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# Evaluation of asymmetric polydimethylsiloxane-polyvinylidene fluoride composite membrane and incorporated with acetone-butanol-ethanol fermentation for butanol recovery

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ABSTRACT

The polydimethylsiloxane-polyvinylidene fluoride (PDMS-PVDF) composite membrane was studied for its pervaporation performance to removal of butanol from butanol/ABE solution, fermentation broth as well as incorporated with acetone-butanol-ethanol (ABE) fermentation. The total flux and butanol titer in permeate through the PDMS-PVDF membrane were up to 769.6 g/m$^2$ h and 323.5 g/L at 80 °C, respectively. The butanol flux and total flux increased with increasing the feed temperature as well as the feed butanol titer. The butanol separation factor and butanol titer in permeate decreased slightly in the presence of acetone and ethanol in the feed due to their preferential dissolution and competitive permeation through the membrane. In fed-batch fermentation incorporated with pervaporation, butanol titer and flux in permeate maintained at a steady level with the range of 139.9–154.0 g/L and 13.3–16.3 g/m$^2$ h, respectively, which was attributed to the stable butanol titer in fermentation broth as well as the excellent hydrophobic nature of the PDMS-PVDF matrix. Therefore, the PDMS-PVDF composite membrane had a great potential in the *in situ* product recovery with ABE fermentation, enabling the economic production of biobutanol.



## 1. Introduction

Butanol is a valuable chemical and potential biofuel that can be derived from renewable resources by microbial acetone-butanol-ethanol (ABE) fermentation (Qureshi et al., 2008). As an alternative for petroleum fuel, butanol is superior to ethanol due to its higher energy density and better compatibility with gasoline *etc.* (Gheshlaghi et al., 2009; Dürre, 2007). However, the main challenge for microbial butanol production is low butanol titer, yield and productivity due to severe butanol toxicity to cells, leading to intensive energy consumption in product recovery (Ezeji et al., 2010; Nicolaou et al., 2010).

In comparison with 12–15% ethanol production in fermentation, butanol titer in ABE fermentation by *Clostridia* spp. is generally less than 2.0% and thus not economically competitive for butanol recovery by conventional distillation (Xue et al., 2010; Chen and Blaschek, 1999). Therefore, *in situ* butanol recovery technologies (such as adsorption, gas stripping and pervaporation) are often adopted to mitigate butanol inhibition to cells during the fermentation, and increase butanol production (Nielsen and Prather, 2009; Xue et al., 2013; Qureshi and Blaschek, 1999).

Among all these butanol recovery methods, pervaporation is regarded to be an energy-efficient process, which allows selective removal of volatiles from model solution/fermentation broth through the membranes. Compared with the conventional homogeneous polymeric membranes such as polypropylene (PP) (Gapes et al., 1996), polysiloxane (Garcia et al., 2009), polytetrafluoroethylene (PTFE) (Vrana et al., 1993), and poly (1-trimethylsilyl-1-propyne) (PTMSP) (Fadeev et al., 2000), the PDMS composite membranes possessed promising properties over others with high hydrophobicity as well as good chemical and mechanical stability (Hecke et al., 2012; Li et al., 2010). Therefore, the PDMS composite membranes have been fabricated to evaluate their potentials for butanol recovery by some authors, shown in Table 1. Adding hydrophobic fillers or a layer composited with the PDMS membrane was an effective way to improve the mass flux and separation factor of butanol in pervaporation. The PDMS-PVDF composite membrane was selected for benzene, toluene, xylene (BTX) and butanol removal due to its good permeation property and stability (Yeow et al., 2002; Jee and Lee, 2014).

In the present study, the homogeneous PDMS and PDMS-PVDF composite membranes were investigated to compare their performances on butanol recovery from butanol/ABE model solution

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**Table 1**
Summary of pervaporation for butanol recovery by various membranes.

| Membrane types | Butanol titer (g/L) | | Flux (g/m$^2$·h) | | Separation factor | Reference |
|---|---|---|---|---|---|---|
| | Feed | Permeate | Butanol | Total | | |
| **The homogenous membrane** | | | | | | |
| Porous PP | ~5.6 | 16.7 | – | 1482 | 6.3 | Gapes et al. (1996) |
| PVDF | 75 | – | – | 2340 | 5.2 | Srinivasan et al. (2007) |
| PTFE | 12.5 | – | – | 170 | 8.5 | Vrana et al. (1993) |
| PEBA 2533 | 19.1 | – | 6.6 | 34 | 13.2 | Liu et al. (2005) |
| **The composite membrane** | | | | | | |
| Silicalite-1-PDMS | 10 | – | 300 | 600–700 | 90–100 | Huang and Meagher (2001) |
| MFI-α-alumina | ~30 | – | – | ~4000 | ~10 | Korelskiy et al. (2013) |
| PDMS-PE-Brass | 20 | – | – | 132 | 32 | Li et al. (2010) |
| PDMS-PVDF | 10 | 300–330 | 48.4 | 159.6 | 43.1 | Jee and Lee (2014) |
| PDMS-PVDF | 15 | 323.5 | 249.0 | 769.6 | 35.2 | This work |
| **The pervaporation membrane incorporated with ABE fermentation** | | | | | | |
| PDMS | 7.6 | 71.0 | 56.9 | 783.9 | 10.3 | Chen et al. (2013) |
| | 7.0 | 46.5 | 26.6 | 566.5 | 7.0 | |
| Porous PP | 2–5 | 7.9 | 3–7.1[a] | – | 3–5 | Friedl et al. (1991) |
| PEBA-CNTs | 8–12 | – | – | 147 | 18 | Yen et al. (2012) |
| PDMS-ceramic | 5.3–9.1 | 81.2–118 | – | 338–847 | 5.1–27.1 | Wu et al. (2012) |
| PDMS-PVDF | 7.4–9.5 | 139.9–154.0 | 13.3–16.3 | 93.3–108.8 | 14.4–21.2 | This work |

[a] Solvent flux.

and fermentation broth. Furthermore, the PDMS-PVDF composite membrane was directly integrated with ABE fermentation using *Clostridium beijerinckii* 55025 to remove ABE from fermentation broth and mitigate butanol inhibition to cells. To be highlighted, the performance of the composite membrane was very effective for butanol recovery from active fermentation broth in the ABE fermentation coupled with pervaporation.

## 2. Materials and methods

### 2.1. Culture and media

*C. beijerinckii* ATCC 55025 was used in this study. The seed culture was prepared in the Clostridial growth medium (CGM) containing 30 g/L glucose, 2 g/L yeast extract, 1 g/L Tryptone, minerals, and vitamins in a phosphate buffer as described in Xue et al. (2013), and incubated at 37 °C for ~16 h until active growth was observed. ABE fermentation was studied using the P2 medium containing: glucose (80 g/L), yeast extract (1 g/L), $KH_2PO_4$ (0.5 g/L), $K_2HPO_4$ (0.5 g/L), ammonium acetate (2.2 g/L), vitamins (1 mg/L para-amino-benzoic acid, 1 mg/L thiamin and 0.01 mg/L biotin), and mineral salts (0.2 g/L $MgSO_4{\cdot}7H_2O$, 0.01 g/L $MnSO_4{\cdot}H_2O$, 0.01 g/L $FeSO_4{\cdot}7H_2O$, 0.01 g/L NaCl), prepared according to the procedures described previously (Xue et al., 2012). The media were sterilized by autoclaving at 121 °C and 15 psig for 30 min. All solutions were purged with nitrogen for 1 h through a sterile 0.2 μm filter, either before or after autoclaving.

### 2.2. Preparation of the homogeneous PDMS and PDMS-PVDF composite membranes

For the homogeneous PDMS membrane fabrication, the base solution from the Sylgard®184 silicone elastomer kit (Dow Corning, USA) was mixed with the curing agent in the ratio of 10:1 using pentane as the solvent to dilute the mixture. The mixture was stirred completely for 5 min and then 8000 × *g* centrifuged for 5 min to wipe off air bubble. The mixture was placed on a cleaning glass plate and cast evenly using a micron film applicator (Paul N. Gardner Company, USA), then heated in oven for 3 h at 100 °C. After the membrane cure, the membrane was carefully peeled off for pervoparation. The thicknesses of the PDMS membranes were fabricated as 100 and 200 μm, respectively.

For the PDMS-PVDF composite membrane shown in Fig. 1, the porous PVDF as the support layer was made by phase inversion method, using the following dope compositions: 12 wt.% PVDF in 88 wt.% N,N-dimethylformamide (DMF), and 0.8 g polyvinylpyrrolidone (PVP) and 1.6 g water were added in every 100.0 g of PVDF-DMF solution as additives. The mixture was stirred completely for 5 min and followed by 8000 × *g* centrifuged for 5 min to wipe off air bubble. Then, the mixture was cast evenly on a cleaning glass plate using a micron film applicator and then immersed in the water bath at 37 °C for 30 s. After drying the PVDF layer at 50 °C for 24 h, the PDMS mixture was cast on the dried PVDF layer with the total PDMS-PVDF membrane thickness of 200 μm. At last, the membrane was heated in oven for 3 h at 100 °C for the membrane cure. The effective area of the PDMS and PDMS-PVDF membranes was 58 cm$^2$. The morphology and structure of the membranes were examined using scanning electron microscopy (SEM) (Quanta 450, FEI, USA) and the images were shown in Fig. 2.

### 2.3. Pervaporation with the PDMS and PDMS-PVDF composite membranes

The butanol-water solution, ABE solution and fermentation broth containing ~15.0 g/L butanol were used to investigate the pervaporation performance of the membranes at the designated temperature. The ABE weight ratio in ABE solution was 3:6:1 to simulate the usual ABE fermentation broth. The feed solution was circulated at a flow rate of 1.2 L/min to minimize the boundary layer thickness and maximize mass transfer. Vacuum was provided on the downstream side of the membrane using a vacuum pump with <5 kPa as the driving force. The recovered permeate was collected in the vacuum tank immersed in liquid nitrogen.

The flux (ABE and total) and separation factor (SF) were calculated as follows:

$$\text{Flux} = \frac{W}{At}$$

$$\text{SF} = \frac{y/(1-y)}{x/(1-x)}$$

where $W$ is the weight of the recovered permeate in gram, $A$ is the membrane area in m$^2$ and $t$ is the time (h) for the sample collection. $x$ and $y$ is the weight fractions of components in the feed and permeate samples in the pervaporation, respectively.