Initial Results from a Pilot Scale Pretreatment Reactor Using Very Dilute Sulfuric Acid on a Hardwood Feedstock

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Abstract

A continuous two stage reactor system to fractionate yellow poplar hardwood at high yields at the pilot scale (200 kg/day) has been installed and operated in an initial campaign of over 100 hours. The reactor design is based upon a horizontal screw plug-flow first stage using steam (170-185 C) and a vertical countercurrent second stage using flowing very dilute sulfuric acid (<0.1 wt %, 205-225 C). The vertical countercurrent stage reactor employs an interrupted flight design to mimic the "shrinking bed" effect. The bench-scale system has been previously been reported to achieve **soluble sugar yields from both cellulose and hemicellulose in excess of 90% from hardwood yellow poplar sawdust.** Initial results from the **pilot scale system** included **soluble xylose yields approaching 90%** (combined oligomers and monomers), and **glucose yields** from cellulose **just slightly less than predicted** from bench work using a **5 minute residence time** at just under a normalized **25% yield**. In addition, **total soluble sugar concentrations** were routinely above **50 g/L** and reached a **maximum of over 65 g/L**, despite the relatively low cellulose conversions (~30%). Several reactor modifications to the reactor system, particularly to the screw flight design of the vertical stage reactor, have been proposed to allow for more effective solids movement that could allow for operation at longer residence times. Finally, recently developed fundamental hemicellulose and cellulose hydrolysis reaction concepts are being utilized to guide additional reactor system modifications.

Predictions from Bench-Scale Reactor Results

(Steam 1st Stage, 0.07 wt% Sulfuric Acid 2nd Stage)

Stage 1

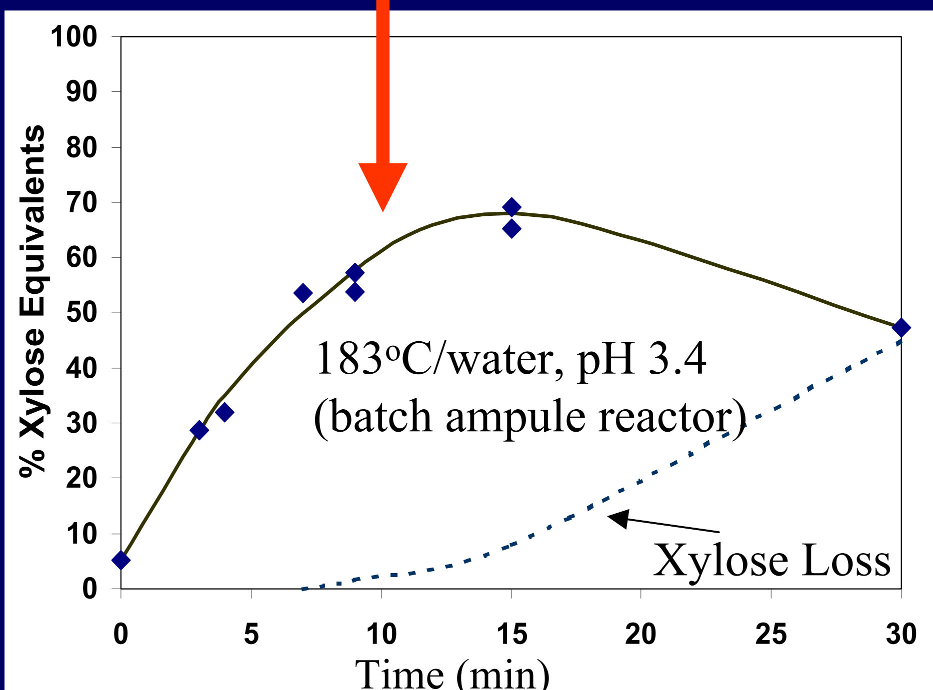
183°C Steam (water)/10 min
Batch Reactor – Predict:

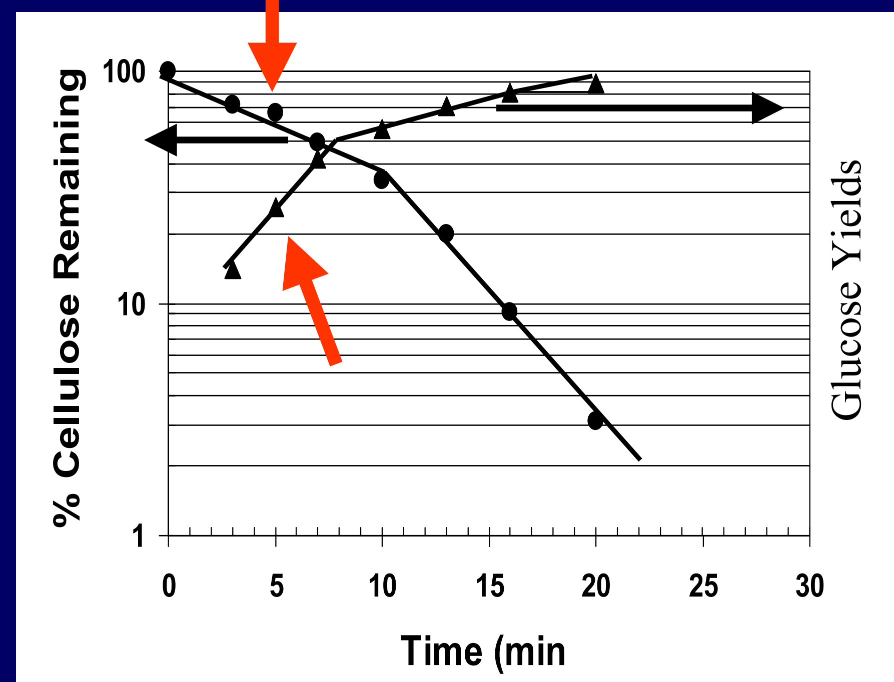
- ~60% conversion
- ~57% xylose equivalents
- ~3% loss

Stage 2

205°C 0.07 wt% acid/5 min
Shrinking Bed Reactor – Predict:

- ~32% conversion
- ~27% glucose equivalents
- ~5% loss





Pilot Reactor Results

(Steam 1st Stage, 0.1 wt% Sulfuric Acid 2nd Stage)

Xylose Mass Balance Results

170°C/10 min 1st Stage 205°C/5 min 2nd Stage	Horizontal Squeezate	Hydrolyzate	Solids	Discharge Squeezate	Total	Standard Deviation	Normal. Total
% as Unconverted Xylan	0.4	0.0	1.9	0.6	2.9	0.3	2.6
% as Soluble Sugar	29.6	52.0	8.0	6.0	96.1	19.7	86.6
% as Furfural	0.0	8.0	2.6	1.6	12.0	3.9	10.8
					111.0		**100.0**

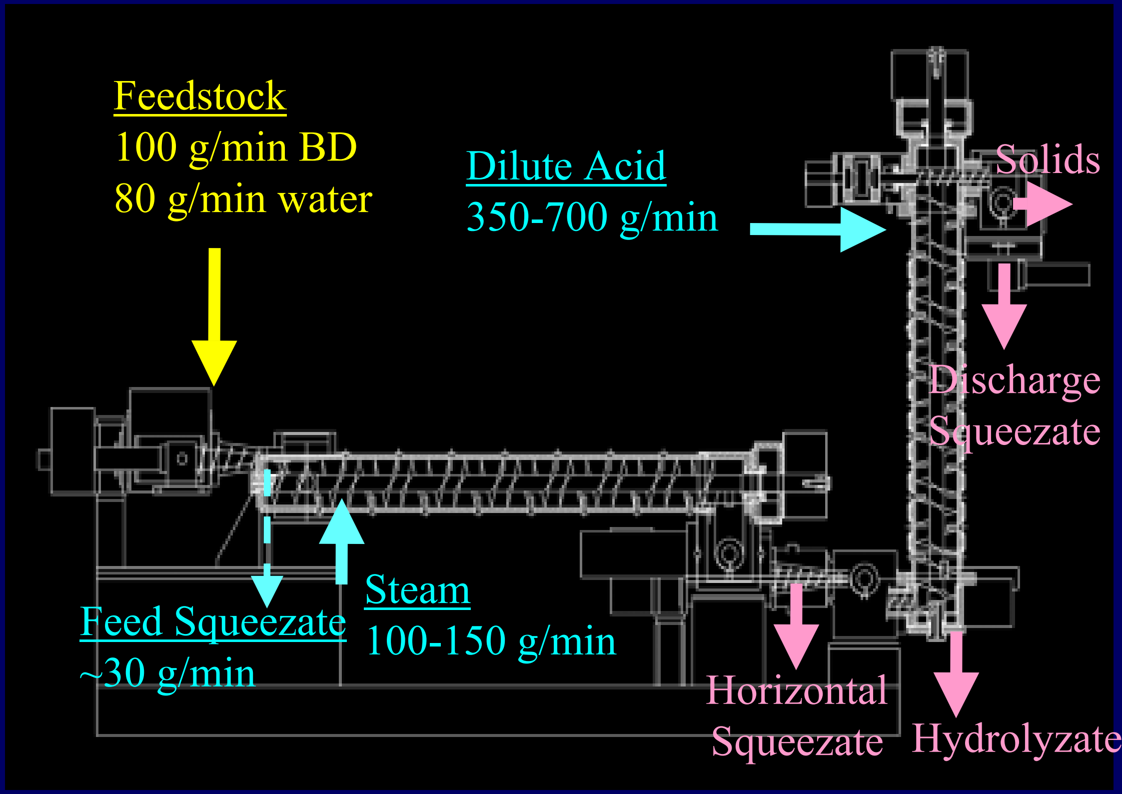
Glucose Mass Balance Results

170°C/10 min 1st Stage 205°C/5 min 2nd Stage	Horizontal Squeezate	Hydrolyzate	Solids	Discharge Squeezate	Total	Standard Deviation	Normal. Total
% as Unconverted Cellulose	9.8	0.0	44.5	13.7	68.0	7.9	76.1
% as Soluble Sugar	2.3	7.5	7.2	2.4	19.7	1.8	22.1
% as HMF	0.2	0.8	0.4	0.3	1.7	0.3	1.9
					89.3		**100.0**

Lignin Mass Balance Results

170°C/10 min 1st Stage 205°C/5 min 2nd Stage	Horizontal Squeezate	Hydrolyzate	Solids	Discharge Squeezate	Total	Standard Deviation	Normal. Total
% as Insoluble Lignin	8.6	0.0	42.4	12.5	64.4	5.8	73.9
% as Soluble Lignin	9.8	9.8	2.4	1.1	22.7	3.8	26.1
					87.2		**100.0**

Liquid:Solid Ratios and Sugar Concentrations



Liquid:Solid Ratio

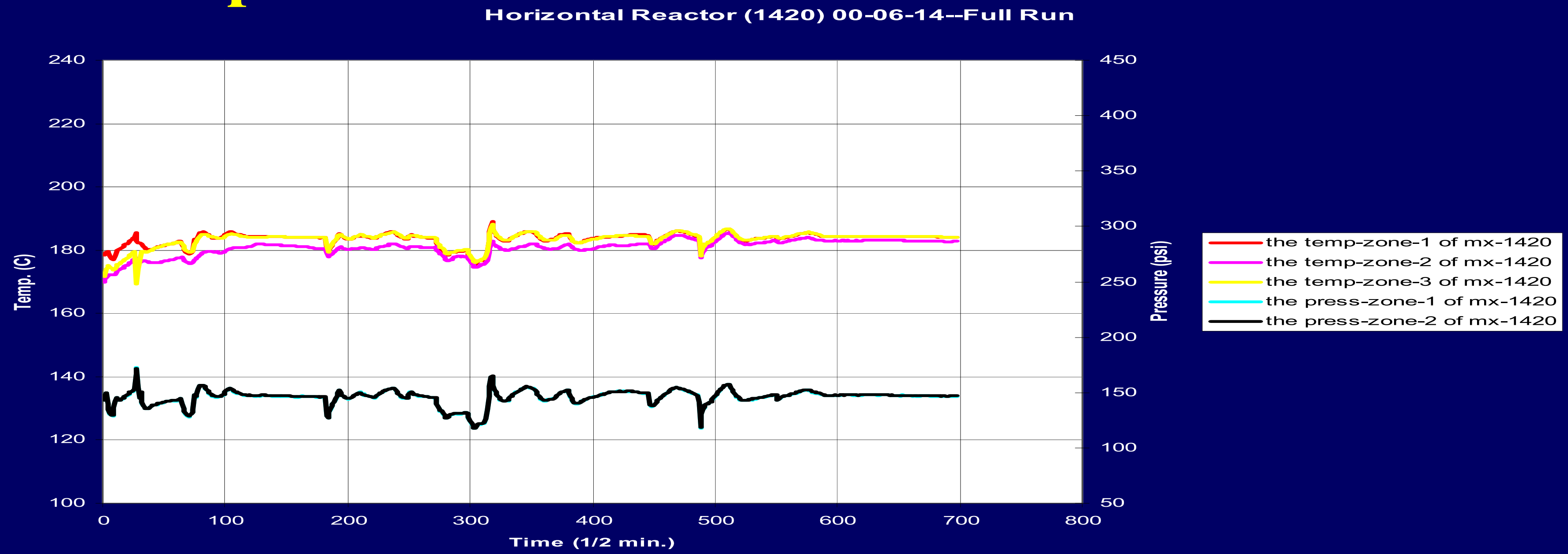
High: $\dfrac{(80-30) + 150 + 700}{100} = 9$

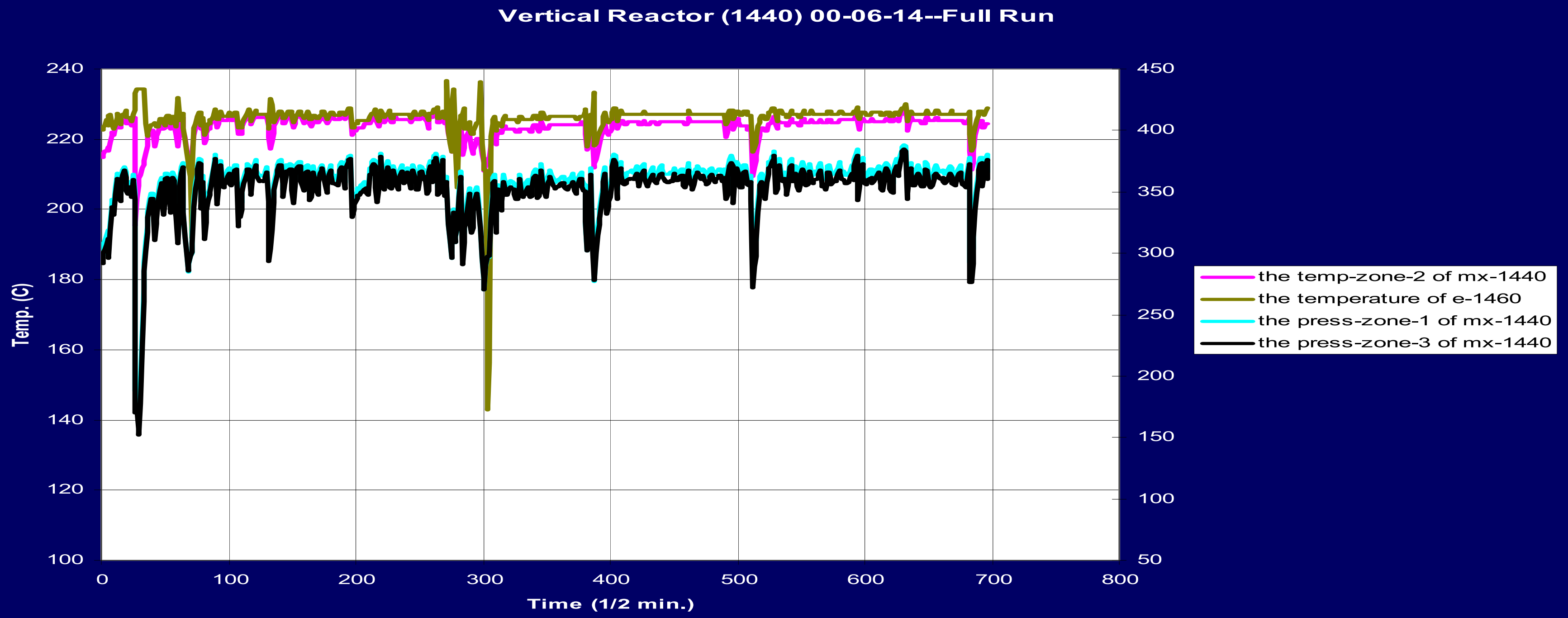
Low: $\dfrac{(80-30) + 100 + 350}{100} = 5$

Soluble Sugar Concentrations (monomer + oligomer)

	Avg. All Runs (g/L)	Avg. Top 5 Runs (g/L)	Highest Run (g/L)
Glucose	8.7	14.3	16.5
Xylose	34.2	43.7	50.0
Total	42.9	58.0	66.5

Temperature/Pressure Data--6 hour run





Potential Re-design of Vertical Reactor Screw Conveyor

Initial Design

- Too much mixing, leads to uneven flow pattern
- Design a conical helical "lifter" in bottom zone at vertical reactor inlet
- Eliminate upper flights to produce a plug flow movement of solids
- Utilize mildly-treated fibrous biomass at vertical reactor inlet to catch fine residual particles from upper reactor zone

Summary of Initial Pilot Reactor Operations

- Pilot-scale reactor system has been operated at targeted conditions in a steady state manner for well over 100 hours of operation time

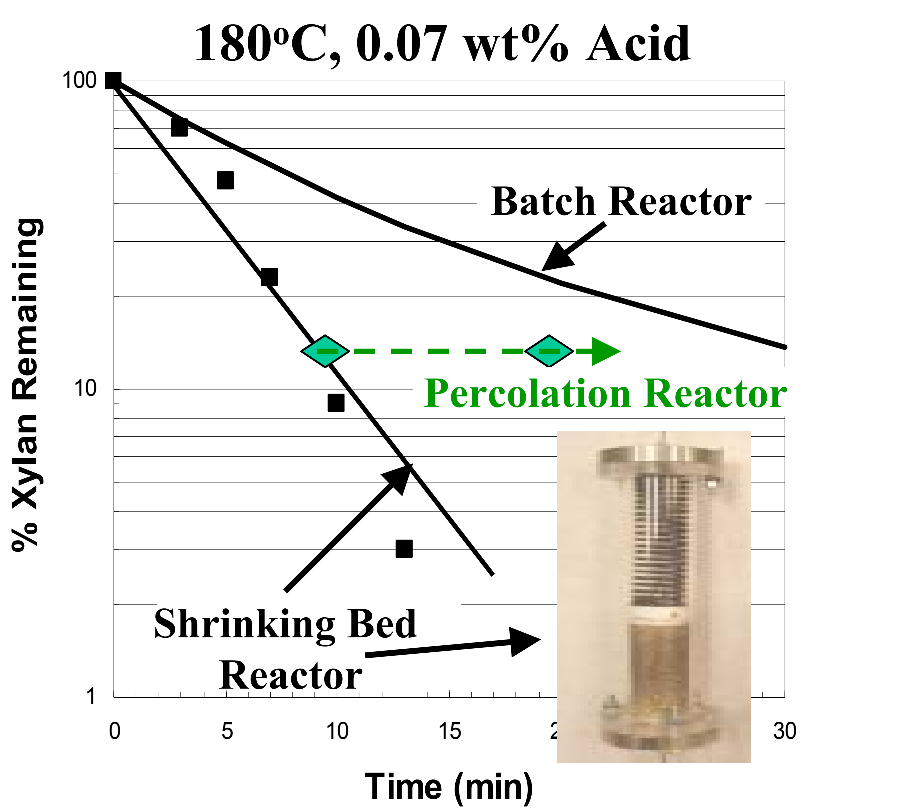
- Xylose yields have substantially met initial target values (>85%) with little optimization

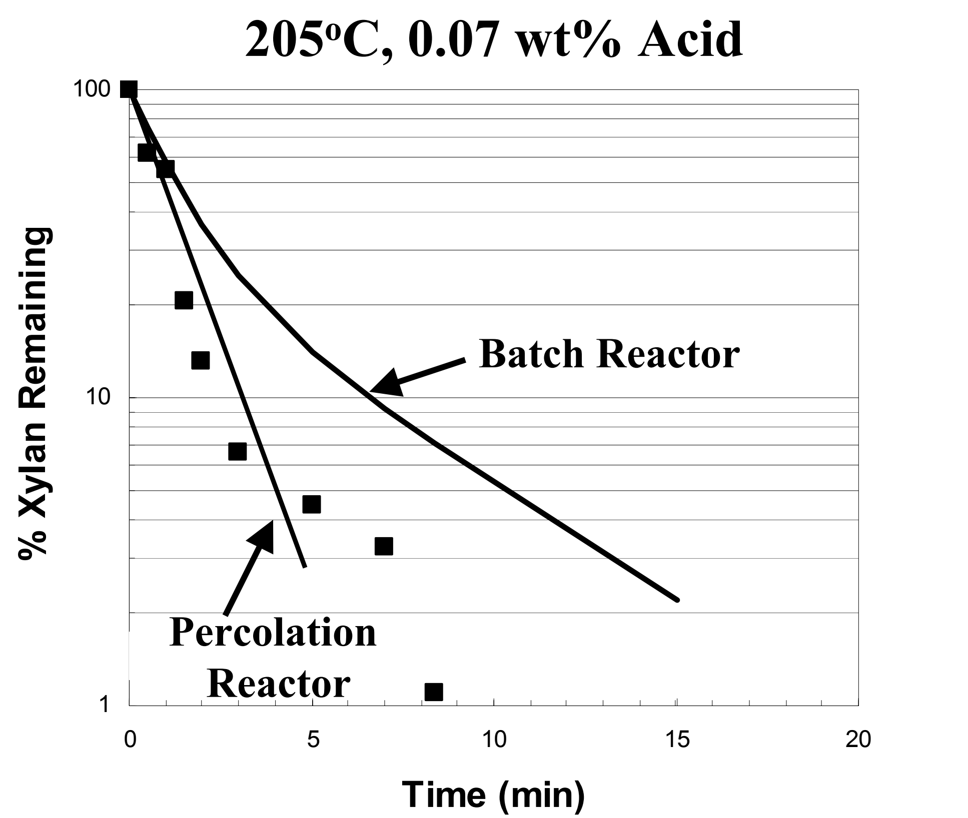
- Using a second stage design height giving an estimated 5 minute residence time, glucose yields are close to expected values based on shrinking bed kinetics

- Initial liquid:solid ratio and hydrolyzate soluble sugar concentration targets have been largely been met; increased residence time in vertical stage leading to greater cellulose conversion should significantly increase glucose concentration

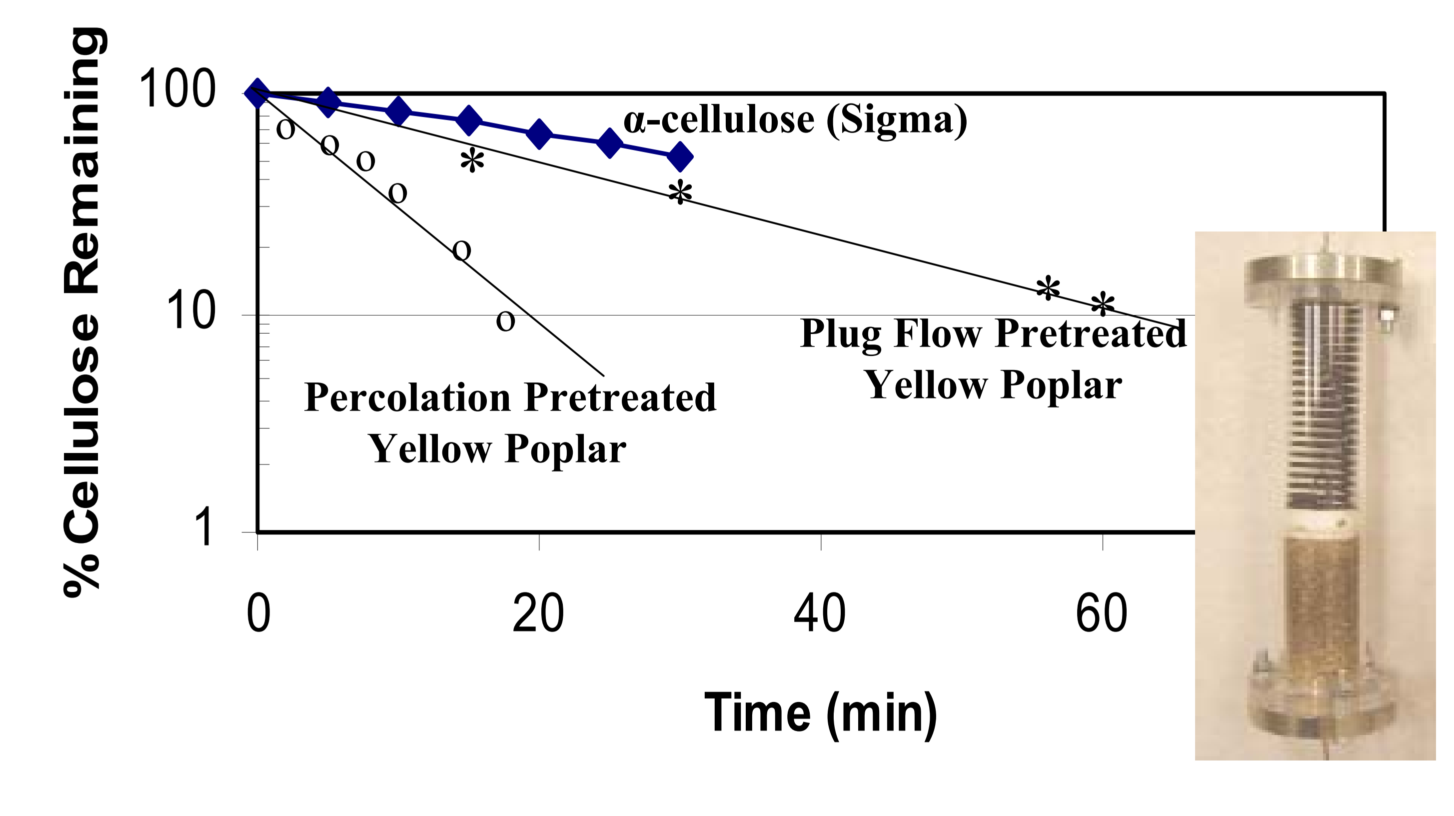
Although the reactor system was initially designed using homogeneous kinetics for both xylan and cellulose hydrolysis and bench results, the kinetics are heterogeneous. The observed global kinetics will, for both polymers, differ with reactor configuration.

Xylan Release Kinetics from Untreated Yellow Poplar as a Function of Reactor Design (0.07 wt% H_2SO_4)



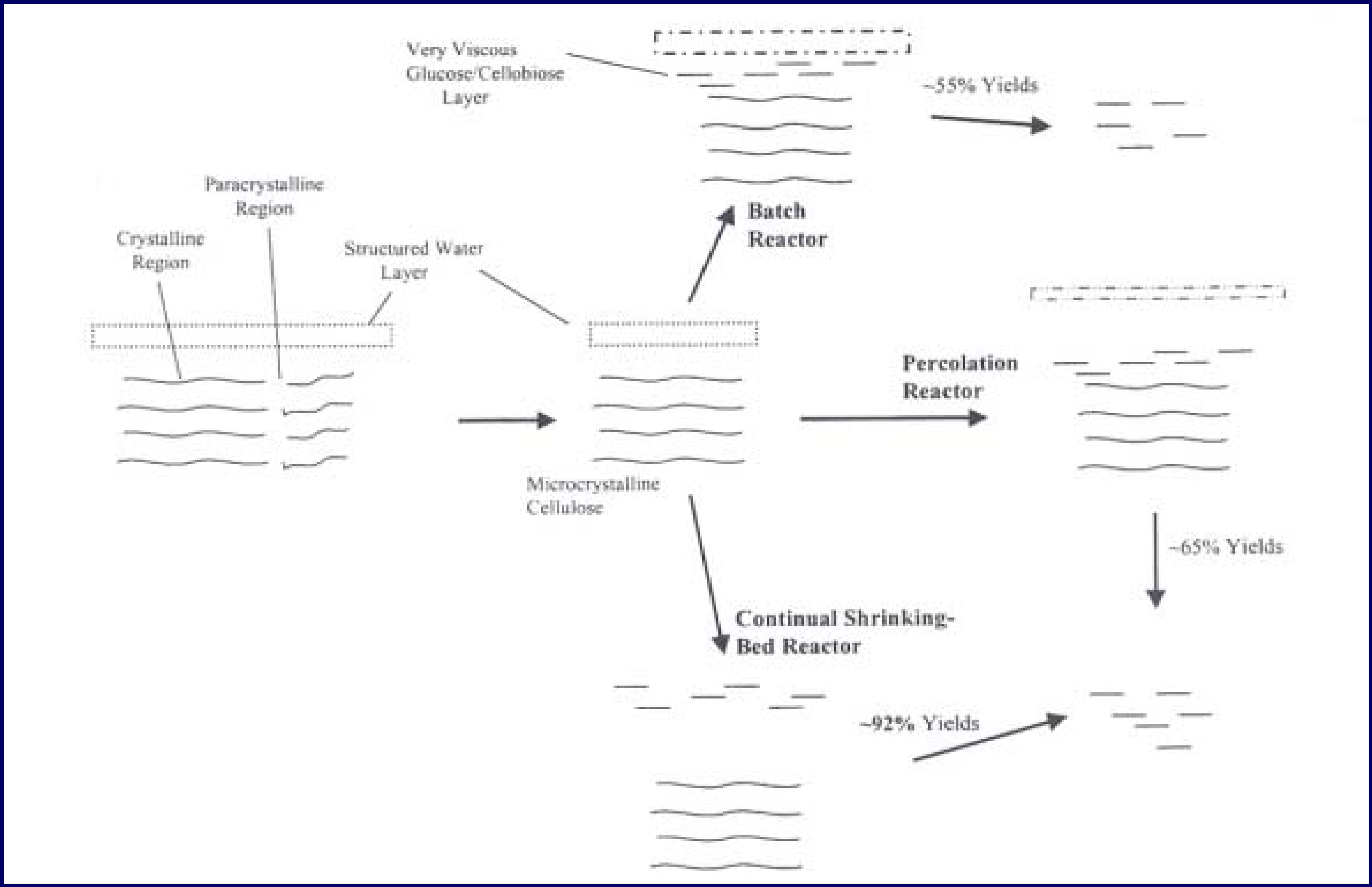


Cellulose Hydrolysis Kinetics using 0.07 wt% acid/205°C and the Shrinking Bed Reactor using Three Different Cellulosic Substrates



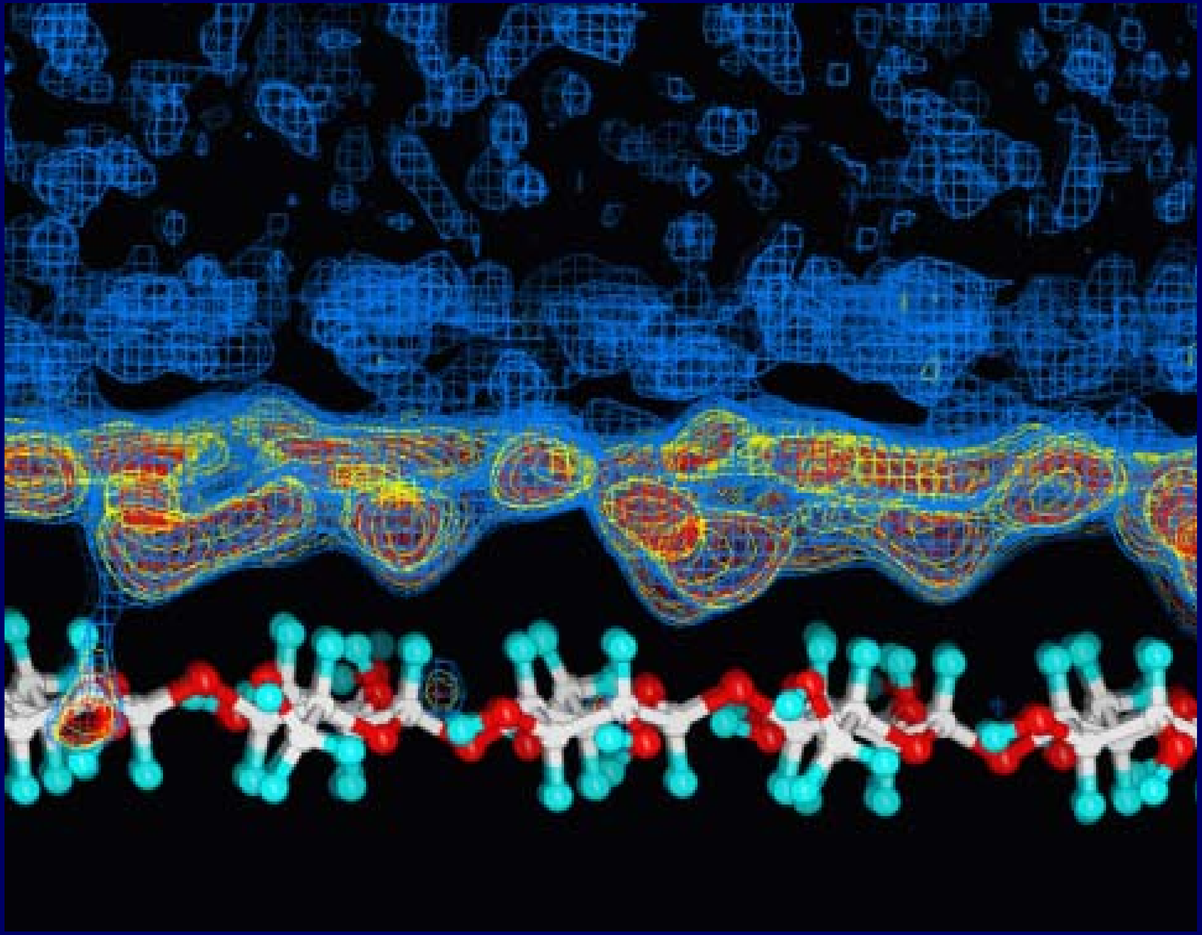
Hypothesized Global Dilute-Acid Hydrolysis Kinetics of Cellulose From Hardwood

Torget et al., *Ind. Eng. Chem. Res.*, Vol. 39, No. 8, 2000



Highly Dense Structured Water Layer Above the Parallel Face of Cellulose at 205 C

A Molecular Dynamics Simulation



bulk density or below

25% above bulk density

50% above bulk density

75% above bulk density

Courtesy of Dr. John Brady, Cornell University

Summary of Global Kinetics for Yellow Poplar Xylan and Cellulose Hydrolysis using Very Dilute Sulfuric Acid (0.07 wt%)

- Bench scale kinetics experiments using different reactor configurations with yellow poplar feedstock indicate the importance of mass transfer considerations in the heterogeneous reaction mechanism

- A structured water boundary layer at the parallel face of a cellulose microcrystal model has been demonstrated to exist through molecular dynamic simulations at 205°C

- These bench and modeling results support the observations that the dilute-acid mediated kinetic release of both polymers cannot be modeled by homogeneous kinetics in all reactor configurations

- These observations have led to new insights for a more global mechanism for thermochemical biomass hydrolysis that will be useful in reactor design modifications and operations

Acknowledgements

This work was funded by the Biochemical Conversion Element of the Office of Fuels Development of the US Department of Energy

Anders Mokvist and Chris Kajzer of Metso Paper, Inc. (formerly Sunds Defibrator), Norcross, GA

Drs. Ray Katzen, Al Converse, Keith Mackie, and Davis Clements for review and constructive criticism of this work

A special thanks to Drs. Y.Y. Lee at Auburn University and John Brady at Cornell University