Continuous Acetone–Butanol–Ethanol (ABE) Fermentation with in Situ Solvent Recovery by Silicalite-1 Filled PDMS/PAN Composite Membrane

Li, Jing; Chen, Xiangrong; Qi, Benkun; Luo, Jianquan; Zhuang, Xiaojie; Su, Yi; Wan, Yinhua

Published in:
The Open Fuels & Energy Science Journal

Link to article, DOI:
10.1021/ef401706k

Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

energy&fuels

Article

pubs.acs.org/EF

Continuous Acetone–Butanol–Ethanol (ABE) Fermentation with in Situ Solvent Recovery by Silicalite-1 Filled PDMS/PAN Composite Membrane

Jing Li,[†,‡,§] Xiangrong Chen,[†] Benkun Qi,[†] Jianquan Luo,[†] Xiaojie Zhuang,[†,‡] Yi Su,[†] and Yinhua Wan*[,†]

[†]State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

[‡]University of Chinese Academy of Sciences, Beijing 10049, People's Republic of China

[§]College of Biology Science & Engineering, Hebei University of Economics & Business, Shijiazhuang 050061, People's Republic of China

ABSTRACT: The pervaporation (PV) performance of a thin-film silicalite-1 filled PDMS/PAN composite membrane was investigated in the continuous acetone–butanol–ethanol (ABE) production by a fermentation–PV coupled process. Results showed that continuous removal of ABE from the broth at three different dilution rates greatly increased both the solvent productivity and the glucose utilization rate, in comparison to the control batch fermentation. The high solvent productivity reduced the acid accumulation in the broths because most acids were reassimilated by cells for ABE production. Therefore, a higher total solvent yield of 0.37 g/g was obtained in the fermentation–PV coupled process, with a highly concentrated condensate containing 89.11–160.00 g/L ABE. During 268 h of the fermentation–PV coupled process, the PV membrane showed a high ABE separation factor of more than 30 and a total flux of 486–710 g/m^{2}h. Membrane fouling was negligible for the three different dilution rates. The solution-diffusion model, especially the mass transfer equation, was proved to be applicable to this coupled process.

1. INTRODUCTION

The depletion of petroleum fuel reserves and the serious environmental issues have triggered an increased attention in technologies that use renewable resources for liquid fuel production.[1,2] Butanol has been regarded as one of the most promising biofuels, due to its characteristics of an alternative liquid fuel to meet the needs of sustainable and green energy systems.[3,4] However, butanol is highly toxic to the fermenting microorganism, resulting in low product concentration in the fermentation broth. Therefore, the conventional butanol fermentation process suffers from low productivity and large energy consumption in the subsequent distillation operation. It was reported that, if the level of butanol concentration in the reactor could be increased from 1.2% to 2% (w/v), the cost of distillation energy for solvent recovery would be reduced by half.[5] It is generally believed that integrating the fermentation with the product separation process by using a suitable in situ product recovery (ISPR) technique could overcome the shortage of low solvent (ABE) resistance of these strains. To date, various techniques, such as gas-stripping, pervaporation (PV), liquid–liquid extraction, and adsorption,[6] have been investigated to reduce the effect of butanol inhibition, and enhance solvent productivity and sugar utilization. Among those techniques, PV is considered to be the most promising technique because of its energy efficiency, cost effectiveness, as well as no harmful effects on the microorganisms.[7]

Among various PV membranes, poly(dimethylsiloxane) (PDMS) membranes have shown good comprehensive performance, including good thermal, chemical, and mechanical stability, moderate selectivity and flux, as well as ease of manufacture and cost effectiveness. The feasibility of PDMS membranes in continuous removal of butanol from the ABE fermentation broth was examined in previous studies.[8−10] Hecke et al. reported continuous two-stage ABE fermentation coupled to the PV process using a PDMS composite membrane. The coupled process lasted 475 h with an average flux of 367 g/m^{2}h.[8] Chen et al. investigated ABE fermentation by combining a PDMS membrane fermentor in a closed-circulating fermentation system.[9] The low flux and/or low separation factor of the PV membrane used in the above reports require a larger membrane area or a higher operation temperature, or obtaining a low total butanol concentration in the permeate solution from the pervaporation unit and require more energy per weight unit of butanol in the subsequent distillation procedure, thus increasing the cost of the PV process and reducing its viability in industrial applications.

Recently, a thin-film composite membrane with the incorporation of silicalite-1 was developed for separating butanol from a model solution.[11,12] The relatively higher flux and higher separation factor of this composite membrane compared to those of the pure PDMS membrane shows its great promise in commercial application in in situ ABE recovery from broth.

In this work, high-performance ultra-thin-film silicaliet-1 filled PDMS composite membrane was prepared by curing a prepolymer on a porous PAN substrate. The behaviors of

Received: August 26, 2013
Revised: December 6, 2013
Published: December 6, 2013

dx.doi.org/10.1021/ef401706k | *Energy Fuels* 2014, 28, 555−562

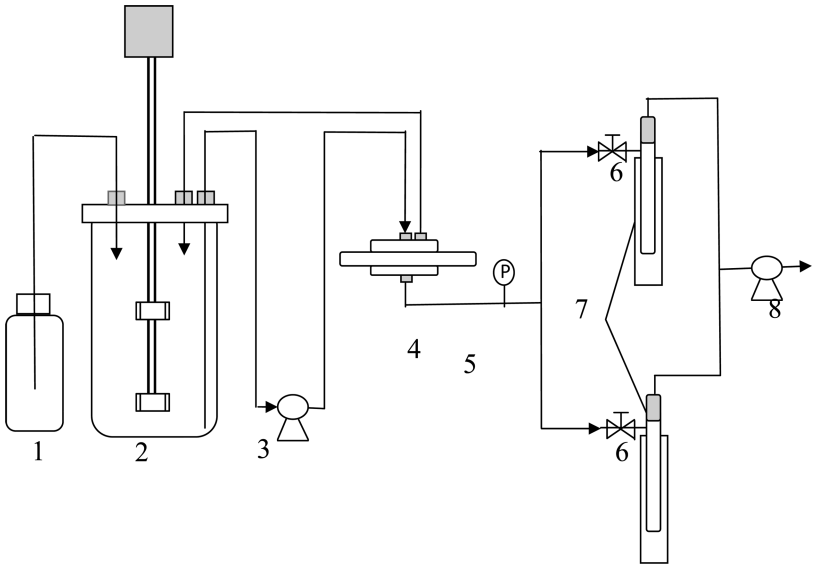

Figure 1. Schematic diagram of the apparatus for pervaporation experiment: (1) concentrate glucose feed tank, (2) fermentator, (3) peristaltic pump, (4) pervaporation unit, (5) pressure gauge, (6) triple valve, (7) cold trap, (8) vacuum pump.

continuous ABE fermentation with in situ solvent recovery by PV with the composite membrane were investigated. The performances of the silicalite-1 filled PDMS/PAN membrane were also studied in continuous the ABE fermentation−PV coupled process.

2. EXPERIMENTAL SECTION

2.1. Materials. PDMS was purchased from GE Toshiba Silicones Co., Ltd., Japan. Silicalite-1 was prepared in our laboratory according to the method reported by Zhou et al.[11] The size of silicalite-1 particles was about 1 μm. An asymmetric microporous poly(acrylonitrile) (PAN) membrane (20 kDa, Shanghai Jitian Co. Ltd., China) was employed as the support substrate. Acetone, butanol, ethanol, and *n*-heptane were of analytical reagent grade and purchased from Beijing Chemical Plant, Beijing, China. Deionized water was used in all experiments.

2.2. Preparation of Thin-Film Silicalite-1 Filled PDMS/PAN Composite Membrane. A silicalite-1 filled PDMS/PAN composite membrane was prepared by first mixing 1.8 g of PDMS, 36 g of *n*-heptane, and 2.25 g of silicalite-1 in a three-neck round-bottom flask, and then the resulting solution was stirred at 70 °C for about 2 h. After degassing under vacuum, the mixing solution was coated as thin layers on the top of a PAN support membrane, using an automatic film applicator (K303 Multi Coater, RK Print Coat Instruments Ltd., UK), with a coating gear of 10. Subsequently, the composite membrane was dried overnight at room temperature, and then cured at 80 °C in a vacuum oven for more than 8 h to ensure complete curing. The finished membrane was cut into round discs with diameters of 48 or 88 mm for PV tests, respectively.

2.3. PV Experiments. The membrane module with an effective membrane area of 0.0072 and 0.0243 m^2 was used, respectively. Details of the membrane module have been given previously.[13] When coupled with fermentation, as reported by Li et al.,[14] 30% ethanol solution was used to sterilize the PV membrane by circulating the ethanol solution through the system for 12 h, followed by washing with 500 mL of sterilized deionized water. The feed tank with butanol/water solution or ABE model solution was maintained at 37 °C by the heater band, and a peristaltic pump was used for recirculation of the liquid mixture. The pressure at the permeate side was maintained at less than 280 Pa all the time. Samples were collected by two parallel cold traps in a liquid nitrogen bath and analyzed during the PV experiment. Flux (J) and selectivity (α) were calculated as follows

$$J = w/At \tag{1}$$

$$\alpha = [y/(1-y)]/[x/(1-x)] \tag{2}$$

where W is the weight of the condensate (g), A is the membrane area (m^2), t is the time (h) for the sample collection, and x and y are weight fractions of components in retentate and permeate samples, respectively.

The solution-diffusion model has been adopted in many studies to simulate the butanol separation from the butanol/water solution,[14,15] the transport behavior of permeates across the PV membrane can be expressed as

$$J_i = K_{i,ov}C_i \tag{3}$$

where J_i is the flux of permeate i with the units of g/m^2h, $K_{i,ov}$ is the overall mass transfer coefficient of permeate i with the units of mm/h, and C_i is the concentration of permeate i in the reactor-side solution with the units of g/L.

2.4. Culture and Inoculum Preparation. Inoculum was prepared from a spore suspension of a hyper-butanolagenic mutant *C. acetobutylicum* DP 217. Spores were suspended in 70 g/L corn mash medium at 4 °C. Spores (10 mL) were heat-shocked for 90 s at 100 °C, followed by cooling in ice−water for 60 s. The culture was inoculated into 100 mL of cooked 70 g/L corn mash medium in a 150 mL screw capped Pyrex bottle, and then incubated anaerobically for 20−24 h at 37 °C as the primary seed culture. A 20 mL portion of the primary seed culture was transferred into 250 mL sealed anaerobic bottles containing 200 mL of 70 g/L corn mash medium and incubated at 37 °C for 20−24 h as the secondary seed culture. When the suspension appeared, the secondary seed culture was inoculated into the ABE production medium.

2.5. Fermentation−PV Coupled Processes. A schematic diagram of the fermentation−PV coupling apparatus is presented in Figure 1. Control batch fermentations were conducted in a 2 L fermentor (New Brunswick Scientific, Edison, NJ). The fermentation medium contained the following: glucose 60 g/L, yeast extract 3 g/L, CH_3COONa 1.1 g/L, NaCl 0.05 g/L, KH_2PO_4 0.25 g/L, K_2HPO_4 0.25 g/L, $MgSO_4$ 0.05 g/L, $FeSO_4{\cdot}7H_2O$ 0.05 g/L, and $MnSO_4{\cdot}H_2O$ 0.05 g/L. The reaction volume and the membrane areas varied with different dilution rates, and all parameters are listed in Table 1. The fermentation medium was autoclaved at 121 °C for 20 min, followed by cooling to 37 °C under an O_2-free N_2 atmosphere. The fermentor was inoculated with 10% (v/v) of the secondary seed culture.

The fermentation experiment was allowed to run for 20 h to reach the initiation of the solventogenesis phase of ABE fermentation, and then the sterile membrane unit coupled to the fermentor was put into operation and in situ ABE removal by PV started. Fermentation broth

dx.doi.org/10.1021/ef401706k | *Energy Fuels* 2014, 28, 555−562

Table 1. Parameters Used in Continuous ABE Production by Fermentation−PV Coupled Process

	test I	test II	test III
fermentation volume (L)	1	1.5	1
membrane area (m^2)	0.0072	0.024	0.024
dilution rate (h^{-1})	0.0038	0.0081	0.0117

was circulated in the fermentor through the membrane module using a peristaltic pump at 2 L/min. Glucose and the organism cells were retained in the fermentor by the PV membrane. The volatile compounds, mainly acetone, butanol, and ethanol, were permeated through the PV membrane, and then cooled in the cooling traps, and no glucose was detected in the permeate solution. Highly concentrated fresh feed solution was added into the fermentor continuously at the same flow rate of in situ removal of solvent to maintain the constant broth volume and the sugar content in the fermentation broth. Continuous experiments with three different dilution rates were conducted, respectively, when the steady condition was maintained. The performance of the thin-film composite membrane during the continuous coupled experiments was investigated.

2.6. Analysis. Acetone, butanol, and ethanol concentrations were determined using a gas chromatograph equipped with a flame ionization detector (FID) and a 20 ft stainless steel packed column (7890A, Agilent Technologies, USA). The oven temperature was programmed from 100 to 250 °C at a rate of 16 °C/min. Both injector and detector temperatures were set at 250 °C. Organic acids in the fermentation culture solutions were analyzed by high-performance liquid chromatography (LC-20A, Shimadazu Corp., Japan). The ultraviolet detector was used to detect acetic acid and butyric acid (SPD-20A, Shimadazu Corp., Japan). Perchloric acid solution (5 mM) was used as the mobile phase at 0.6 mL/min. Cell density was measured at 620 nm using an ultraviolet spectrophotometer (UV757 CRT, Shanghai Precision & Scientific Instrument Co., Ltd., China). Glucose concentration was measured using a biosensor with glucose oxide electrodes (SBC-40C, Institute of Biology, Shandong Academy of Science, China).

3. RESULTS AND DISCUSSION

3.1. Characterization and Evaluation of Thin-Film Silicalite-1 PDMS/PAN Composite Membrane. In this work, membranes have been prepared by using PAN as the support substrate and silicalite-1 as filler. The surface and the cross-sectional morphology of the composite membranes was characterized by SEM. Figure 2a is an SEM surface image of the membrane. There was a dense membrane structure free of pores and cracks, and silicalite-1 particles were evenly dispersed in the PDMS polymer. Figure 2b represents the cross-section image of the composite membrane. In this micrograph, the composite membrane showed two obvious layers from top to bottom: silicalite-1 filled polymer layer and substrate layer. The thickness of the active layer was about 7 μm, which guaranteed the high flux of the membrane.

To evaluate the PV performance of the silicalite-1 PDMS/PAN composite membrane, the butanol/water binary solutions were first tested in the experimental system. PV experiments were conducted with varied butanol concentrations ranging from 2.3 to 10.4 g/L, which are relevant to that in the control ABE fermentation. Membrane performance for the model solution is shown in Figure 3.

As can be seen from Figure 3a, the butanol separation factor of the thin-film membrane decreased slightly from 33 to 30 with increasing feed concentration. In the condensate, 244 g/L of butanol concentration was obtained. Vane et al. evaluated the economics of pervaporation, and claimed that the PV system could be sufficiently energy efficient when the separation

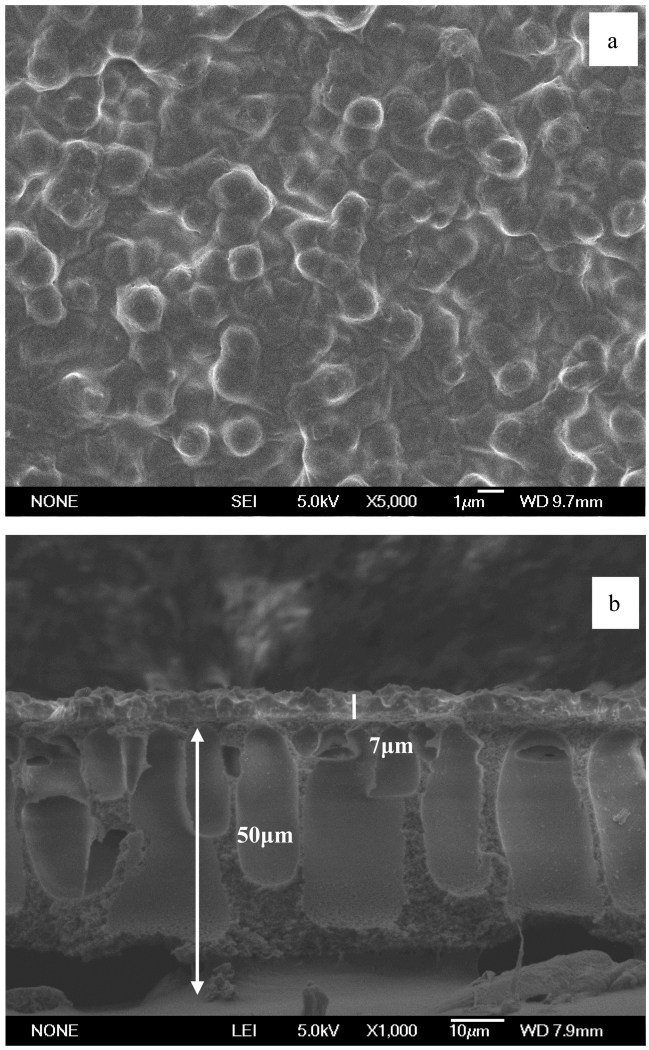

Figure 2. SEM images of the silicalite-1 filled PDMS/PAN membrane: (a) top view, (b) cross section.

factors of membranes were higher than 30.[16] It seemed that the silicalite-1 filled PDMS/PAN composite membrane could meet this requirement. As shown in Figure 3b, under the experimental conditions examined, the total flux and the butanol flux increased from 550 to 708 g/m^2h and from 40 to 173 g/m^2h, respectively, while the water flux was more or less constant. According to the solution-diffusion mechanism, the increase of butanol flux is almost linear with butanol concentration. The transport behavior can be mathematically described by eq 3, and the overall mass transfer coefficient of butanol was 16.84 mm/h. These phenomena were in agreement with the previous observations of the pervaporative separation of butanol−water solution.[14] The total fluxes of the membrane were much higher than those of the reported membranes under the same conditions[12,17] due to its very thin active separating layer (about 7 μm), which could meet the flux requirement of the fermentation−PV coupled processes. The results indicated that the thin-film silicalite-1 filled PDMS/PAN membrane possessed very good PV performance. Its applicability in the long term fermentation−PV coupled process was further investigated in the following experiments.

3.2. Continuous ABE Fermentation by the Coupled Process. The ABE fermentation was first run as a controlled experiment without coupling with PV. Figure 4a shows the

dx.doi.org/10.1021/ef401706k | Energy Fuels 2014, 28, 555−562

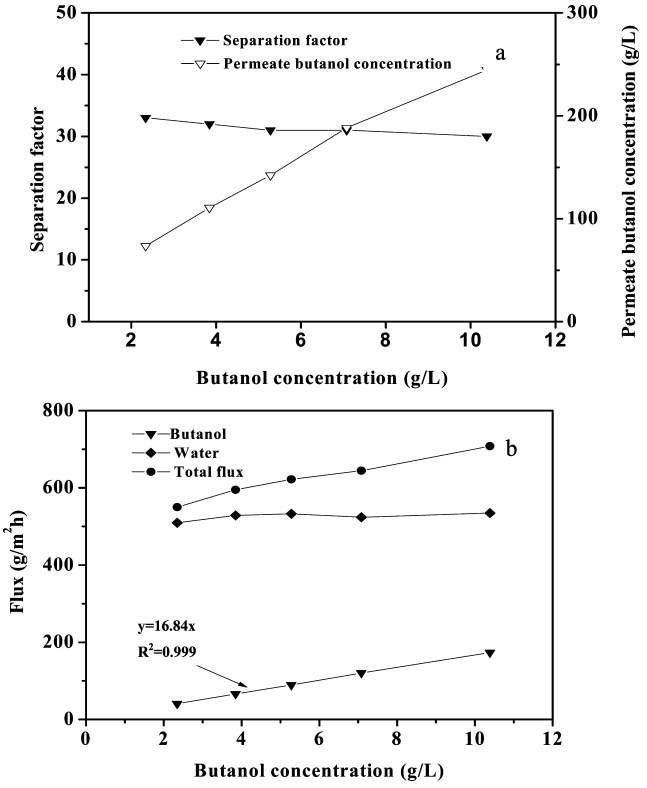

Figure 3. Pervaporation performance of the silicalite-1 filled PDMS/PAN membrane with butanol/water model solutions at 37 °C. (a) Separation factor and permeate butanol concentration, and (b) flux.

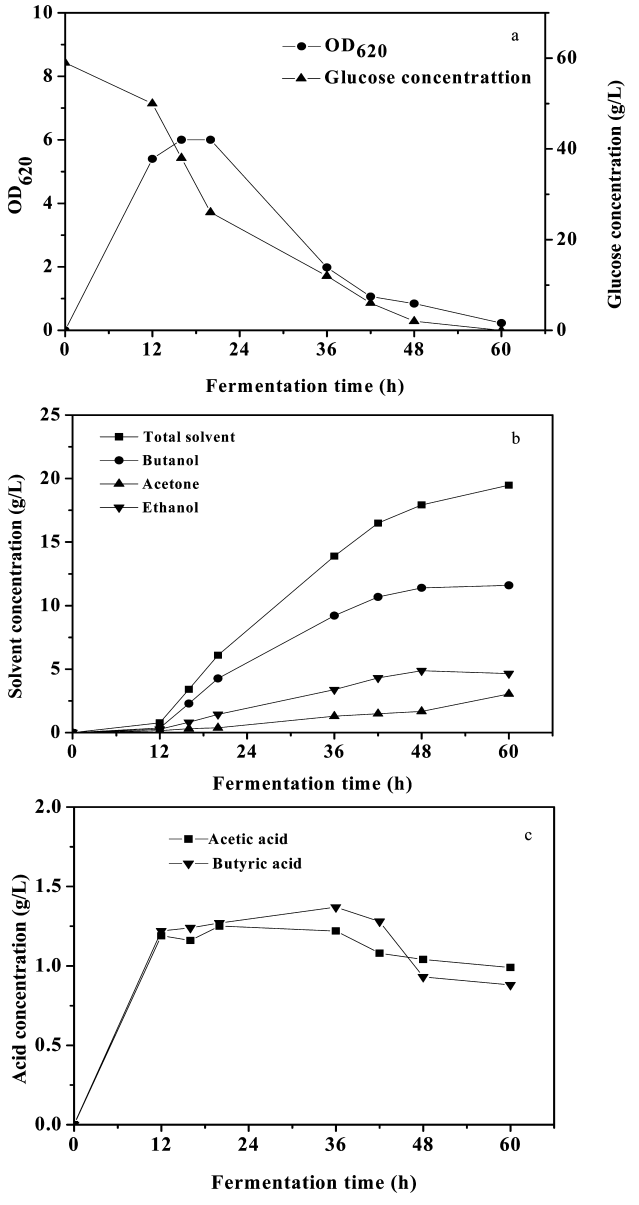

Figure 4. Production of ABE in control batch fermentation: (a) OD_{620} and glucose concentrations, (b) solvent concentrations, (c) acid concentrations.

growth of *C. acetobutylicum* DP 217 and the consumption of glucose. Maximum cell growth rate was obtained during the first 12 h, followed by a stationary phase for 4 h, then declined drastically at a fermentation time of 20 h because of the butanol inhibition on the microorganism. Simultaneously, the glucose utilization rate was high during the first 16 h, and then slowed down after 20 h of inoculum. The average volumetric glucose consumption rate was 1.00 g/Lh during the whole fermentation process. ABE and acid production profiles are shown in Figure 4b,c. The culture produced 19.49 g/L total solvent from 60 g/L glucose, with a productivity of 0.32 g/Lh and a yield of 0.32 g/g, respectively. Acid concentration increased greatly at the initial 12 h of fermentation, and maintained at a higher level of more than 1 g/L between 12 and 36 h, and then decreased slightly due to the assimilation by the organism (Figure 4c).

To evaluate the performance of simultaneous butanol fermentation and solvent recovery by PV, continuous ABE production by the fermentation−PV coupled process was carried out. Fermentation was first started with batch mode and operated at 37 °C in a 2 L fermentor with a working volume of 1 L. When the fermentation progressed to 20 h, the butanol concentration reached 4.41 g/L, and microorganism was in a physically active form and it was transformed from acidogenesis to solventogenesis, the fermentation−PV coupled process was started with a membrane having an area of 0.024 m^2. Simultaneously, the broth volume in the fermentor was maintained constant by continuously introducing fresh feed at the same flow rate of in situ removal of solvent.

Continuous ABE fermentation by the coupled process was normally performed for at least 268 h, and the data during 288 h of fermentation (20 h initial batch fermentation plus 268 h continuous fermentation) are presented in the present work. As can be seen from Figure 5a, when PV was turned on, the cell density increased continuously with the operation time. This phenomenon could be explained by the constant removal of solvent from the fermentor by the PV process, avoiding butanol accumulation in the fermentor to inhibit the growth of bacteria cells. Moreover, in a preliminary study, it was found that the severe fluctuation of glucose concentration would result in the decline of activity of the organism and then a drastic variation of solvent production. This phenomenon was also found by Tashiro et al. and Hecke et al.[18,19] Therefore, in the experiments, the precise regulation of glucose concentration at 26.56 g/L was performed when feeding concentrated fresh medium of 200 g/L glucose, which could support the rapid growth of cells. Furthermore, the cells were retained and accumulated in the fermentor due to retention of the PV membrane. Consequently, the maximum OD_{620} reached 14.3, much higher than that in control batch fermentation without PV (1.98). The effect of PV on the fermentation was also

dx.doi.org/10.1021/ef401706k | *Energy Fuels* 2014, 28, 555−562

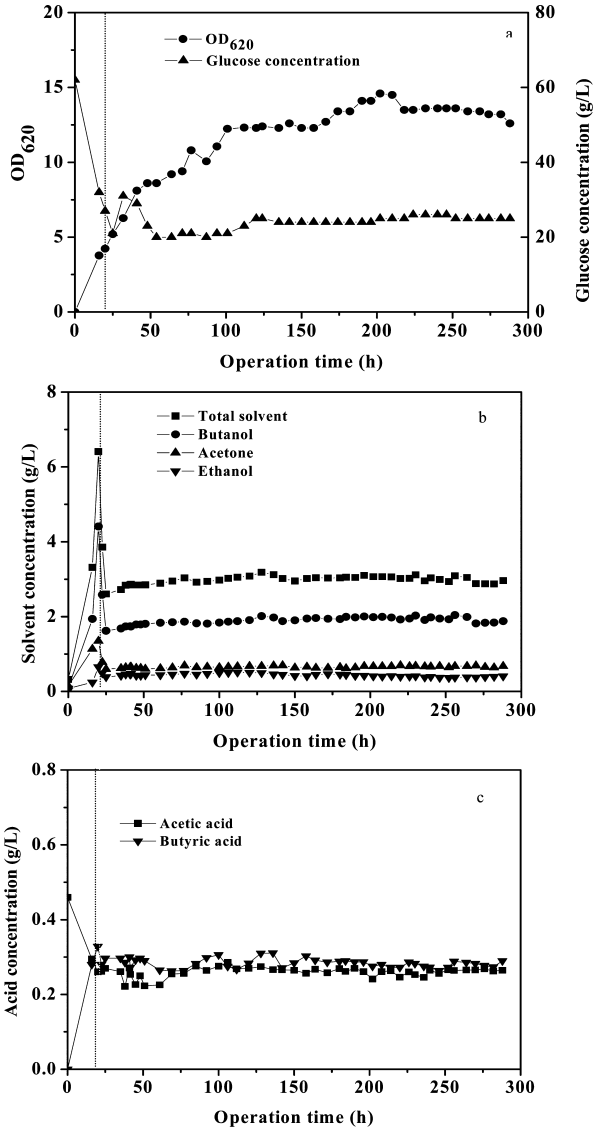

Figure 5. ABE fermentation profiles in continuous ABE fermentation–PV coupled process; D = 0.0117 h^{-1}. The vertical line at 20 h represents the start line of pervaporation. (a) OD_{620} and glucose concentrations, (b) solvent concentrations, (c) acid concentrations.

examined in terms of volumetric glucose consumption rate, where the average volumetric glucose consumption rate was 2.55 g/Lh, which was 155% higher than that in the control batch process without PV. The increased glucose utilization rate could be due to the fact that, on account of the reduction of butanol inhibition, the cell population was much higher than that in the control batch fermentation without PV; thus, a higher cell population resulted in an increased glucose consumption rate. The average sugar conversion was 96.34%.

The variation of solvent concentration observed during the long-term operation is illustrated in Figure 5b. The solvent concentration in the fermentor increased during the first 20 h, reaching 6.41 g/L, and then decreased drastically due to its removal from the fermentation broth by the pervaporation process. Finally, the solvent concentration in the fermentation broth maintained at a stable level thanks to the regulation of the PV process. As can be seen from Figure 3, the flux of the membrane was related to the butanol concentration in the feeding solution. This implies that the solvent removal rate was related to the solvent concentration in the fermentor. As the solvent concentration in the fermentor increased, the solvent removal rate would also increase, which, in turn, resulted in the reduction of the solvent concentration in the fermentor, and vice versa. During this experiment, average acetone, ethanol, butanol, and total solvent concentrations in the fermentor were 0.67, 0.43, 1.96, and 3.06 g/L, respectively, below the threshold of toxicity. This demonstrated that the thin-film silicalite-1 filled PDMS/PAN composite membrane was highly effective for removing butanol from the fermentation broth.

With regard to acid production, the average concentrations of acetic acid and butyric acid were 0.26 and 0.28 g/L, respectively, in the fermentation broth at steady state (Figure 5c). These values were lower than those in the control batch fermentation. This phenomenon could be explained by the fact that the higher butanol productivity obtained resulted in an increasing reassimilation rate of acids in the fermentor when coupled to PV. Furthermore, a small amount of acetic acid was detected in the permeate solution (0.20–0.71 g/L), indicating continuous removal of acetic acid from the fermentor through PV, which also led to a lower concentration of acids in the fermentation broth. However, there was no butyric acid detected in the permeate solution. Similarly, Querish et al.[20] reported that acids concentrations were very low, almost not detected at the end of most of the operation of fed-batch fermentation with PV. Gapes et al. also reported[21] that the butyric acid concentration remained very low after the startup of continuous online PV.

Figure 6 shows the variation of solvent concentration in the permeate solution. The solvent concentration in the permeate

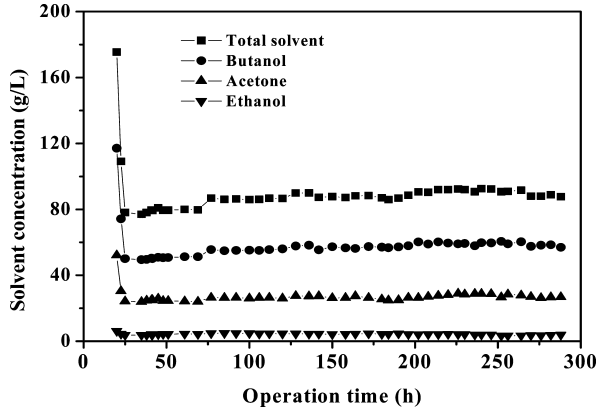

Figure 6. Permeate profiles in continuous ABE fermentation–PV coupled process; D = 0.0117 h^{-1}.

solution decreased drastically from 175 to 78 g/L within 15 h after the PV process started, and, eventually, maintained at a constant level. It was clearly observed that the change of butanol concentration in the permeate solution was closely related to its concentration in the fermentation broth. Average acetone, ethanol, butanol, and total solvent concentrations in the condensate solution (permeate solution) were 27.10, 4.24, 57.77, and 89.11 g/L, respectively. The total solvent concentration obtained in the permeate solution was much higher than the maximum solvent concentration of 19.49 g/L in the control batch fermentation.

In an attempt to increase the solvent concentration in the permeate solution, the working volume of the fermentor was increased to 1.5 L. Fresh feed with 240 g/L glucose was

dx.doi.org/10.1021/ef401706k | Energy Fuels 2014, 28, 555–562

supplied into the fermentor, and the dilution rate was decreased to 0.0081 h^{-1}. A steady state was attained after 12 h of PV startup; the average residual glucose concentration was 25.31 g/L throughout the continuous fermentation period of 268 h. The results are given in Table 2. The increasing working volume induced an increasing of total solvent amount in the fermentor; therefore, the solvent concentration in the fermentor was higher than that with the relatively higher dilution rate of 0.0117 h^{-1}. This resulted in a higher solvent concentration in the permeate solution of 106.76 g/L (73.50 g/L butanol, 28.36 g/L acetone, and 4.09 g/L ethanol, respectively). Similar results were also observed by Friedl et al.[22]

Table 2. Steady-State Solvent and Acid Concentrations in Continuous ABE Fermentation–PV Coupled Process at a Dilution Rate of 0.0081 h^{-1}

	retentate	permeate
acetone (g/L)	0.71	28.36
ethanol (g/L)	0.42	4.09
butanol (g/L)	2.46	73.50
total solvents (g/L)	3.59	106.76
acetic acid (g/L)	0.48	0.42
butyric acid (g/L)	0.52	
total acids (g/L)	1.00	0.42

Operated at 37 °C for 288 h.

To further increase the total solvent concentration in the permeate solution, the dilution rate was further decreased to 0.0038 h^{-1}. To maintain the broth volume in the fermentor constant, a membrane with a lower membrane area of 0.0072 m^2 and 1 L working volume were used. This resulted in an increase of the solvent concentration in the fermentor (see Table 3). In the coupled process, fresh medium with 280 g/L glucose was fed into the fermentor and the average residual glucose concentration was maintained at about 24.78 g/L. As expected, the acetone, butanol, ethanol, and total solvent concentrations in the permeate solution were increased to 47.25, 8.12, 104.63, and 160.00 g/L, respectively. According to the Material Safety Data Sheet (MSDS) for butanol, the solubility of butanol in water is about 7.7% at 20 °C. When the butanol concentration in the mixture solution is more than 8%, the overall butanol solution undergoes phase separation. It was indeed observed that there were two phases in the permeate solution, i.e., the organic phase and the aqueous phase. The organic phase contained a higher concentration of 533 g/L ABE with 446 g/L butanol. Such a highly concentrated butanol solution would significantly reduce the energy consumption required in final product recovery by distillation.[5,6] The aqueous phase contained 160.7 g/L ABE with 89.6 g/L butanol, which could be further concentrated by a second-stage PV system.[23]

Table 3. Steady-State Solvent and Acid Concentrations in Continuous ABE Fermentation–PV Coupled Process at a Dilution Rate of 0.0038 h^{-1}

	retentate	permeate
acetone (g/L)	1.23	47.25
ethanol (g/L)	0.93	8.12
butanol (g/L)	3.81	104.63
total solvents (g/L)	5.97	160.00
acetic acid (g/L)	0.53	0.51
butyric acid (g/L)	0.48	
total acids (g/L)	1.01	0.51

Operated at 37 °C for 288 h.

Productivity, yield, glucose utilization rates, and conversions achieved under the three dilution rates for a long period of continuous operation are presented in Figure 7. The highest productivity and glucose utilization rate obtained were 0.97 and 2.55 g/Lh, respectively, during continuous operation with the dilution rate D = 0.0117 h^{-1}, which were 203% and 155% higher than those obtained in the control experiment, respectively. Decreasing the product recovery rate and dilution rate would help to increase the solvent concentration in the permeate solution; however, productivity and glucose utilization rates decreased. When dilution rate D was decreased to 0.0038 h^{-1}, the maximum average total solvent concentration reached 160.0 g/L with productivity and glucose utilization rates of 0.57 and 1.54 g/Lh, respectively. The productivity and glucose utilization rates were also 78% and 54% higher, respectively, than those obtained in the control batch experiment without the PV process. The productivity enhancement was also found between continuous fermentation with and without the PV process by Hecke et al.[8] They found that, as compared with continuous fermentation without the PV process as control, the continuous fermentation–PV coupled process increased the productivity to 0.30 g/Lh from 0.13 g/Lh. It is interesting to note that there was little acid in the broth when the fermentation–PV coupled process was adopted. This indicates that most of the glucose and acids were converted to solvents. Therefore, a total solvent yield of 0.37 g/g was obtained in the continuous fermentation–PV coupled process, which was higher than the yield (0.32 g/g) in the control batch culture. This would improve the economic competitiveness of the process for butanol production from renewable resources. Experimental results also indicated that glucose conversions for the dilution rates of 0.0117, 0.0081, and 0.0038 h^{-1} were 96.34, 97.18, and 94.42%, respectively.

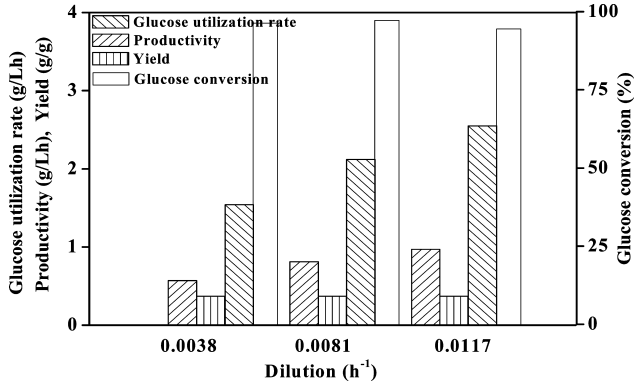

Figure 7. Comparison of solvent production in continuous ABE fermentation–PV coupled process at three dilution rates.

3.3. Membrane Performance in Continuous Fermentation–PV Coupled System. Continuous fermentation experiments at three different dilution rates were carried out at steady state. The membrane performance during the fermentation–PV coupled processes was investigated in detail. Figure 8 shows the variation of total solvent fluxes and separation factors with operation time at the dilution rate of 0.0117 h^{-1}. Under the experimental conditions examined, the

dx.doi.org/10.1021/ef401706k | Energy Fuels 2014, 28, 555–562

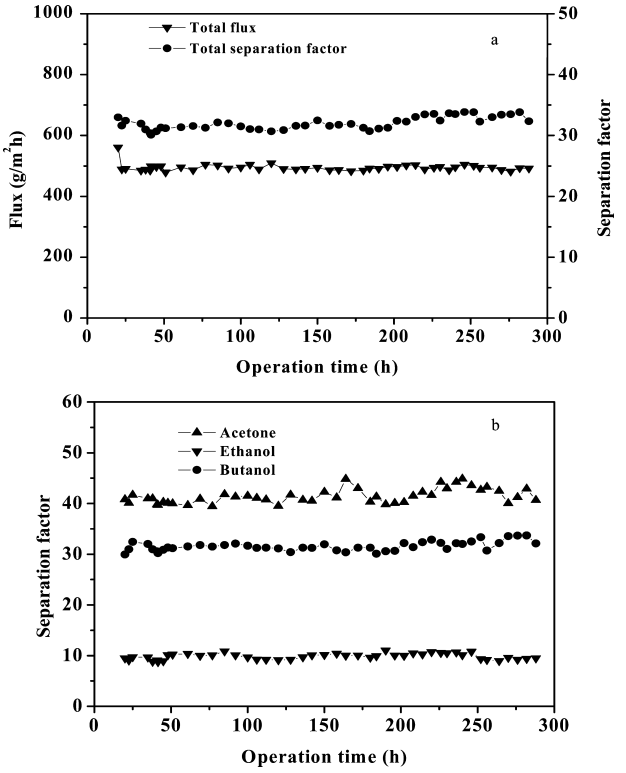

Figure 8. Pervaporation performance of the silicalite-1 filled PDMS/PAN composite membrane in continuous ABE fermentation−PV coupled process; D = 0.0117 h^{-1}.

total solvent fluxes dropped promptly from 561 to 491 g/m^{2}h within the fermentation period from 20 to 25 h. This was because the ABE concentration in the broth decreased as PV went on until a steady state was obtained (see Figure 5b), and according to the solution-diffusion model, individual solvent flux decreases with decreasing solvent concentration in the feed solution. The total flux maintained at approximately 486 g/m^{2}h and lasted for 268 h without an obvious decrease. No significant variation in separation factor was observed, and the average separation factor of ABE, acetone, butanol, and ethanol was 32.0, 41.4, 31.6, and 9.8, respectively (Figure 8b). These results indicated that the composite membrane was not fouled by the complex fermentation broth. A similar result was also obtained by Hecke et al. They reported that no fouling was observed during 475 h of continuous fermentation when a commercial PDMS membrane was coupled to ABE fermentation.[8]

For the experiments with the dilution rates of 0.0081 and 0.0038 h^{-1}, the average total fluxes at steady state were 505 and 585 g/m^{2}h, respectively. According to the solution-diffusion model, the total flux is a function of ABE concentrations. Figure 9 shows the effect of average butanol concentration in the feed on butanol, total, and water flux during continuous ABE fermentation under different dilution rates. It can be seen that the water flux maintained at around 448 g/m^{2}h, whereas the butanol flux had a linear relationship with respect to the butanol concentration in the broth. Therefore, the total solvent flux increased with butanol concentration. Using eq 3, the overall mass transfer coefficient of butanol can be calculated to be 14.71 mm/h. This is 12.65% lower than that in butanol/water solution (16.84 mm/h). As compared with water flux in butanol/water solution (about 526 g/m^{2}h), water flux in the

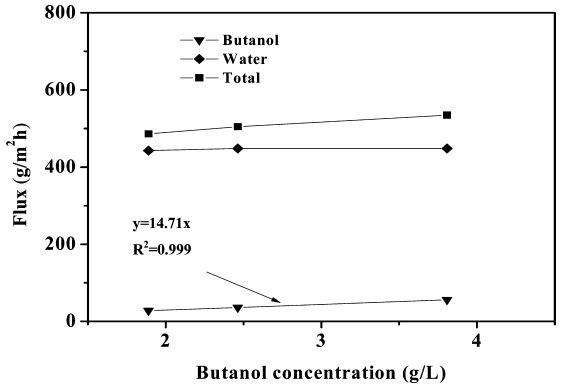

Figure 9. Fluxes of silicalite-1 filled PDMS/PAN composite membrane in continuous ABE fermentation−PV coupled process at three different dilution rates.

fermentation broth decreased by 14.83%. These results indicated that the coupling effect occurred during the fermentation−PV process. The coupling effect of other components in complex fermentation systems on the target component has become a major concern for the PV.[14] Lipnizki et al.[24] investigated the influence of impermeable components on the permeation of aqueous 1-propanol mixtures in commercial PV. They found that NaCl, $MgCl_2$, and glucose tended to increase flux of the organic compared with a binary mixture, whereas citric acid, acetic acid, glycerine, and Na_2SO_4 acted to decrease flux. Zhou et al.[11] reported that acetone and ethanol could cause a decrease of water flux in the separation of acetone and ethanol aqueous solutions using a dense silicalite-1 filled PDMS membrane. Li et al.[14] investigated the recovery of butanol from ABE model solutions and binary solutions with the same butanol concentrations using a PDMS/dual support composite membrane and observed that the butanol fluxes in the ABE model solutions were lower than that in the binary solutions. In the present work, the decrease of water flux and the overall mass transfer coefficient could be caused by other components in the ABE fermentation broth, such as acetone, ethanol, glycerine, or other metabolites. After the ABE fermentation operation with the coupled process, the thin-film silicalite-1 filled PDMS/PAN membrane was flushed with deionized water for 2 min, and then its PV performance was tested in butanol/water binary solution. The total flux and separation factor of the water-washed membrane were the same as those of the fresh membrane (Figure 10), implying that the coupling effect of the other composition on the membrane was reversible.

4. CONCLUSIONS

With the adoption of the thin-film silicalite-1 filled PDMS/PAN composite membrane, continuous ABE production without periodic membrane cleaning could be applicable using the fermentation−PV coupled process. Compared to the control experiments, the coupled process exhibited a very high glucose consumption rate, productivity, and solvent yield. Moreover, the coupled process produced a high titer of butanol, which could decrease the energy consumption required in subsequent distillation for solvent recovery.

The membrane showed an excellent stability during 268 h of operation in the coupled process; i.e., flux and separation factor of the membrane were more or less constant during continuous ABE fermentation. Analyses of the overall mass transfer

dx.doi.org/10.1021/ef401706k | Energy Fuels 2014, 28, 555−562

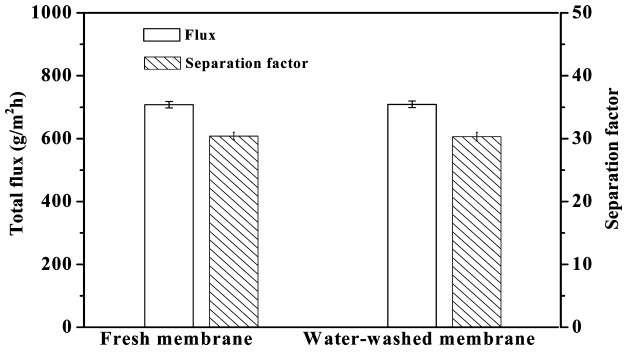

Figure 10. PV performance of the fresh and water-washed composite membranes. Feed: 10.5 g/L butanol in water.

coefficient of the composite membrane showed that there existed a negative coupling effect of other components in the ABE fermentation broth on butanol flux and water flux. After the water wash, the performance of membranes could be restored as a fresh membrane. This work demonstrated that the silicalite-1 filled PDMS/PAN composite membrane was a promising membrane for butanol production with the fermentation−PV coupled process. In situ product recovery by PV could increase the economic competitiveness of biobutanol against the petroleum-based butanol.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: 86-10-62650673. E-mail: yhwan@home.ipe.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant no. 21176239), the National High Technology Research and Development Program of China (863 Program, Grant no. 2012AA03A607), and the Visiting Scholar Foundation of the Key Laboratory of Low-grade Energy Utilization Technologies and Systems (Chongqing University), Ministry of Education of China.

■ REFERENCES

(1) Kumar, M.; Gayen, K. *Appl. Energy* **2011**, *88*, 1999−2012.
(2) Qureshi, N.; Saha, B. C.; Cotta, M. A.; Singh, V. *Energy Convers. Manage.* **2013**, *65*, 456−462.
(3) Dürre, P. *Curr. Opin. Biotechnol.* **2011**, *22*, 331−336.
(4) Liu, H.; Lee, C.-f. F.; Huo, M.; Yao, M. *Energy Fuels* **2011**, *25*, 2426−2426.
(5) Badr, H. R.; Hamdy, M. K. *Biomass Bioenergy* **1992**, *3*, 49−55.
(6) Xue, C.; Zhao, J. B.; Lu, C. C.; Yang, S. T.; Bai, F. W. *Biotechnol. Bioeng.* **2012**, *109*, 2746−2756.
(7) Leland, M. V. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 603−629.
(8) Hecke, W. V.; Vandezande, P.; Claes, S.; Vangeel, S.; Beckers, H.; Diels, L.; DeWever, H. *Bioresour. Technol.* **2012**, *111*, 368−377.
(9) Chen, C.; Xiao, Z.; Tang, X.; Cui, H.; Zhang, J.; Li, W.; Ying, C. *Bioresour. Technol.* **2013**, *128*, 246−251.
(10) Liu, G. P.; Wei, W.; Wu, H.; Dong, X. L.; Jiang, M.; Jin, W. Q. *J. Membr. Sci.* **2011**, *373*, 121−129.
(11) Zhou, H. L.; Su, Y.; Chen, X. R.; Wan, Y. H. *Sep. Purif. Technol.* **2011**, *79*, 375−384.
(12) Liu, X. L.; Li, Y. S.; Liu, Y.; Zhu, G. Q.; Liu, J.; Yang, W. S. *J. Membr. Sci.* **2011**, *369*, 228−232.
(13) Yi, S. L.; Su, Y.; Wan, Y. H. *J. Membr. Sci.* **2010**, *360*, 341−351.
(14) Li, S. Y.; Srivastava, R.; Parnas, R. S. *Biotechnol. Prog.* **2011**, *27*, 111−120.
(15) Zanati, E. E.; Hakim, E. A.; Ardi, O. E.; Fahmy, M. *J. Membr. Sci.* **2006**, *280*, 278−283.
(16) Vane, L. M. *Biofuels, Bioprod. Biorefin.* **2008**, *2*, 553−588.
(17) Li, S. Y.; Srivastava, R.; Parnas, R. S. *J. Membr. Sci.* **2010**, *363*, 287−294.
(18) Tashiro, Y.; Takeda, K.; Kobayashi, G.; Sonomoto, K.; Ishizaki, A.; Yoshino, S. *J. Biosci. Bioeng.* **2004**, *98*, 263−268.
(19) Hecke, W. V.; Tim, H.; Wever, D.; Heleen. *Bioresour. Technol.* **2013**, *129*, 421−429.
(20) Qureshi, N.; Meagher, M. M.; Huang, J. C.; Hutkins, R. W. *J. Membr. Sci.* **2001**, *187*, 93−102.
(21) Gapes, J. R.; Nimcevic, D.; Friedl, A. *Appl. Environ. Microbiol.* **1996**, *62*, 3210−3219.
(22) Friedl, A.; Qureshi, N.; Maddox, I. S. *Biotechnol. Bioeng.* **1991**, *38*, 518−527.
(23) Wan, Y. H.; Li, J.; Chen, X. R.; Su, Y.; Qi, B. K.; Shen, F., China patent CN 201210265526.3, Sep 14, 2012.
(24) Lipnizki, F.; Hausmanns, S.; Field, R. W. *J. Membr. Sci.* **2004**, *228*, 129−138.