Investigating mass transport limitations on xylan hydrolysis during dilute acid pretreatment of poplar

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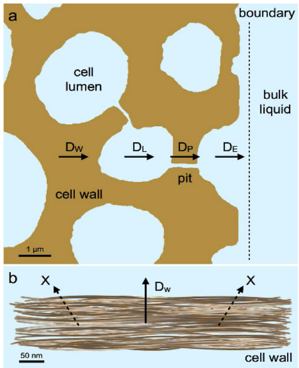
Objectives

•The objective of this work was to characterize and measure mass transfer limitations that could occur during dilute acid pretreatment of biomass.
•Experiments were designed to determine if ~~the~~ apparent xylan acid hydrolysis reaction rates changed with the size of the biomass particles.
•We have studied the mass transfer restrictions imposed by the structure of biomass on the hydrolysis of xylan during dilute acid pretreatment using xylobiose, beechwood xylan, and poplar wood at particle sizes ranging from 10 µm to 10 mm. Additionally, xylan hydrolysis was also investigated using O-acetyl-4-O-methylglucurono-β-D-xylan and DMSO extracted xylan.
•A mathematical model has been developed to describe the kinetics of xylan hydrolysis that includes diffusion of the products through biomass. The model has been used to fit experimentally measured xylose yields at different temperatures.

Length scales of diffusion

- *The cartoon of plant cell walls highlights some of the important diffusion processes that may occur at the tissue and cellular level in biomass*
- *At the surface of a biomass particle there will be external diffusion through the boundary layer, D_E. This diffusion rate can be increased by adequate mixing of the solution*
- *Diffusion through the lumen (~30 µm average size in cross section) is indicated by D_L.*
- *D_P represents the diffusion through the pits that are situated in adjacent cell walls. Finally, there is diffusion through the solid cell wall, D_W. The cell wall is known to be very dense and, therefore, this diffusion rate is likely to be extremely slow.*

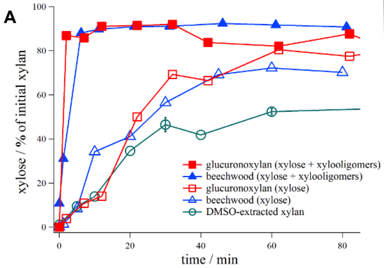


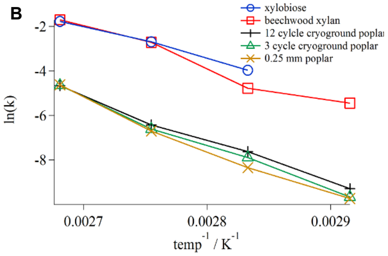
Hydrolysis with no mass transport limitations

(A)Isolated xylan hydrolysis

(B) Arrhenius plots of the hydrolysis rate constants for xylobiose, isolated xylan and poplar

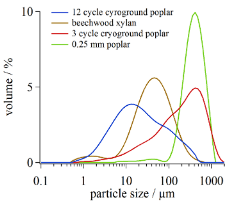
- *Batch reactions – microwave reactor*
- *Solids: 1% w/v*
- *H_2SO_4: 1.2 wt%*
- *Well-stirred*





- *Hydrolysis of isolated xylan and xylobiose appear to follow simple first-order kinetics*
- *The rate of xylose formation from xylobiose and beechwood xylan is an order of magnitude or two larger than the rate from poplar wood.*

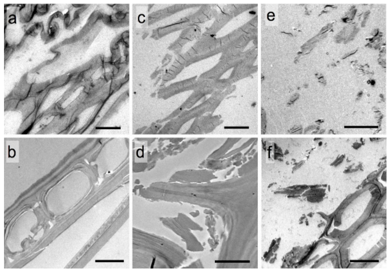
Particle size data



Representative particle sizes
•commercial beechwood xylan
•cryoground poplar (12 cycle, 3 cycl) prepared using SPEX SamplePreP 6770 Freezer Mill (1min grind, 1min hold between cycles)

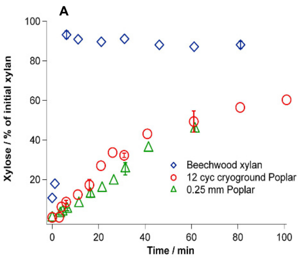
TEM micrographs of variably milled poplar wood

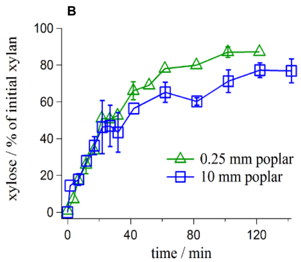
In 0.25 mm and larger particles, both fiber (a) and ray cells (b), appear intact and connected to adjacent cells. After 3 cycles of cryogrinding, many particles display intact cells, but with fractured walls and cell wall fragments (c, d). After 12 cycles, most particles appear fractured with few intact cells remaining (e, f). Scale bars = 10 µm.



Xylan hydrolysis kinetics in poplar

•Xylan hydrolysis in poplar at three different particle sizes (vs. isolated xylan) at 110 ° C
(A) 0.25 mm; 12 cycle cryoground poplar and (B) 0.25 mm vs. 10 mm poplar
•Differences in xylose release were minimal over entire particle size range





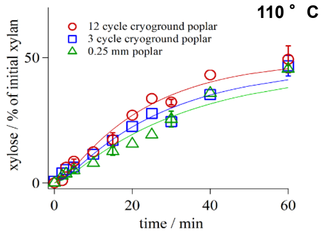
Mass Transfer Modeling

Species A (xylan; solid phase) → ***Species B (xylooligomers + xylose; liquid phase)***

$$\frac{M_A}{M_A^{RM}} = 1 - \alpha\left(1 - e^{-kt}\right)$$

$$\frac{M_{B,pore}}{M_A^{RM}} = \frac{\alpha}{1+\beta}\left[\left(1 - e^{-(1+\beta)K_{OB}t}\right) - \frac{\left(K_{OB} - k\right)}{K_{OB} - k/\left(1+\beta\right)}\left\{e^{-kt} - e^{-(1+\beta)K_{OB}t}\right\}\right]$$

$$\frac{M_{B,bulk}}{M_A^{RM}} = \alpha\left(1 - e^{-kt}\right) - \frac{M_{B,pore}}{M_A^{RM}}$$



Fit parameters for modeling xylose formation from poplar

T (C)	α	β	K_{OB} (s^{-1})	k (s^{-1})	$(1+\beta)K_{OB}$ (min^{-1})	D_{fiber} (order of magnitude estimate, cm^2/s)
110	0.59	4.03	1.3×10^{-4}	7.4×10^{-3}	0.038	2.6×10^{-15}
90	0.42	0.29	4.5×10^{-4}	2.7×10^{-3}	0.034	6.8×10^{-15}
80	0.40	0.11	6.4×10^{-4}	1.7×10^{-3}	0.043	1.2×10^{-14}
70	0.35	0.06	4.1×10^{-4}	5.5×10^{-4}	0.026	6.5×10^{-15}

Notation
- **α** — ***susceptible or accessible fraction of xylan in wood***
- **β** — ***dimensionless partition coefficient for species B between bulk and pore liquid***
- **k** — ***first-order reaction rate constant for xylan hydrolysis (min^{-1})***
- **K_{OB}** — ***overall volumetric mass-transfer coefficient (min^{-1}) for species B***
- **M_A** — ***mass of A (kg) in the solid phase at any time t (min)***
- **M_A^{RM}** — ***initial mass of xylan (species A(kg)) in the biomass at time t = 0***
- **$M_{B,pore}$** — ***mass (kg) of B in the pore-liquid phase at any time t***
- **$M_{B,bulk}$** — ***mass (kg) of B in the bulk-liquid phase at any time t***

Conclusions

•Mass transfer restriction significantly reduces the observed rates of hydrolysis from the intrinsic hydrolysis rates that are possible in the absence of mass transfer.
•The hydrolysis results show the rate of xylose formation from beechwood xylan is about an order of magnitude larger than from the smallest particle size poplar (10 µm) we have studied.
•Moreover, we observed no significant difference in the rates of xylan hydrolysis in poplar over two orders of magnitude in particle size. Therefore, we believe that that the xylan hydrolysis rate in this particle size range are limited primarily by the diffusion of the products across the plant cell walls.
•The modeling results suggest that diffusion rates are only modestly affected by temperature. Thus, the mass transport restrictions cannot be significantly overcome by increasing temperature.

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