes for Butanol Recovery

organophilic membranes	feed butanol content (wt %)	temp. (°C)	total flux (g/m^2 h)	separation factor	ref
PDMS (PERVAP 1060)	1 (n-BtOH)	40	300	27	15
PDMS (PERVAP 2200)[a]	1.1 (n-BtOH)	33	33	10	66
PDMS/tubular ceramic	1 (n-BtOH)	40	457	26	48
PDMS/tubular ceramic	1.1 (in ABE)	37	1065	18	8
PDMS/hollow fiber ceramic	1 (n-BtOH)	40	1282	43	21
PDMS/PE/brass	1 (n-BtOH)	40	95	34	49
PDMS/PVDF	1.5 (n-BtOH)	55	670	44	19
PDMS/PAN	1 (n-BtOH)	42	1580	22	67
silicalite-1/PDMS	1 (n-BtOH)	30	63	86	16
silicalite-1/PDMS	1 (in ABE)	50	90	99	18
ZIF-8/PMPS	1 (i-BtOH)	80	6400	40	42
PTMSP (22 μm)[a]	1 (n-BtOH)	25	60	52	23
silica/PTMSP	5 (n-BtOH)	50	9500	104	22
PEBA (100 μm)[a]	1 (n-BtOH)	23	32	12	27
ZSM-5/PEBA	2.5 (n-BtOH)	35	390	30	25
CNTs/PEBA (50 μm)[a]	1 (n-BtOH)	37	139	18	43
ZIF-71/PEBA	1 (n-BtOH)	37	520	19	28
OA/PP liquid membrane	0.95 (n-BtOH)	30	80	180	31
TOA/PP liquid membrane	1.5 (n-BtOH)	54	53	240	32
silicalite-1	2 (n-BtOH)	70	100	150	39
silicalite-1	3 (n-BtOH)	60	4000	10	37
PDMS-coated silicalite-1	1 (n-BtOH)	45	31	60	60
silicalite-1-PDMS	1 (i-BtOH)	80	7100	32	40

[a] Dense membrane; available membrane thickness is given in the bracket.

tremendous attention because of their exceptional thermal and chemical stability. It was demonstrated that butanol can be efficiently separated from aqueous mixtures by the adsorption of ZIF-8.[65] When incorporating ZIF-8 nanoparticles into polymethylphenylsiloxane (PMPS), the ZIF-8/PMPS MMMs exhibited a high flux of 6.4 kg/m^2 h and separation factor of 40 for the pervaporation of 1 wt % iso-butanol/water solution at 80 °C, which transcended the upper limit of state-of-the-art organophilic membranes.[42] Also, our recent work[28] demonstrated that ZIF-71 was efficient enough to simultaneously enhance the flux and separation factor of PEBA membranes (membrane schematic is shown in Figure 2b). The ZIF-71/PEBA MMMs also showed high and stable butanol recovery performance in ABE fermentation broth. The main reason for the performance improvement should be that ZIF nanoparticles can create preferential pathways for butanol molecules by virtue of their ultrahigh adsorption selectivity. In addition, an interesting alternative is that MMMs were prepared with CNTs, which is an inorganic filler material that differs substantially from those molecular sieves in the inorganic dispersed phase. With the addition of 5 wt % CNTs, the flux of a PEBA membrane could be increased from 85 to 139 g/m^2 h with a constant separation factor of ~18.[43]

Comparison of Organophilic Membranes. The pervaporation performance of various organophilic membranes for butanol recovery is summarized in Table 1. For practical application, most of the organophilic membranes were fabricated as composite membranes, which generally exhibited higher permeate flux than the dense membranes. It is demonstrated that PDMS-based membranes are still the benchmark of organophilic membranes, owing to their good and stable separation performance and cost-effective preparation. Remarkable improving the flux and/or selectivity of PDMS membranes included the coating of thin defect-free PDMS active layer on low-transport resistance supports, and the incorporating high-selective inorganic fillers into PDMS matrix to fabricate MMMs. PEBA membranes are neither very permeable nor selective for butanol recovery application. Although exhibiting very high initial performance, PTMSP membranes' aging problem is the major obstacle for its practical application yet. Liquid membranes have extremely high selectivity due to the high adsorption selectivity toward butanol. However, besides of the inherent toxicity to fermentation broth, much efforts have to be carried out to continue improving the permeate flux and permanent liquid immobilization. Up to now, the usage of silicalite-1 membranes for butanol recovery is not competitive compared with the polymeric membranes, on account of the permeate flux and fabrication cost. Nevertheless, inorganic fillers such as zeolite, MOFs and CNTs have been proven to be very useful building blocks for MMMs development.

Effect of Feed Conditions on Pervaporation Performance. Besides the membrane, the performance of the pervaporation process is also determined by the feed conditions (e.g., temperature, composition, and flow rate).[12] We have systematically investigated the effect of these parameters on the performance of the PDMS/ceramic composite membrane.[48] An interesting phenomenon was found that with raising the feed temperature the separation factor of butanol had nearly little change, which was different from the general relationship between feed temperature and membrane selectivity. It could be attributed to the confinement effect of rigid ceramic support on the excessive swelling of the PDMS active layer. The influence of the molecular structure of the feed component on pervaporation of butanol/water binary mixtures was studied by Petrychkovych et al.[68] Their results showed that the fluxes of butanol isomers decreased in the order of sec-butanol > n-butanol > tert-butanol > iso-butanol, resulting from their differences both in molecular shapes and vapor pressure. The diffusivity decreased with decreasing of "linearity" of butanol molecules in the sequence of n-butanol, sec-butanol, iso-butanol, and tert-butanol, while the solubility of butanol isomers corresponded to their vapor pressure with the sorption amount decreased from tert-butanol, sec-butanol, iso-butanol, to n-butanol.

Treatment of Butanol Multicomponent Mixtures. In contrast to the binary butanol/water mixtures, the pervaporation performance in ABE aqueous solution is more complicated. It is dependent on the adsorption selectivity and molecular size of individual components. When the PDMS/ceramic composite membrane was applied for pervaporation of ABE/water mixtures, we found the separation factor followed the order of acetone > n-butanol > ethanol, corresponding to their affinities with the PDMS membrane.[8] Niemistö et al.[67] conducted a comprehensive study on the pervaporation performance of the PDMS/PAN composite membrane in binary aqueous mixtures of acetone, butanol, and ethanol, along with different kind of aqueous ternary mixtures and quaternary ABE/water mixtures. The membrane permselectivity by means of partial fluxes and permeate concentrations was found to be in the order of acetone ≈ butanol > ethanol. Separation factors of acetone and butanol were much higher than ethanol and reached the highest in the case of ternary mixtures. It was demonstrated that the permeation of butanol was preferable in solutions of several organic compounds, indicating that the PDMS membrane has the potential to be used in the ABE fermentation process. Because hydrophobic pervaporation membrane removes ABE solvents, their further separation and purification would be performed using distillation and/or pervaporation dehydration.[69] The ABE/water solution obtained in the membrane permeate could first flow into an acetone distillation column to get acetone. The bottom solution then can be distilled by an ethanol column to get ethanol/water azeotrope and butanol/water mixtures. These mixtures could be dehydrated using hydrophilic pervaporation membranes, resulting in the ethanol and butanol products.

Pervaporation-Based Integration Process. In situ product recovery can improve the performance of biomass fermentation to biobutanol. Because the end product inhibition could be reduced by the in situ separation of butanol from fermentation broth, the butanol productivity and sugar utilization are improved. Continuous ABE fermentation is realized, and eventually, the cost of biobutanol would be cut down. The practical application of butanol recovery depends on the economic feasibility of the process on a large scale. The traditional method for recovery of butanol is distillation, which is energy intensive, as the boiling point of butanol (118 °C) is higher than water (100 °C). The energy requirement for butanol recovery by pervaporation has been calculated to be 14 MJ/kg butanol as compared to 24 MJ/kg butanol by steam-stripping distillation.[70] The attractiveness of pervaporation strongly depends on its flux, selectivity, and equipment cost. If a pervaporation system with high selectivity and 100% operating efficiency is applied, it was predicted that the energy requirement of butanol recovery could be reduced to <4 MJ/kg,[71] which is similar to ~10% of the internal combustion energy of butanol. Recently, Qureshi et al.[69] carried out a cost estimation study for a biological butanol production plant using wheat straw as feedstock with a capacity of 150×10^6 kg butanol/year. It was found that the use of traditional technologies such as batch fermentation and distillation recovery result in a butanol production price of \$1.23/kg. Pervaporation recovery could reduce the butanol price to \$1.00/kg as the membrane cost was assumed \$$1.00 \times 10^6$/year.

Groot et al.[72] compared the existing technologies (stripping, adsorption, liquid–liquid extraction, pervaporation, and membrane solvent extraction) for in situ product recovery on the basis of design parameters and energy efficiency. It was indicated that pervaporation and liquid–liquid extraction are considered to have the greatest potentials. Additionally, adsorption was found to be an energy-efficient process for butanol recovery. Qureshi's group carried out a comprehensive study on different butanol recovery technologies integrated with ABE fermentation.[73] The results suggested that the extraction method containing oleyl alcohol directly contacted with the culture led to cell toxicity. Additionally, the intermediates would be removed during the extraction, and the ABE concentration in the extractant was not so high. Although perstraction maybe minimize the loss and emulsion of extractant, the cell toxicity was still a major problem. Gas stripping and pervaporation were regarded as the most promising butanol recovery techniques. The advantage of pervaporation is its operational simplicity.

Currently, most studies used PDMS membranes for butanol recovery integrated with ABE fermentation,[8,9,17,20] and additionally, PP[29] and liquid membranes[31] were used in some cases. Early researches have demonstrated that with the integration of the pervaporation process, the butanol content in broth could be maintained at a low level that has little toxicity to the microbes, leading to an increase in the sugar conversion rate and solvent productivity. Meanwhile, the fermented solvent would be enriched in the membrane permeate.[17,29,31,74] For example, the silicalite-1/PDMS membrane was coupled with fed-batch ABE fermentation, which ran with 10 cycles for 870 h.[17] It was found that 155.0 g/L of ABE with a yield of 0.35 was achieved in the coupled fermentation process, and this performance was much higher than the 72 h batch fermentation with an ABE concentration of 19.2 g/L and yield of 0.29. We also demonstrated that with in situ removal of ABE by the PDMS/ceramic composite membrane, the fed-batch fermentation–pervaporation-coupled process continued for over 200 h, and ABE in the broth was concentrated to 96.2 g/L in the membrane permeate.[9] It will be more attractive when pervaporation is applied for continuous fermentation because ABE productivity could be further improved. Recently, a long continuous and closed-circulating ABE fermentation system has been achieved by combining pervaporation with ABE fermentation.[20] Because the pervaporation membrane effectively reduced the butanol inhibition and extended the fermentation duration, fermentation performance under continuous coupling mode was superior to that under intermittent coupling mode. Moreover, Van Hecke et al. reported a two-stage continuous fermentation by integrating PDMS composite membranes. As a result, the overall productivity was increased from 0.45 to 1.13 g/L/h.[75] The duration of the pervaporation process could last for 654 h, with a total flux and butanol separation factor of 561–621 g/m^2h and 17–20, respectively. This process shows a promising practical application for biobutanol production.

Membrane Fouling. The membrane performance in the ABE fermentation–pervaporation-coupled process is usually lower than that in ABE or butanol aqueous system. The difference between ABE fermentation broth and the aqueous solution is not only the different density, pH and viscosity, but also with or without the inorganic salts, glucose, active and inactive microbial cells and several other metabolic compounds. After the coupled fermentation experiment, Matsumura et al.[31] observed the liquid membrane was totally fouled by some viscous matters, leading to the sharp decline of membrane performance: the butanol flux decreased from 12.1 g/m^2h to 3.3 and the original separation factor of 160 was reduced to 66. Also, Qureshi's group reported three times drop of separation factor in the application of PDMS membrane in pervaporation integrated ABE fermentation process.[76] Their further study revealed that the membrane could hold its separation performance in fermentation medium, spent fermentation broth and cell-free fermentation broth.[77] A reasonable explanation for this phenomenon was that the membrane fouling should be originated from active cells in the fermentation broth.

Recently, our group thoroughly investigated the evolution of microstructures, properties, and performance of PDMS membrane in the ABE fermentation−pervaporation-coupled process.[8] This membrane exhibited a high flux of 0.670 kg/m^2 h, with an applicable ABE separation factor of 16.7. With the combination of pervaporation data and SEM and IR analysis, it was clearly indicated that the microbial active cells that adsorbed on the hydrophobic PDMS membrane surface during the coupled process were the main cause of membrane fouling, resulting in the membrane performance drop. Fortunately, the fouled membrane could be easily restored by a simple water rinse. Until now, an effective way to avoid membrane fouling is adding a microfiltration or ultrafiltration process to retain the cells before the fermentation broth goes into the pervaporation membrane module.[17] However, this approach would increase the process complexity and capital investment. A recent article reported a separation of diluted butanol−water solutions via vapor phase by organophilic membranes based on high permeable polyacetylenes.[78] Because the method is based on a combination of the gas stripping with membrane vapor separation, it could be a possible route for fouling resistance in fermentation system. Moreover, more effort should be afforded to develop anti-biofouling materials for fabricating organophilic membranes in the future.

Besides the biofouling from microorganisms, several other byproducts in the fermentation broth would decrease the membrane performance. The pervaporation test in model mixtures revealed the negative impact of butyric acid and long-chain fatty acids on the permeate flux, and long-chain fatty acids could also decrease the separation factor of PTMSP membranes.[55] Thus, an off-line upstream nanofiltration step was proposed in order to remedy the loss of membrane performance caused by the fouling during the in situ n-butanol recovery from an ABE fermentation broth. Additionally, when applying MMMs for pervaporation of fermentation broth, one should be aware of the possible adsorption of minor constituents in the broth (e.g., organic acids, esters, and alcohols) into the pores of inorganic fillers, causing performance reduction. Vane et al.[79] proposed an effective regeneration scheme of soaking the ZSM-5/PDMS MMMs in 100% n-butanol, which fully recovered the original performance.

HYDROPHILIC MEMBRANES FOR BUTANOL DEHYDRATION

It is needed for further purification of butanol/water mixtures after they are removed from the fermentation broth. Butanol and water can form an azeotrope at low water content (e.g., azeotropic composition of tert-butanol/water is about 11.8 wt % water at 79.9 °C). The traditional method to treat these azeotropes is extraction distillation, which generally has the drawbacks of energy-intensive consumption and the addition of impurities. Pervaporation has been considered as an alternative technique for butanol dehydration that is not limited by gas−liquid equilibrium, along with having energy-saving and cost-effective advantages.[12]

There are two main types of membrane materials for the dehydration purpose. One is polymeric membranes with cavities/free volumes formed by the packing and mobility of polymer chains that could provide molecular diffusion. The other is inorganic membranes, made from zeolites or ceramics, which have intrinsic pores or channels for fast and selective diffusion of small molecules. With the combination of polymeric membranes and inorganic membranes, mixed matrix membranes with hydrophilic inorganic particles filled in polymer matrix have become a third type of pervaporation membrane for butanol dehydration. Overall, the common hydrophilic membrane materials for pervaporation dehydration of butanol/water mixtures include poly(vinyl alcohol) (PVA),[80−84] chitosan (CS),[83,85,86] alginate (Alg),[80,87] polyimide (PI),[88−92] (PBI),[90,93,94] polybenzoxazole (PBO),[95] polyelectrolytes,[96−99] silica,[100−105] zeolites,[106] etc.

PVA Membranes. PVA is the most frequently used hydrophilic membrane material with excellent water permselective properties due to it containing a large number of hydroxyl groups that provide strong hydrophilicity. Because of the inherent linear molecular structure, PVA membranes exhibit good mechanical strength and chemical stability. The PVA membrane is the first commercialized pervaporation membrane developed by GFT (now Sulzer Chemtech) in 1980s. Until now, most of the commercial hydrophilic membranes were still made from PVA material, which was cross-linked by maleic acid or citric acid and cast on a polyacrylonitrile (PAN) substrate, namely, PVA/PAN composite membranes.[14]

During the past decades, porous ceramic membranes, with their inherent properties of chemical, thermal, and mechanical stability, have been used to fabricate ceramic-supported polymer composite membranes. Peters et al.[81] developed a high-performance cross-linked PVA composite membrane on top of hollow fiber ceramic support with an average pore size of 4 nm. The γ-Al_2O_3/α-Al_2O_3 ceramic support provided a sufficiently smooth surface; thus, ultrathin and defect-free PVA active layers with the thickness of 300−800 nm were obtained, leading to a very low transport resistance. In the dehydration of n-butanol (5 wt % water content at 80 °C), the prepared PVA/ceramic composite membranes exhibit a simultaneously high water flux of 0.8−2.6 kg/m^2 h and high separation factor of 500−10000. This performance was much higher than that obtained from cross-linked PVA membranes using polymeric supports.

Nowadays, there are increasing numbers of polymeric membrane materials that contain hydrophilic groups that benefit the adsorption and diffusion of water molecules. Nevertheless, the hydrophilic groups sometimes lead to excessive swelling of the membrane that would result in selectivity decline. Hence, how to simultaneously keep the hydrophilic groups and structural stability is one of the key issues to prepare high-quality hydrophilic polymeric membranes. For example, in order to further improve the performance of pristine PVA membranes, essential routes could be the molecular design or modification on PVA material,

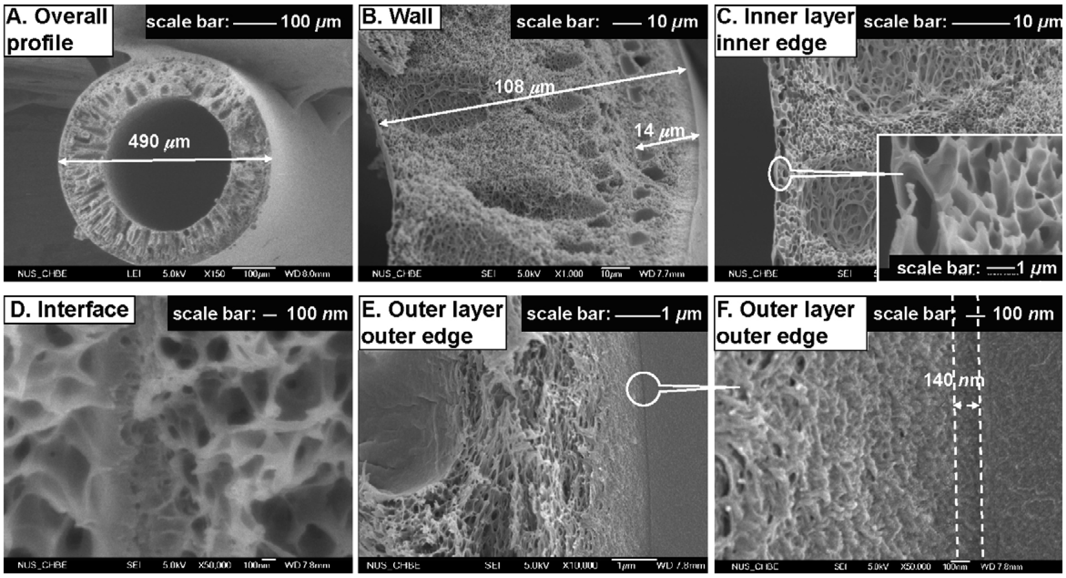

Figure 3. SEM images of the outer surface and inner surface of the PAI/PEI dual-layer hollow fiber membranes. Reproduced from ref 108. Copyright Elsevier.

such as blending, grafting, plasma treatment, incorporating inorganic particles, etc.

Our group reported the preparation of PVA-CS blending membranes on the surface of macroporous ceramic supports that were pretreated by a solvent prefilling method.[83] Part of the intramolecular hydrogen bonds were replaced by several intermolecular hydrogen bonds that formed by the blending of PVA with CS. Thus, introducing CS into PVA increased the amorphous region of the PVA membrane that facilitated the enhancement of membrane permeation flux. As for pervaporation of 10 wt % t-butanol/water mixtures at 70 °C, the ceramic-supported PVA-CS composite membrane showed a total flux of 1.1 kg/m^2 h with a separation factor of over 1000.

Polyimides Membranes. According to the solution−diffusion model, the high-efficient dehydration achieved in hydrophilic polymers such as PVA, CS, and Alg is basically based on the enhancement of solubility selectivity of water toward the membrane by hydrogen bond interactions. On the contrary, glassy polymers such as rigid and stiff polyimides would improve the diffusivity selectivity of water upon the molecular sieving effect. Although PVA membranes have been widely studied and used in various industrial applications, the maximum operating temperature for PVA membranes were generally no higher than 100 °C.[14] Thus, for further extending the application of hydrophilic polymeric membranes to high-temperature dehydration, polyimide membranes, a class of popular gas separation membranes owing to superior thermal stability and mechanical strength, have begun to be used for butanol dehydration in recent years.[92]

Polyimides are typical glass polymers derived from the condensation of bifunctional carboxylic acid anhydrides and primary diamines. According to the numerous investigations, the aromatic and heterocyclic polyimides appear to be the most promising materials for pervaporation application.[92] A comparison investigation was carried out by Kreiter et al.[89] in which three PI polymers with different molecular structures (Torlon, P84, and Matrimid) were used to prepare ceramic-supported polymer composite membranes. The pervaporation test in a 95 wt % n-butanol/water solution at 95 °C indicated that the PI/ceramic composite membrane based on P84 showed high and stable performance for at least 300 days with a water flux of 1.2−1.4 kg/m^2 h and separation factor of 931. With further raising of the operating temperature to 150 °C, a stable performance was still observed for the t-butanol dehydration up to at least 250 days.

Besides the PI molecular structure, manipulation of the membrane structure is another key point for large-scale industrial applications of PI membranes because anisotropic membranes with an ultrathin dense selective layer could remarkably improve the separation efficiency. On the basis of the diverse chemical structures and superior film-forming characteristics of polyimides, the configuration of anisotropic PI membranes could be asymmetric membranes, composite membranes, and dual-layer asymmetric hollow fibers.[92] Chung's group developed a new type of Psf/Matrimid dual-layer hollow fiber membrane with a coextrusion technique that exhibited excellent separation performance far surpassing the prior polymeric membranes and approaching ceramic membranes for t-butanol dehydration.[107] Similarly, they prepared novel Torlon polyamide-imide (PAI)/Ultem polyetherimide (PEI) dual-layer hollow fiber membranes that also exhibited high and stable performance for butanol dehydration (membrane microstructures are shown in Figure 3).[108] The superior performance is attributed to the balanced properties of PAI as the water permselective layer and the low water uptake and less swelling characteristics of the PEI as the supporting layer, in addition to desirable membrane morphology with intermolecular diffusion and interactions at the interface.

The performance of the PI membrane is not only affected by the chemical composition and molecular structure of material, membrane microstructure, and configuration but is also dependent on operating conditions and history. Guo and Chung[91] studied the thermal hysteresis behavior of PI (Matrimid 5218) membranes for pervaporation of 85 wt % t-butanol/water mixtures. They found that three factors played important roles in the hysteresis behavior: feed component−membrane interactions, nonequilibrium nature of separation layer, and swelling of asymmetric membrane. The butanol flux and separation factor were closely related to the chain-packing

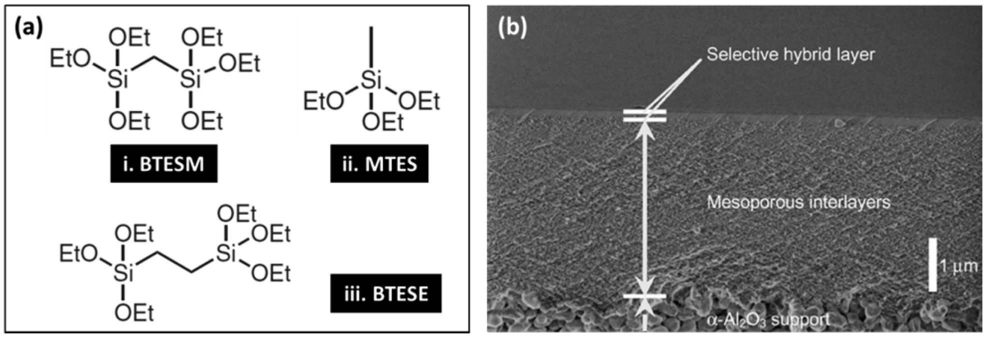

Figure 4. (a) Precursors used for the HybSi membrane layer. Reproduced from ref 103. Copyright Elsevier. (b) Typical SEM cross-section image of HybSi membrane. Reproduced from ref 114. Copyright Royal Society of Chemistry.

density and orientation that would determine the transportation resistance and selective diffusion.

Polyelectrolyte Membranes. The alternate electrostatic layer-by-layer (LbL) adsorption of cationic and anionic polyelectrolytes at the charged substrate has proven to be a simple and effective method for developing ultrathin membranes with defined composition. By using polyelectrolytes of high charge density and controlling pH and ion content of polyelectrolyte solutions, the prepared polyvinylamine/polyvinylsulfate polyelectrolyte membranes (PEMs) exhibited a flux of 1.2 kg/m^2 h and separation factor of 8500 for dehydration of 90 wt % t-butanol aqueous solution at 60 °C.[98] For pushing the application of hollow fiber PEMs, Zhang et al.[96] developed a dynamic LbL adsorption technique by alternatively dynamically filtrating poly(acrylic acid) (PAA) and polyethyleneimine on the inner skin of hollow fiber PAN substrate under a negative pressure condition.

Alternatively, Qian et al.[99] have explored a series of polyelectrolyte complex (PEC) membranes based on PEC aggregate nanoparticles instead of polyelectrolyte chains. The PEC membranes displayed high dehydration performances due to their ultrapermeable and selective channel structures. Recently, it was reported that the separation performance of PEC membranes could be tailored with the side chain length of the cationic polyelectrolyte while maintaining similar polymer backbones. A high flux of 2241 g/m^2 h and 99.2 wt % permeate water can be obtained with the fabrication of quaternized poly(4-vinylpyridine) (QP4VP)/carboxymethyl cellulose (CMCNa) PEC membranes (feed: 90 wt % n-butanol at 60 °C).

Other Polymeric Membranes. PBI is a class of heterocyclic amorphous polymers with excellent chemical resistance and thermal stability (e.g., commercially available PBI has a chemical structure of poly-2,2′-(m-phenylene)-5,5′-bibenzoimidazole with a high T_g of 425−435 °C). Moreover, this material is a highly hydrophilic amorphous polymer with a reported water sorption up to 15−18 wt %. The use of PBI membranes for pervaporation dehydration of solvents has been explored by Chung's group.[90,93,94,109] Because of its outstanding thermal stability and chemical resistance, PBI was used to blend with Matrimid to improve the chain stability of Matrimid membranes due to the strong molecular interactions between the carbonyl group of Matrimid and the N−H group of PBI.[90] At the same time, the hydrophilic nature of PBI and the close chain packing were in favor of increasing the Matrimid membrane selectivity.

As a superior class of glassy polymer, PBO consists of a rigid rod structure with good thermal and chemical stability and is considered as a promising membrane material for pervaporation dehydration. Park et al.[110] first reported a novel fabrication of PBO membranes from a PI precursor via the thermal rearrangement (TR) approach, which acquired superior gas separation performance. Subsequently, the feasibility of TR-PBO membranes for solvent dehydration was examined.[95] It was found that the free volume and *d*-spacing of the membranes increased after the TR process, and the TR-PBO membranes showed a stable performance in dehydration of n-butanol at 80 °C for 250 h continuous operation.

Other reported polymeric membranes for butanol dehydration include a sodium alginate (SA)/hydroxyethylcellulose (HEC) blending membrane[85] and toluylene diisocyanate (TDI) cross-linked CS membranes.[86]

Inorganic Membranes. Inorganic materials such as ceramic and zeolite offer significant advantages over polymers like high chemical and thermal stability. Thus, compared with polymeric membranes, inorganic membranes can be operated at higher temperature and in harsh solvent environments, which are the essential parts of hydrophilic membranes. Nowadays, two main types of inorganic membranes have been involved in solvent dehydration: silica membranes and NaA zeolite membranes.[14] In the past decade, most of the literature focused on the research of silica membranes for butanol dehydration, which may be attributed to both the already mature NaA membrane technique and diversity of silica membranes.

Silica membranes consisting of microporous amorphous silica materials on mesoporous ceramic supports fabricated by either chemical vapor deposition or sol−gel hydrolysis and condensation could give effective dehydration of solvent. Within this amorphous silica, small Si−O rings of about 0.3 nm in diameter are formed, similar to the kinetic diameter of small molecules such as water (kinetic diameter 2.6 Å).[111] Thus, silica membranes could exhibit a high permeability for small molecules meanwhile a very low permeability for larger ones (>~3 Å). Silica membranes with nanosized thickness were successfully prepared on tubular[112] and hollow fiber[113] alumina supports, respectively. Both of them showed very high flux and separation factor in dehydration of 95 wt % n-butanol/water solution at 80 °C, but the performance decreased during the continuous pervaporation test. Actually, inorganic silica is known to be hydrothermally unstable, which becomes apparent at temperatures as low as ~70 °C. Upon exposure to moisture, hydrolysis and net transport of silicon species lead to substantial loss of permeability within hours. Furthermore, the interaction between permeate components and silica, namely, butanol and water molecules could be adsorbed on a silica membrane surface and then react with hydroxyl groups of

Table 2. PV Performance of Hydrophilic Membranes for Butanol Dehydration

hydrophilic membranes	feed butanol content (wt %)	temp. (°C)	flux (g/m^2 h)	separation factor	ref
PVA/hollow fiber ceramic	95 (n-BtOH)	80	800−2600	500−10000	81
PVA-CS/ceramic	90 (i-BtOH)	70	1100	1000	83
P84/ceramic	95 (n-BtOH)	95	1200−1400	931	89
Matrimid hollow fiber	85 (t-BtOH)	60	630−965	91−491	91
PI/PEI dual-layer hollow fiber	85 (n-BtOH)	60	846	1174	108
polyvinylamine/polyvinylsulfate	90 (t-BtOH)	60	1200	8500	98
PAA/polyethyleneimine	95 (t-BtOH)	50	769	481	96
QP4VP/CMCNa	90 (n-BtOH)	60	2241	1100	99
ZIF-8/PBI (50 ± 15 μm)[a]	85 (n-BtOH)	60	81	3417	94
TR-PBO[a]	90 (n-BtOH)	80	58	390	95
CS	96 (t-BtOH)	30	210	2657	86
SA-HEC	87 (t-BtOH)	30	2300	3237	87
tubular silica	95 (n-BtOH)	70	4500	600	112
hollow fiber silica	95 (n-BtOH)	80	1310−2920	900−1200	113
BTESE/MTES hybrid silica	95 (n-BtOH)	150	10000	931	114
BTESE hybrid silica	95 (n-BtOH)	150	20000	4000	115
BTESE hybrid silica (ETP-CVD)	95 (n-BtOH)	95	1800	1100	102
hydrophobic silica	5 (n-BtOH)	90	1500	15	100
NaA product (Mitsui eng. and shipbuilding)	90 (n-BtOH)	70	2700	8000	106

[a] Dense membrane; available membrane thickness is given in the bracket.

silica membranes (i.e., $\equiv$ Si−O−Si $\equiv$ + $H_2O \rightarrow 2 \equiv$ Si−OH), leading to the formation of nonselective pores and defects in silica membrane and then resulting in loss of selectivity.[104]

Several strategies have been proposed for improving the stability of silica membranes. Compared with post-treatment in humid air and substitution or doping with inorganic oxides, the introduction of hydrolytically stable organic groups into the silicon moieties to prepare organic−inorganic hybrid silica membranes was regarded as one of the most successful attempts.[105] By incorporating organic Si−C_xH_y−Si links into the inorganic network of silica, the high thermal and solvent stability of Si−O−Si bonds could be complemented with a high hydrothermal stability. The research groups from Energy Research Centre of The Netherlands (ECN), University of Twente, and University of Amsterdam have done lots of interesting work on hybrid silica membranes, which are so-called HybSi membranes.[103−105,114,115] By using different precursors, active layers of HybSi membranes contain either pure bis(triethoxysilyl)methane (BTESM), pure bis-(triethoxysilyl)ethane (BTESE), or a 50/50 mol % mixture of BTESE and methyltriethoxysilane (MTES) (molecular structures of precursors and typical membrane morphology are shown in Figure 4). It was shown that the HybSi membranes are suitable for demanding separations using pervaporation at temperatures up to at least 190 °C in aggressive aprotic solvents including N-methyl-2-pyrrolidone (NMP) and in the pH range of 2−8. The high stability, corresponding to the high flux (10−20 kg/m^2 h) and separation factor (1000−4000), was proven in the continuous dehydration of n-butanol at 150 °C that lasted for 1000 days, which overcomes the limitations of currently available commercial polymer and zeolite membranes and should meet current industrial demands and expectations.

More recently, the development of silica membranes on a porous polymeric substrate was demonstrated by applying plasma-enhanced chemical vapor deposition (ETP-CVD) to the synthesis of BTESE-derived hybrid silica membranes using the PEI substrate.[101,102] The pervaporation performance of this new type of silica membrane for butanol dehydration was comparable with those of conventional ceramic-supported membranes made by sol−gel technology (i.e., a water flux of 1.8 kg/m^2 h and separation factor of >1100). Another interesting work is that the affinity of silica membranes could be tailored from hydrophilic to hydrophobic by incorporating different R-triethoxysilanes into BTESE-based materials.[100] Longer R-groups resulted in lower permeate water purity, falling from >99 wt % for BTESE to ~40 wt % for C10 in the dehydration of n-butanol/water (95/5 wt %) by pervaporation. The C10-triethoxysilanes/BTESE silica membrane showed a n-butanol flux of 1.5 kg/m^2 h with a separation factor of 15 for butanol recovery from 5 wt % butanol/water mixtures at 90 °C.

Hydrophilic Mixed Matrix Membranes. Likewise, organophilic MMMs with the incorporation of inorganic fillers that exhibited high affinity with water and/or fast diffusion of water into polymeric matrix could fabricate hydrophilic MMMs for biobutanol dehydration. It is reported that the PVA membrane performance could be improved by introducing delaminated microporous aluminophosphate ($[Al_3P_4O_{16}]^{3-}$, AlP).[84] The AlP-filled PVA membrane with low AlP content performed much better than ordinary zeolite (NaA and NaX)-filled membranes. This was attributed to the high hydrophilicity caused by both the P negative electricity centers and the P+O··· HOH hydrogen bonding and the molecular sieving effect of AlP related to 8 member rings on the layers. Recently, nanosized ZIF-8 particles with a aperture size of 3.4 Å and large cavity size of 11.6 Å were incorporated into PBI to fabricate ZIF-8/PBI MMMs.[94] It was found that the water-induced swelling can be severely suppressed because of the hydrophobic nature and rigid structure of ZIF-8 particles, while the butanol-induced swelling was enhanced owing to a greater free volume in the PBI/ZIF-8 membrane revealed by positron annihilation lifetime spectroscopy (PALS) technique.[93] As a result, the flux of the PBI membrane was increased by four times with 33.7 wt % ZIF-8 loading.

Comparison of Hydrophilic Membranes. The pervaporation performances of different hydrophilic membranes for butanol dehydration are listed in Table 2. It can be found that PVA membranes are still the representative hydrophilic polymeric membranes, especially for the commercialized products and industrial applications. Meanwhile, hollow fiber PI membranes are becoming a promising candidate for butanol dehydration because of their superior performance at high operating temperature. Membranes fabricated by PEC, PBI, and PBO materials are regarded as the emerging hydrophilic membrane materials whose free volumes could be easily regulated for fast transport of water molecules. Further efforts could be taken to make dense PBI and PBO membranes into composite membranes. Although NaA zeolite membranes account for the major market of industrial solvent dehydration, in the recent 10 years, great progress has been made for developing hybrid silica membranes with excellent and stable performance under high temperatures and a harsh environment. Silica membranes are expected to be a new kind of competitive hydrophilic membrane product when the bottlenecks of large-scale and cost-effective production are overcome.

■ PERSPECTIVES

Pervaporation membrane technology is expected to play a significant role in biobutanol production. Its practical application strongly relies on the development of high-quality membranes and high-efficiency membrane processes. More specifically, improvement of the flux and/or selectivity of the existing pervaporation membranes especially for the organophilic membranes is urgently needed in order to meet the requirement of energy consumption and cost of investment. Meanwhile, high-performance membrane materials are required to be engineered to further reduce the membrane cost for biobutanol production. How to develop antibiofouling membranes and stable pervaporation-based systems to suppress or avoid membrane fouling is also a key issue for industrial implementation of pervaporation in the biomass fermentation process.

Some effective strategies could be employed for the future development of pervaporation membranes either for butanol recovery or dehydration: (1) fabrication of ultrathin active layers and utilization of low-transport resistance substrates (e.g., hollow fiber) to obtain high-flux composite membranes, (2) screening of optimal inorganic filler—polymer matrix pairs and effective synthesis methods for the development of high-quality mixed matrix membranes to overcome the permeability—selectivity trade-off in polymeric membranes, (3) developing more approaches for molecular design and post-treatment to tune the membrane-free volumes (e.g., TR membranes), (4) extending the "organic—inorganic hybrid" idea into more kinds of inorganic membranes to increase their diversity and performance stability, (5) designing and preparing practical application-oriented membranes (e.g., antifouling organophilic membranes or hydrophilic membranes with high hydrothermal stability), and (6) exploring new materials for efficient separation of butanol/water mixtures by creating high-preferential adsorption and/or fast-selective diffusion toward butanol or water molecules.

As for the rational design and optimization of the pervaporation process, more attention should be paid to the establishment of matching parameters in the fermentation—pervaporation or distillation—pervaporation integrated process. Additionally, further research is required into the economic assessment for the entire pervaporation-based biobutanol production process, which possibly could be studied by life cycle assessment (LCA). As a result, the practical demands for pervaporation membranes would more clearly promote the development of membrane products with specific separation performance and some other properties (e.g., increased lifetime, chemical and thermal stability, mechanical strength).

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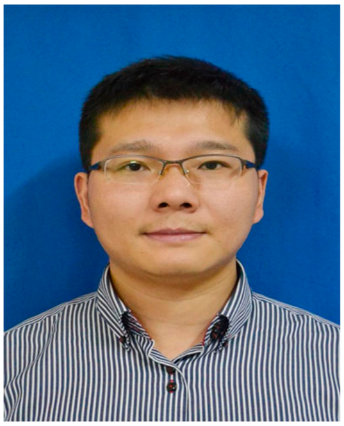
Notes

The authors declare no competing financial interest.

Biographies

Dr. Gongping Liu was born in Ji'an, Jiangxi Province, China in 1988. After receiving his Ph.D. under the supervision of Professor Wanqin Jin from Nanjing University of Technology in 2013, he joined Nanjing University of Technology as a lecturer. His current research interest focuses on the rational designing and engineering of advanced pervaporation membranes that can be used for biofuels recovery and purification, as well as developing pervaporation-intensified processes.



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