Comparative Data from Application of Leading Pretreatment Technologies to Corn Stover

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Outline of Talk

- Overview of Consortium
- USDA IFAFS project overview
- Participants and Advisory Board
- Pretreatment technologies
- Selected results and preliminary material balances to date
- Preliminary economic comparisons
- Future work

Brief History of Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI)

- Pretreatment researchers working together in a coordinated, disciplined way to understand the fundamentals underlying lignocellulosic biomass pretreatment and hydrolysis
- Organized in late 1999, early 2000
- CAFI recognizes that pretreatment operates as part of a **system** that includes hydrolysis and fermentation—pretreatment effects on downstream processes <u>must</u> be better understood
- IFAFS opportunity arose in March 2000, and a subset of CAFI pursued and won an award

USDA IFAFS Project Overview

- Multi-institutional effort funded by USDA Initiative for Future Agriculture and Food Systems Program for $1.2 million to develop comparative information on cellulosic biomass pretreatment by leading pretreatment options with common source of cellulosic biomass (corn stover) and identical analytical methods
  - Aqueous ammonia recycle pretreatment - YY Lee, Auburn University
  - Water only and dilute acid hydrolysis by co-current and flowthrough systems - Charles Wyman, Dartmouth College
  - Ammonia fiber explosion (AFEX) - Bruce Dale, Michigan State University
  - Controlled pH pretreatment - Mike Ladisch, Purdue University
  - Lime pretreatment - Mark Holtzapple, Texas A&M University
  - Logistical support and economic analysis - Rick Elander/Tim Eggeman, NREL through DOE Biomass Program funding
- Emphasis on quality not quantity

USDA IFAFS Project Tasks

1. Apply leading pretreatment technologies to prepare biomass for conversion to products
2. Characterize resulting fluid and solid streams
3. Close material and energy balances for each pretreatment process
4. Determine cellulose digestibility and liquid fraction fermentability/toxicity
5. Compare performance of pretreatment technologies on corn stover on a consistent basis

Project period: 2000-2003

USDA IFAFS Project Advisory Board

Serve as extension agents for technology transfer
Provide feedback on approach and results
Meet with team every 6 months

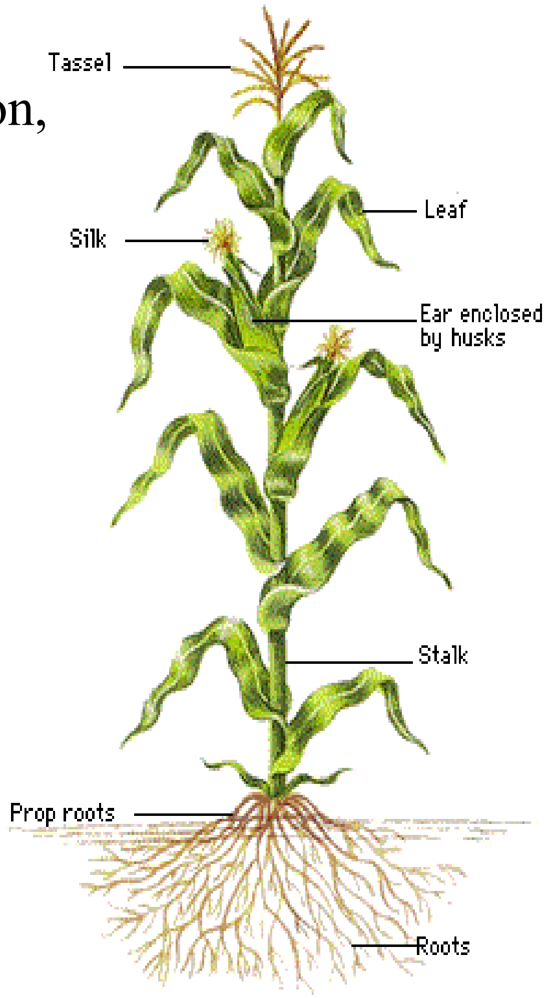
Mat Peabody, Applied CarboChemicals
Greg Luli, BC International
Paris Tsobanakis, Cargill
Robert Wooley, Cargill Dow
James Hettenhaus, CEA
Kevin Gray, Diversa
Paul Roessler, Dow
Susan Hennessey, DuPont

Michael Knauf, Genencor
Don Johnson, GPC (Retired)
Dale Monceaux, Katzen Engineers
John Nghiem, MBI
Rene Shunk, National Corn Growers Association
Joel Cherry, Novozymes
Leo Petrus, Shell

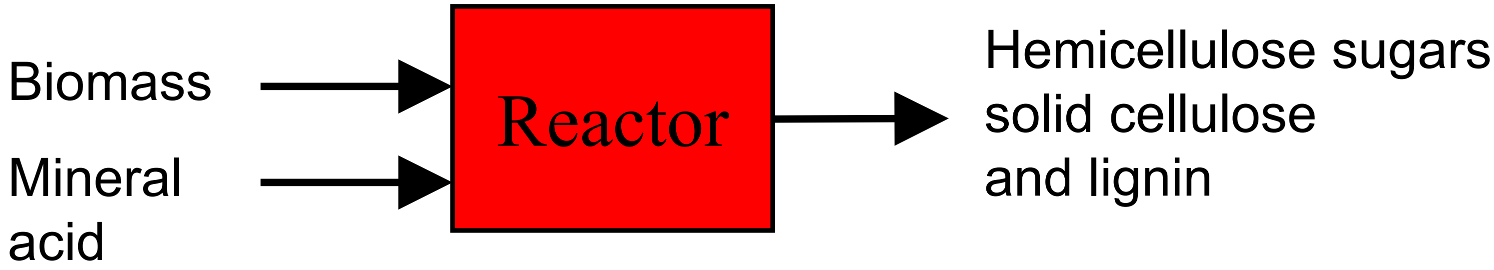
Corn Stover Composition

- NREL supplied corn stover to all project participants (source: BioMass AgriProducts, Harlan IA)
- Stover washed and dried in small commercial operation, knife milled to pass ¼ inch round screen

Glucan	**36.1 %**
Xylan	**21.4 %**
Arabinan	**3.5 %**
Mannan	**1.8 %**
Galactan	**2.5 %**
Lignin	**17.2 %**
Protein	**4.0 %**
Acetyl	**3.2 %**
Ash	**7.1 %**
Uronic Acid	**3.6 %**
Non-structural Sugars	**1.2 %**



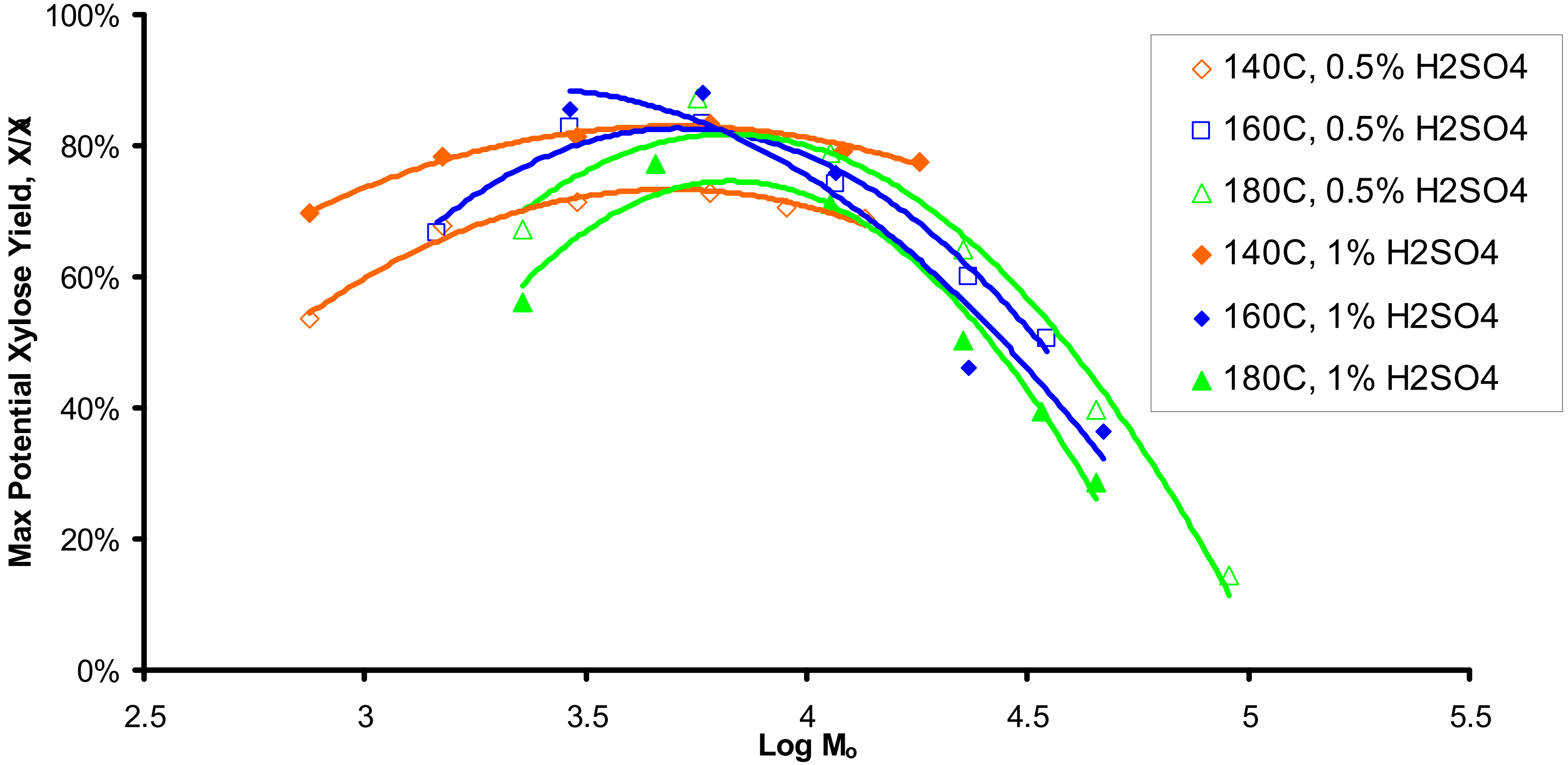
Dilute Acid Pretreatment



- Mineral acid gives good hemicellulose sugar yields and high cellulose digestability
- Sulfuric acid usual choice because of low cost
- Requires downstream neutralization and conditioning
- Typical conditions: 100-200^{o}C, 50 to 85% moisture, 0-1% H_2SO_4
- Some degradation of liberated hemicellulose sugars

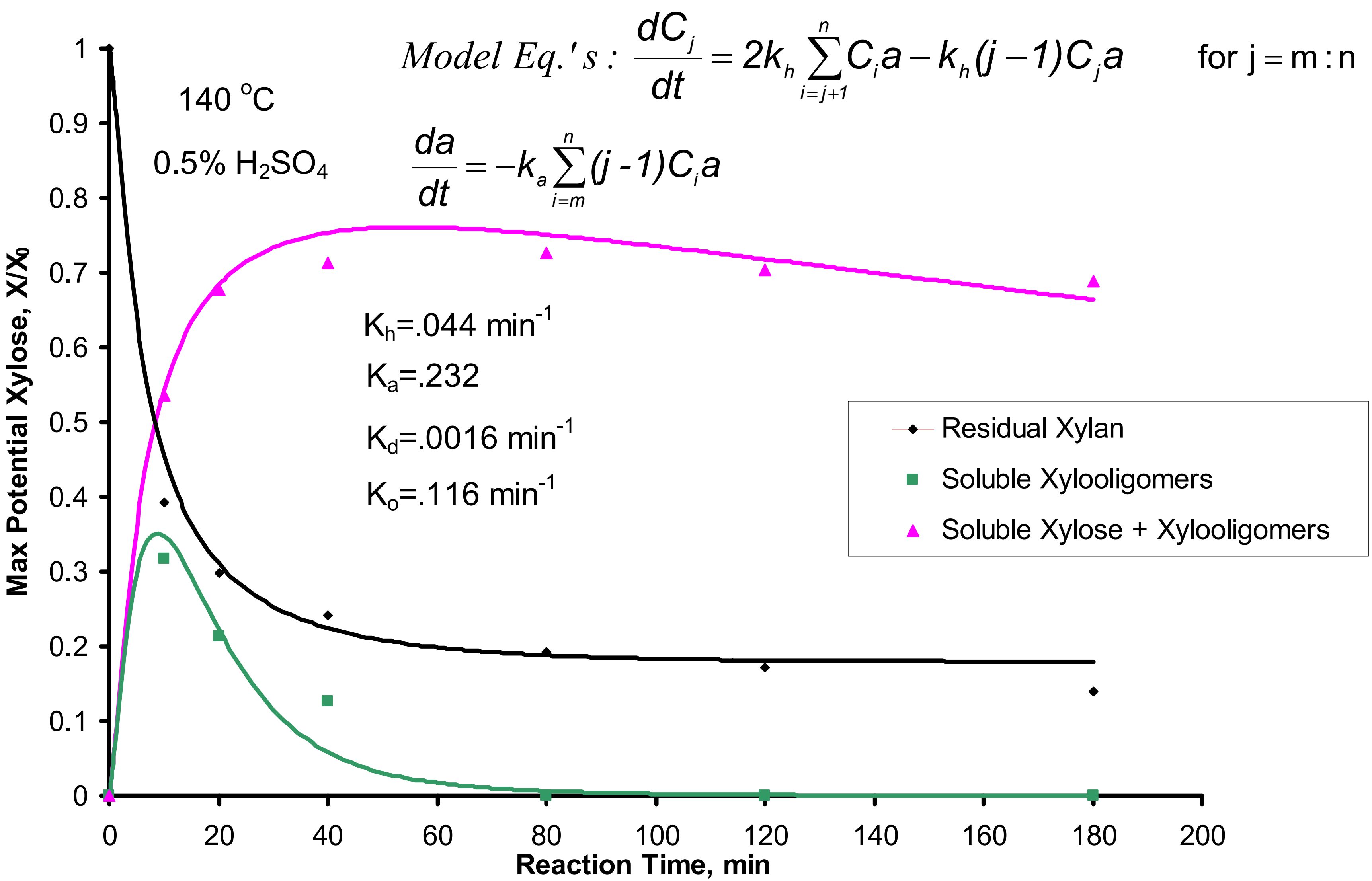
Reactor Systems Employed

Solubilized Xylan Partition vs. LogM_o – Dilute Sulfuric Acid

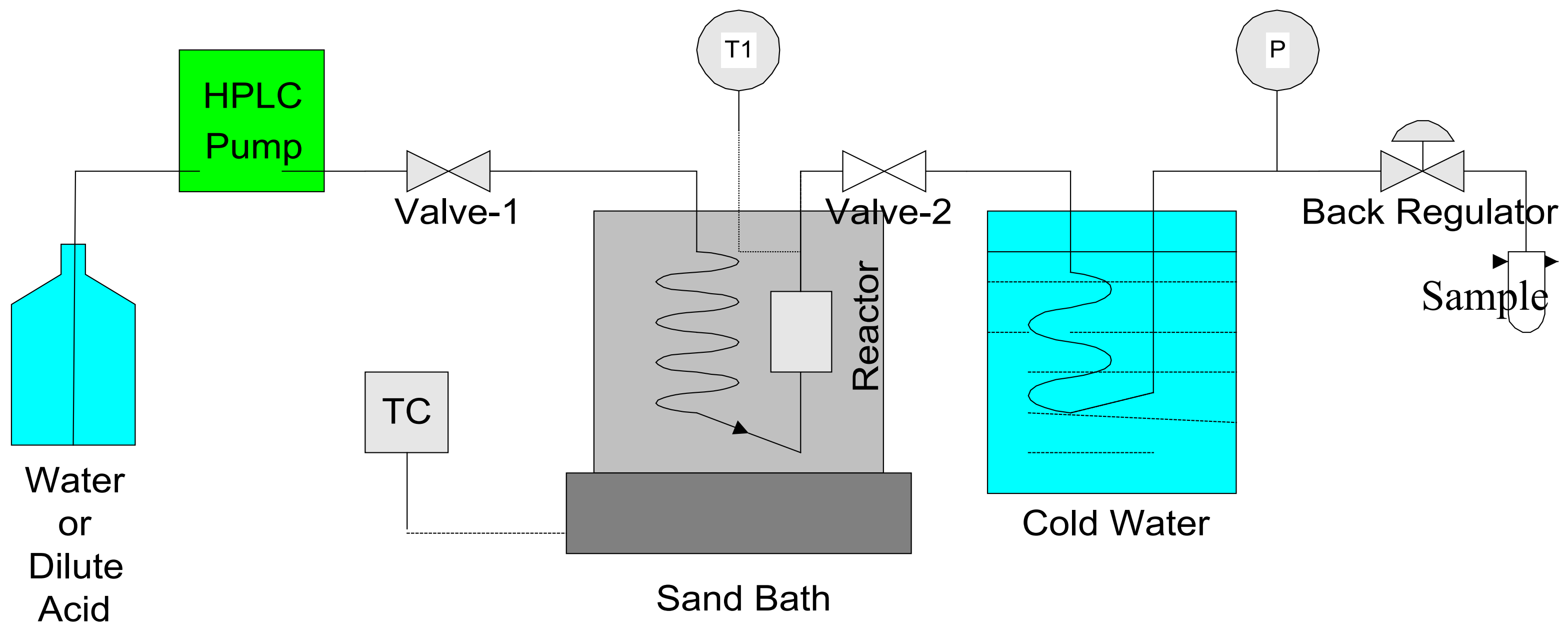


$$Mo = t\ A^n \exp\{(T - 100)/14.75\} \text{ – for acid}$$

Fate of Xylan for Dilute Acid Hydrolysis

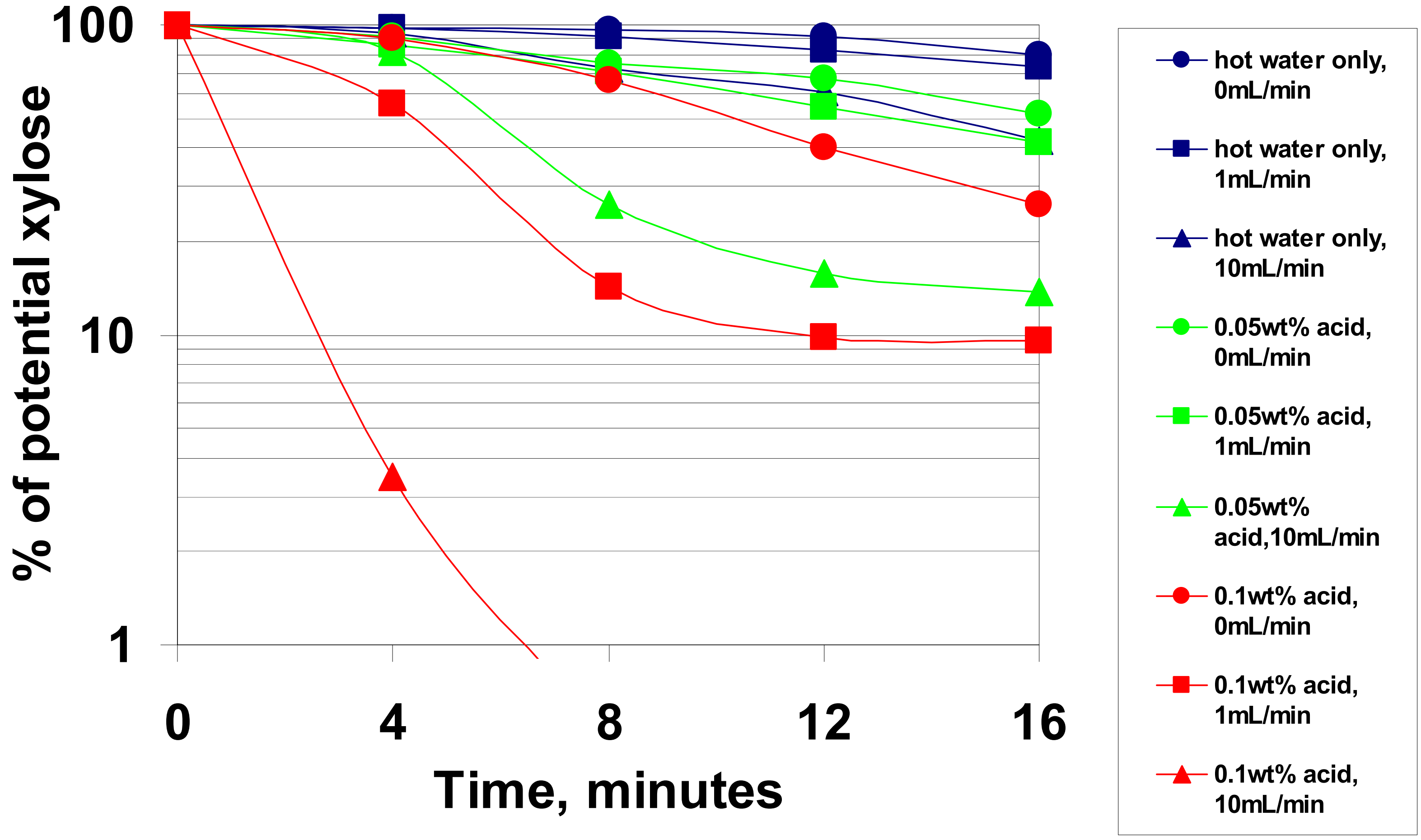


Schematic Diagram of Flowthrough Pretreatment

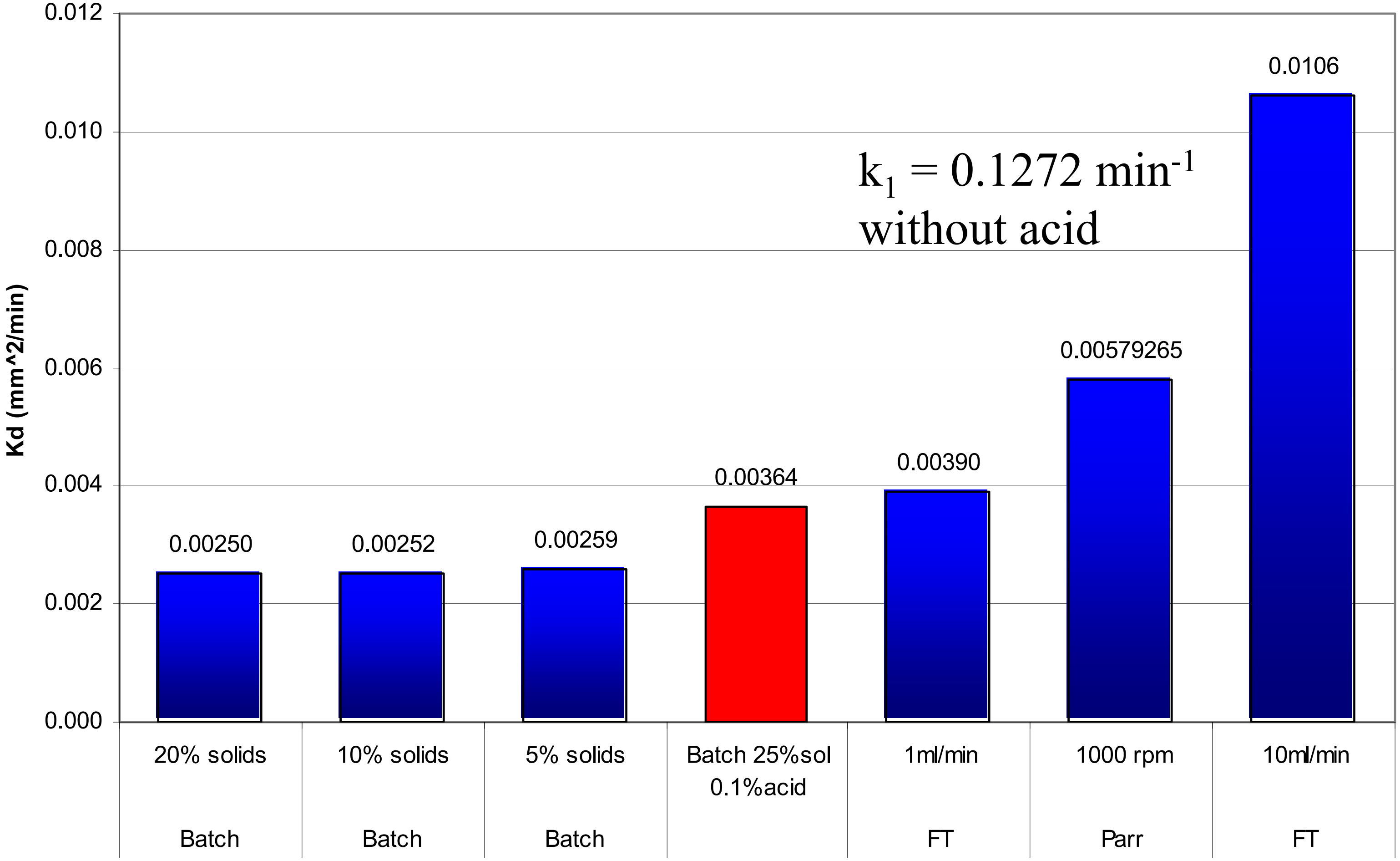


Thayer School of Engineering at Dartmouth College

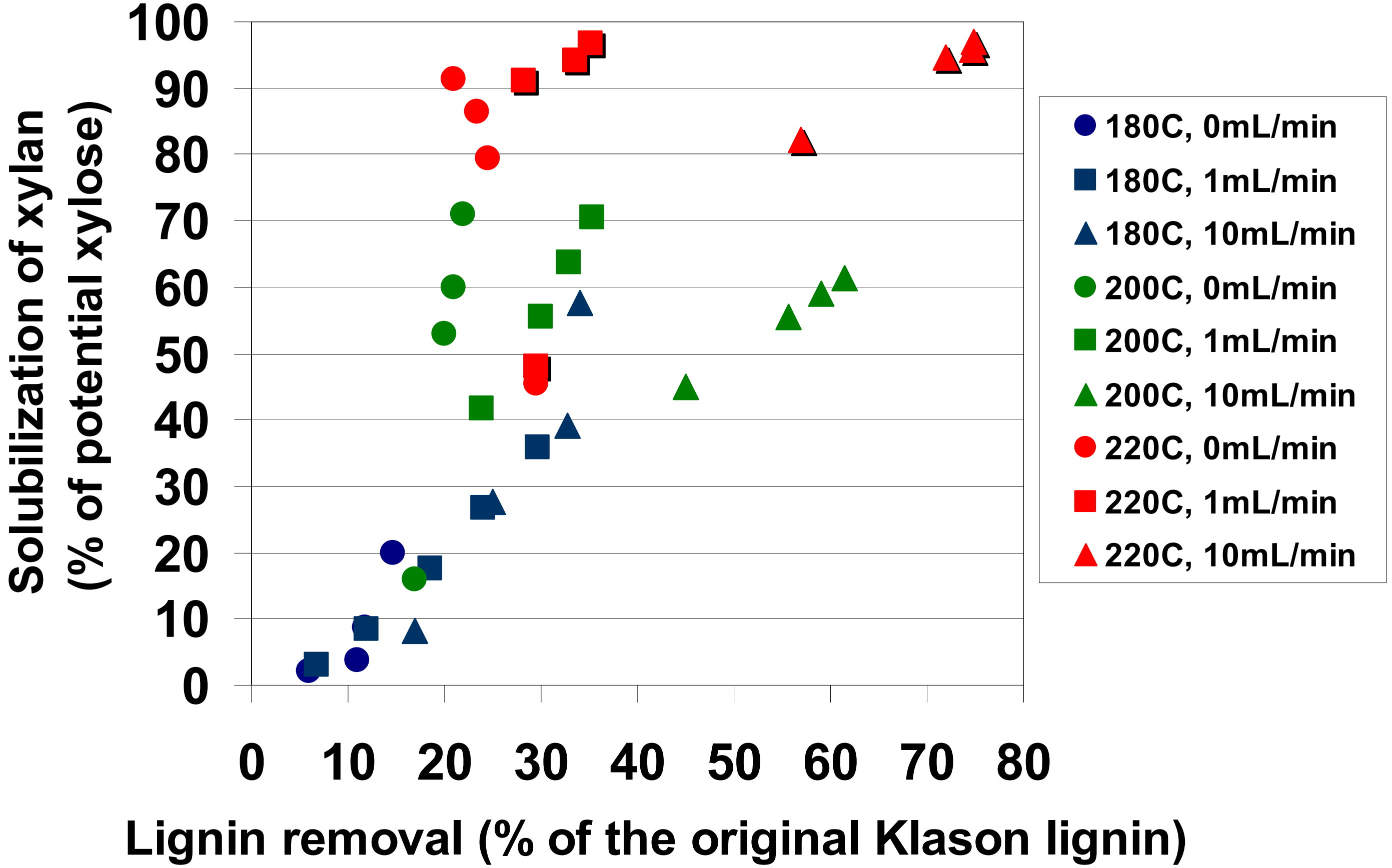
Effect of Flow Rate and Acid on Residual Xylose at 180°C



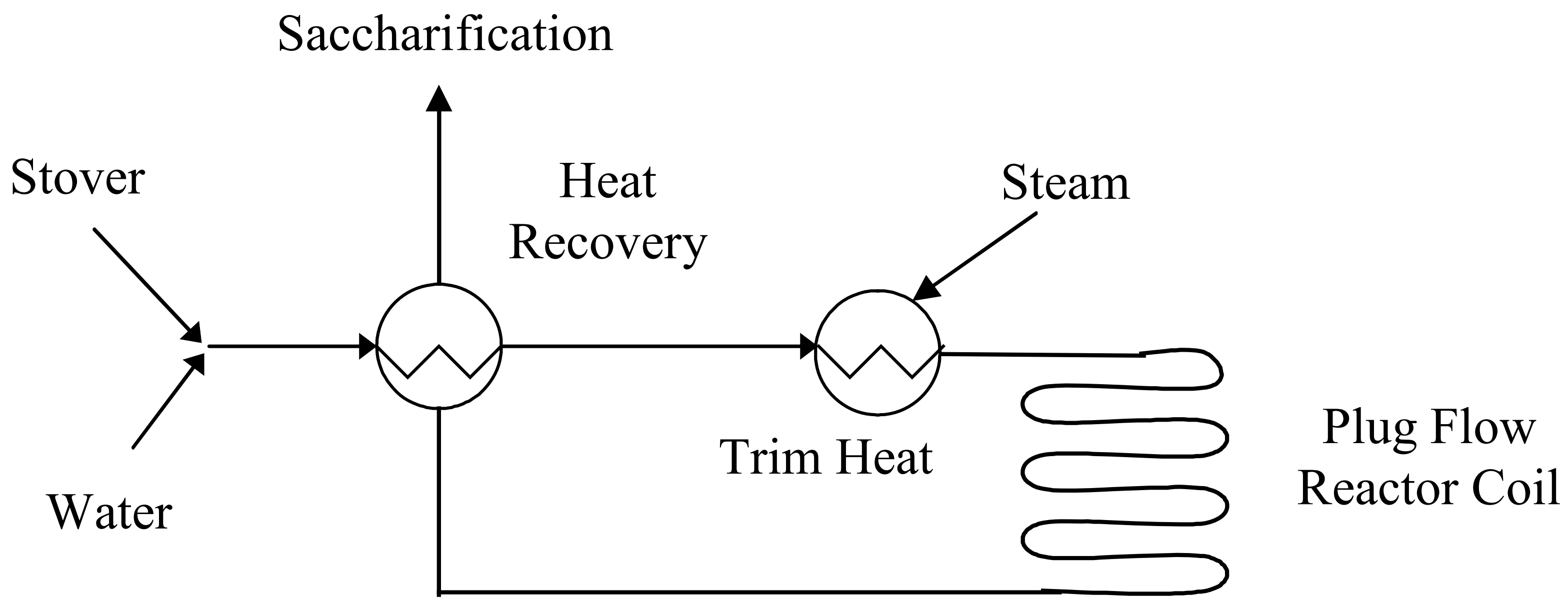
Initial Mass Transfer Coefficient k_d for Water Only Hydrolysis Changes with Reactor Type (180°C)



Solubilization of Xylan and Lignin for Water Only Hydrolysis

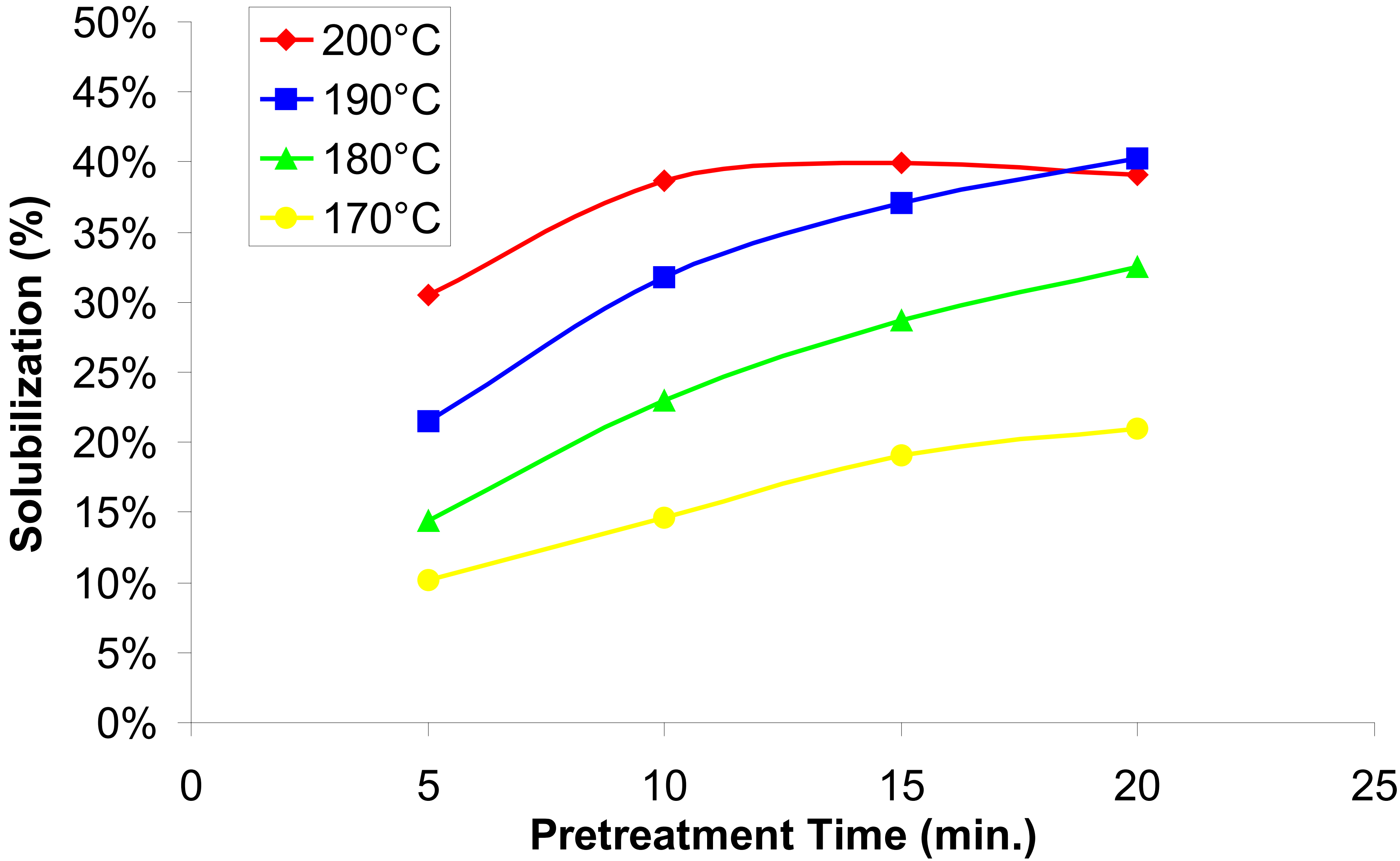


Controlled pH Pretreatment



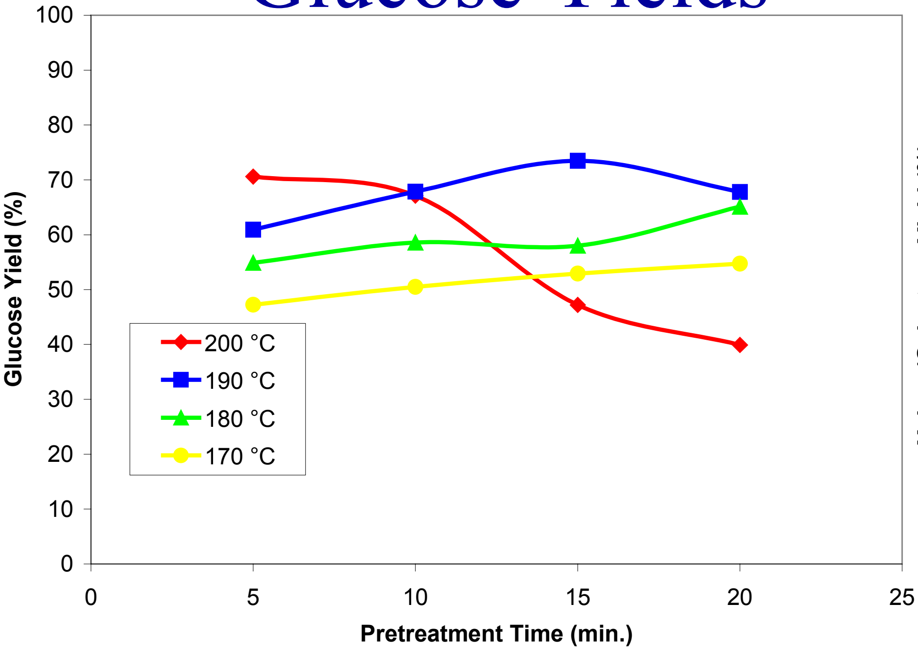
- pH control through buffer capacity of liquid
- No fermentation inhibitors, no wash stream
- Minimize hydrolysis to monosaccharides thereby minimizing degradation

Solubilization of Corn Stover by Controlled pH Pretreatment

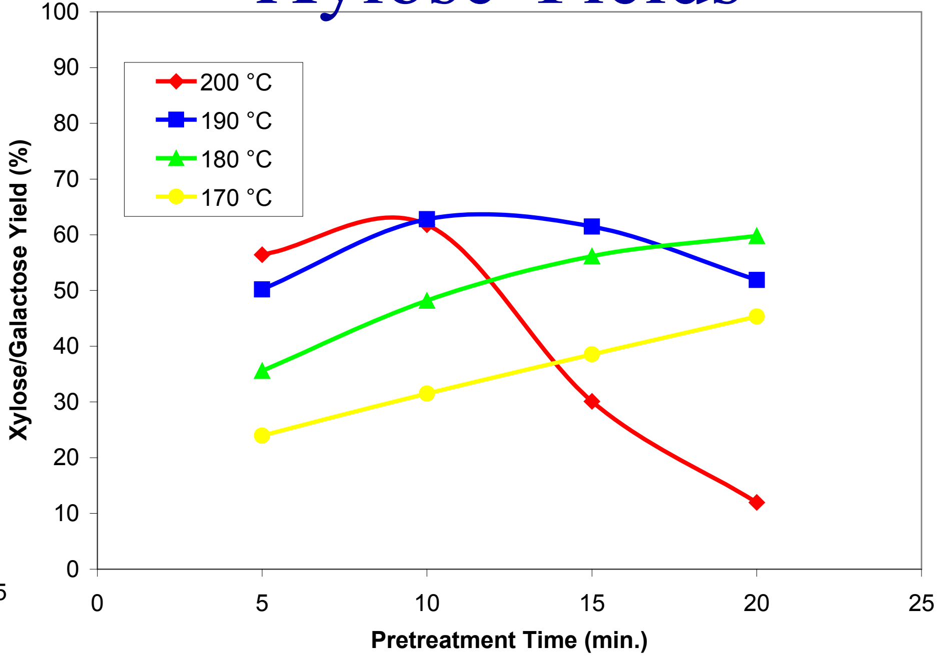


Cellulose Digestibility vs Hemicellulose Solubilization

Glucose Yields

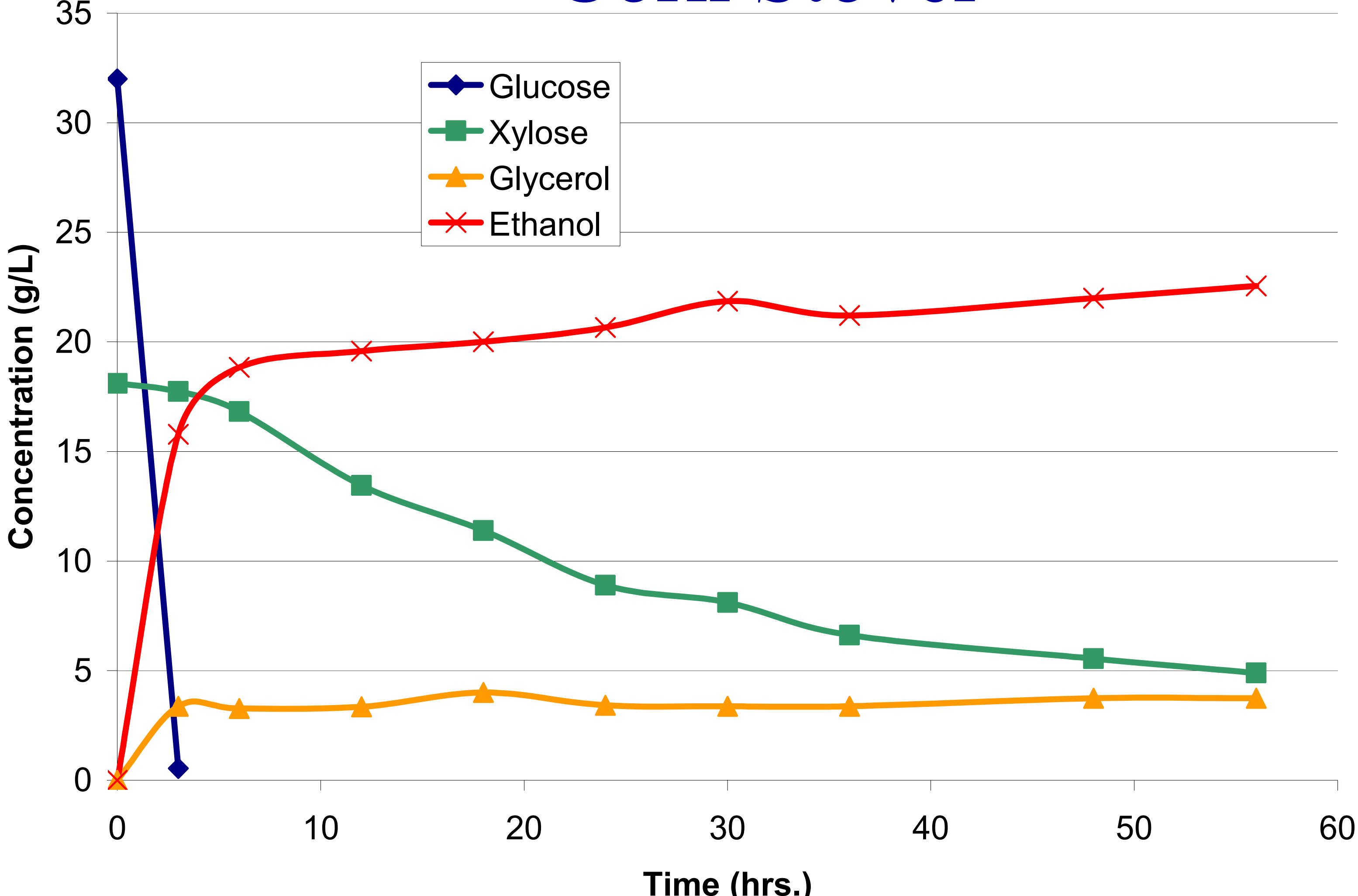


Xylose Yields



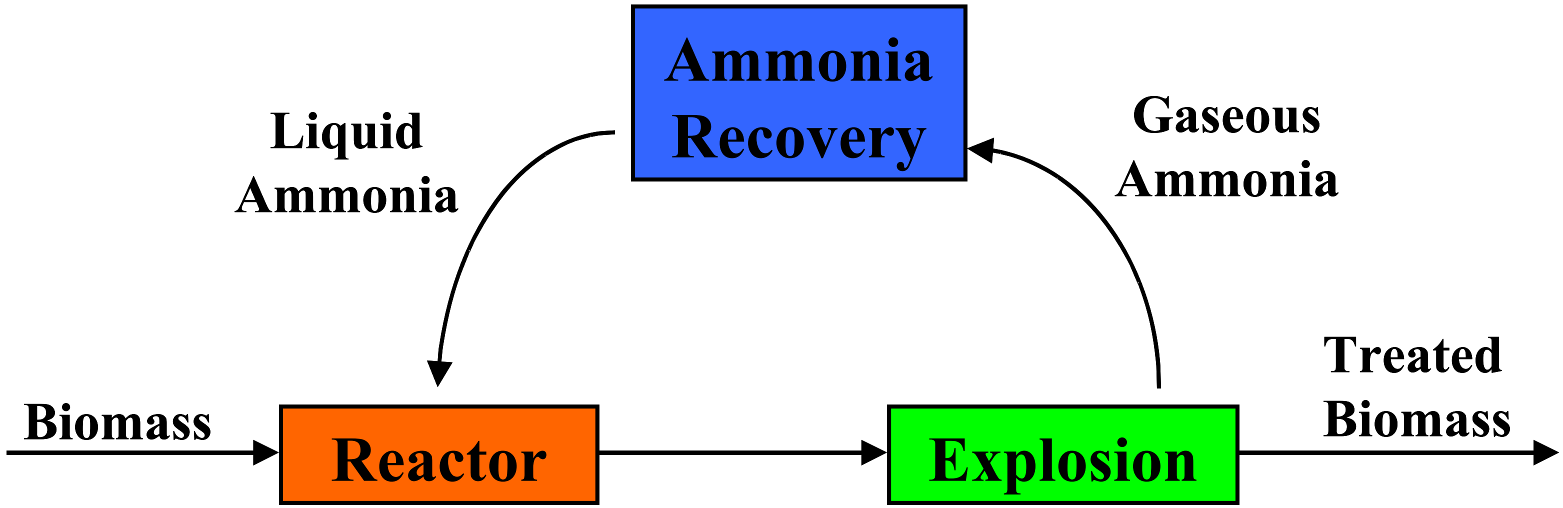
Controlled pH Hot Water Pretreatment (non flow-through) improves digestibility primarily by removal of hemicellulose <u>without</u> degrading the monosaccharides → improved porosity / enzyme accessibility

Fermentation of Pretreated, Saccharified Corn Stover



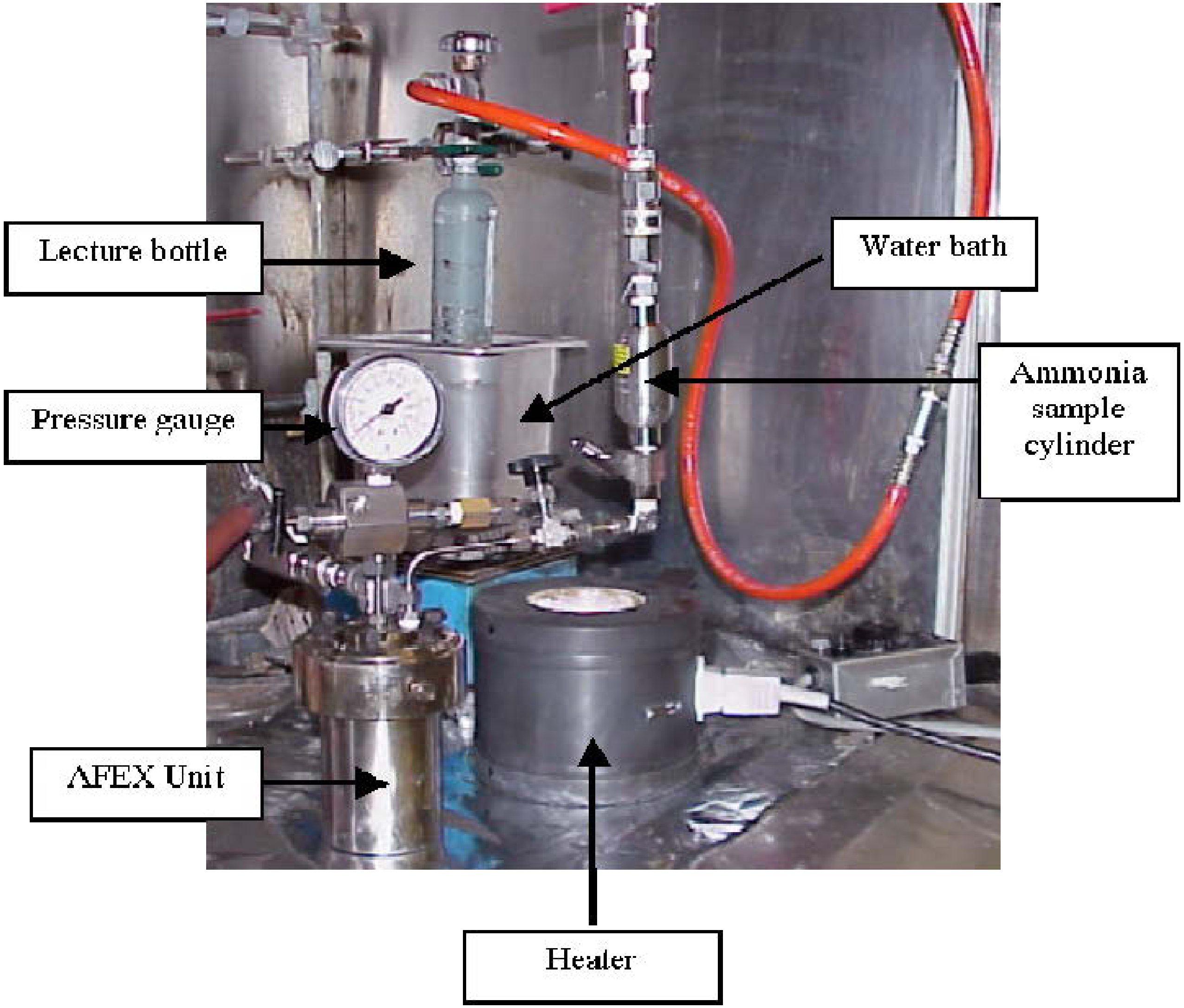
Xylose Fermenting Recombinant Yeast 426A (LNH-87).
Data provided by Dr. Nancy Ho.

What is AFEX/FIBEX?

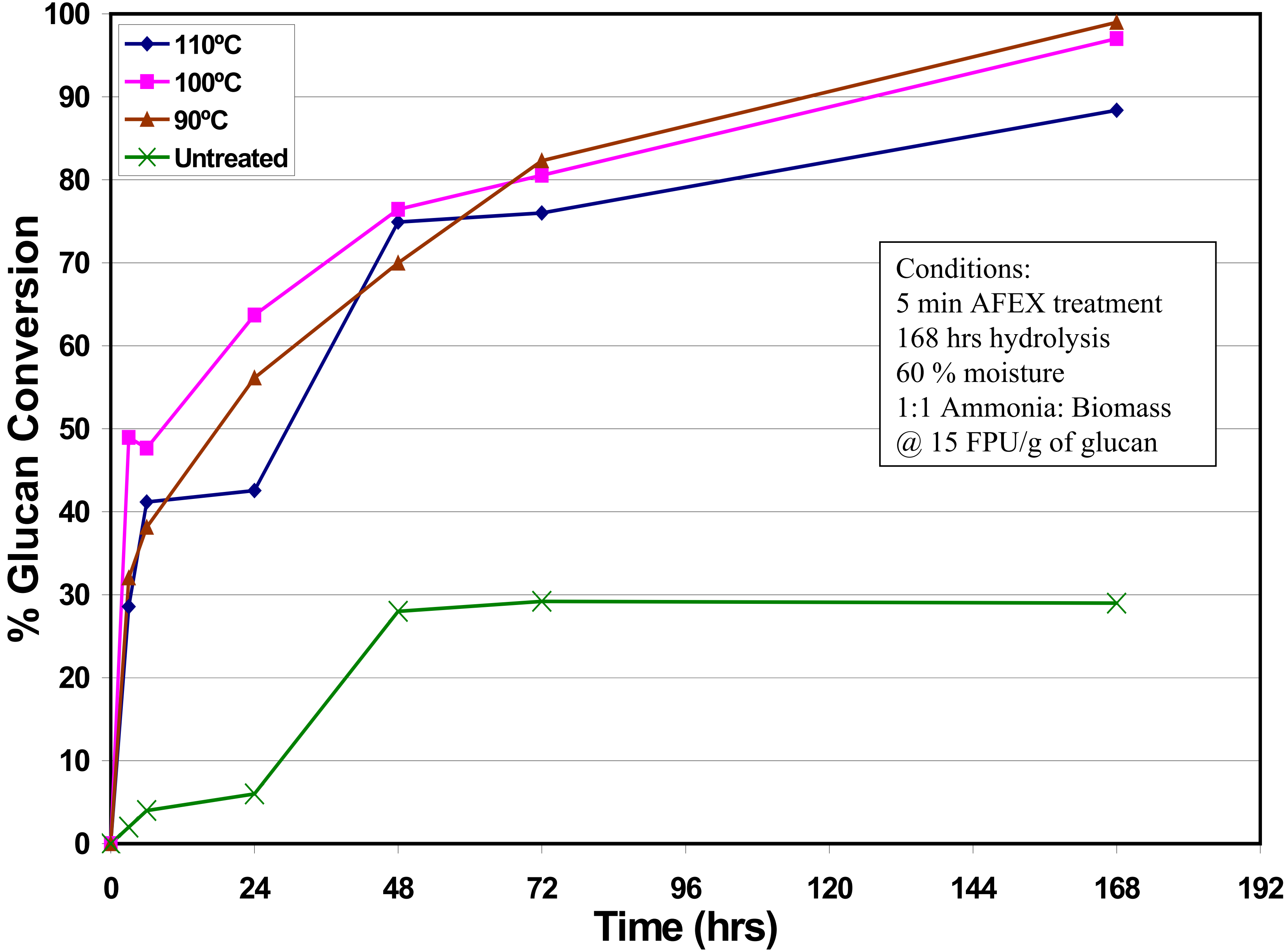


- Liquid "anhydrous" ammonia treats and explodes biomass
- Ammonia is recovered and reused
- Ammonia can serve as N source downstream
- Batch process is AFEX; FIBEX is continuous version
- Conditions: 60-110°C, moisture 20-80%, ammonia:biomass ratio 0.5-1.3 to 1.0 (dry basis)
- Moderate temperatures, pH prevent/minimize sugar & protein loss
- No fermentation inhibitors, no wash stream required, no overliming
- Only sugar oligomers formed, no detectable sugar monomers
- Few visible physical effects

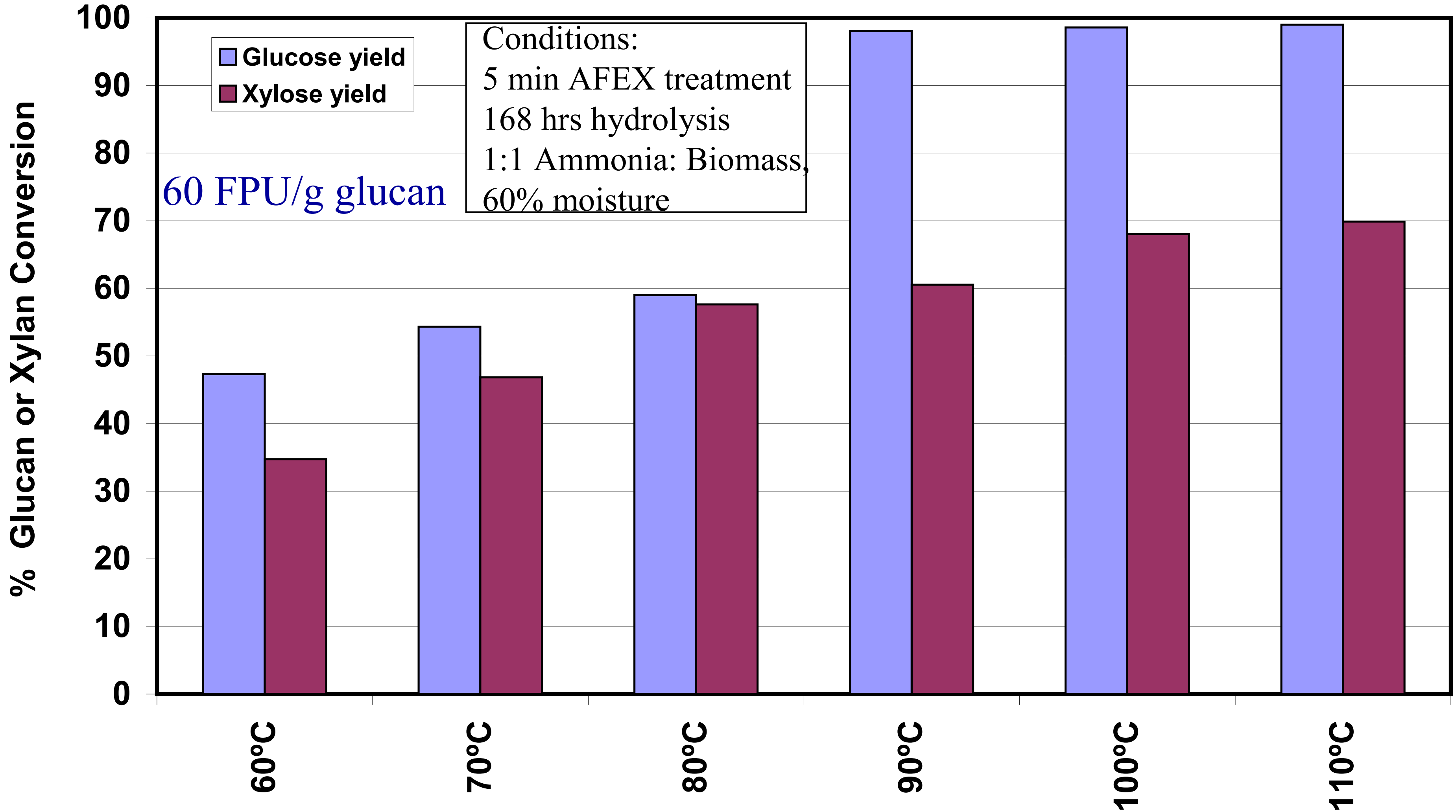
Experimental Ammonia Fiber Explosion (AFEX) System



Kinetics of Glucan Hydrolysis



Conversion of Glucan and Xylan vs. AFEX Treatment Temperature



Features of Ammonia Recycle Pretreatment (ARP)

- Aqueous ammonia is used as the pretreatment reagent:
  - **Efficient delignification**
  - **Volatile nature of ammonia makes it easy to recover**
- Flowthrough column reactor is used
- Value-added byproducts are obtained
  - **Low-lignin cellulose ("filler fiber" grade)**
  - **Uncontaminated lignin**

Composition and Digestibility for ARP Pretreatment

Flow rate [mL/min]	Solid[1]			Liquid[1]		Digestibility[2]	
	Lignin	Glucan	Xylan	Glucan	Xylan	60FPU	15FPU
Untreated	17.2	36.1	21.4	-	-	21.2	15.7
2.5	6.4	35.9	10.7	0.5	10.6	91.5	83.2
5.0	*5.1*	*35.6*	*10.3*	*0.5*	*10.1*	*91.3*	*86.9*
7.5	5.6	35.7	10.1	0.8	10.5	93.4	86.9

Note.; 1. All data based on original feed. 2. **Enzymatic hydrolysis conditions**; 60 or 15 FPU/g of glucan, pH 4.8, 50°C, 150 rpm, at 72h

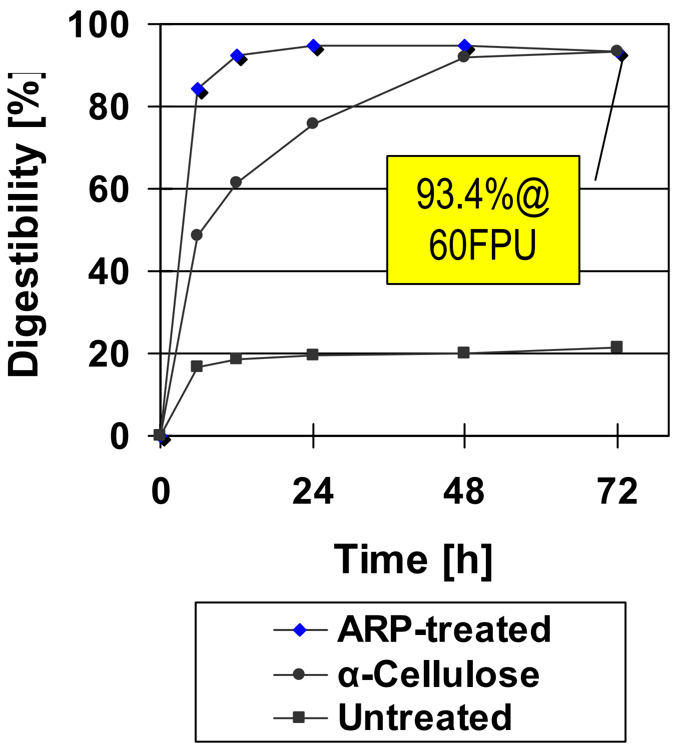
- **Pretreatment conditions**

✓ Liquid throughput: 3.3 mL of 15 wt% NH_3 per g of corn stover at 170 °C

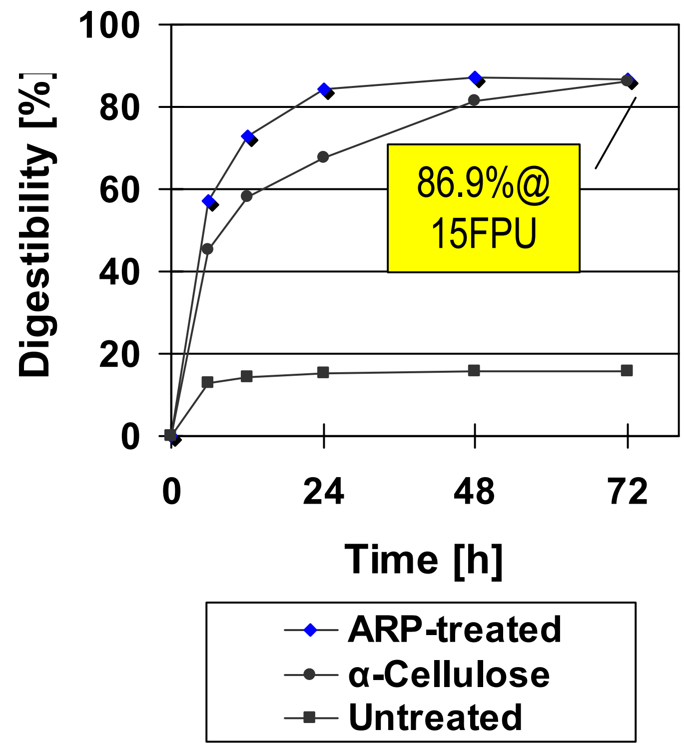
✓ Air dried corn stover is used without presoaking.

Enzymatic Hydrolysis of a Representative ARP Sample (15 wt% NH_3, 170ºC)

60 FPU/g of glucan

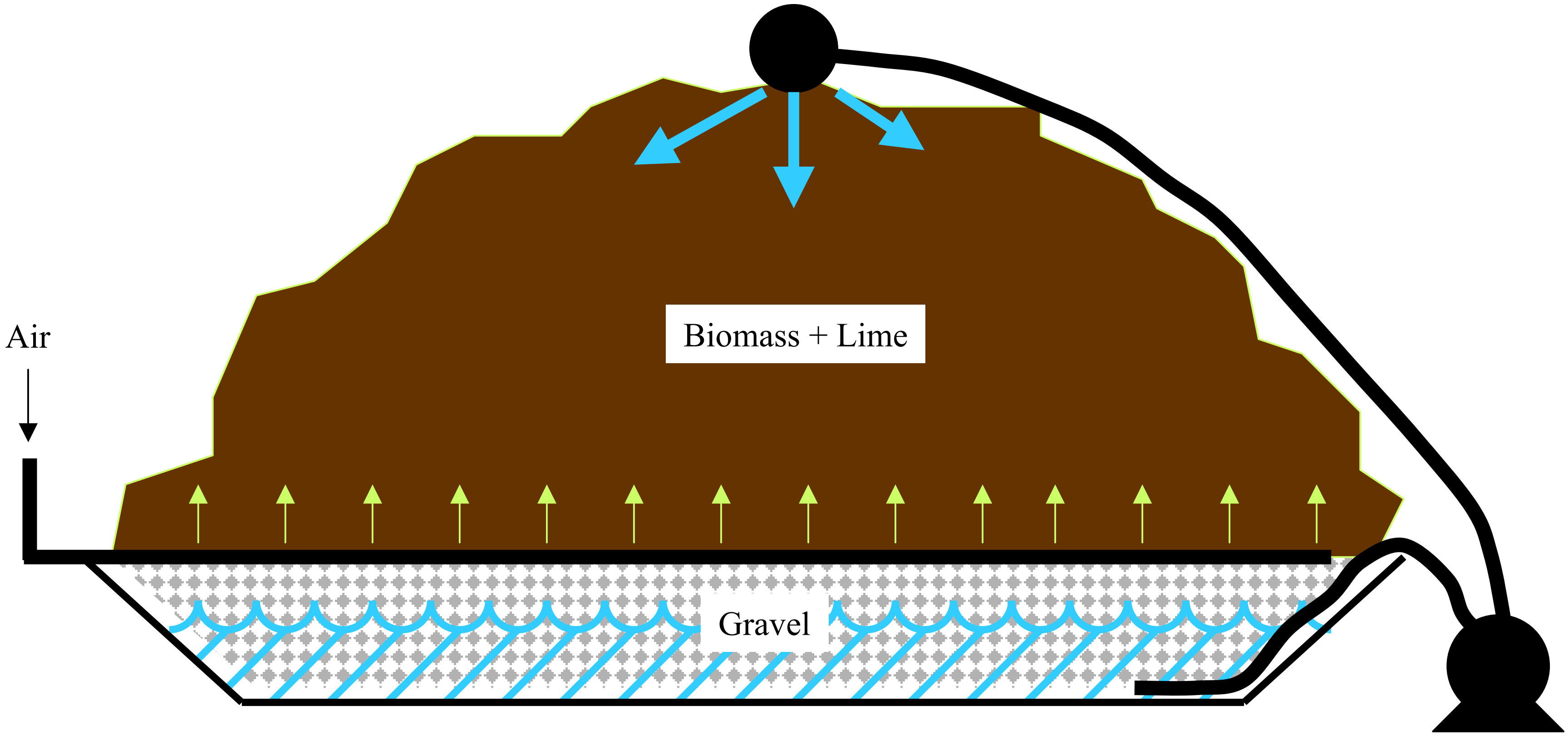


15 FPU/g of glucan



Pretreatment conditions: 170°C, 3.3 mL of 15 wt% of ammonia per g of corn stover, 2.3 MPa;
Enzymatic hydrolysis conditions : 60 or 15 FPU/g cellulose, pH 4.8, 50°C, 150 rpm ; α

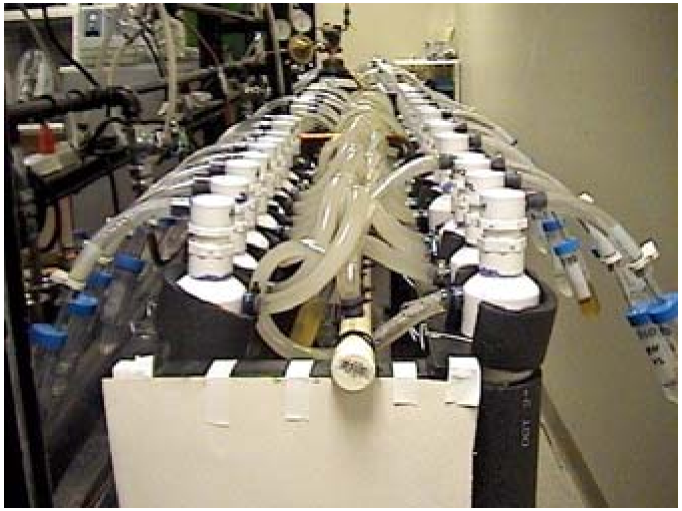
Lime Pretreatment

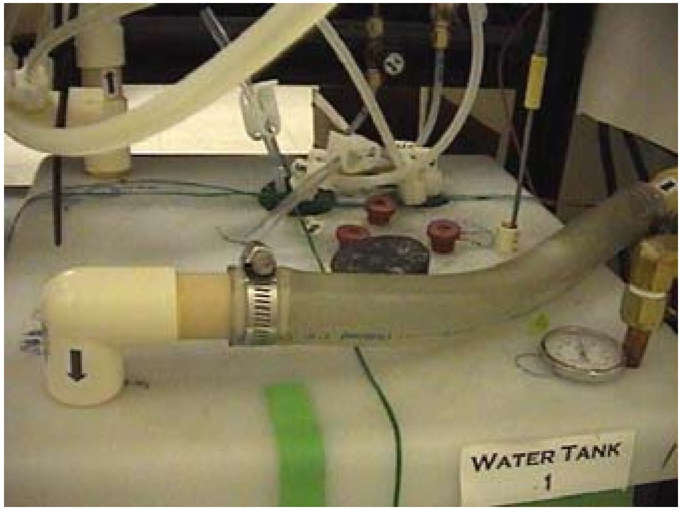


Typical Conditions:

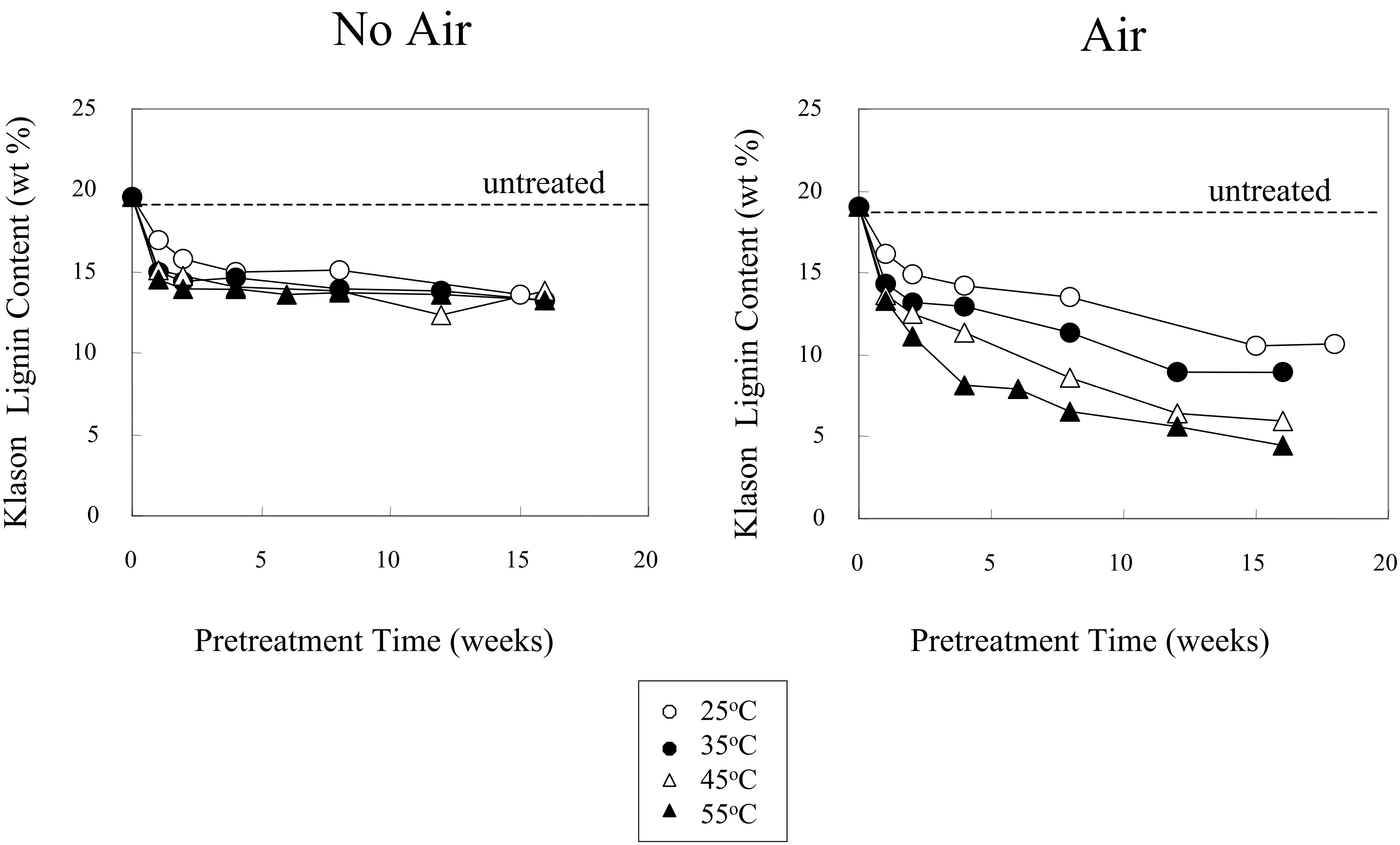
- Temperature = 25 – 55°C
- Time = 1 – 2 months
- Lime Loading = 0.1 – 0.2 g $Ca(OH)_2$/g biomass

Reactor System for Lime Pretreatment

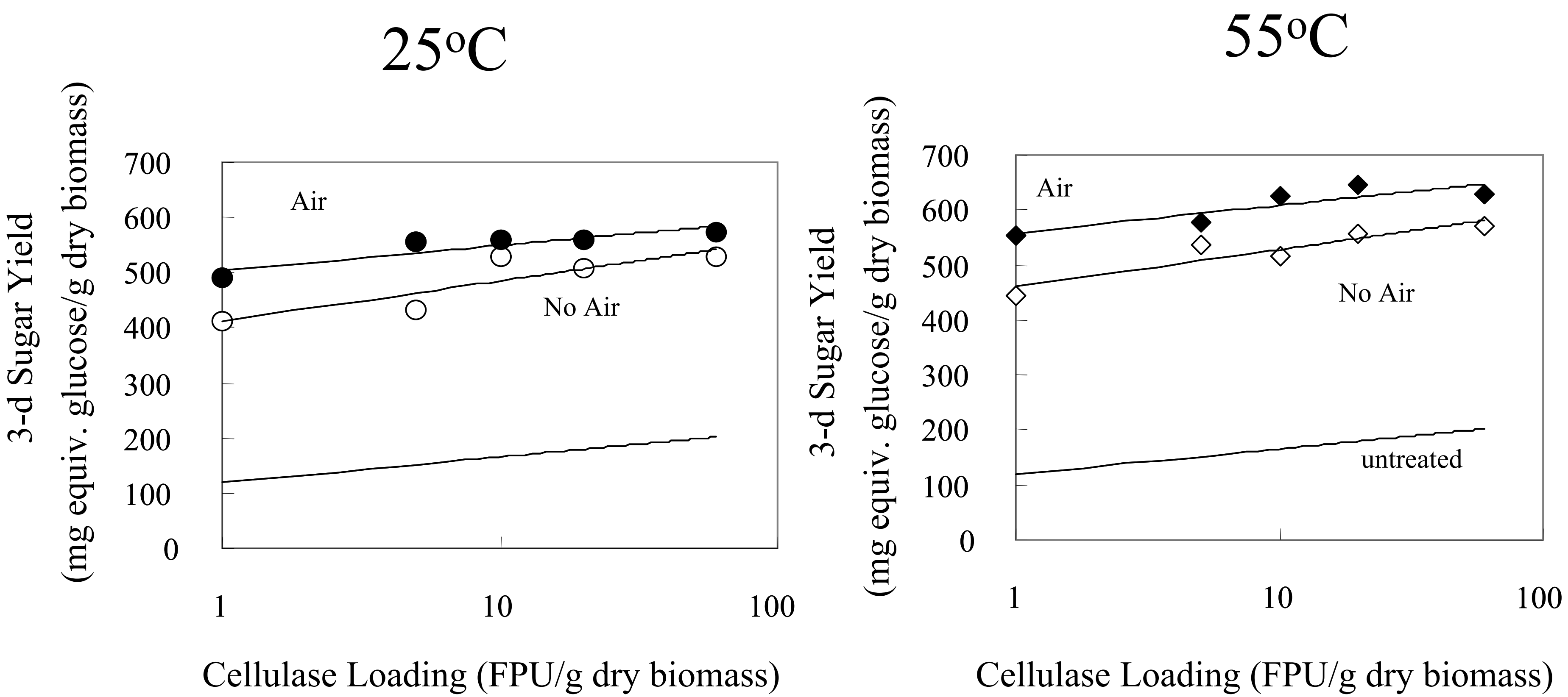




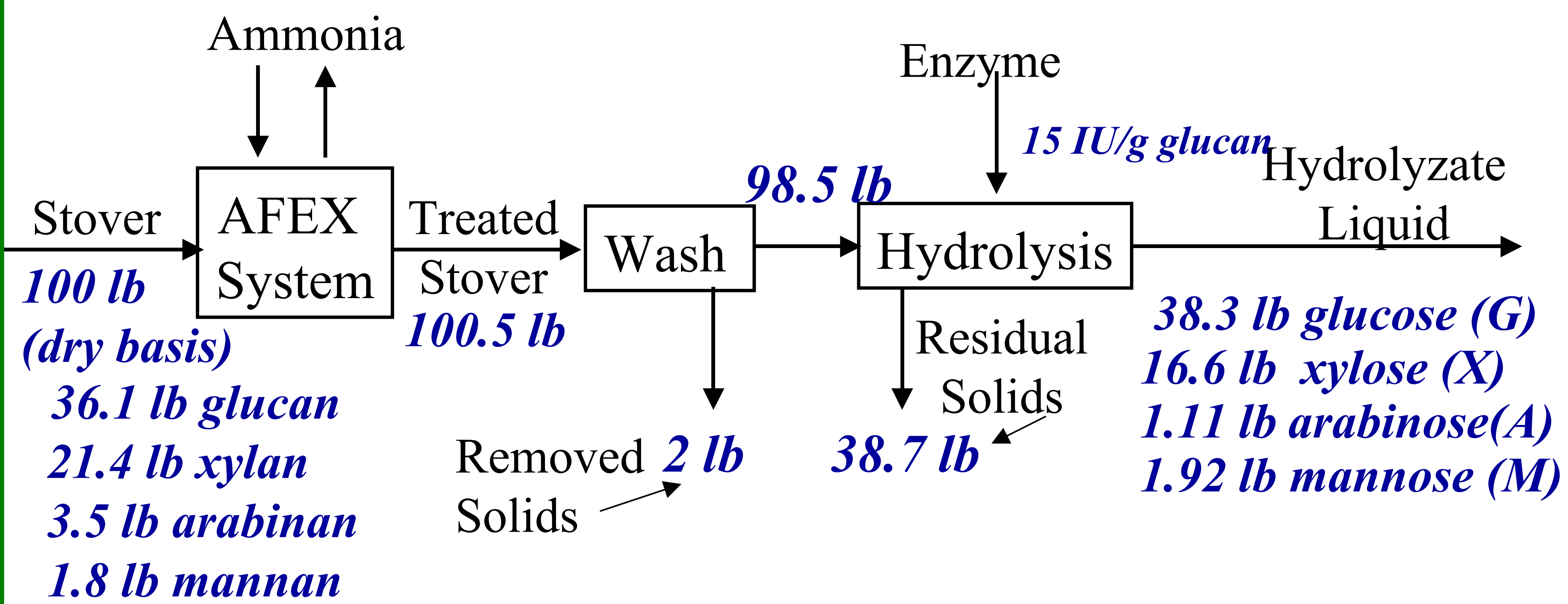
Effect of Air/Temperature on Lignin



Enzymatic Digestibility for Lime Treated Biomass



Preliminary Mass Balances: Example for AFEX Pretreatment



95% glucan to glucose, 68% xylan to xylose
(93% overall glucan + xylan solubilization)
97% overall mass balance closure (All solids + G + X + A + M)
3.76 gallons ethanol (90% yield of glucose plus xylose)

Preliminary Yield Comparisons

Increasing pH

Process	Xylose yields	Glucose yields
Dilute acid	~85% increasing to ~95% w cellulase @ 60 FPU/g glucan	~90 @ 15 FPU/g SSF[1] to 95% w cellulase @ 60 FPU/g glucan
Flowthrough	~97-98% in pretreatment	~93-98% @ 15 FPU/g glucan cellulase
Controlled pH	~62% after pretreatment and enzyme	~73% @ ~30 FPU/g glucan
AFEX	~68% after both steps	~95% @ 7.5 FPU/g glucan
ARP	~70% from both steps at 15 FPU/g glucan	~87% at 15 FPU/g glucan ~95% at 60 FPU/g glucan
Lime	~77-93% overall as cellulase raised from ~2 to 20 FPU/g glucan	

1 – NREL data on Sunds

NREL CAFI Project Contributions

- Properly store and provide feedstock
- Provide/monitor cellulase preparation
- Train students on analytical procedures, etc.
- Perform process engineering evaluations
- Conduct periodic comparative SSF evaluations
- Supported by US DOE Office of the Biomass Program

Economic Modeling Methodology

Capital Costs

Fixed - Direct
Purchased Equipment
Installation
- Indirect
- Contingency
- Start-up

Working

Operating Costs

Variable - Stover
Enzymes
Other

Fixed - Labor
Maintenance
Insurance
Depreciation

Revenues

Ethanol Sales
Electricity Sales

Discounted Cash Flow

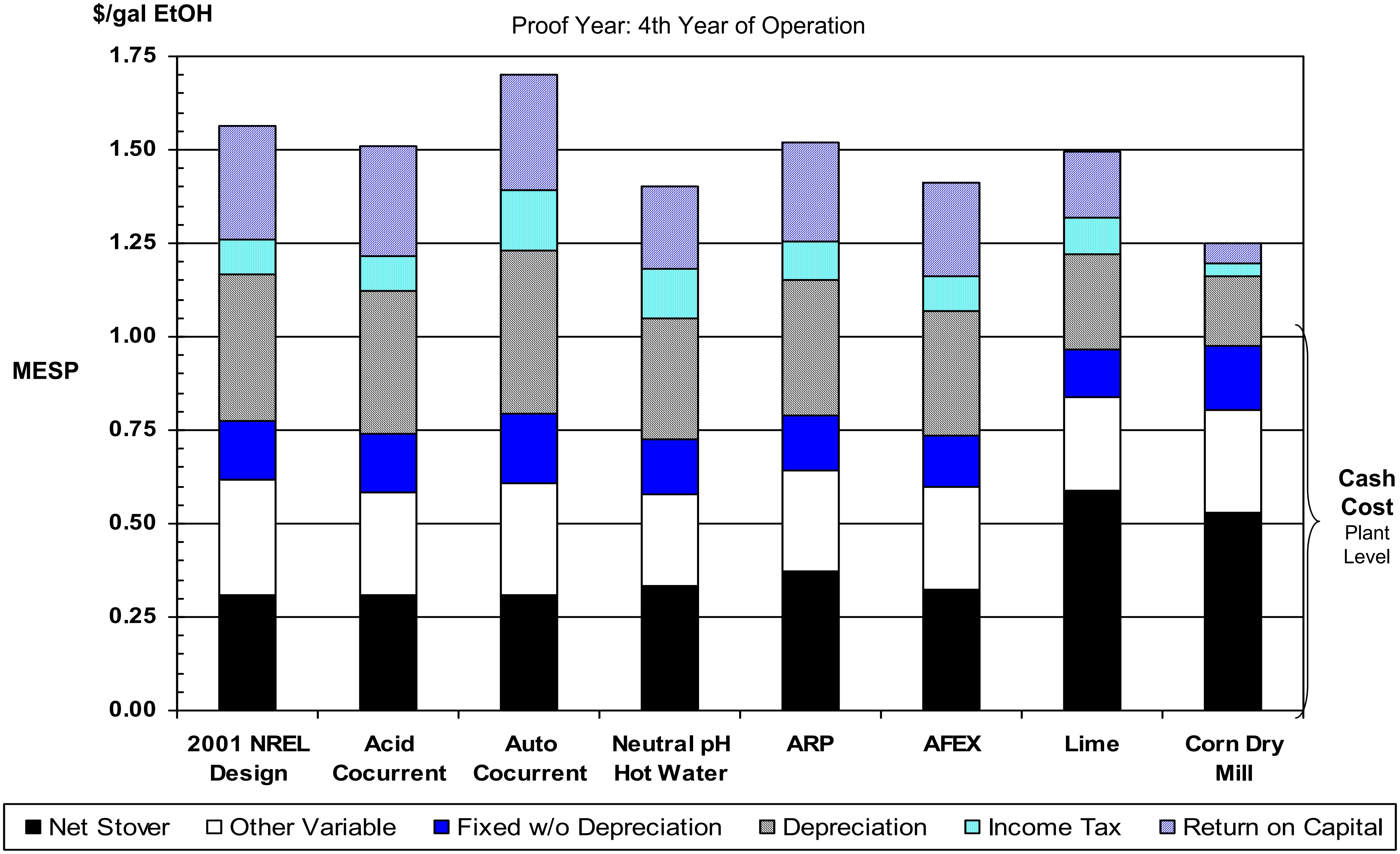
2.5 yr Construction, 0.5 yr Start-up 20 yr Operation
100% Equity, No Subsidy
Rational EtOH Pricing Rather Than Market Pricing
10% Real After Tax Discount Rate

Performance Measures

Total Fixed Capital Per Annual Gallon of Capacity
Minimum Ethanol Selling Price (MESP)—$/gallon
Plant Level Cash Costs

Based on NREL economic model for ethanol from cellulosics
-Pricing per 2001 NREL design
-2,000 dry mtons/day stover

MESP and Cash Cost



Caveats About Economic Projections

- Current economic models…Not final!
  - Pretreatment assumptions: Modeling currently based on many assumptions—will be updated with more data at conclusion of project
  - Assumptions in other areas: All cases have similar assumptions….thus similar performance—will be updated with additional data
- No distinctions for level of development

Some Conclusions to Date

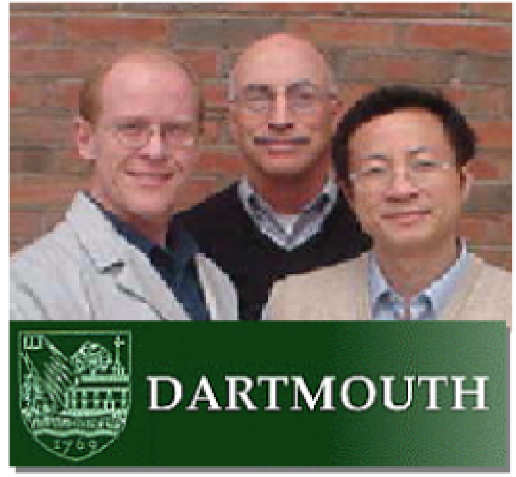
- Dilute acid and neutral pH pretreatments solubilize mostly hemicellulose while ammonia and lime remove mostly lignin. AFEX removes neither.
  - Hemicellulose hydrolysis to monomers can reduce post processing
  - Lignin removal can reduce cellulase use although AFEX reduces cellulase without lignin removal
- Greater hemicellulase activity would improve yields from higher and controlled pH approaches
- All are capital intensive for differing reasons
  - Costly reactor materials and waste treatment, in some cases
  - Pretreatment catalyst recovery, in others
- Some advantages in operating costs
  - e.g., low waste generation with AFEX

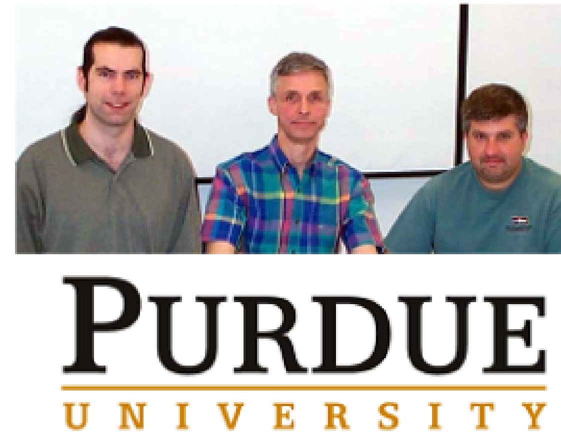
Future Work

- Complete pretreatments with each technology
- Complete data on enzymatic digestibility
  - Gather max yield data at 15 and 60 FPU/g glucan
  - Determine yields in SSF configuration
- Characterize hydrolyzate toxicity to organisms
- Characterize pretreated materials to improve picture of key differences and similarities, e.g., acetyl content, crystallinity
- Update process economic models with more developed pretreatment and enzymatic digestibility performance data

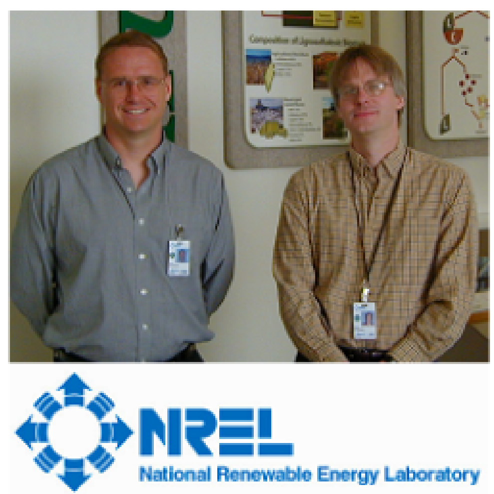
Acknowledgments

- The United States Department of Agriculture Initiative for Future Agricultural and Food Systems Program through Contract 00-52104-9663 for funding this CAFI research
- The United States Department of Energy Office of the Biomass Program and the National Renewable Energy Laboratory for NREL's participation
- Our team from Dartmouth College; Auburn, Michigan State, Purdue, and Texas A&M Universities; and the National Renewable Energy Laboratory





IFAFS Project Participants



Questions?