Effects of Synthesis Conditions on the Pervaporation Properties of Poly[1-(Trimethylsilyl)-1-Propyne] Useful for Membrane Bioreactors

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ABSTRACT: An integrated fermentation and membrane-based recovery (pervaporation) process has certain economical advantages in continuous conversion of biomass into alcohols. This article presents new pervaporation data obtained for poly[1-(trimethylsilyl)-1-propyne] (PTMSP) samples synthesized in various conditions. Three different catalytic systems, $TaCl_5$/*n*-BuLi, $TaCl_5$/Al(*i*-Bu)$_3$, and $NbCl_5$ were used for synthesis of the polymers. It was found that the catalytic system has a significant influence over the properties of membranes made from PTMSP. Although a combination of a high permeation rate and a high ethanol–water separation factor (not less than 15) was provided by all PTMSP samples, the PTMSP samples synthesized with $TaCl_5$/*n*-BuLi showed significant deterioration of membrane properties when acetic acid was present in the feed. In contrast, the PTMSP samples synthesized with $TaCl_5$/Al(*i*-Bu)$_3$ or $NbCl_5$ showed stable performance in the presence of acetic acid. When using a multicomponent mixture of organics and water, the copermeation of different organic components results in lower separation factor for both ethanol and butanol. These data are consistent with nanoporous morphology of PTMSP. It was demonstrated that pervaporative removal of ethanol improved the overall performance of the fermentation process. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2271–2277, 2004

Key words: poly[1-(trimethylsilyl)-1-propyne] (PTMSP); membranes; biological applications of polymers; structure–property relations; membrane bioreactor

INTRODUCTION

The production of fuel-grade ethanol from renewable lignocellulosic feedstocks by using microorganisms has a potential to reduce burgeoning world dependence on petroleum, while decreasing the net emission of carbon dioxide, the principal greenhouse gas. However, alcohol-producing microorganisms usually exhibit strong product inhibition. The continuous removal of alcohols from the fermentor is desired for increased fermentor productivity, complete substrate utilization, and high-process yield.

One of the approaches for overcoming product inhibition is to continuously remove the fermentation product from the fermentor effluent and recycle the retentate stream back to the fermentor, allowing residual sugar to be converted to product. In pervaporation membrane systems, a liquid feed mixture is contacted with a membrane and a permeate is removed as a vapor. A pervaporation unit coupled with a fermentor can recover ethanol[1] and enhance the fermentation process by keeping the ethanol concentration in the fermentor below concentrations that are inhibitory for microorganisms, thus reducing the cost of bioethanol.[2,3]

For this purpose, the membranes with organophilic properties (organic component of water/organic mixtures permeates preferentially through such a membrane) should be used. Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) is an organophilic material that has one of the highest gas-permeability coefficients reported for polymers and has been intensively studied for membrane gas separation and pervaporation.[4–12] Despite many unique and outstanding properties, PTMSP has not found commercial application as a membrane material. This is due in large part to its tendency toward physical and/or chemical aging.[13–15] This aging results in significant decline of flux and separation factor over time.[8,9]

Several studies have evaluated the specific relationships between membrane properties and PTMSP preparation conditions.[4,15–17] However, there is limited information on the effects of different PTMSP catalysts on pervaporation and many issues remain

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TABLE I
The Synthesis Conditions for PTMSP Samples[a]

Sample	Catalyst	C_{mon}/C_{cat} (mol/mol)	$C_{cat}/C_{co\text{-}cat}$	T (°C)	Polymer yield (% mass)	$[\eta]$ (dl/g) in toluene 25°C
PTMSP-1	$TaCl_5$/n-BuLi	100	1	25	95	16.0
PTMSP-2	$TaCl_5$/n-BuLi	50	1	40	90	9.6
PTMSP-3	$TaCl_5$/n-BuLi	50	1	25	88	10.3
PTMSP-4	$TaCl_5$/Al(i-Bu)$_3$	50	3	40	98	5.2
PTMSP-5	$TaCl_5$/Al(i-Bu)$_3$	50	3	25	98	5.4
PTMSP-6	$TaCl_5$/Al (i-Bu)$_3$	200	2	25	66	8.0
PTMSP-7	$NbCl_5$	50	—	25	98	0.6
PTMSP-8	$NbCl_5$	150	—	25	96	1.3

[a] The molecular masses were determined for samples: PTMSP-2: M_w = 1,651,300, M_w/M_n = 1.63; PTMSP-4: M_w = 1,270,000, M_w/M_n = 1.88; PTMSP-5: M_w = 925,300, M_w/M_n = 1.19; PTMSP-8: M_w = 383,700, M_w/M_n = 1.20. The determinations were performed by GPC (Waters, detector R-401, toluene, 50°C).

unresolved.[18] We have found that the ethanol sorption characteristics of PTMSP differ markedly[17] for different catalysts and are interested in the pervaporation properties of membranes made from different PTMSP samples.

This article presents performance data obtained for pervaporation membranes prepared from PTMSP samples synthesized under different conditions. The following three catalytic systems were investigated: $TaCl_5$/*n*-BuLi, $TaCl_5$/Al(*i*-Bu)$_3$, and $NbCl_5$.

EXPERIMENTAL

PTMSP synthesis

Polymerization was carried out in glass reactors under argon or in vessels sealed after removal of air. Trimethylsilylpropyne (TMSP; 99.5% purity) was redistilled under argon over calcium hydride prior to polymerization. Toluene was redistilled, dried for 24 h by boiling over sodium, and then redistilled over CaH_2 in a flow of an inert gas directly before polymerization. A solution of triisobutylaluminum (TIBA) in toluene (40 wt %) was used as a cocatalyst. *N*-butyllithium (*n*-BuLi) was synthesized in the lab. The $NbCl_5$, $TaCl_5$, and *n*-BuLi catalysts of known concentration were dosed into the polymerization system from the sealed, calibrated ampoules with a thin glass seal that could be broken to initiate the polymerization reaction. TIBA was added from the Schlenk-type vessels.

After a desired time (24 h, 25°C and 1 h, 40°C), the polymerization reaction was quenched with 20/80 (w/w) methanol/toluene solution to deactivate the catalyst. The precipitated polymer was dissolved in toluene and reprecipitated into methanol. The polymer was dried at ambient conditions and then under vacuum. The TMSP polymerization, yields, intrinsic viscosities, and molecular masses of the polymers are summarized in Table I.

Membrane preparation

PTMSP solution in toluene (0.5 wt %) was cast onto cellophane surface and the solvent was evaporated for 100–200 h at ambient conditions. The dense membranes (14–43 μm thick) were removed from the cellophane and dried under vacuum to constant weight. As recommended by Ulutan and Nakagawa,[19] to prevent aging, the membranes were stored in ethanol until they were used.

Pervaporation

Pervaporative performance of PTMSP samples was investigated by using 6 wt % solution of ethanol in water, multicomponent mixture, and fermentation broth. The multicomponent mixture contained ethanol (6 wt %), acetic acid (1 wt %), methyl acetate (0.5 wt %), *n*-butanol (0.2 wt %), acetone (0.2 wt %), and water (92.1 wt %).

Pervaporation of the ethanol/water mixture and the multicomponent mixture was carried out by conventional methods by using the apparatus shown schematically in Figure 1. The effective membrane area in the stainless steel cell was 31.2 cm^2. The feed solution was circulated through the membrane cell at 30°C, and the permeate pressure was maintained at 2 mm Hg. The membrane flux was determined gravimetrically. A 1-L feed reservoir was used to minimize the change in the feed concentration during the experiment (typically 1 day).

A Minitan-S unit (Millipore) with an effective membrane area of 60 cm^2 was used in pervaporation of fermentation broth. The experimental setup is described elsewhere.[10]

The feed and permeate concentrations were determined by a refractometer or gas chromatography (GC). The separation factor, α, and enrichment factor, β, were determined according to the following equations:

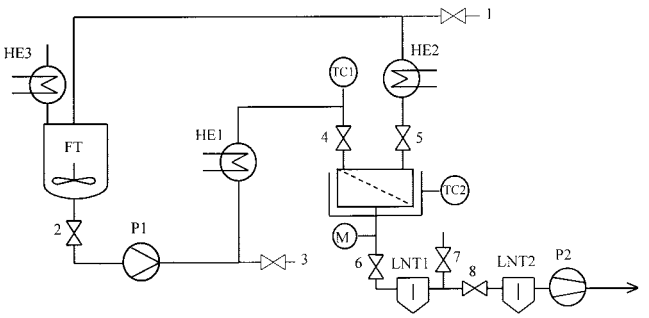

Figure 1 Schematic representation of apparatus for pervaporation of ethanol/water and synthetic mixtures: LNT1 and LNT2, permeate condensers; FT, feed tank; P1, feed pump; P2, vacuum pump; HE1, HE2, and HE3, heat exchangers; 1–8, valves; M, pressure manometer; TC1 and TC2, thermocouples.

$$a = \frac{y_o/y_w}{x_o/x_w} \quad (1)$$

$$\beta = y_o/x_o \quad (2)$$

where x_i and y_i are the weight fractions in the feed and permeate, respectively. The subscripts o and w stand for organic component and water.

Fermentation

Saccharomyces cerevisiae D5A was used in the yeast fermentations. The inoculum was grown for 15 h at 30°C, 150 rpm, in a baffled shake flask with Morton closure by using 2% w/v yeast extract, 1% w/v bacto peptone, and 15% w/v glucose. It was then used 5–10% v/v to inoculate a baffled shake flask containing yeast extract, peptone, and glucose of the same concentration. The broth was harvested after 24–48 h.

Membrane bioreactor

The effect of pervaporative removal of ethanol on the performance of the continuous fermentation was studied by using a BioFlo III bioreactor coupled with a Minitan-S unit. The medium composition and inoculum preparation procedure were similar to those described in the Fermentation section. The fermentation was run in a batch mode at 39°C for 50 h to achieve reasonable cell mass and then it was switched into continuous mode with a dilution rate of 0.01 h^{-1}. The fermentor temperature was lowered to the optimal value of 37°C. Within the next 75 h, fermentation reached a steady state and the pervaporation unit was turned on. The ethanol concentration was measured with high-performance liquid chromatography (HPLC); glucose concentrations were measured with a YSI 2300 STAT Plus Glucose and Lactate Analyzer, while dry cell mass was estimated from turbidity measurements by using a preestablished calibration.

RESULTS AND DISCUSSION

Pervaporation of ethanol/water mixture

The ethanol concentration dependencies of the permeation rate and separation factor for a membrane prepared from PTMSP-2 are shown in Figure 2. The range of ethanol feed concentrations (3–10 wt % of ethanol) were selected to bracket the range of ethanol concentrations that might be found in real fermentation broths. The permeation rate increased from 5 to 8 [mg m/m^2 h], whereas the separation factor remained constant at value 18, as the ethanol concentration in the feed increased from 3 to 10 wt %. To our knowledge, there is no systematic data on concentration dependences of flux and separation factor for PTMSP membranes for feed solutions with less than 10 wt % ethanol. The effect of feed composition on the ethanol–water pervaporation through PTMSP was studied for the feed mixtures containing 10–100 wt % ethanol.[19,20] It was shown that the separation factor sharply increased with decreasing ethanol content in the feed to give $\alpha = 13$[19] or $\alpha = 17$[20] at 10 wt % ethanol. As seen in Figure 2, decreasing the ethanol concentration in the feed below 10 wt % does not influence the separation factor. These results are in good agreement with our findings on PTMSP swelling (sample elongation) behavior in ethanol aqueous solutions.[21] In the region 0–10 wt % ethanol, the ethanol concentration has no effect on elongation (no elongation at all). Above 10 wt % ethanol, there is a linear increase in elongation up to a maximum elongation of 9.5% at a 100 wt % ethanol concentration. The high and stable separation factor values at low ethanol contents show that PTMSP membrane is suitable for concentrating ethanol from dilute aqueous solutions. This might be especially useful in membrane bioreactor applications where the

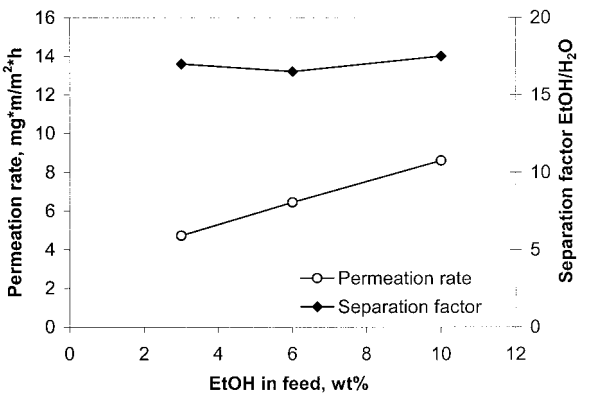

Figure 2 Concentration dependence of permeation rate and separation factor for pervaporation of ethanol–water mixtures through PTMSP-2.

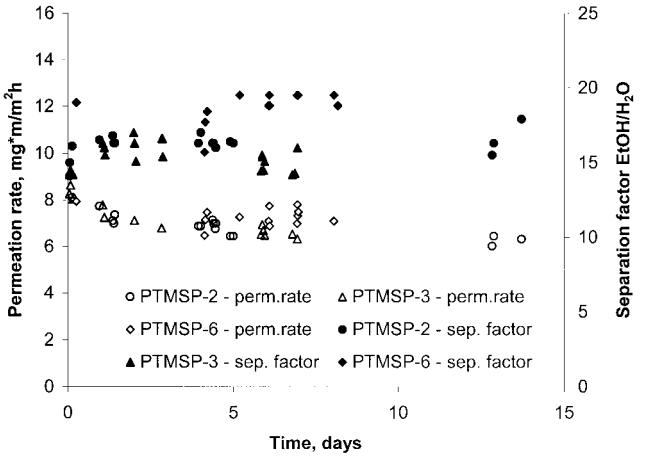

Figure 3 Permeation rate and separation factor versus operating time for PTMSP-6, PTMSP-2, and PTMSP-3. Feed is 6 wt % ethanol.

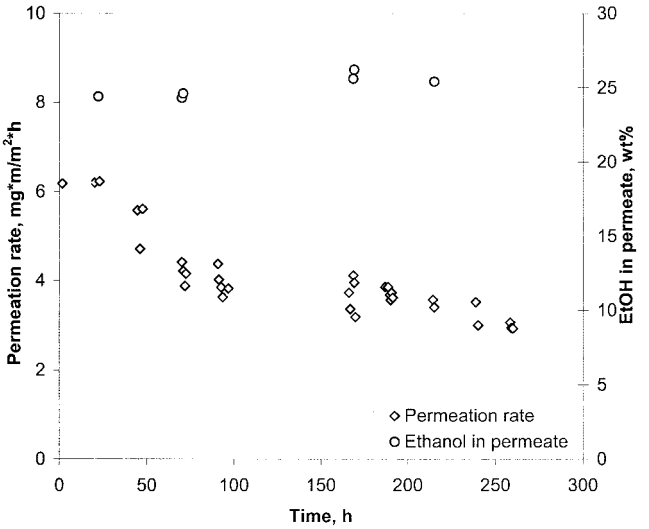

Figure 4 Permeation rate and ethanol content in the permeate versus operating time for PTMSP-3. Feed is water (92.1 wt %), ethanol (6 wt %), acetic acid (1 wt %), methyl acetate (0.5 wt %), *n*-butanol (0.2 wt %), and acetone (0.2 wt %).

ethanol concentration is low but changes during the fermentation process.

The start-up transient permeation behavior was investigated by using fresh membranes. For all the samples studied, the flux and separation factor approached a steady state within several hours and reached steady state after 5 days (Fig. 3). The pervaporation data corresponding to the steady state are shown in Table II. All of the membranes studied here exhibited a combination of high-permeation rate and good separation factor (not less than 15).

Based on the polymer yield, viscosity, and data on ethanol/water separation, the samples PTMSP-2, PTMSP-3, PTMSP-4, PTMSP-5, and PTMSP-8 are most promising for preparing membranes with commercially attractive properties. Low-yield polymerization results in higher cost polymers and high molecular weight polymers are difficult to form into solutions with the proper viscosity/concentration properties for membrane formation.

Pervaporation of synthetic mixture

Mori and Inaba[9] reported that PTMSP membrane ($TaCl_5$ as a catalyst) showed significant selectivity deterioration when fermentation broth was used as a feed. These changes were attributed to the presence of lactate and acetate in the fermentation broth.

The present study examined the stability of PTMSP pervaporation membranes in the presence of acidic byproducts, as well as other organic compounds commonly found in fermentation broths. A multicomponent organic mixture containing the major components present in yeast fermentation broth was used for this portion of the work: ethanol (6 wt %), acetic acid (1 wt %), methyl acetate (0.5 wt %), *n*-butanol (0.2 wt %), and acetone (0.2 wt %).

The multicomponent mixture caused deterioration of the membrane properties of the PTMSP-3 (catalytic system $TaCl_5$/*n*-BuLi) sample (Fig. 4). The permeation rate declined over time and did not reach steady state even after 250 h. The ethanol content in the permeate was 25 wt %, which is one-half the value observed for pervaporation of a pure ethanol–water mixture (Table II). The poor stability of the catalytic system $TaCl_5$/*n*-

TABLE II
Pervaporation Data for PTMSP Samples Synthesized under Different Conditions (Feed: 6 wt % of EtOH in Water)

Sample	Thickness (μm)	Flux (kg/m²h)	Permeation rate (mg*m/m²h)	Separation factor EtOH/H_2O	EtOH in permeate (wt %)
PTMSP-1	20	0.42	8.4	15.5	49.8
PTMSP-2	14	0.50	7.0	16.5	51.3
PTMSP-3	15	0.42	6.5	16.0	50.5
PTMSP-4	25	0.34	8.4	19.9	56.0
PTMSP-5	15	0.44	6.6	15.1	49.0
PTMSP-6	19	0.35	6.7	19.3	55.5
PTMSP-7	18	0.42	7.6	15.7	50.0
PTMSP-8	20	0.30	6.0	18.5	53.5

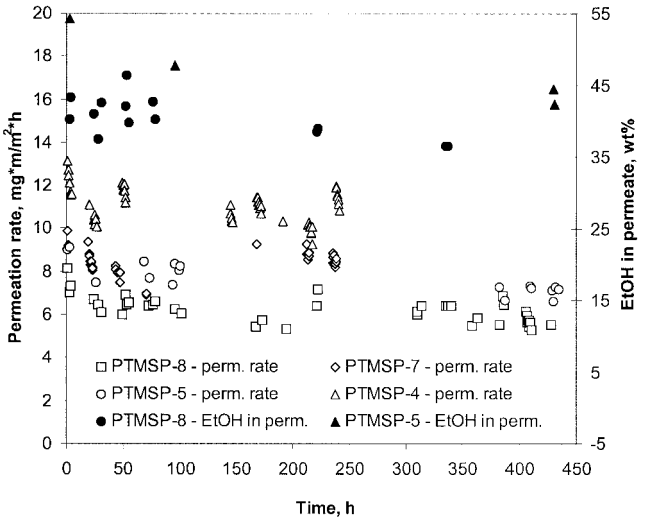

Figure 5 Permeation rate and ethanol content in permeate versus operating time for PTMSP-5, PTMSP-6, PTMSP-8, and PTMSP-4. Feed is water (92.1 wt %), ethanol (6 wt %), acetic acid (1 wt %), methyl acetate (0.5 wt %), *n*-butanol (0.2 wt %), and acetone (0.2 wt %).

BuLi PTMSP membranes is most likely related to the fact that $TaCl_5$/*n*-BuLi appears to cause metallation of the PTMSP.[22,23] Metallation of the PTMSP leads to the formation of repeat units with a double bond in the β-position to the silicon atom. It has been shown that Si—C bonds tend to break down in acidic environment.[22,23] Exposure of this PTMSP to acidic environment could lead to polymer degradation and a resulting deterioration of its membrane properties.

On the other hand, the PTMSP samples synthesized with $TaCl_5$/Al(*i*-Bu)$_3$ and $NbCl_5$ (PTMSP-5, PTMSP-6, and PTMSP-8) demonstrated stable performance during pervaporation of the multicomponent mixture (Fig. 5). The permeate compositions are shown in Table III. PTMSP-5 and PTMSP-8 provided high-ethanol concentration in permeate (42 and 40 wt %, respectively) along with permeation rates comparable to those observed for pure ethanol/water (6/94) mixtures (Table II). With the exception of acetic acid, all of the organic components are concentrated in the permeate. The concentration of acetic acid is lower in the permeate than in the feed. Thus, acetic acid should be regarded as the least-permeable component of the multicomponent mixture. These data indicate that the $TaCl_5$/*n*-BuLi catalyst produces polymers with significantly lower pervaporation stability than do $TaCl_5$/Al(*i*-Bu)$_3$ and $NbCl_5$ catalysts. The improved stability of PTMSP synthesized by using $NbCl_5$ as a catalyst was also observed in gas-separation membranes.[14,15]

TABLE IV
Influence of Feed Mixture Composition on Enrichment Factor for PTMSP-5 with Respect to Different Target Components

Target component	Feed	Enrichment factor, β
EtOH	6% EtOH in water	8.2
	6% EtOH in multicomponent mixture	7.0
BuOH	0.2% BuOH in water	40.0[a]
	0.2% BuOH in multicomponent mixture	26.0

[a] Published data[12].

It is interesting to compare the influence of the feed mixture composition on the enrichment factor for the same membrane (PTMSP-5) and different target components (ethanol and butanol) (Table IV). The ethanol enrichment factor, β, for binary and multicomponent mixtures of ethanol is 8.2 and 7.0, respectively. The same tendency of a lower enrichment factor for the multicomponent mixture is also observed for butanol where the enrichment factors for binary and multicomponent mixtures are 40 and 26, respectively. Thus, permeation rates are influenced by copermeation of additional organic species in multicomponent mixtures, consistent with the nanoporous morphology of PTMSP.

It is generally agreed that PTMSP acts more like a fine nanoporous material (e.g., nanoporous carbon) rather than a conventional glassy polymer.[5,24–28] The polymer has a very high fraction of nonequilibrium (unrelaxed) free volume, 20–26%.[5,24] This free volume forms a network of interconnecting nanopores in the polymer matrix with the narrowest pore diameter of 3–5 Å.[5,12,24] This morphology also explains why the permeability of light gases such as helium or nitrogen are drastically reduced by the copermeation of a more strongly sorbing species such as SF_6[25] (so-called pore-blocking effect). This pore-blocking effect has also been observed for *n*-butane–methane[25] and *n*-butane–hydrogen[29] mixtures in gas separation and *n*-butanol–water mixture in pervaporation.[12]

TABLE III
Pervaporation Characteristics of PTMSP Samples with Regard to Multicomponent Mixture (Ethanol, 6 wt %; Acetic Acid, 1 wt %; Methyl Acetate, 0.5 wt %; *n*-Butanol, 0.2 wt %; Acetone, 0.2 wt %; Water, 92.1 wt %)

	Content in permeate (wt %)				
Sample	Ethanol	Butanol	Acetone	Methyl acetate	Acetic acid
PTMSP-5	42.1	5.2	6.4	19.8	0.6
PTMSP-8	40.4	5.7	6.1	20.9	0.4

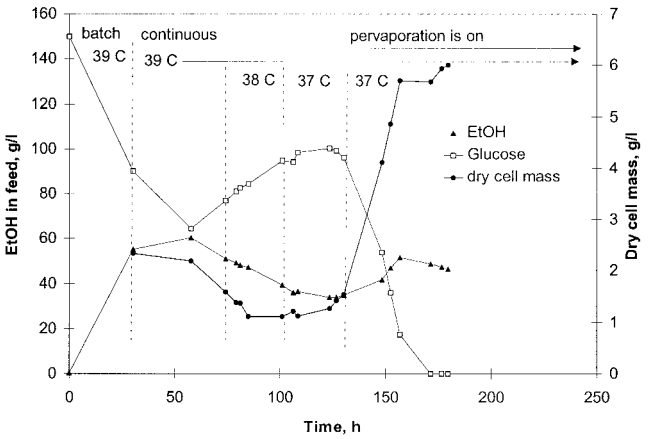

Figure 6 Change in the composition of fermentation broth when inhibitory ethanol is continuously removed by pervaporation through PTMSP-4 membrane.

The data presented here confirm this phenomenon for pervaporation of multicomponent mixtures through PTMSP, when the copermeating species have to share the same permeation pathways in PTMSP. Consistent with Mori and Inaba[9] this work shows that methyl acetate behaves as a strongly sorbing species, showing the highest enrichment factor among the compounds tested ($\beta = 40$, Table III).

Membrane bioreactor test

The effect of pervaporative ethanol removal on the performance of the continuous fermentation was investigated by using PTMSP-4. Pervaporative removal of the inhibitory product promoted growth of cell mass, which increased from under 2 to almost 6 g/L, and improved fermentation productivity as reflected by the decrease in residual glucose concentration (Fig. 6). These results demonstrate that significant performance improvement in a fermentor can be achieved by coupling the fermentor to a pervaporation unit. It should be noted, however, that at this dilution rate the pervaporation cell reduced the direct fermentor overflow, which also leads to an increase in cell mass retention.

The long-term stability of PTMSP-5 and PTMSP-8 by using yeast fermentation broth has been reported.[30] Both membranes showed very similar performance. Although fermentation broth caused a decline in both flux and separation factor, a steady state was reached in 200 h. It was concluded that the internal fouling of the membrane plays a major role in the deterioration of PTMSP membrane properties over time. Specifically, it was found that the free volume of the fouled PTMSP membrane was occupied with the low volatile byproducts of the fermentation broth, the most likely compounds being diols. It was also found that soaking PTMSP membrane in ethanol restores the membrane properties to some extent.[30] These findings highlight the potential for developing a continuous membrane regeneration process by using a portion of the organic rich permeate, which is under investigation.

CONCLUSION

It was shown that the type of catalytic system used to synthesize PTMSP polymer has a significant impact on the pervaporation properties of membranes made from PTSMP. In the case of binary ethanol–water mixtures, a combination of high-permeation and high-separation factors (not less than 15) are seen for all PTMSP samples. The PTMSP samples synthesized with $TaCl_5$/*n*-BuLi showed significant selectivity and flux deterioration when either a synthetic mixture containing acetic acid or actual fermentation broths were used as the feed. In contrast, PTMSP samples synthesized by using $TaCl_5/Al(i\text{-}Bu)_3$ or $NbCl_5$ catalysts showed a stable membrane performance during pervaporation of a multicomponent mixture. Continuous ethanol removal by pervaporation improved overall fermentor performance.

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