Pervaporation-assisted catalytic conversion of xylose to furfural

Alex Wang^{a,b}, Nitash P. Balsara^{a,b,c*}, Alexis T. Bell^{a,b*}

^a Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, USA

^b Energy Biosciences Institute, University of California, Berkeley, CA 94704, USA

^c Material Sciences Division and Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Electronic Supplementary Information

We modeled xylose dehydration with simultaneous furfural extraction by pervaporation and liquid-liquid extraction (LLE) in accordance to Scheme 1 (which we reproduced here as Scheme S1), using the constants provided Table 1. For LLE-assisted reactions, we assumed that the mass transfer rate of furfural across the two phases was very rapid, resulting in an equilibrium distribution and allowing us to write the following differential equations:

$$\frac{d[X]}{dt} = -(k_1 + k_4[I])[X][H^+]$$
(S1)

$$\frac{d[I]}{dt} = \left(k_1[X] - k_2[I] - k_3[I][F] - k_4[I][X]\right) \left[H^+\right]$$
(S2)

$$\frac{d[F]^{aq}}{dt} = \left(\frac{1}{K\nu+1}\right) \left(k_2[I] - k_3[I][F] - k_5[F]\right) \left[H^+\right]$$
(S3)

$$\frac{d[F]^{org}}{dt} = \left(\frac{K}{K\nu+1}\right) \left(k_2[I] - k_3[I][F] - k_5[F]\right) \left[H^+\right]$$
(S4)

where [X], [I], $[H^+]$, and $[F]^{aq}$ are the concentrations of xylose, intermediate product, protons, and furfural in the aqueous phase, respectively, and $[F]^{org}$ is the concentration of furfural in the organic phase. The constants K and v are the equilibrium constant (*i.e.* $[F]^{org}/[F]^{aq}$) and the volume ratio (*i.e.* toluene-phase volume/aqueous-phase volume), respectively. The constants k_1 , k_2 , k_3 , k_4 , and k_5 correspond to the same constants in Scheme S1. We invoked the pseudo-steady state assumption, *i.e.* $d[I]/dt \approx 0$, so that

$$[I] = \frac{k_1[X]}{k_2 + k_3[F] + k_4[X]}$$
(S5)

We treated the pervaporation-assisted reactions with a similar approach. We used Equation (5) to calculate permeation rates, but neglected the term corresponding to the permeate pressure in permeation rates because the permeate pressure was nearly zero. Mass balances were written in terms of moles, rather than concentrations, because water could permeate through the membrane and change the volume of the reactor:

$$\frac{dN_X}{dt} = -\left(k_1 + k_4 \left(\frac{k_1 N_X / V}{k_2 + k_3 N_F^{ret} / V + k_4 N_X / V}\right)\right) \frac{N_X}{V} N_H^{+}$$
(S6)

$$\frac{dN_{F}^{ret}}{dt} = \left[\left(k_{2} - k_{3} \frac{N_{F}^{ret}}{V} \right) \left(\frac{k_{1} N_{X}/V}{k_{2} + k_{3} N_{F}^{ret}/V + k_{4} N_{X}/V} \right) - k_{5} \frac{N_{F}^{ret}}{V} \right] N_{H} + -A \frac{P_{F}}{l} \frac{N_{F}^{ret}}{N_{X} + N_{F}^{ret}}$$
(S7)

$$\frac{dN_W^{ret}}{dt} = -A \frac{P_W N_W^{ret}}{l_{N_X} + N_F^{ret} + N_W^{ret}} \gamma_W p_W^{sat}$$
(S8)

$$\frac{dV^{ret}}{dt} = \frac{M_W dN_W^{ret}}{\rho_W dt}$$
(S9)

$$\frac{dN_{F}^{perm}}{dt} = A \frac{P_{F}}{l} \frac{N_{F}^{ret}}{N_{X} + N_{F}^{ret} + N_{W}^{ret}} \gamma_{F} p_{F}^{sat}$$
(S10)

$$\frac{dN_{W}^{perm}}{dt} = -A \frac{P_{W}}{l} \frac{N_{W}^{ret}}{N_{X} + N_{F}^{ret} + N_{W}^{ret}} \gamma_{W} p_{W}^{sat}$$
(S11)

$$\frac{dV^{perm}}{dt} = \left(M_F \frac{dN_F^{perm}}{dt} + M_W \frac{dN_W^{perm}}{dt}\right) \frac{1}{\rho_W}$$
(S12)

Here, the subscripts represent components and the superscripts denote phases. Thus, N_i^j is the moles of component *i* in phase *j*. The subscripts *X*, *F*, *H*⁺, and *W* represent xylose, furfural, protons, and water, respectively, while the superscripts *ret* and *perm* represent the retentate and permeate, respectively. Xylose was only found in the retentate, so its phase index is neglected. V^j represents the volume of phase *j*, *A* is the area of the membrane, P_i is the permeability of component *i*, *l* is the thickness of the membrane, γ_i is the activity coefficient of *i* in the liquid feed, and p_i^{sat} is the saturation vapor pressure of *i* at the feed conditions.

We used least squares minimization of the sum of errors between experimentally observed and simulated concentrations for reactions assisted by LLE and pervaporation with PDMS. These concentrations were that of xylose and furfural 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 resultant reaction rate constants are given in rows 23-27 of Table 1, which we reproduced here in Table S1.

Data from the reaction without extraction was not included 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. This observation, in conjunction with Reactions 3 and 5 in Scheme S1. Reaction network for furfural production from xyloseScheme

S1, would lead one to expect the furfural consumption to be greater during the pervaporationassisted reaction. This expectation is inconsistent with our experimental data, which showed that pervaporation improved the furfural yield, and led us to exclude the case of reaction without extraction from the reaction-rate-constant calculations and subsequent simulations of experimentally inaccessible reaction times with those reaction rate constants (see Figure 6).

Figure S1 shows the comparison of experimental data and simulated results for the case of reaction without extraction, using the reaction rate constants for xylose dehydration with simultaneous furfural extraction (provided in Table S1). We used Equations (S1), (S3), and (S5) while setting the volume ratio v equal to zero. The xylose conversion is predicted well, but the furfural yield is overestimated by a factor of 2. We analyzed each of the five reaction rate constants in order to improve the simulated furfural yield only in the case of reaction without extraction, assessing how sensitive the xylose conversion and furfural yield at 120 min were to changes in each parameter.

Rate constant k_1 , which represents xylose dehydration, has the most significant effect on xylose conversion and, by extension, also significantly affects furfural yield. Changes in this constant do not result in proportionate changes in the xylose conversion and furfural yield at 120 min because of their exponential dependence on time and on multiple rate constants. Ultimately, k_1 should be left unchanged to ensure reasonable agreement between the experimental and predicted xylose conversions.

Rate constant k_4 , which represents xylose-intermediate condensation, could be increased to increase the production of humins *via* Reaction 4. A secondary effect would be the reduction in [*I*] (see Equation (S5)), which would lead to less furfural production. However, the difference in xylose conversion between the reactions with LLE and without extraction is minimal (see

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Figure 2a), suggesting that $k_4[I]$ is, and must remain, much smaller than k_1 (see Equation (S1)); k_4 should remain unchanged.

Rate constant k_5 , which represents furfural resinification, could also be increased to increase the production of humins and decrease furfural yield. However, the rate of Reaction 5 is small because of the low furfural concentration, so large changes in k_5 are necessary to significantly impact the furfural yield: a 15-fold increase in k_5 results in the 2-fold decrease in furfural yield required to match the simulated and experimental furfural yields, as shown in Figure S2a.

Rate constant k_2 , which represents furfural production, could be decreased to decrease furfural yield. A side effect of decreasing k_2 is that [*I*] is increased slightly, leading to a minor increase in xylose conversion *via* Reaction 4, which causes the simulated and experimental xylose conversion to diverge. However, the most pronounced impact is on furfural yield, with a modest 1.8-fold decrease in k_2 leading to a 1.3-fold decrease in furfural yield.

Rate constant k_3 , which represents furfural-intermediate condensation, could be increased to decrease furfural yield, as well as reduce [*I*] and consequently decrease xylose conversion *via* Reaction 4. On its own, a 1.8-fold increase in k_3 results in a 1.2-fold decrease in furfural yield. However, when this increase is coupled with the 1.8-fold decrease in k_2 , the two effects work together to accurately predict the xylose conversion and furfural yield in the case of reaction without extraction, as shown in Figure S2b.

We applied the aforementioned adjustments to k_5 and to the pair of k_2 and k_3 and simulated the extraction-assisted reactions for experimentally inaccessible durations, similarly to how we produced Figure 6. The results from increasing k_5 by a factor of 15 are shown in Figure S3, while the results from decreasing of k_2 by a factor of 1.8 and simultaneously increasing k_3 by

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a factor of 1.8 are shown in Figure S4. In both cases, the xylose conversion, furfural yield, and extraction selectivity trends matched what we found with our unadjusted reaction rate constants (in Figure 6): conversions were the same regardless of extraction method, yields increased in the order of LLE < PDMS < SDS < SDS (5x $P_i A/l$) < Infinite Extraction, and the LLE extraction selectivity remained constant while all pervaporation extraction selectivities approached 100%. The extracted furfural concentrations trended similarly across all three cases, except with LLE when furfural resinification was inflated (see Figure S3c) because the furfural concentration rose enough that the rate of furfural resinification exceeded that of furfural production, leading to the maxima observed in both the furfural yield and the furfural concentration in toluene (see Figure S3b and Figure S3c, respectively). We can conclude from this analysis that while the exact values of xylose conversion, furfural yield, and extracted furfural concentration are somewhat sensitive to the values of the reaction rate constants k_1 - k_5 , the trends with respect to extraction method are rather insensitive; pervaporation holds the potential to improve furfural yield, concentration of furfural in the extractant phase, and the proportion of furfural in the extractant phase.



Scheme S1. Reaction network for furfural production from xylose

Parameter	Symbol	Value
Xylose dehydration (L/mol/s)	k_1	3.4.10-4
Furfural production (L/mol/s)	k_2	7.0.10-4
Furfural-intermediate condensation $(L^2/mol^2/s)$	k_3	$4.6 \cdot 10^{-3}$
Xylose-intermediate condensation $(L^2/mol^2/s)$	k_4	5.7.10-4
Furfural resinification (L/mol/s)	k_5	1.3.10-4

Table S1. Reaction rate constants for xylose dehydration with extraction



Figure S1. Comparison among experimental data and simulated results of xylose conversion and furfural yield during the conversion of 375 mM xylose to furfural at 140 °C with 133 mM H⁺ from Amberlyst 70 without furfural extraction. Reaction rate constants are listed in Table S1.



Figure S2. Comparison among experimental data and simulated results of xylose conversion and furfural yield during the conversion of 375 mM xylose to furfural at 140 °C with 133 mM H⁺ from Amberlyst 70 without furfural extraction. Reaction rate constants are listed in Table S1, except in (a) k_5 was changed to 2.0·10⁻⁴ L/mol/s and in (b) k_2 was changed to 3.9·10⁻⁴ L/mol/s while k_3 was changed to 8.3·10⁻³ L²/mol²/s.

Figure S3. Comparison among simulated results of (a) xylose conversion; (b) furfural yield; (c) concentration of furfural in the extractant phase (toluene or permeate); and (d) extraction selectivity of furfural during the conversion of 375 mM xylose to furfural at 140 °C with 133 mM H⁺ from Amberlyst 70 with increased furfural resinification ($k_5 = 2.0 \cdot 10^{-3}$ L/mol/s). Extraction configurations are listed in Table 2.

Figure S4. Comparison among simulated results of (a) xylose conversion; (b) furfural yield; (c) concentration of furfural in the extractant phase (toluene or permeate); and (d) extraction selectivity of furfural during the conversion of 375 mM xylose to furfural at 140 °C with 133 mM H⁺ from Amberlyst 70 with decreased furfural production ($k_2 = 3.9 \cdot 10^{-4}$ L/mol/s) and increased furfural-intermediate condensation ($k_3 = 8.3 \cdot 10^{-3}$ L²/mol²/s). Extraction configurations are listed in Table 2.