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Pervaporation-assisted catalytic conversion of xylose to furfural†

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Furfural produced from the biomass-derived xylose may serve as a platform molecule for sustainable fuel production. The Brønsted acid-catalyzed dehydration of xylose to furfural is plagued by side reactions that form a set of soluble and insoluble degradation products, collectively known as humins, which reduce the yield of furfural. The formation of humins can be minimized by removal of furfural, either by steam stripping or by liquid–liquid extraction (LLE). However, both these techniques are very costly. The goal of this study was to demonstrate the feasibility of using pervaporation, a membrane process, to remove furfural as it is produced. A laboratory-scale reactor/membrane system was designed, built, and tested for this purpose and its performance for furfural production was compared with that achieved by carrying out the reaction with and without furfural extraction by LLE. Furfural production assisted by pervaporation (with a commercially available membrane or a triblock copolymer membrane) or LLE produced comparable amounts of furfural, and more than could be achieved by reaction without extraction. A model of the reaction kinetics and the rate of furfural extraction was fit to the pervaporation- and LLE-assisted furfural production data and was used to predict the performances of these processes at near-complete xylose conversion. Pervaporation is shown to have two advantages over LLE: pervaporation extracts a greater fraction of the furfural produced and the furfural concentration in the permeate phase is significantly higher than that present in the extractant phase obtained by LLE. It is noted that further improvement in the separation of furfural from the aqueous phase where it is produced can be achieved by using a more-permeable, thinner pervaporation membrane of larger area, and by operating the membrane at the reaction temperature.

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Introduction

A significant component of lignocellulosic biomass is hemicellulose (20–40% by weight), a polysaccharide consisting primarily of xylose units.^{1–3} Upon physical or chemical pretreatment, most notably with dilute sulfuric acid, hemicellulose depolymerizes to produce xylose.^{3,4} Further treatment with dilute Brønsted acid results in the dehydration of xylose to furfural, a platform molecule for the production of gasoline, diesel, and jet fuel.^{2,5–10}

The dehydration of xylose, most often in water, proceeds as shown in Scheme 1.^{4,10,11} During this process, side reactions that consume xylose and furfural detract significantly from the furfural yield. These side reactions produce soluble and in-

soluble humic substances, or humins.^{4,11–13} Industrial manufacturers of furfural have improved furfural yields and minimized humins production through furfural extraction by continuous steam stripping.^{1,11,12} More recently, higher furfural yields have been achieved by liquid–liquid extraction (LLE) with an organic phase, such as toluene,^{14–16} methyl isobutyl ketone,^{17–19} various alcohols,^{18,19} dichloromethane,¹⁸ tetrahydrofurans,^{19–21} or cyclopentyl methyl ether.^{22,23} Both forms of furfural extraction (*i.e.*, steam stripping and LLE) improve the yield of furfural, but introduce significant processing costs. Steam stripping requires approximately 30 tons of steam per ton of furfural produced^{10,12} while LLE utilizes large volumes of organic solvents, with organic:aqueous volume ratios reaching as high as 3.7.¹⁸ Moreover, both processes significantly dilute the furfural, necessitating downstream furfural purification. These costly furfural separation processes limit its potential as a cost-competitive fuel precursor,^{10,12} indicating that cheaper and more energy efficient production processes must be developed. An attractive option for meeting this challenge is pervaporation.

Pervaporation is a membrane-based process in which a liquid mixture contacts the feed side of a membrane while a

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Scheme 1 Reaction network for furfural production from xylose.

vacuum is maintained on the permeate side. The vacuum reduces the chemical potential of the permeating components below their respective chemical potentials in the feed liquid, thus providing the driving force for mass transfer. Pervaporation has been used to separate organic compounds from water,^{24–28} and is currently used commercially to remove water from concentrated ethanol solutions.²⁹ Membranes suitable for the selective pervaporation of furfural have also been reported.^{30–36} Furfural separation by pervaporation has a noteworthy advantage over steam stripping and LLE: both of the latter two processes significantly dilute furfural in the product stream, whereas pervaporation concentrates furfural in the permeate, provided a furfural-selective membrane is used. This eases the downstream purification of furfural, and is expected to reduce overall production costs. In the present study, we demonstrate that pervaporation is a promising extraction process for the production of furfural and offers advantages over LLE.

Experimental methods

Materials

D-(+)-Xylose ($\geq 99\%$), furfural (99%), toluene ($\geq 99.5\%$), dodecane (99%), and cyclohexane ($\geq 99\%$) were purchased from Sigma-Aldrich and used as received. Amberlyst 70, an ion-exchange resin donated by Dow Chemical Co., was washed with nanopure water until the pH of the supernatant was >5.5 , then dried overnight at $80\text{ }^{\circ}\text{C}$ in a vacuum oven. The concentration of acid sites on Amberlyst 70 was confirmed to be equal to the manufacturer's reported value of 2.55 eq. H^+ per kg by H^+/Na^+ exchange with NaCl solution, then titration of the resulting acidic supernatant with NaOH solution using phenolphthalein as the indicator. Cross-linked polydimethylsiloxane (PDMS) thin-film composite membranes were purchased from Pervatech and had a $130\text{ }\mu\text{m}$ -thick polyethylene terephthalate support layer, a $100\text{ }\mu\text{m}$ -thick polyisoprene intermediate ultrafiltration membrane layer, and a $3\text{--}5\text{ }\mu\text{m}$ -thick pervaporation PDMS layer ($4\text{ }\mu\text{m}$ was used in all calculations requiring membrane thickness). These membranes were received as sheets and were cut

to fit the membrane cell. The block copolymer polystyrene-*block*-polydimethylsiloxane-*block*-polystyrene (SDS), which was previously shown to be permeable to furfural,^{34,36} was purchased from Polymer Source and was used as received. The number-averaged molecular weight of the polydimethylsiloxane block is 104 kg mol^{-1} , and that of the polystyrene blocks is 22 kg mol^{-1} . The dispersity of the polymer sample is 1.3, and 86 wt% of the sample is the triblock copolymer with the balance being mostly diblock copolymer.

SDS membrane preparation

A solution consisting of 1 g of SDS dissolved in 20 mL of cyclohexane was used to prepare each solvent-cast SDS membrane. The solution was poured onto a 100 mm polytetrafluoroethylene (PTFE) evaporation dish (Fisher, 02-617-148), which was covered and allowed to dry in a fume hood for three days. The resulting membrane was then peeled off the dish, sandwiched between two filter papers, and cut to fit the pervaporation cell. The thickness of each solvent cast membrane was measured at 15 points by a micrometer and the mean thickness was found to be $120\text{ }\mu\text{m}$.

A solution consisting of 0.8 g of SDS dissolved in 8 mL of cyclohexane was used to prepare each spin-coated SDS membrane. The solution was deposited onto a $10\text{ cm} \times 10\text{ cm}$ square of Biomax 50 PBQK polyethersulfone nanofiltration support membrane taped to a 3 in diameter silicon wafer and then spun at 300 rpm for one minute. The membrane was then covered, allowed to dry in a fume hood for one day, then cut to fit the membrane cell. The thicknesses of the SDS layers of the spin-coated membranes were determined by pervaporation of DI water at $75\text{ }^{\circ}\text{C}$. The thickness of these membranes was determined by equating the products of membrane thickness times DI water flux for the spin-cast membranes of unknown thickness to that of a $120\text{ }\mu\text{m}$ -thick solvent-cast membrane. By this means the average thickness of the spin-cast membranes was found to be $4.8\text{ }\mu\text{m}$.

Xylose dehydration

Batch reactions without simultaneous product separation by pervaporation were carried out in 10 mL thick-walled glass

vials (Sigma-Aldrich, 27198) sealed with PTFE/silicone crimp top septa (Agilent, 8010-0420) and immersed in a silicone oil bath. Separate reactors were used for each reaction time. The temperature of the oil bath was maintained with a magnetic-stirring hotplate (Sigma-Aldrich, Z645060). Reactor contents were stirred using PTFE-coated stir bars rotating at a rate of 600 rpm. When LLE was not conducted, each reactor received 4 mL of the reactant solution comprising $375 \mu\text{mol mL}^{-1}$ xylose in water and 52.3 mg mL^{-1} Amberlyst 70 (equivalent to 133 mM H^+ based on the liquid volume). When *in situ* LLE was conducted, each reactor received 2 mL of the reactant solution and 4 mL of toluene. Upon completion of the reaction, the reactors were removed from the oil bath and quenched in an ice bath. An aliquot of each phase (water and toluene, if applicable) was removed from the reactor for analysis by high-performance liquid chromatography (HPLC) or gas chromatography-mass spectroscopy (GC-MS). An internal standard (5 mg per mL dodecane in toluene) was added to toluene-phase samples prior to analysis by GC-MS.

Reactions with simultaneous product separation by pervaporation were carried out in a custom-built apparatus, shown schematically in Fig. 1. This reactor was a stirred stainless steel autoclave equipped with $40 \mu\text{m}$ -fritted dip tubes (Parr, 4564). The reactor was heated with a heating mantle controlled by a temperature controller (Parr, 4848). To carry out product pervaporation, the contents of the reactor were withdrawn through an inline filter with $2 \mu\text{m}$ pores and a shell-and-tube heat exchanger cooled with circulating water (Cole-Parmer, EW-12122-02) using a gear pump (Cole-Parmer, EW-74013-70) and passed through a custom-built membrane pervaporation cell, after which the retentate flowed past a sampling port, and was then directed back to the reactor. A thermocouple (Omega,

TC-K-NPT-U-72) and temperature sensor (Omega, DP7002) were used to measure the temperature of the membrane. All components of the membrane reactor were connected by 1/4-in stainless steel tubing and fittings to give a total available volume of 210 mL (150 mL in the autoclave and 60 mL in the rest of the unit). The tubing between the heat exchanger and the membrane thermocouple was wrapped in silicone heating tape (BriskHeat, HSTAT101010), which was not turned on. With the exception of the autoclave, the circulation pump, and the membrane cell, all components were wrapped in thermally insulating silicone tape (Sigma Aldrich, Z175633). Unless otherwise stated, all components of the membrane reactor were purchased from Swagelok. The interstage cooling provided by the shell-and-tube heat exchanger was used to keep the membrane at temperatures below the glass transition temperature ($\sim 100^\circ\text{C}$) of the structural units of SDS (polystyrene), so as to maintain the mechanical stability of the membrane. The membrane module was a flat, circular cell made of polyether ether ketone (PEEK) in which the membrane was supported by a porous stainless steel frit and was restrained by an o-ring to obtain a permeation area of 37 cm^2 . The feed entered the cell normal to the membrane at the center of the circular housing while the retentate exited the cell at a point on the circumference. The feed-side fluid within the cell was mixed by a custom-built PTFE-coated magnetic stirring bar suspended above the membrane surface. A vacuum of $\leq 3 \text{ mbar}$ was maintained on the permeate side of the membrane using a vacuum pump (Welch, 2014). The permeate vapor was condensed in a cold trap (ChemGlass, CG-4516-02) cooled with liquid nitrogen.

At the start of each experiment, the membrane module was loaded with a new membrane (either PDMS or $4.8 \mu\text{m}$ -thick

Fig. 1 Pervaporation-assisted dehydration reactor featuring (a) a heated and stirred stainless steel tank reactor, (b) an inline filter, (c) a shell-and-tube heat exchanger, (d) a circulating cooling water bath, (e) a gear pump, (f) a thermocouple, (g) a flat membrane cell, (h) a sampling port, (i) a cold trap for permeate collection cooled by liquid nitrogen, and (j) a vacuum pump.

spin-coated SDS) and the reactor was filled with 180 mL of 375 $\mu\text{mol mL}^{-1}$ xylose in water. At any given moment, 60 mL of solution were located outside the heated autoclave, *i.e.* in the rest of the unit, while the heated tank contained the remainder of the solution. The autoclave was also charged with 9.41 g Amberlyst 70 (equivalent to 133 mM H^+ based on the initial 180 mL in the reactor), all of which was kept in the autoclave by the fritted dip tubes. The circulation rate through the gear pump was set to 40 mL min^{-1} , the stirring rate in the tank was set to its maximum value of 690 rpm, and the stirring rate in the membrane cell was fixed at 120 rpm. The steady-state temperature of the autoclave was 140 °C and the steady-state temperature of the membrane was 75 °C. The autoclave (which contained the catalyst) reached 132 °C by 20 min from the start of heating and circulation and it reached the reaction temperature of 140 °C by 40 min. The membrane reached 71 °C in 20 min, and 75 °C in 40 min.

The reactor was sampled using the sampling port, first taking a sample to flush the sampling port, then taking another sample for analysis. The total volume removed per sample was 1 mL, a small fraction of the total reactor volume (180 mL). The permeate was collected at the same time as the reactor was sampled by switching the accumulating cold trap with a fresh one. The thawed permeate was a single-phase mixture under the conditions used in this study. The accumulated cold trap was weighed and an aliquot was removed for analysis. The total flow rate through the membrane was about 18 g h^{-1} when using PDMS membranes and about 12 g h^{-1} when using SDS membranes.

Equilibrium distribution of furfural

The equilibrium distribution of furfural between water and toluene was measured by filling 10 mL thick-walled glass vials (Sigma-Aldrich, 27198) with 4 mL of toluene, 2 mL of aqueous furfural solution, and a PTFE-coated stir bar. Each vial was matched to a time point from the LLE-assisted reactions with the total furfural in each vial corresponding to the total furfural produced in its matched time point. The vials were then sealed with PTFE/silicone crimp top septa (Agilent, 8010-0420), shaken vigorously by hand for 10 s, then placed on a stir plate for one hour, with the stir bar rotating at 600 rpm. The vials were then opened and an aliquot of each phase was removed for analysis by HPLC or GC-MS, with an internal standard (5 mg per mL dodecane in toluene) added to toluene-phase samples prior to analysis by GC-MS.

Product analysis

Samples of the aqueous phase were analyzed by HPLC using an Ultra High Performance Liquid Chromatograph system (Shimadzu, Kyoto, Japan). 10 μL aliquots of the samples were injected onto a Phenomenex Rezex RFQ-Fast Acid H+ column (100 $\times$ 7.8 mm; 0.01 N H_2SO_4 ; 1.0 mL min^{-1} ; 55 °C) equipped with a refractive index detector (RID). Product quantities were determined by converting integrated peak areas into concentrations using a 9-point calibration curve generated from standards created with analytical grade chemicals.

Samples of the organic phase from the LLE-assisted reactors were analyzed by GC-MS using a Varian CP-3800 Gas Chromatograph equipped with a FactorFour Capillary Column (UF-5 ms 30 m, 0.25 mm, 0.25 μm , P/N CP8944) connected to a Varian quadrupole-mass spectrometer (MS) and flame ionization detector (FID). After product identification by mass spectrometry, product concentrations were determined from integrated FID peak areas using a 7-point calibration curve generated from standards created with analytical grade chemicals.

Calculations

Xylose conversions and furfural yields are reported as molar percentages relative to the initial moles of xylose and furfural, *i.e.*

Conversion

$$= \frac{(\text{Initial moles of xylose}) - (\text{Remaining moles of xylose})}{(\text{Initial moles of xylose})} \times 100\% \quad (1)$$

$$\text{Yield} = \frac{(\text{Moles of furfural}) - (\text{Initial moles of furfural})}{(\text{Initial moles of xylose})} \times 100\% \quad (2)$$

The moles of xylose and furfural were calculated by multiplying the molar concentration of each species in a given phase by that phase's volume. In the case of reactions without simultaneous product separation by pervaporation, the phase volumes were assumed to be equal to their initial values. In the case of reactions with simultaneous product separation by pervaporation, the total initial liquid volume was assumed to be constant throughout the experiment. Any permeated mass collected in cold traps was converted to volume by assuming a density of 1 g mL^{-1} . That volume, in addition to that which was removed by the reactor sampler, was subtracted from the initial liquid volume to calculate the volume in the reactor at each time point.

For reactions conducted without a membrane, initial moles were determined by preparing and analyzing extra reactors (time = 0 min) as stated previously, but without heating in an oil bath. For reactions with a membrane, initial moles were taken to be those in the reactor and in the permeate 20 min after heating and circulation began when the autoclave reached at least 132 °C and the membrane reached at least 71 °C. Conversion of xylose and production of furfural were minimal in those first 20 min.

The equilibrium distribution of furfural is reported as the proportion of the total furfural loaded that was present in the toluene phase, *i.e.*

$$\text{Equilibrium distribution} = \frac{\text{Moles of furfural in toluene phase}}{\text{Total moles of furfural loaded in vial}} \times 100\% \quad (3)$$

The equilibrium distribution is related to the equilibrium constant K , defined as the ratio of furfural concentration in

the toluene phase to the aqueous phase, and the toluene: water volume ratio v , as follows:

$$\text{Equilibrium distribution} = \frac{Kv}{Kv + 1} \times 100\% \quad (4)$$

The molar permeation rate of component i , $\dot{n}_i$, in pervaporation is described as follows:^{29,37}

$$\dot{n}_i = \frac{\Delta m_i}{M_i \Delta t} = A \cdot J_i = A \cdot \frac{P_i}{l} (x_i \gamma_i p_i^{\text{sat}} - y_i p_{\text{permeate}}) \quad (5)$$

where Δm_i is the change in mass of the permeate during the length of time Δt , M_i is the molecular weight, A is the area of the membrane, J_i is the molar flux, P_i is the permeability, l is the thickness of the membrane, x_i is the mole fraction in the liquid feed, γ_i is the activity coefficient in the liquid feed, p_i^{sat} is the saturation vapor pressure at the feed conditions, y_i is the mole fraction in the vapor permeate, and p_{permeate} is the total permeate pressure. Activity coefficients were assumed to be constant at 75 °C of water (1) and furfural (85), and were estimated from binary water–furfural vapor–liquid equilibrium data.³⁸ Saturation vapor pressures were determined by the Antoine equation, using constants calculated from binary water–furfural vapor–liquid equilibrium data.³⁸ Eqn (5) was then used to calculate the membrane permeabilities of water and furfural.

All experiments in this study, with the exception of the equilibrium distribution of furfural measurement, were duplicated. Each plot showing experimental data was constructed using the mean values for each time point, with the error bars representing the range of the two trials. Some error bars are not visible because the ranges for those time points are smaller than the symbols used in the plots. The data point at 120 min time for the LLE-assisted reaction has large error bars caused by significantly different results obtained during the two trials; however, the mean values shown coincide with the values one would expect, given the data points that precede them.

Results and discussion

Comparisons of furfural production methods

Xylose was dehydrated to form furfural in three reactor configurations: without extraction, with LLE, and with pervaporation using commercially available PDMS membranes. Xylose conversions and furfural yields from these experiments are shown in Fig. 2a. All three sets of xylose conversion data followed the same trend, reaching approximately 31% conversion after 120 min when pervaporation was not used and 37% conversion after 120 min when pervaporation was used. The parity in conversion in reactors without extraction and with LLE indicates that LLE of furfural had no significant impact on the rate of xylose conversion. We attribute the increase in conversion when comparing reactions without pervaporation to reactions with pervaporation to the removal of water by the membrane; the liquid volume in the reactor decreased over time, leading

to higher concentrations of catalyst and xylose than would have been present at a given conversion in a constant-volume reactor, and consequently higher rates of xylose conversion. The furfural yield for all three systems increased monotonically over the course of 120 min, the highest yield of furfural being achieved with LLE, followed by pervaporation with PDMS membranes, and finally the base case of no extraction. The higher furfural yield with either separation method demonstrates that both methods improve the furfural yield.

One important quantity to consider when comparing the two processes is the cumulative concentration of furfural in the extracted phase. As seen in Fig. 2b, the furfural concentration in the permeate phase obtained by pervaporation with a PDMS membrane was 6 times higher than that obtained in the extractant phase produced by LLE. The much higher furfural concentration produced by pervaporation was a consequence of using a furfural-selective membrane that more readily absorbed and transported furfural relative to water.

To quantify the effectiveness of extraction, we define an extraction selectivity in the following way:

$$\text{Extraction Selectivity} = \frac{\text{Moles of furfural extracted}}{\text{Total moles of furfural formed}} \times 100\% \quad (6)$$

Extraction selectivity is bound by 0% and 100% since the denominator is composed of the extracted furfural and the furfural present in the reactive phase (*i.e.*, the aqueous phase in LLE-assisted reactions and the retentate in pervaporation-assisted reactions). We show extraction selectivity as a function of reaction time for reactions assisted by LLE and by pervaporation with a PDMS membrane in Fig. 2c. Under the conditions employed in this study, extraction by LLE was more selective than by pervaporation; after 120 min of reaction, the extraction selectivity for LLE was 85% compared to 67% for pervaporation. Extraction selectivity in the case of LLE was constant with reaction time, whereas extraction selectivity for pervaporation increased monotonically with time.

The observed differences in extraction selectivity with reaction time can be attributed to differences in the extraction method. In the case of LLE, the aqueous and organic phases were not sampled during the reaction; the reactors were removed from the heated oil bath, quenched in an ice bath, and sampled after approximately one hour. The equality of the extraction selectivity for LLE-assisted reactions (data points in Fig. 2c) and the measured equilibrium distribution indicates that the furfural had equilibrated between the two phases during LLE-assisted reaction at the time of sampling. What this means is that the extent of furfural partitioning into the toluene phase is governed solely by the equilibrium constant and the ratio of toluene to water volumes. An increase in the toluene:water ratio would increase the LLE selectivity, but would also result in further dilution of furfural in the extracting phase. By contrast, the extraction selectivity for pervaporation increases monotonically with time, as it is governed by

Fig. 2 Comparison among furfural extraction configurations of (a) xylose conversion and furfural yield; (b) concentration of furfural in the extractant phase (toluene or permeate); and (c) extraction selectivity of furfural; during the conversion of 375 mM xylose to furfural at 140 °C with 133 mM H⁺ from Amberlyst 70. Extraction configurations include liquid–liquid extraction (2 : 1 toluene : water by volume), pervaporation with a PDMS membrane, and no extraction. All curves are provided to guide the eye, with the exception of the dashed line in (c) representing the equilibrium distribution of furfural in 2 : 1 toluene : water by volume.

the rate of furfural permeation through the membrane relative to the rate of its formation by reaction.

Comparisons of pervaporation membranes

Additional pervaporation-assisted reactions were carried out using SDS triblock copolymer membranes, which have been shown previously to exhibit high furfural permeability.^{34,36} The results achieved with these membranes are compared to those achieved using PDMS membranes in Fig. 3. As demonstrated in Fig. 3a, similar xylose conversions and furfural yields were obtained with either membrane type. However, both the concentration of furfural in the permeate (Fig. 3b) and the extraction selectivity (Fig. 3c) were higher when using SDS membranes rather than PDMS membranes. The permeate obtained using the SDS membrane reached a furfural concentration that was 62% higher than that attained using the PDMS membrane, indicating that the SDS membrane has a

higher selectivity for furfural over water. We also note that the extraction selectivity was 33% higher using the SDS membrane than the PDMS membrane, signifying that the rate of furfural mass transfer through the SDS membrane was higher and that a greater fraction of the furfural was transported into the permeate, leaving the concentration of furfural in the retentate lower. The reduced retentate furfural concentration reduced the formation of humins and, consequently, increased the reaction selectivity, as shown in Fig. 3a; the furfural yields are matched across membranes, but the xylose conversion is slightly lower for the SDS membrane, resulting in a higher reaction selectivity. The observed difference is fairly minor, demonstrating the relative insensitivity of furfural yield to changes in mass transfer coefficient. We, therefore, conclude that large improvements in furfural extraction rate are required to significantly increase the total furfural yield.

Fig. 3 Comparison among PDMS or SDS membranes of (a) xylose conversion and furfural yield; (b) concentration of furfural in the permeate; and (c) extraction selectivity of furfural; during the pervaporation-assisted conversion of 375 mM xylose to furfural at 140 °C with 133 mM H⁺ from Amberlyst 70. All curves are provided to guide the eye.

While SDS membranes exhibited better furfural permeability and selectivity than did PDMS membranes, the furfural permeability of SDS membranes decreased by nearly 50%, over the course of an experiment, whereas the furfural permeability of the PDMS membranes remained relatively constant, as is shown in Fig. 4. In both cases, though, the water permeability remained unaffected. The decreasing furfural permeability through SDS membranes led to relatively slower furfural permeation rates at longer reaction times, resulting in a lower furfural yield and extraction selectivity compared to what could have been achieved had the furfural permeability remained constant. Since the water permeability did not change while the furfural permeability did, the permeate furfural concentration was also lower than what it could have been had the furfural permeability been constant. While the change in furfural permeability was clear, its effects on furfural yield, extraction selectivity, and permeate furfural concentration were rather subtle, reinforcing the notion that these

metrics of reaction performance are relatively insensitive to changes in mass transfer rates.

It is possible that the lack of cross-links in SDS allowed the humins produced during the reaction to change its morphology, which may in turn have led to the selective decrease in furfural permeability through the membrane. Morphological changes have previously been shown to affect permeability, as was observed in PDMS-containing copolymers used for pervaporation of aqueous ethanol solutions^{39,40} and in polystyrene-*block*-polybutadiene block copolymers used for permeation of CO₂ gas.⁴¹ We intend to investigate this possibility in our systems in the future. If the PDMS cross-links were indeed responsible for maintaining constant furfural permeability, one might be able to replicate the effect in a triblock copolymer by cross-linking the structural block (polystyrene in our case) while still leaving the transporting block (PDMS in our case) flexible. This may allow for the preservation of the high permeability of non-cross-linked PDMS, which was

Fig. 4 (a) Furfural and (b) water permeabilities of SDS and PDMS membranes during the pervaporation-assisted conversion of 375 mM xylose to furfural at 140 °C with 133 mM H^+ from Amberlyst 70. Each data point is representative of the 20 minute range starting 10 minutes before and ending 10 minutes after the point. All curves are provided to guide the eye.

evident when comparing SDS to PDMS (see initial furfural permeabilities in Fig. 4a), and the simultaneous incorporation of the resistance to morphological change from the cross-linked structural block.

Simulations of reaction and LLE or pervaporation

A theoretical model of simultaneous xylose dehydration and furfural extraction (by LLE or pervaporation) was developed in order to understand the effects of operating conditions on the achievable levels of furfural recovery. The set of equations we used in this model are provided in the ESI.[†] The reaction network outlined in Scheme 1 was used to model the reaction kinetics of the systems. It was assumed that the intermediates in the xylose-to-furfural conversion are in pseudo-steady state. For LLE-assisted reactions, only furfural was allowed to transfer between phases and the rate of mass transfer was assumed to be very rapid, resulting in an equilibrium distribution. For the pervaporation-assisted reactions, both furfural and water were allowed to permeate through the membrane. The mass transfer rate of each component was represented by eqn (5), with membrane permeabilities calculated from the data in Fig. 4. Permeabilities through PDMS membranes were taken to be the mean of the data presented in Fig. 4, while the furfural permeability of SDS membranes was taken as the first data point in Fig. 4, and the water permeability of SDS membranes was taken as the mean of the data in Fig. 4. These mass transfer constants and the remainder of the modeling parameters which we held constant are listed in rows 1–22 of Table 1. Reaction rate constants k_1 , k_2 , k_3 , k_4 , and k_5 were determined through least squares minimization of the sum of errors between the predicted and observed concentrations for reactions assisted by LLE and pervaporation with PDMS. Specifically, these were xylose and furfural concentrations in the aqueous phase for the LLE-assisted reaction, xylose concentrations in the retentate for the pervaporation-assisted reaction, and furfural concentrations

in both the retentate and the permeate for the pervaporation-assisted reaction. The values of those reaction rate constants can be found in rows 23–27 of Table 1.

We did not include the case of reaction without extraction in the calculation of reaction rate constants. This was because the measured furfural concentration in the retentate during the pervaporation-assisted reaction was higher than that in the reactor during the reaction without extraction. One would then expect, by reactions (3) and (5) in Scheme 1, that the furfural consumption would be greater during the pervaporation-assisted reaction, but that was not what we observed; pervaporation improved the furfural yield. This observation led to our exclusion of the case of reaction without extraction from these calculations and as a result, the reaction rate constants we report in rows 23–27 of Table 1 only represent xylose dehydration with simultaneous furfural extraction. Further analysis and explanation for this exclusion is provided in the ESI.[†]

Fig. 5 compares the simulated results with the corresponding experimental results for the LLE-assisted, PDMS-pervaporation-assisted, and SDS-pervaporation-assisted reactions. The simulated and experimental results compare very well for all three cases, albeit less so for SDS-pervaporation data. Some of this deviation can be ascribed to the decrease in furfural permeability of SDS membranes with time of use, as discussed previously. It is also clear that the model we developed slightly underestimates both the extraction selectivity and the permeate furfural concentration for pervaporation-assisted reactions carried out with either PDMS or SDS membranes.

Predictions of reaction and LLE or pervaporation over experimentally inaccessible durations

The model was used to predict the results of xylose dehydration with simultaneous furfural extraction for much longer reaction times than were achievable experimentally. We chose five furfural extraction configurations, using the parameters

Table 1 Parameters used in this study for experiments, membrane calculations, and simulations

Row	Parameter	Symbol	Value
Common parameters			
1	Proton concentration (mmol L ⁻¹)	[H ⁺]	133
2	Initial xylose concentration (mmol L ⁻¹)	[X] ₀	375
Liquid-liquid extraction parameters			
3	Equilibrium constant ((mol L ⁻¹) _{org} /(mol L ⁻¹) _{aq})	<i>K</i>	2.74
4	Volume ratio (L _{org} L _{aq} ⁻¹)	<i>ν</i>	2.0
Pervaporation parameters			
5	Initial volume (mL)	<i>V</i> ₀	180
6	Initial xylose loading (mmol)	<i>N</i> _{X,0}	67.5
7	Furfural molecular weight (g mol ⁻¹)	<i>M</i> _F	96.08
8	Water molecular weight (g mol ⁻¹)	<i>M</i> _W	18.02
9	Water density (g mL ⁻¹)	<i>ρ</i> _W	1.0
10	Membrane area (cm ²)	<i>A</i>	37
11	Membrane temperature (°C)	<i>T</i> _{mem}	75
12	PDMS membrane thickness (μm)	<i>l</i>	4.0
13	SDS membrane thickness (μm)	<i>l</i>	4.8
14	Furfural permeability of PDMS (mol m ⁻¹ s ⁻¹ Pa ⁻¹)	<i>P</i> _F	8.3 × 10 ⁻¹²
15	Water permeability of PDMS (mol m ⁻¹ s ⁻¹ Pa ⁻¹)	<i>P</i> _W	7.6 × 10 ⁻¹²
16	Furfural permeability of SDS (mol m ⁻¹ s ⁻¹ Pa ⁻¹)	<i>P</i> _F	1.6 × 10 ⁻¹¹
17	Water permeability of SDS (mol m ⁻¹ s ⁻¹ Pa ⁻¹)	<i>P</i> _W	6.0 × 10 ⁻¹²
18	Furfural activity coefficient	<i>γ</i> _F	85 ^a
19	Water activity coefficient	<i>γ</i> _W	1 ^a
20	Furfural saturation vapor pressure at <i>T</i> _{mem} (Pa)	<i>p</i> _F ^{sat}	3804 ^b
21	Water saturation vapor pressure at <i>T</i> _{mem} (Pa)	<i>p</i> _W ^{sat}	38 457 ^b
22	Permeate pressure (Pa)	<i>p</i> _{permeate}	3
Reaction rate constants			
23	Xylose dehydration (L mol ⁻¹ s ⁻¹)	<i>k</i> ₁	3.4 × 10 ⁻⁴
24	Furfural production (L mol ⁻¹ s ⁻¹)	<i>k</i> ₂	7.0 × 10 ⁻⁴
25	Furfural-intermediate condensation (L ² mol ⁻² s ⁻¹)	<i>k</i> ₃	4.6 × 10 ⁻³
26	Xylose-intermediate condensation (L ² mol ⁻² s ⁻¹)	<i>k</i> ₄	5.7 × 10 ⁻⁴
27	Furfural resinification (L mol ⁻¹ s ⁻¹)	<i>k</i> ₅	1.3 × 10 ⁻⁴

^a Ref. 38, activity coefficients at 75 °C estimated from vapor-liquid equilibrium data. ^b Ref. 38, saturation vapor pressures (mmHg) at 75 °C calculated by Antoine equation, *A*_{furfural} = 8.402, *B*_{furfural} = 2338.49, *C*_{furfural} = 261.638, *A*_{water} = 8.07131, *B*_{water} = 1730.63, *C*_{water} = 233.426.

listed in Table 1: (1) LLE; (2) pervaporation with a PDMS membrane; (3) pervaporation with an SDS membrane with constant, rather than decaying, furfural permeability (which we refer to as “pervaporation with SDS”); (4) pervaporation with a membrane that had five times the value of (*P*_F*A*/*l*) of the experimental SDS membranes, also with constant furfural permeability (which we refer to as “SDS (5× *P*_F*A*/*l*)”); and (5) a hypothetical configuration in which furfural extraction is instantaneous and infinite in capacity (*i.e.* extraction selectivity always equals 100%). These five configurations are summarized in Table 2. We note here that while the simulated results of pervaporation-assisted reactions plotted in Fig. 5 included the effects of a decreasing reactor volume caused by water permeation, those in this analysis did not, since the water permeation was significant enough to deplete the reactor of its solvent within the time considered. To account for this, the model was modified slightly: the rate of water permeation remained the same, but the amount of water in the reactor did not change. Physically, this means that any water passing through the membrane is rapidly replaced.

We compared xylose conversions, furfural yields, extracted furfural concentrations, and extraction selectivities for different extraction configurations, as shown in Fig. 6a–c. Xylose conversion remained unaffected by the method of extraction, reaching 95% after 1000 min. Fig. 6a shows that

furfural yield increases monotonically throughout the reaction, signifying that every extraction method reduced the concentration of furfural within the reactor sufficiently so that the rates of furfural consumption (reactions (3) and (5) in Scheme 1) are never able to exceed the rate of furfural production. In the infinite extraction case, the hypothetical limit of furfural yield at 95% xylose conversion is 73%. What this reveals is that reaction (4) in Scheme 1, on its own, is responsible for a humins yield of 22%. When furfural separation is by LLE or when furfural separation is achieved by pervaporation through a PDMS or an SDS membrane with properties given in Table 1, the furfural yield decreases to between 52% and 59% – 72–82% of the hypothetical limit with infinite extraction. By increasing the value of (*P*_F*A*/*l*) for an SDS membrane by fivefold, it is possible to attain a furfural yield of 69% at a xylose conversion of 95% – a 17% increase over the case of pervaporation with SDS.

Shown in Fig. 6b are the predicted extracted furfural concentrations for each extraction configuration over the course of the reaction, except for the case of infinite extraction. As we saw experimentally, the predicted furfural concentrations in the permeate resulting from both pervaporation using either an SDS or a PDMS membrane exceeds the predicted furfural concentration in toluene obtained by LLE. However, in the SDS (5× *P*_F*A*/*l*) case, the predicted furfural concentration is

Fig. 5 Comparison among experimental data and simulated results of (a) xylose conversion and furfural yield; (b) concentration of furfural in the extractant phase (toluene or permeate); and (c) extraction selectivity of furfural; during the conversion of 375 mM xylose to furfural at 140 °C with 133 mM H⁺ from Amberlyst 70. Extraction configurations include liquid-liquid extraction (2 : 1 toluene : water by volume), pervaporation with a PDMS membrane, and pervaporation with an SDS membrane.

Table 2 Reactor configurations simulated for experimentally inaccessible reaction times

Number	Name	Description
1	LLE	Liquid-liquid extraction with 2 : 1 toluene : water by volume
2	PDMS	Pervaporation with PDMS
3	SDS	Pervaporation with an SDS membrane with constant, rather than decaying, furfural permeability
4	SDS ($5 \times P_A/I$)	Pervaporation with a membrane with five times the value of (P_A/I) of the experimental SDS membranes
5	Infinite extraction	A hypothetical configuration in which furfural extraction is instantaneous and infinite in capacity

initially higher than that obtained by LLE, but becomes lower than that obtained by LLE at 520 min and continues to decrease thereafter.

It is worth noting that the change with time in the predicted furfural concentration in the extracted phase differs for LLE and pervaporation. Simulations of LLE show that the furfural concentration in the extract rises monotonically and proportionally to the furfural yield. This is a consequence of the constant extraction selectivity combined with the assumption of rapid mass transfer. In the simulations of pervaporation, the extracted furfural concentration rises rapidly initially, peaks within 260 min, and then falls. This behavior differs qualitatively from what is predicted for LLE because both furfural and water permeate the membrane during pervaporation. As shown in Fig. 6d, the predicted furfural concentration in the reactor rises initially then decreases. This behavior stems from the changing and competing rates of furfural production *versus* consumption or pervaporation. Initially, the rate of furfural production is high because the xylose concentration is high. At later times, though, the furfural production rate diminishes and is overcome by the combination of pervapora-

Fig. 6 Comparison among simulated results of (a) xylose conversion and furfural yield; (b) concentration of furfural in the extractant phase (toluene or permeate); (c) extraction selectivity of furfural; (d) concentration of furfural in pervaporation-assisted reactors; and (e) furfural yield in the extractant phase (toluene or permeate) during the conversion of 375 mM xylose to furfural at 140 °C with 133 mM H^+ from Amberlyst 70. Extraction configurations are listed in Table 2.

tion and consumption to form humins. A consequence of the trends in reactor furfural concentration is that the furfural permeation rate also rises initially and then decreases. However, since the furfural concentration is low, the water concentration and hence the water permeation rate is essentially constant. The combined result leads to the trends shown in Fig. 6b. The times to the maximum in permeate furfural concentration and the reactor furfural concentration do not match because the permeate furfural concentration is the result of the cumulative effect of changing furfural permeation rates, and not the

instantaneous permeate furfural concentration; the cumulative permeate needs time to be diluted by the increasingly dilute permeate flux in order to reach its maximum value.

The predictions shown in Fig. 6c demonstrate that by 360 min all three pervaporation configurations give greater extraction selectivity than LLE, ultimately reaching >98% while LLE is limited to 85%, further underscoring the advantage of pervaporation over LLE. Multiplying the extraction selectivity by the total furfural yield gives the furfural yield in the extracted phase, or extracted furfural yield, which we plot for

all four simulated extraction configurations in Fig. 6e. The extracted furfural yield represents the yield of furfural that would be captured in the end, assuming no loss during purification. In our simulations, the extracted furfural yields of all three pervaporation configurations were 21–56% higher than that for LLE, showing an additional benefit of pervaporation over LLE.

The present study demonstrates that pervaporative separation of furfural from an aqueous solution not only reduces the loss of product due to formation of humins, but also results in a much more concentrated product than could be achieved by LLE. It is expected that further enhancements in pervaporative extraction could be achieved by improving the membrane properties, *i.e.* increasing the permeability of furfural through the film through the use of a different membrane material, increasing the membrane area, and decreasing the membrane thickness. In this study, we demonstrated an improvement in furfural permeability by changing our PDMS membranes to SDS block copolymer membranes. One could envision improving the membranes further through the use of a transporting phase with more intrinsic free volume, such as poly[1-(trimethylsilyl)-1-propyne] (PTMSP)^{29,42} or by changing the volume fraction of the transporting phase, with which the permeability is expected to be proportional.^{39,43} Additionally, pervaporative extraction could be improved by increasing the operating temperature of the film. Clearly, operation of the membrane separator at the temperature of the reaction (140 °C) would be desirable, since this would eliminate the need for the heat exchanger placed between the reactor and the membrane unit. An increase in the membrane temperature would also increase the saturation vapor pressure of furfural in the membrane feed 13 times,³⁸ which would, in turn, increase the furfural mass transfer rate by a similar magnitude (see eqn (5)).

Conclusions

A laboratory-scale reactor/membrane separation system was built and tested in order to assess the feasibility of using pervaporation to remove furfural from an aqueous solution as it is formed by the Brønsted-acid catalyzed dehydration of xylose. We found that LLE and pervaporation with either PDMS or SDS membranes improved the yield of furfural over the case of reaction without extraction. SDS membranes had high furfural permeabilities, offering a promising alternative to cross-linked PDMS membranes, but their furfural permeabilities declined during the course of the reaction, ultimately limiting their use. The data from reactions with simultaneous furfural extraction were simulated using a model of the system, which enabled an analysis of the benefits of pervaporation-assisted xylose dehydration at near-complete conversion to be explored more fully. When compared to LLE, pervaporation was found to produce an extractant phase of significantly greater purity and to extract a larger proportion of the furfural produced. Both of these advantages improve the potential economic viability of

pervaporation-assisted xylose dehydration compared to an LLE-assisted process.

Improvements in pervaporation could come from changing the dimensions of the membrane (*i.e.* increasing the area and decreasing the thickness) and from changing the membrane material itself. As shown in rows 14 and 16 of Table 1, the tri-block copolymer SDS membranes have a furfural permeability twice that of cross-linked PDMS, despite having a smaller volume fraction of the furfural-transporting block. Pervaporation membranes may be further improved by utilizing more-permeable block copolymer transporting units or by cross-linking the structural unit, which may lead to increased membrane resistance to changes in furfural permeability during its production.

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