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Review

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# Recent progresses in separation membranes and their fermentation coupled processes for biobutanol recovery

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**Abstract:** In recent decades, pervaporation membrane separation coupled with fermentation is recognized as a promising process in biofuel production. This review presents latest progress in membrane materials applied for the biobutanol separation from dilute aqueous solution or fermentation broth. It also summarizes various membrane-based separation processes for *in-situ* recovering biobutanol during the fermentation. Opportunities and challenges in future development of pervaporation organophilic membrane materials and fermentation coupled processes for biobutanol production are outlook.

*Keywords:* butanol recovery, membranes, pervaporation, fermentation, coupled process

## 1. Introduction

Butanol is not only a common organic solvent and important chemical raw material, but also a kind of advanced fuel.[1-3] In comparison with bioethanol, biobutanol possesses more advantages in fuel economy and performance: good compatibility with petrol, low vapor pressure, high energy density, and greater tolerance to water.[4-7] To date, the production of butanol is mainly composed of chemical synthesis and biological fermentation.[8, 9] The chemical synthesis of butanol includes the carbonyl synthesis of propylene and acetaldehyde condensation.[10] With the shortage of petroleum resources and environmental problems such as the greenhouse effect, biofuels have attracted great attention.[11, 12] Biobutanol, one of the widely studied biofuels, is produced by biomass fermentation.[13, 14] In addition to the traditional grain-based fermentation technology, the economic feasibility of low cost non-grain crops as feedstocks have been also studied. [15-17]

Separation and purification are important processes in chemical industry. It is estimated that the energy consumption required for separation process is ~40% of the total chemical energy consumption.[18] Given

high energy demand for butanol recovery from biomass fermentation broth using conventional separation technologies such as distillation, alternative energy-efficient separation processes are developed.[19, 20] Pervaporation (PV) membrane separation, based on selective adsorption and diffusion of the certain component, has potential application in butanol recovery.[21] Compared with liquid-liquid extraction, distillation, gas stripping, adsorption and other conventional separation approaches, pervaporation technology has significant features of high selectivity and low energy requirement.[22] Studies have shown that compared with distillation process, pervaporation separation can save up to 50 % of energy consumption in the application of bio-alcohol separation.[23, 24]

Like other membrane separation processes, the core of pervaporation technology lies in the membrane material.[25] That is, the unique material structure and physicochemical performance act a pivotal part in separation system. The membrane materials should not only have good permeability (flux) and selectivity (separation factor), but also stability.[26] In terms of the produced solvents (e.g., butanol) toxicity on the microbial cells, *in-situ* solvent removal from the fermenter is favorable for enhancing the fermentation productivity.[27, 28] Different from the sole biomass fermentation, in the biobutanol fermentation integrated with pervaporation process, the pervaporation membrane can selectively concentrate the fermented solvents in the permeate side, and meanwhile the nutrients and microorganism cells are retained in the fermentation broth.[29]

This review aims to present recent progresses in biobutanol production from the fermentation broth with different feedstocks by membrane pervaporation separation technology. Over the past decade, much work has been carried out to design and fabricate pervaporation membranes to enhance butanol/water property and membrane stability. In particular, the membrane materials used for biobutanol recovery mainly include rubbery and glassy polymer, inorganic and hybrid materials. Meanwhile, with the biobutanol separation from fermented solvents, batch, fed-batch and continuous fermentation modes integrated with pervaporation were explored respectively. In addition, future direction of the development of membrane materials and fermentation coupled process for biobutanol recovery is prospected.

## 2. Principle of pervaporation separation and fermentation-pervaporation coupled process

### *2.1. Pervaporation separation process*

The mass transport mechanism through pervaporation membrane is based on solution-diffusion model.[30] The key parameters for evaluating the pervaporation membrane are permeation flux and separation

factor, which are expressed from Eqs. 1 and 2, respectively.

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

$$\beta = \frac{y_a / y_b}{x_a / x_b} \tag{2}$$

where $M$ is the weight of permeate product, $A$ is the effective area in membrane module, and $t$ is the permeation time; $y$ and $x$ are the weight percentages of each components in permeation and feed, respectively. The symbol of *a* and *b* is the component *a* and *b in binary system*, respectively.

For multi-component aqueous system, the permeation flux $J_i$ and separation factor $\beta_i$ of component *i* are calculated as follows:

$$J_i = y_i * J \tag{3}$$

$$\beta_i = \frac{y_i / y_{H_2O}}{x_i / x_{H_2O}} \tag{4}$$

For acetone-butanol-ethanol (ABE)-water system, the $y_i$ and $x_i$ are the total of ABE concentration in the permeate and feed side, respectively.

Generally, organophilic membrane materials are used for the recovery of biobutanol from fermentation process, which currently focused on polymeric membrane and its modified membranes, such as polydimethylsiloxane (PDMS), poly(ether block amide) (PEBA), poly[1-(trimethylsilyl)-1-propyne] (PTMSP), polymers possessing microporosity (PIM) and liquid membranes. In addition to acetone, butanol and ethanol (ABE), microbial bacteria, a small amount of inorganic salts and organic acid, and other substances are existed in the biobutanol fermentation broth. Therefore, the membrane material used for biobutanol recovery from fermentation process should consider not only separation performance, but also long-term stability.

### *2.2. Pervaporation coupled with fermentation process*

Bio-fermentation is an effective method for producing biobutanol. The most critical problem in biofuel fermented solvents is the toxic effect of product on the fermentation strains. As shown in Figure 1, based on the characteristics of selective permeation of the pervaporation membrane, biobutanol fermentation and separation are performed simultaneously in the integration of fermentation and PV process. The main parameters to evaluate the integration process are permeation flux, separation factor, feedstock consumption rate and product productivity. The pervaporation membrane biofouling often occurs in the

separation process, mainly because the bacteria in the fermentation broth adhere to the membrane surface and eventually develop a biofilm, which will lead to the deterioration of the membrane separation performance, as well as the accumulation of products in the fermentation broth. Currently, broth pretreatment could reduce the biofouling, and anti-fouling pervaporation membrane can also be developed for the efficient recovery of biobutanol.

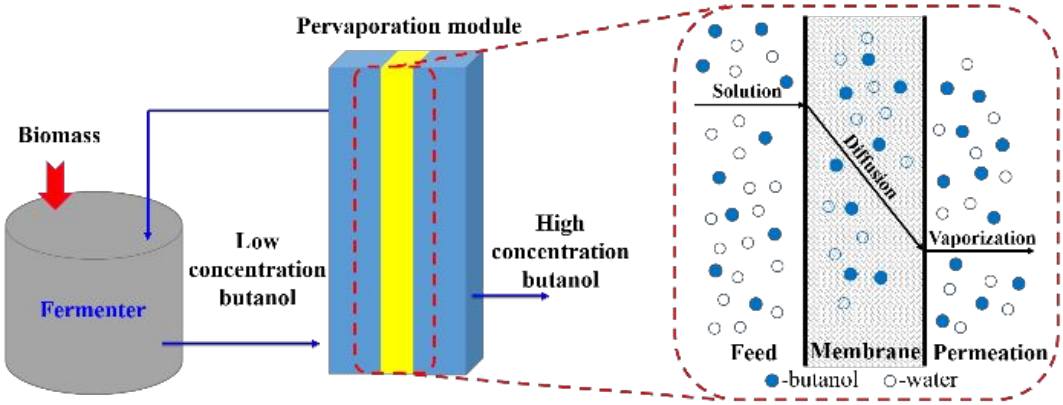


Figure 1. Biobutanol fermentation-pervaporation coupled process

## 3. Separation membranes for biobutanol recovery

### *3.1. PDMS-based membranes*

Polydimethylsiloxane membranes is the most commonly applied to separate n-butanol from aqueous solution or fermentation broth because of the benefit in good thermal, chemical and mechanical stability, as well as easy fabrication, high separation performance.[21, 31] Commercial PDMS membranes (Pervatech PDMS, Pervap 1060, Pervap 2200, Pervap 4060) were applied to study the membrane separation of butanol from binary system. The total flux and separation factor of Pervap 4060 membrane are 3400 g/m$^2$h and 39 with 5 wt% butanol-water mixtures at 50 $^o$C, respectively.[32] On the basis of pure PDMS membrane, different physical or chemical methods have been investigated to enhance the separation property of PDMS membrane layer including surface modification, new fabrication methods, optimizing substrate with different materials and pore size.

One of our recent interests focused on optimizing the interface between separation layer and support layer, which was probed by *in-situ* nano-indentation/scratch technique.[33] The excellent interfacial adhesion of PDMS/PVDF composite membrane was attributed to pore size of poly(vinylidene fluoride) (PVDF) layer and viscosity of PDMS coating solution under finely control.[34] In addition, compared PDMS/PE/Brass alloy composite membrane with PDMS/Brass alloy, an improvement of the separation property was

attributed to the existence of hydrophobic porous polyethylene (PE) layer.[35] Apart from the traditional preparation method of PDMS/PVDF composite membrane, Qin and co-workers proposed a green approach selecting water as a solvent in the presence of a surfactant, dodecylbenzene sulfonic acid instead of organic solvents like n-heptane.[36] Recently, they further proposed an UV-induced polymerization approach, realizing an ultrafast fabrication of the methacrylate-functionalized PDMS (MA-PDMS) membrane on PVDF substrate (Figure 2).[37] This ultrafast preparation approach was also applied for continuous preparation of homogeneous PDMS mixed matrix membranes incorporated with silicalite-1 zeolite.

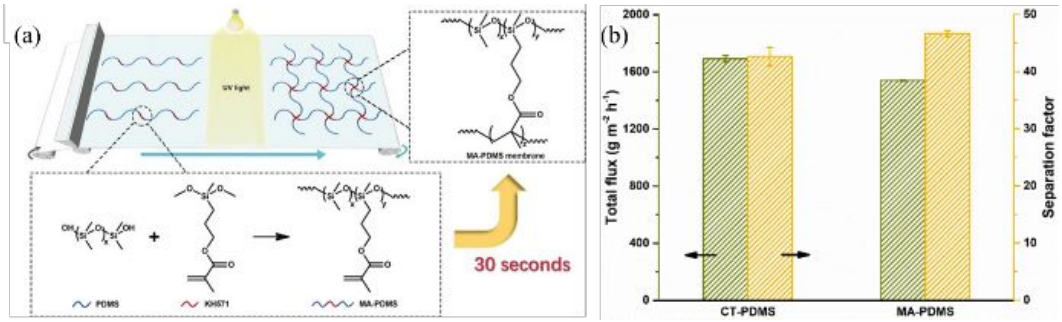


Figure 2. (a) Fabrication processes of PDMS membrane via UV-polymerization approach. (b) The pervaporation performance of conventional thermal crosslinked PDMS (CT-PDMS) membrane and MA-PDMS membrane for n-butanol recovery from 1.5 wt% aqueous solution at 55 °C.[37] Reproduced with permission from John Wiley and Sons.

Hollow fiber has an asymmetric structure including sponger-like and finger-like structure. Owing to the special support structure with low transport resistance, hollow fiber supported composite membranes show high separation property, especially in permeate flux. Our group reported a new kind of PDMS/ceramic hollow fiber composite membrane with the permeate flux of 1282 g/m$^2$h and the separation factor of 42.9 for low concentration butanol-water (1 wt%) binary system at 40 $^o$C.[38] Furthermore, the membrane exhibited permeate flux of 1116 g/m$^2$h and butanol/water separation factor of 23.8 for real ABE fermentation broth. We also designed modules for such PDMS/ceramic hollow fiber composite membranes with the packing density of 560 m$^2$/m$^3$, performing averaged permeate flux of 1.0 kg/m$^2$h and butanol/water separation factor of 22.2 in ABE fermentation broth.[39] In comparison, Lee et al. fabricated the PDMS active layer on the organic polyetherimide (PEI) hollow fiber.[40] The membrane pervaporation performance showed low total flux (249 g/m$^2$h) and high separation factor (59) in 1 wt% butanol aqueous solution at 40 $^o$C.

To further enhance the mechanical strength and packing density of inorganic hollow fiber composite membranes, our group fabricated a PDMS separation layer on the inner surface of four-channel $Al_2O_3$ hollow fiber via coating/cross-flow method (Figure 3).[41] The optimized membrane performance exhibited permeate flux of 1810 g/m$^2$h and separation factor of 35 in dilute butanol-water (1 wt%) system at 60 $^o$C.

Furthermore, the interfacial adhesion of PDMS/ceramic hollow fiber composite membrane can be enhanced by grafting $C_{16}$ chains on the surface of ceramic hollow fiber.[42] The above two kind of PDMS membrane possessed high property for n-butanol separation from dilute aqueous solution. In our group, from outer membrane to inner membrane, and even four-channel inner membrane, the changes of fabrication approaches are to enhance the separation performance, packing density and mechanical strength of the PDMS/ceramic composite membranes.

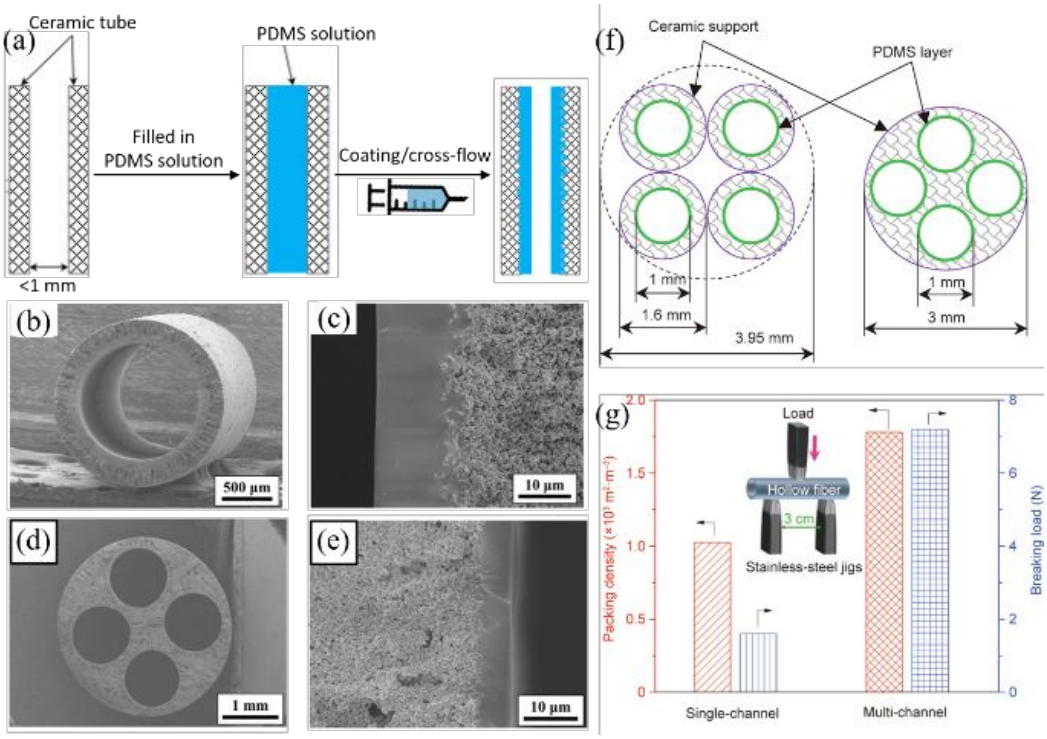


Figure 3. (a) Schematic of preparing an inner-surface PDMS/ceramic hollow composite membrane by coating/cross-flow method. Typical morphologies of inner surface PDMS/ceramic hollow fiber composite membrane: (b-c) single-channel; (d-e) multi-channels. Comparison of the inner-surface PDMS/ceramic composite membranes using single-channel and multi-channel hollow fibers: (f) Cross-sections of an ideal packing pattern with the same membrane area of the PDMS layer, which requires four fibers for the single-channel hollow fiber, but only one fiber for the four-channel hollow fiber; (g) packing density calculated using the ideally designed patterns in part (f) and breaking load measured by the three-point method; inset shows a schematic of the measurement.[41] Reproduced with permission from Elsevier.

Mixed matrix membranes (MMMs), with the addition of fillers into polymeric layer, can overcome the trade-off between permeability and selectivity for polymeric membranes, which is a promising strategy for enhancing the butanol recovery performance. Wan and co-workers used silane to graft the surface of silicalite-1 zeolite filler to enhance its dispersion and eliminate the nonselective voids with polymer matrix.[22, 43] Thus, the separation factor of PDMS membrane was highly improved with incorporating the surface modified silicalite-1 particles. Liu et al. introduced ZIF-8 (window size: 0.34 nm) into

polymethylphenylsiloxane (PMPS) matrix to prepare MMM layer on the alumina capillary tube.[44] Due to favorable aperture size and hydrophobic channels, the ZIF-8/PMPS MMM exhibited high separation properties ($J$=8600 g/m$^2$h and $\beta$=34.9) for 3 wt% i-butanol aqueous solution at 80 $^o$C. Given the excellent properties of ZIF-8 as a superhydrophobic fillers in polymeric matrix for organophilic pervaporation, Fan et al. reported highly loaded ZIF-8/PDMS nanohybrid membranes via a simultaneous spray self-assembly approach (Figure 4).[45] When the ZIF-8 nanoparticles loading of MMMs reached 40 wt%, the nanohybrid membrane exhibited high property in the permeation flux (4846.2 g/m$^2$ h) and separation factor (81.6) (1.0 wt% butanol-water at 80 $^o$C). In addition, they incorporated hydrazone-linked covalent organic-frameworks (COFs) into polymeric matrix to fabricate COF-based MMMs for butanol recovery.[46] The COF-42-PDMS MMM exhibited permeation flux of 1577.1 g/m$^2$h and separation factor of 85.2 in 1 wt% butanol solution at 80 $^o$C. Recently, Zhao's group incorporated ZIF-8-capped halloysite nanotubes into PDMS layer to enhance n-butanol recovery performance.[47] The resulting membrane obtained permeation flux of 683 g/m$^2$h and separation factor of 61.3 for dilute butanol (1 wt%) solution at 40 $^o$C.

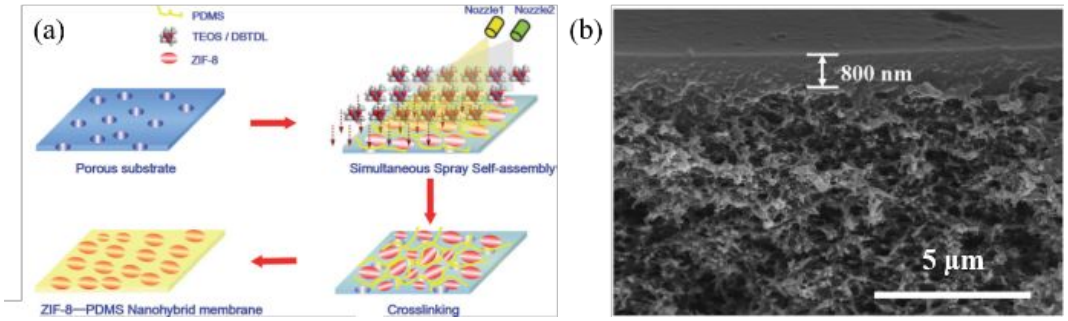


Figure 4. (a) Formation of the ZIF-8-PDMS nanohybrid composite membrane by the simultaneous spray self-assembly technique. (b) Cross-sectional SEM image of the ZIF-8-PDMS membrane (40%, w/w) prepared through two cycles of the spray self-assembly technique.[45] Reproduced with permission from John Wiley and Sons.

In addition to zeolite and metal organic frameworks (MOFs), other fillers were also used to fabricate PDMS MMMs for butanol recovery. Our group designed and fabricated polyhedral oligomeric silsesquioxanes (POSS)/PDMS MMMs with tunable free volumes driven by filler-polymer molecular interactions.[48] The butanol permeance and butanol/water selectivity were simultaneously enhanced with increasing the POSS loading up to 40 wt%. To avoid fillers aggregation at high loading, we further developed a type of low-loading POSS/PDMS MMMs via creating chemical bonding between vinyl-POSS and PDMS.[49] The butanol permeance and butanol/water selectivity of vinyl-POSS/PDMS (2 wt%) MMMs is comparable to the performance of methyl-POSS/PDMS (40 wt%). Yang et al. fabricated vertically aligned (VA) CNT (open-ended)/PDMS membranes.[50] The homogeneous PDMS membrane showed total flux of 1093.7 g/m$^2$h and separation factor of 37.6 for 1.5 wt% n-butanol aqueous solution at 80 $^o$C.

### *3.2. PEBA-based membranes*

As a soft-hard block copolymer, poly (ether-block-amide), is composed of rigid polyamide (PA) segments and flexible polyether (PE) blocks.[51] Therefore, due to the different property and proportion of PA and PE segments, PEBA (1657, 1740, 2533, 3533, 4033) has been used as membrane material for pervaporation and gas separation. In molecular structure of PEBA, PA segments provide mechanical strength, while PE segments provide good affinity to organic solvents. PEBA 2533, the highest proportion of PE segment, possesses the highest hydrophobicity and the best separation effect on the dilute organic solutions. Feng and co-workers studied PEBA 2533 dense films for pervaporation separation of butanol/water mixtures.[52, 53] Their results demonstrated the great potential of the PEBA 2533 membrane material for butanol recovery from both binary and ABE aqueous solution. Different from polymeric substrates, ceramic substrates can be applied to fabricate high separation property organic/inorganic composite membrane depended on high packing density and low transportation resistance. Our group successfully fabricated PEBA 2533/ceramic hollow fiber composite membrane with finely tailoring the dip-coating parameters such as concentration and viscosity of PEBA casting solution (Figure 5).[54] The permeate flux of the composite membrane was up to 4196 g/m$^2$h for separating butanol from low concentration butanol (1 wt%) solution with the separation factor of 21 at 60 $^o$C.

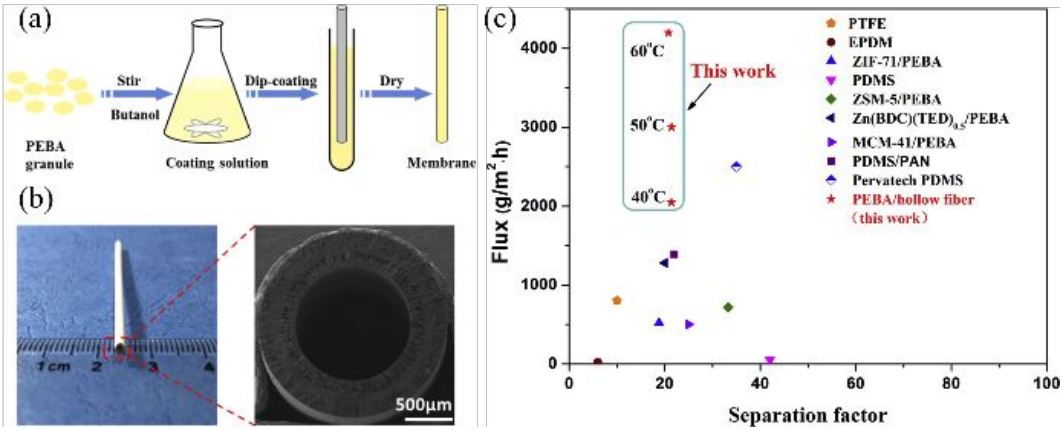


Figure 5. (a) Schematic illustration of the preparation of PEBA/ceramic hollow fiber composite membrane. (b) Digital photograph (left) and SEM image (right) of PEBA/ceramic hollow fiber composite membrane. (c) Graphical representation of polymeric membrane performance for n-butanol recovery.[54] Reproduced with permission from Elsevier.

Similar to PDMS-based membranes, high-performing fillers were introduced into PEBA membrane to enhance its butanol recovery performance. Our group incorporated hydrophobic ZIF-71 nanoparticles into PEBA 2533 matrix for biobutanol recovery.[55] The resulting 20 wt% ZIF-71/PEBA MMM exhibited

stable separation property in model ABE solution, with total flux of 520.2 g/m$^2$h and separation factor of 18.8 at 37 $^o$C. In comparison, another MOF filler, Zn(BDC)(TED)$_{0.5}$, endowed the PEBA MMMs with higher total flux (630.2 g/m$^2$h) while lower separation factor (17.4) in the same ABE solution.[56] Tan et al. fabricated ZSM-5 zeolite incorporated PEBA 2533 matrix and applied in the removal of butanol-water mixtures by pervaporation.[57] The highest separation factor is 30.7 and the permeate flux is 569 g/m$^2$h at 45 $^o$C for 5 wt% ZSM-5-PEBA membrane. They also incorporated MCM-41 into PEBA 2533 membrane to improve the butanol separation property with the use of the hydrophobicity of MCM-41 filler.[58] In recent studies, the performance of POSS/PEBA membrane were studied by Nigiz et al. for butanol recovery from dilute butanol-water mixtures.[59] An optimal flux of 1.33 kg/m$^2$h was obtained accompanied with separation factor of 27.2 with the 4 wt% POSS of the hybrid membrane at 40 $^o$C. Li et al. proposed hydrophobic ZIF-8 modified graphene oxide (GO) nanosheets (ZGO) preferential deposited on the ceramic tube and then dip-coated polymer PEBA.[60] The ZGO/PEBA composite membrane exhibited total flux was ~1.0 kg/m$^2$h and separation factor of 29.3 within the concentration of butanol-water (5 wt%) solution at 55 $^o$C. Different from the preparation method of pure polymeric membranes and conventional MMMs, the ZGO skeleton plays a role of preferential butanol adsorption and restricts PEBA swelling, thereby improving membrane performance and stability.

### *3.3. PTMSP-based membranes*

PTMSP, with high free volume fraction (34%), attracts a lot of attention because of the advantage of super permeable or ultra-high flux in gas separation and pervaporation.[61, 62] Therefore, for PTMSP membrane, the solution selectivity may become more significant than the diffusion selectivity. However, it might show unstable performance which is attributed to compaction of the polymeric membrane structure, blocking of free volume in permeation process and aging.[63-65] Dubreuil et al. investigated the performance of thin film composite PTMSP pervaporation membranes for *in-situ* product recovery of biobutanol.[66] During the separation process, significant decline of membrane flux was observed because of the existence of ageing and fouling in the membrane. The aging of the PTMSP membranes was monitored under the experimental conditions by using X-ray photoelectron spectroscopy (XPS) and infra-red spectroscopy (IR). The physical aging rate in glassy polymers is closely related to the membrane thickness, being much more rapid in thin films than in thicker films.[67] Many reports focused on the reduction of aging by incorporating different particles into polymeric matrix. Kelman and co-workers showed that the incorporation of 10 wt% POSS nanoparticles delayed the physical aging of thin PTMSP films, but decreased its permeability.[68]

Matteucci et al. investigated that permeability in the film with 75 wt% MgO increases over time, which also reduced the physical ageing in the polymer phase.[69] Olivieri et al. reported that reducing ageing of thin PTMSP films by adding few-layer graphene and monolayer GO, which enhance the separation performance and slow down the aging process.[70] The explanation for this behavior is that the fillers act as physical barriers to the rearrangement of the polymer chains. Therefore, the PTMSP membrane structure is optimized with the incorporation of the fillers into polymeric matrix, thereby improving the long stability of the PTMSP membrane.

### *3.4. PIMs-based membranes*

Polymers of intrinsic microporosity, emerging membrane materials, possess high free volume fraction, rigid molecular chains and apply in fields such as gas separation and pervaporation.[71, 72] In particular, the special ladder-like structure of PIMs with contorted sites can prevent polymer chains from packing and rotating efficiently, resulting in superior gas separation performance. Ž ák et al. firstly demonstrated a self-supported PIM-1 membrane applied to remove n-butanol from aqueous solution.[73] Furthermore, the effects of aging on the PIM-1 membrane and separation properties were explained by comparing the properties of the fresh and 370 days aged membranes. Gao et al. reported high-flux PIM-1/PVDF composite membrane (active layer thickness 1 μm) for butanol (5 wt%) solution at 65 $^{o}$C (Figure 6 ).[74] Total flux of 9.08 kg/m$^2$h and separation factor of 13.3 were reached. MMMs of PIM-1 and graphene-like fillers has also been researched for pervaporation. Alberto et al. prepared PIM-1-based MMMs with the reduced alkylamine-functionalized graphene oxide (GO) as fillers.[75] Permeation flux and n-butanol/water separation factor reached 541.4 g/m$^2$h and 32.9 for the PIM/0.1 reduced graphene oxide-octylamine (rGO-OA) MMM. It was shown that the incorporation of rGO derivatives in PIM-1 not only improves the membrane affinity towards butanol, but also decreases the affinity towards water. Additionally, organophilic PIMs was directly combined with polymer PDMS to study the recovery of dilute butanol aqueous solution (1 wt%) by Zhang's group.[76] The membrane flux was 1425.7 g/m$^2$h and separation factor was 30.7, respectively. In comparison with pure PIM-1, MMMs exhibited better separation performance.

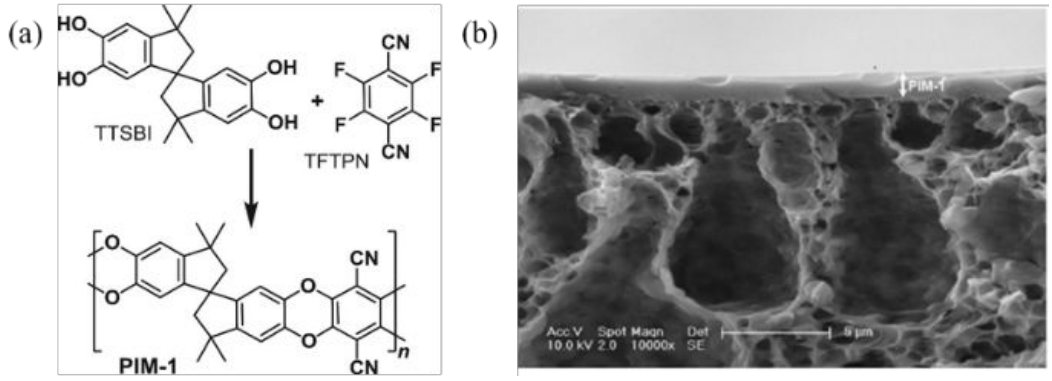


Figure 6. (a) Synthesis of PIM-1 from tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (TTSBI) and tetrafluoroterephthalonitrile (TFTPN). (b) Representative SEM of cross sections of PIM-1 thin film (coated from 2 wt% solution) on PVDF 18.[74] Reproduced with permission from Elsevier.

### *3.5. Liquid membranes*

Ionic liquid (ILs) membrane has been also investigated owing to the characteristics of ILs such as low flammability, negligible volatility and high thermal stability.[77, 78] Generally, liquid membrane is suitable for separation of specific ions and organic solution.[79] Sirkar and Thongsukmak developed a liquid membrane of trioctylamine immobilized in the porous hollow fiber to separate ABE from dilute solution.[80] The butanol flux and butanol/water selectivity were 11 g/m$^2$h and 275 with the butanol concentration of 1.5 wt% at 54 $^o$C. Earlier different types of ILs as solvent extractant for butanol recovery were investigated by Cascon and co-workers.[81] They reported separation performance and biocompatibilities of cation-based room temperature ILs (RTILs) using ABE fermentation broths. The results demonstrated the majority of the RTILs are toxic to bacterial strain. However, all of them showed inhibitory effects in fermentation conditions. Heitmann et al. studied the effect of different ILs on the pervaporation performance of the as-prepared membranes with immobilized by inclusion between silicone layers or by dissolution in PEBA matrix.[82] The best separation performance of the prepared PEBA-Im$_{10,1}$tcb membrane was permeation flux of 560 g/m$^2$h and butanol mass fraction of 55 wt% in the permeate side. Merlet et al. used different commercial hydrophobic ILs as receiving phase, showing the highest butanol flux of 5.5 g/m$^2$h in [P$_{6,6,6,14}$][DCA], and highest butanol separation factor of 64.25 in [omim][Tf$_2$N].[83] The practical application of current, IL-membranes was limited by the challenges of instability.

### *3.6. Inorganic membranes*

The inorganic membranes can be used in harsh conditions (high temperature and high pressure), and

possess superior thermal and chemical properties over polymeric membrane.[84] MFI zeolite is the most representative hydrophobic inorganic membrane material. Korelskiy et al. reported MFI membranes (thickness: 0.5 μm) prepared on a graded $\alpha$-alumina support.[85] The thin MFI membrane exhibited a high total flux of ~4 kg/m$^2$h for n-butanol aqueous solution at 60 $^o$C, while a low separation factor of only 10, indicating the formation of defects in the membrane layer. Shen et al. prepared silicalite-1 membranes with two silicon source by secondary growth method.[86] The permeation flux of the as-prepared membrane were 1.55, 0.10 and 1.51 kg/m$^2$h towards acetone-water (3 wt%), butanol-water (2 wt%) and ethanol-water (5 wt%) binary systems at 70 $^o$C, and the corresponding separation factor was 211, 150 and 39, respectively. Although high separation factors were obtained, reason for the ultra-low flux in butanol/water mixtures is unknown. In addition to zeolite, Kim et al reported a hydrophobic mesoporous silica membrane for pervaporation separation.[87] The silylated mesoporous silica on Torlon hollow fiber exhibited a permeation flux of 1.06 kg/m$^2$h and separation factor of 11 in butanol-water (5 wt%) system.

As discussed above, a wide range of materials have been used for preparation of organophilic membranes applied for n-butanol separation from aqueous solution and fermented solution. Table 1 summarized the separation performance of state-of-the-arts membranes for butanol separation. Besides of the representative polymers, such as PDMS and PEBA, like PIMs and MOFs are developing for pervaporation separation. Meanwhile, developing mixed-matrix membranes is still a dominant approach to improve the butanol recovery property of pervaporation polymeric membranes. Inorganic membranes, which have been successfully applied for ethanol/water separation with excellent performance, however remained challenges in highly selective or permeable recovery of n-butanol from low concentration aqueous solution.

Table 1. Separation property of organophilic pervaporation membranes for butanol/water mixtures

| Membranes | Feed concentration (wt %) | Temperature ($^{o}$C) | Total flux (g/m$^2$h) | Separation factor ($\beta$) | References |
|---|---|---|---|---|---|
| PDMS/ceramic | 1 | 40 | 475.4 | 26.1 | 21 |
| Pervatech PDMS | 1 | 60 | 1500 | 11.3 | 88 |
| Pervap 4060 | 5 | 50 | 3400 | 39 | 32 |
| PDMS/PVDF | 1 | 70 | 2210 | 46 | 34 |
| PDMS/hollow fiber | 1 | 40 | 1282 | 42.9 | 38 |
| PDMS/PEI | 1 | 40 | 249 | 59 | 40 |
| Inner surface PDMS/hollow fiber (single-chanel) | 1 | 60 | 1750 | 38 | 41 |
| Inner surface PDMS/hollow fiber (four-channel) | 1 | 60 | 1810 | 35 | |
| ZIF-8-PDMS | 1 | 80 | 4846.2 | 81.6 | 45 |
| MA-PDMS | 1.5 | 55 | 1538 | 47 | 37 |
| POSS/PDMS | 1 | 40 | 745 | 40 | 48 |
| VA CNT (open-ended)/PDMS | 1.5 | 80 | 1093.7 | 37.6 | 50 |
| PTMS-MCM-41/PDMS | 1.5 | 55 | 1476 | 43 | 89 |
| PTMS-silicalite-1/PDMS | 1.5 | 55 | 1156 | 72.9 | 90 |
| c-PDMS-BPPO | 5 | 40 | 220 | 35 | 91 |
| PPhS/PDMS/PVDF | 1 | 30 | 261.4 | 46.8 | 92 |
| PEBA/ceramic hollow fiber | 1 | 60 | 4196 | 21 | 54 |
| ZSM-5/PEBA | 2.5 | 45 | 569 | 30.7 | 57 |
| PEBA/ZIF-71 | 1 | 37 | 520.2 | 18.8 | 55 |
| Zn(BDC)(TED)$_{0.5}$/PEBA | 1.2 | 40 | 630 | 17.4 | 56 |
| POSS/PEBA | 2 | 40 | 1330 | 27.2 | 59 |
| ZGO/PEBA | 5 | 55 | ~1000 | 29.3 | 60 |
| PTMSP | 1.5 | 70 | 1030 | 70 | 93 |
| Silica filled PTMSP | 5 | 50 | 9500 | 104 | 32 |
| PTMSP/ PDMSM | 2 | 25 | 120 | 128 | 62 |
| PIM-1/PVDF | 5 | 65 | 9080 | 13.3 | 74 |
| PIM/0.1 rGO-OA | 5 | 65 | 541.4 | 32.9 | 75 |
| [omim][Tf$_2$N] | 1.2 | 30 | 4.3 | 64.25 | 83 |
| MFI | 3 | 60 | 3600 | 10.2 | 85 |
| Silicalite-1 | 2 | 70 | 100 | 150 | 86 |
| silylated mesoporous silica on Torlon hollow fiber | 5 | 50 | 1060 | 11 | 87 |
| POMS/OA | 2.5 | 60 | 95.9 | 279 | 94 |
| PERTHESE 500-1 | 1 | 37 | 33.0 | 56.0 | 95 |
| PTFE | 1 | 50 | 805.0 | 10.0 | 96 |

## 4. Fermentation-pervaporation coupled process

### *4.1. Pervaporation-coupled in-situ separation processes*

When coupling organophilic pervaporation membranes with ABE fermentation, solvents were

selectively removed from the fermentation broth. Among these membranes, PDMS-based membranes are most frequently studied. In our group, a tubular PDMS/ceramic composite membrane module was directly integrated with biomass fermentation broth to separate the fermentation products.[27] During the integration of fermentation and PV process, the membrane exhibited the permeation flux of 626-741 g/m$^2$h and the butanol separation factor of 8.3-21.4 at 37 $^o$C. However, the occurrence of membrane fouling was demonstrated by SEM, AFM and FT-IR. Subsequently, the fouled membrane was washed with deionized water for several times and then its separation property was almost recovered. The adhesion of microorganism on membrane surface had contributed to decrease the membrane separation performance. Recently, we compared the separation properties of PDMS composite membrane coated on the inner and outer surface of ceramic tube applied for fermentation-PV coupled process (Figure 7).[97] Compared with the shell side feed for the outer surface PDMS/ceramic composite membrane, the cross-flow created in the bore side for the inner surface PDMS/ceramic composite membrane is beneficial to reduce the adhesion and growth of microorganisms and membrane fouling, leading to a more stable separation performance during the biobutanol separation from the fermented solvents.

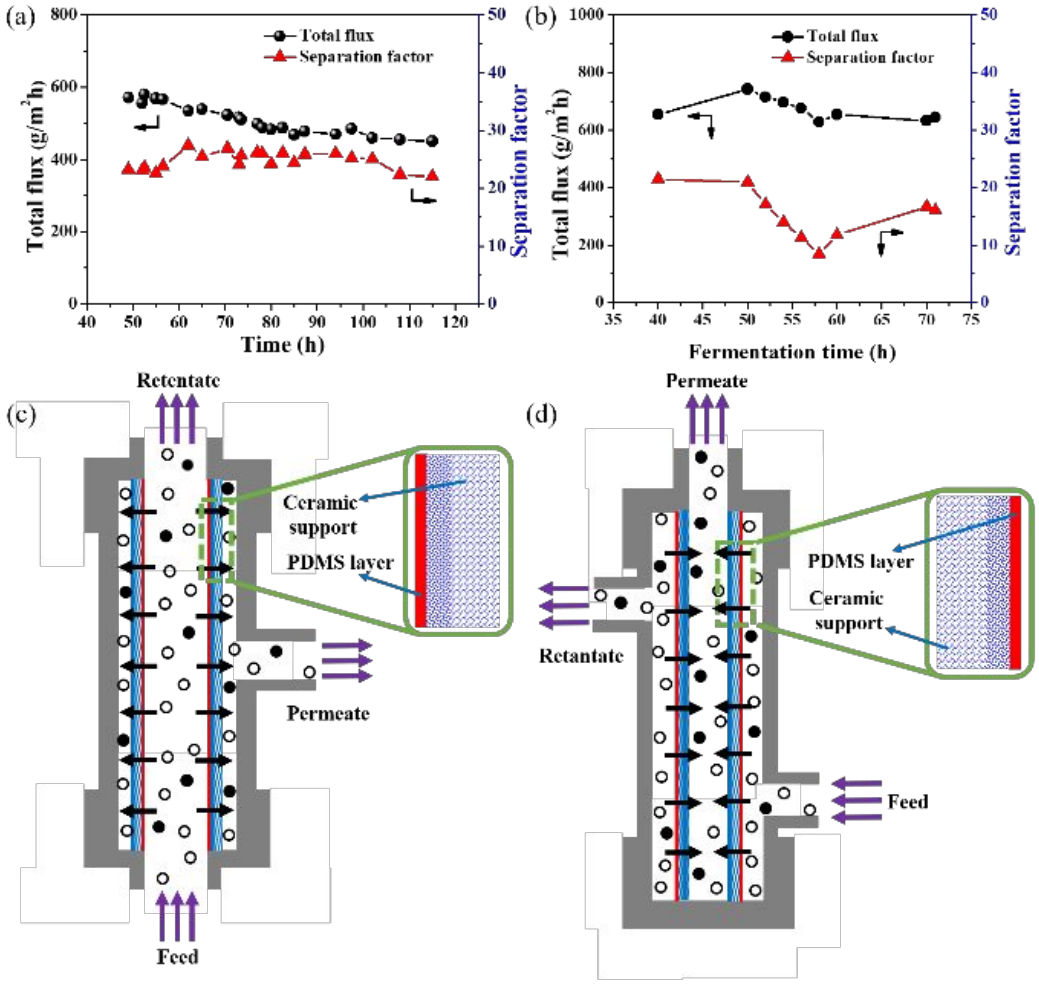


Figure 7. (a-b) Separation property of PDMS composite membranes in the coupled process. PDMS membranes are coated

on the (c) inner and (d) outer surface of ceramic tube, respectively.[97] Reproduced with permission from Elsevier.

Hecke et al. employed PDMS/polyimide thin film composite membrane for the biobutanol recovery from ABE fermented solution.[98] The pervaporation membrane achieved an average permeation flux of 367 g/m$^2$h and butanol/water separation factor of 14.7 at 35 $^o$C during 475 h of fermentation-PV coupled process. They attributed the flux variation to the differences in solvent concentration for the subsequent phases in the *in-situ* separation process. Wan and co-workers applied silicalite-1 filled PDMS/polyacrylonitrile (PAN) composite membrane in the continuous biobutanol production by a ABE fermentation-PV coupled process (Figure 8).[99] During 268 h of the integrated process, the permeation flux of the composite membrane was maintained at approximately 486 g/m$^2$h, and the average separation factor of ABE and butanol were 32.0 and 31.6 with no significant variation, respectively. A total solvent yield of 0.37 g/g and a concentrated condensate containing 89.11-160 g/L ABE were obtained in the coupled process of fermentation and PV. They also used this membrane to investigate the production of ABE from cassava with the integrated of fermentation and PV process.[100] The average total flux of the membrane was 557 g/m$^2$h, while the average separation factor of butanol was 31.2. In the end, it was obtained 574.3 g/L ABE with 501.1 g/L butanol in the final product solution. They showed that continuous *in-situ* recovery ABE from the fermented solution not only increased the solvent productivity, but also enhanced the glucose utilization rate.

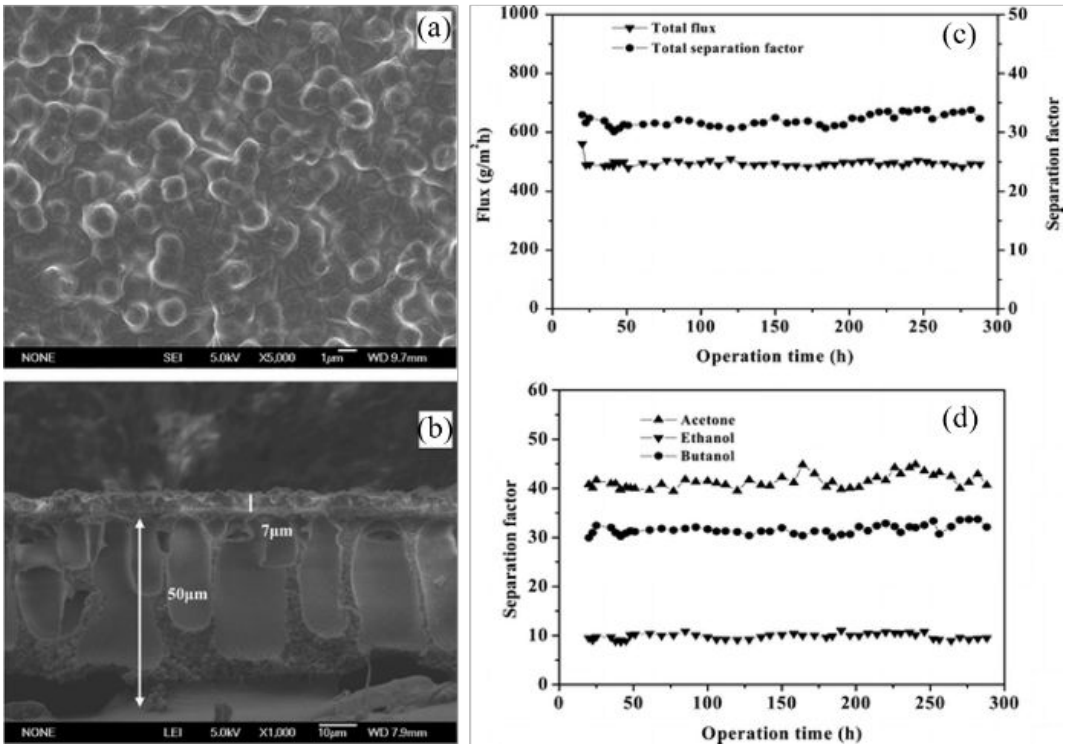


Figure 8. SEM images of the silicalite-1 filled PDMS/PAN membrane: (a) top view, (b) cross section. (c-d) Pervaporation performance of the silicalite-1 filled PDMS/PAN composite membrane in continuous ABE fermentation-PV coupled process.[99] Reproduced with permission from the American Chemical Society.

For increasing the robust of strains and improving the solvent productivity, Cai et al. carried out *in-situ* pervaporation integrated immobilized fermentation process for biobutanol production.[101] The coupled process was achieved 225-394 g/L of ABE solvents (152-225 g/L butanol), 0.38 g/g of ABE yield and butanol separation factor of 15.4-26.4 in a total ~240 h of integration process. They also studied two-stage pervaporation using PDMS/PVDFcomposite membrane for separation from fermented solution.[102] In the first stage pervaporation process, 235.25-384.41 g/m$^2$h of total permeation flux and 275.17-419.47 g/L of ABE were reached for ~190 h. They explained the slight decrease trend of the permeate flux due to the adsorption of cell debris and the lipids on the membrane surface. In the second stage of pervaporation, ABE separation factors increased gradually with the ABE concentration decreased in the feed, while the permeation flux was decreased dramatically from 527.73 g/m$^2$h to 35.51 g/m$^2$h in ~50 h.

*4.2. Hybrid in-situ separation processes*

To further enhance the separation efficiency and productivity of biobutanol, other separation processes were coupled with the fermentation-PV coupled process. To avoid membrane fouling, a gas stripping-PV integrated process was proposed to *in-situ* removal ABE solvents (Figure 9a).[103] After the first-stage of the gas-stripping (GS) condensation, about 177.6 g/L of ABE (108.33 g/L of butanol) was obtained with a slight phase separation. This process offers easy operation, elimination of cell toxicity of butanol and no fouling for the membrane in the second-stage process. It was collected about 706.68 g/L ABE (482.55 g/L of butanol) on the permeate side during the second stage of pervaporation separation unit. The GS-PV integration process shows an advantage in energy-saving and high efficiency with the comparison of the conventional GS-distillation process. Wen et al. proposed a hybrid pervaporation/salting-out process integrated with fed-batch fermentation for solvent production (Figure 9b).[104] At the first-stage separation of 182 h, 330.1-344.2 g/L of total ABE solvents (168.8-236.2 g/L of butanol) were reached in the permeate side. Then, they applied salting-out process as the second-stage to concentrate ABE under phase separation. 851.1 g/kg of total ABE was enriched in the $K_3PO_4$ groups at the salting-out factor of 2.5. Compared with prior reported PV-based techniques, they claimed that almost 100% of butanol was separated by using the PV and salting-out hybrid process.

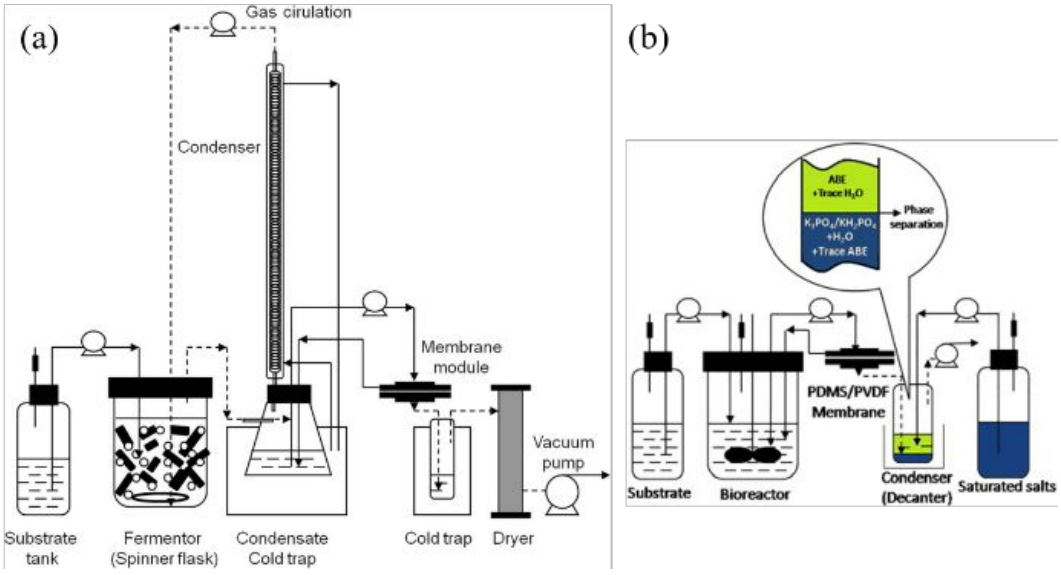


Figure 9. (a) Experimental setup of the GS-PV hybrid process.[103] (b) Experimental setup of the pervaporation and salting-out hybrid process.[104] Reproduced with permission from Elsevier.

Besides of intensifying the separation process, traditional random mutagenesis and rational metabolic engineering have been utilized to study butanol-tolerant strains, which can not only solve the butanol inhibition, but also enhance the solvent production.[105-108] Kong et al. reported a butanol-tolerant mutant generated by atmospheric and room temperature plasmas for higher butanol tolerance during fermentation.[109] Their results showed that this mutant produced 33% higher ABE solvents and 25% higher butanol with the existence of intracellular nicotinamide adenine dinucleotide (NADH) and butanol dehydrogenase during batch fermentation. As coupling with this fermentation process to *in-situ* recover butanol, the PDMS/ceramic composite membrane showed a total flux of 524-707 g/m$^2$h and separation factor of 11-19. The strains mutated and constructed provides a promising strategy to enhance the productivity of fermentation-PV coupled process.

### *4.3. Anti-fouling pervaporation membranes*

The organic components are complex in the fermentation broth, including proteins, microbial flocs and extra-cellular polymeric substances (EPSs). To avoid these components adhering to the membrane surface during *in-situ* separation process, our group recently proposed a new type of anti-biofouling PDMS membrane via a condensation reaction between fluorosilane and PDMS (Figure 10).[110] The fluoroalkyl groups was spontaneously formed on the membrane surface and provided ultra-low surface energy.[111] The fluorinated PDMS membrane showed out-standing anti-fouling performance, as well as 2-fold stabilized permeation flux and 3-fold higher ABE separation factor than the pristine PDMS membrane during 140

PV-fermentation coupled process. Additionally, 51% higher ABE productivity than batch fermentation was achieved in the fluorinated PDMS membrane integrated fed-batch fermentation process.

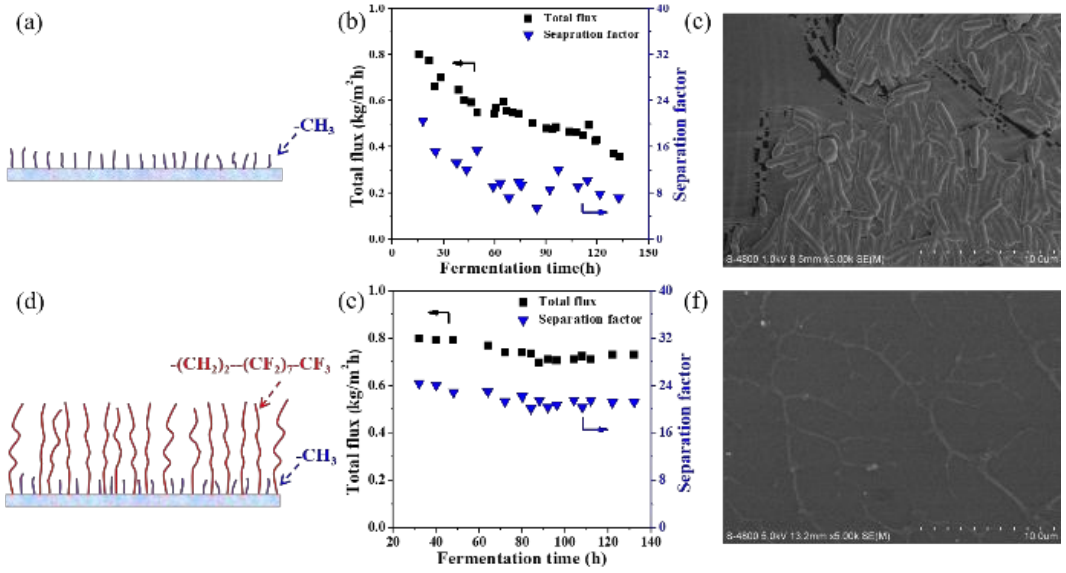


Figure 10. Schematic of (a) pristine PDMS membrane and (d) fluorinated PDMS membrane surface. Separation performance of PDMS membranes in ABE fermentation-pervaporation coupled process: total flux and separation factor for (b) pristine PDMS membrane and (e) fluorinated PDMS membrane. Surface SEM images of used (c) pristine PDMS membrane and (f) fluorinated PDMS membrane surface after the ABE fermentation-pervaporation coupled process.[110] Reproduced with permission from Elsevier.

Table 2 summarized fermentation and separation property of biobutanol fermentation-PV integrated process for biobutanol production in recent decade. Until now, PV membranes applied for *in-situ* biobutanol separation from biomass fermentation process are mainly based on PDMS membrane, owing to its high and stable performance, as well as easy fabrication. Compared with membrane separation in dilute alcohol aqueous solution or simulation solution, the pervaporation membrane property in the biobutanol fermentation-PV integrated process were generally much lower. Therefore, the stability and anti-fouling property of the organophilic pervaporation membranes deserve further attention and developments.

Table 2. Fermentation and separation performance of fermentation-pervaporation coupled process for biobutanol production

| Membrane | ABE in broth (g/L) | | ABE in permeate (g/L) | | ABE productivity (g/(L h)) | ABE yield (g/g) | Total flux ($g/m^2h$) | Separation factor | | | References |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Butanol | ABE | Butanol | ABE | | | | Acetone | Butanol | Ethanol | |
| PDMS/Ceramic | 6.93 | - | 93.49 | 150.06 | 0.98 | 0.38 | 524–707 | 19-27 | 11-19 | - | 109 |
| PDMS/Ceramic | 5.3-9.1 | 7.8-14.9 | - | 81.2-112 | 0.21 | 0.28 | 338-847 | - | 5.1-27 | - | 28 |
| PDMS/Ceramic | 2.6 | - | 39.5 | 90 | 0.62 | 0.31 | 676 | - | 15.8 | - | 112 |
| PDMS/PI | 4.7 | 7.3 | 64.0 | 117.1 | 0.37 | 0.36 | 349-418 | 35.1-46.7 | 13.7-15.7 | 6.7-8.7 | 98 |
| PDMS/PI | 4.0-8.2 | 5.8-11.5 | 61.0-131.6 | 85.6–202 | 0.37-1.13 | 0.24-0.35 | 561.04-621.2 | 20.02-33.36 | 16.76-19.81 | 5.71-10.07 | 113 |
| PDMS/Ceramic | 6-10 | - | 71-84.4 | - | 0.12-0.23 | 0.19-0.2 | 556.5-783.9 | - | 7-10.3 | 2.8-2.9 | 114 |
| PDMS/PVDF | 9.9-11.9 | 15.2-18.1 | 125.2-224.9 | 224.5-394 | 0.41 | 0.38 | 170.2-276.7 | - | 15-28 | - | 101 |
| PDMS/PVDF | | ~173.6 | 482.55 | 706.68 | ~0.67 | ~0.38 | 10.6-775.4 | | | | 103 |
| PDMS/PVDF | 10-12 | 17-21 | 199.09 | 346.45 | - | - | 235.25-384.41 | 24.5-30 | 20-24.5 | 9.5-12.58 | 102 |
| PDMS/PVDF | >8 | | 168.8-236.2 | 330.1-344.2 | 0.22 | 0.35 | | | | | 104 |
| Silicalite-1 filled PDMS/PAN | 1.96 | 3.06 | 57.77 | 89.11 | 0.3 | 0.37 | 486 | 41.4 | 31.6 | 9.8 | 99 |
| Silicalite-1 filled PDMS/PAN | <5 | - | 122.4 | 201.8 | 0.76 | 0.38 | 557 | 39.4 | 31.2 | 8.2 | 100 |
| Zeolite-PDMS | 6.7-8.5 | - | 169.6 | 253.3 | 0.46 | 0.32 | 61.4-97.5 | - | - | - | 115 |
| CNTs-PDMS | 7.7-14.2 | - | 441.7 | 593.2 | - | - | 181-655.2 | 4.4–10.2- | 19.3–38.1 | <2.5 | 116 |

## 5. Conclusions and outlook

Taking into account the vast amount of literature, it can be concluded that organophilic pervaporation membranes and their coupling with fermentation are useful to recover biobutanol and reduce the toxic effect of products in the fermentation broth. To realize efficient biobutanol recovery, the materials for making organophilic pervaporation membranes should be carefully designed and fabricated. Until now, polymers such as PDMS, PEBA are still the dominant membrane materials for butanol recovery, and mixed-matrix membranes are receiving more and more attention due to the enhanced flux and/or butanol/water separation factor. To achieve high biobutanol productivity, various *in-situ* membrane-based separation technologies have been proposed to couple with fermentation process. Compared with traditional fermentation-pervaporation coupled process, integrating two-stage pervaporation or GS-PV with fermentation can further improve the biobutanol productivity and reduce the membrane fouling.

In future, high performance organophilic pervaporation membranes are still required for further improving the recovery of biobutanol products. Among them, mixed-matrix membrane could be a potential candidate owing to the excellent balance in processability and separation performance. Facile methods for fabricating thin and defect-free mixed-matrix separation layer need to be developed towards practical application. Moreover, development of anti-fouling hydrophobic membranes with high interfacial adhesion in the continuous biomass fermentation process should be paid more attention. To satisfy the industrial application, green synthesis of multi-functional membrane materials and ultrafast fabricating high-performance pervaporation membranes would be useful for scale-up fabrication.

Further improvement in biobutanol productivity are achievable by combining metabolic engineering methods with *in-situ* product recovery technologies. Among them, selection of strain is vital since it determines fermentation performance and affects the methods for feedstock pre-treatment/hydrolysis and solvent recovery. For efficient biobutanol production and recovery equally, pervaporation-based in-situ hybrid processes can be directly integrated with fermentation process. Hence, the match between butanol production via fermentation and butanol removal with membrane can be further studied to optimize the design of fermentation-PV coupled process. In addition, further optimization on the configuration of organophilic pervaporation membrane modules included packing density, flow distribution and feed concentration are required for the enhancement of separation and industrial process in practical application.

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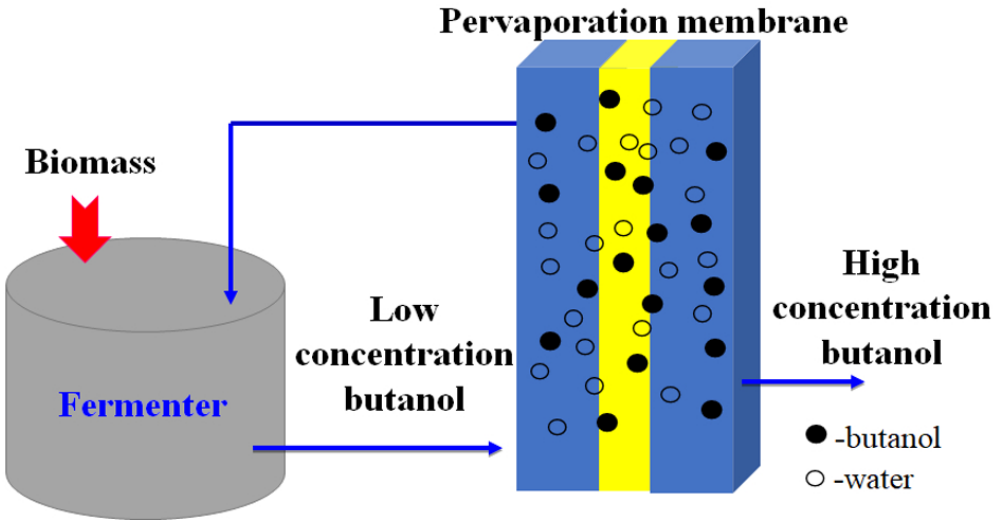


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