

Pretreatment: The Key to Unlocking Low Cost Cellulosic Ethanol

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Cellulosic Ethanol Forum and Technology Roundtable

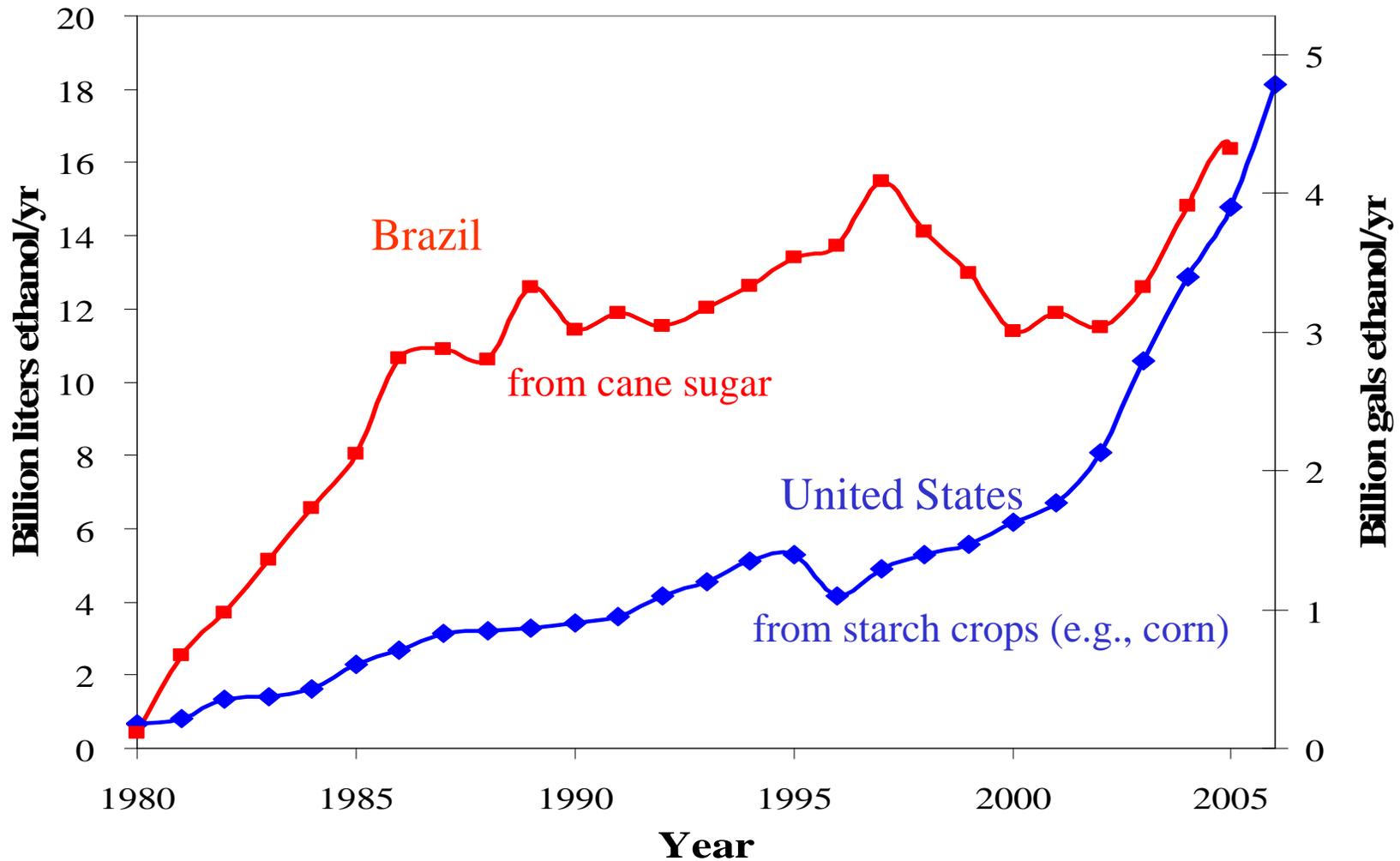
AQMD Headquarters

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Biomass Refining CAFI

Ethanol Production in Brazil and the United States

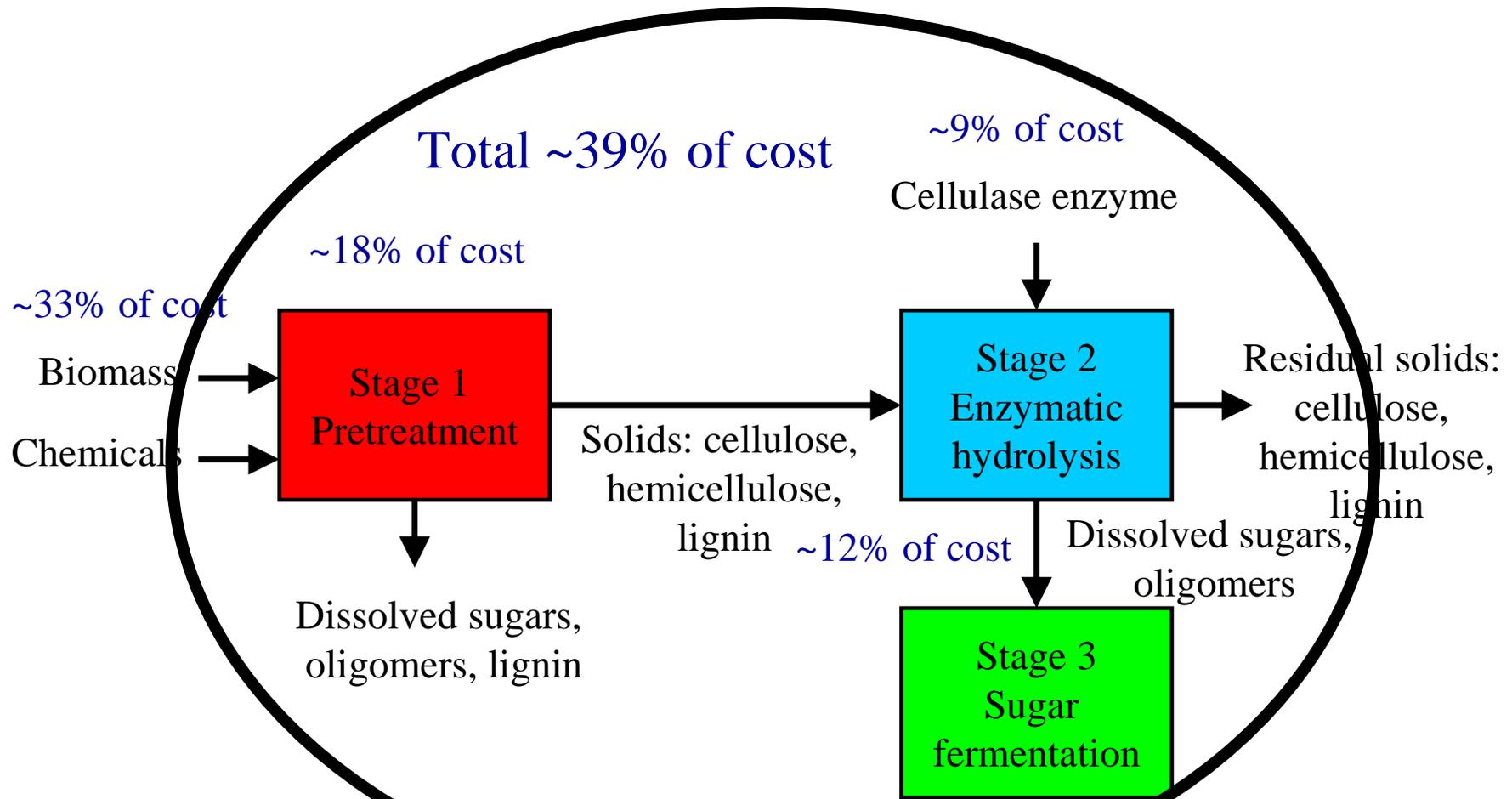




Biological Processing of Cellulosic Biomass

- Biological processing of cellulosic biomass to ethanol and other products offers the potential of high yields vital to economic success
- Biological processing can take advantage of the continuing advances in biotechnology to dramatically improve technology and reduce costs
- In response to recent petroleum price hikes, new initiatives seek to support major research efforts to reengineer plants and biological processes for more efficient conversion of plants into fuels, e.g.
 - \$500 million over 10 years for BP Energy Biosciences Institute
 - \$250 million over 5 years for 2 DOE Bioenergy Research Centers

Major Process Steps



Importance of Pretreatment

- Although significant, feedstock costs are low relative to petroleum
- In addition, feedstock costs are a very low fraction of final costs compared to other commodity products
- Pretreatment is the most costly process step: the only process step more expensive than pretreatment is no pretreatment
 - Low yields without pretreatment drive up all other costs more than amount saved
 - Conversely enhancing yields via improved pretreatment would reduce all other unit costs
- Need to reduce pretreatment costs to be competitive

CAFI Background

- Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) organized in late 1999, early 2000
- Included top researchers in biomass hydrolysis from Auburn, Dartmouth, Michigan State, Purdue, NREL, Texas A&M, U. British Columbia, U. Sherbrooke
- Mission:
 - Develop information and a fundamental understanding of biomass hydrolysis that will facilitate commercialization,
 - Accelerate the development of next generation technologies that dramatically reduce the cost of sugars from cellulosic biomass
 - Train future engineers, scientists, and managers.

USDA IFAFS Project Overview: CAFI 1

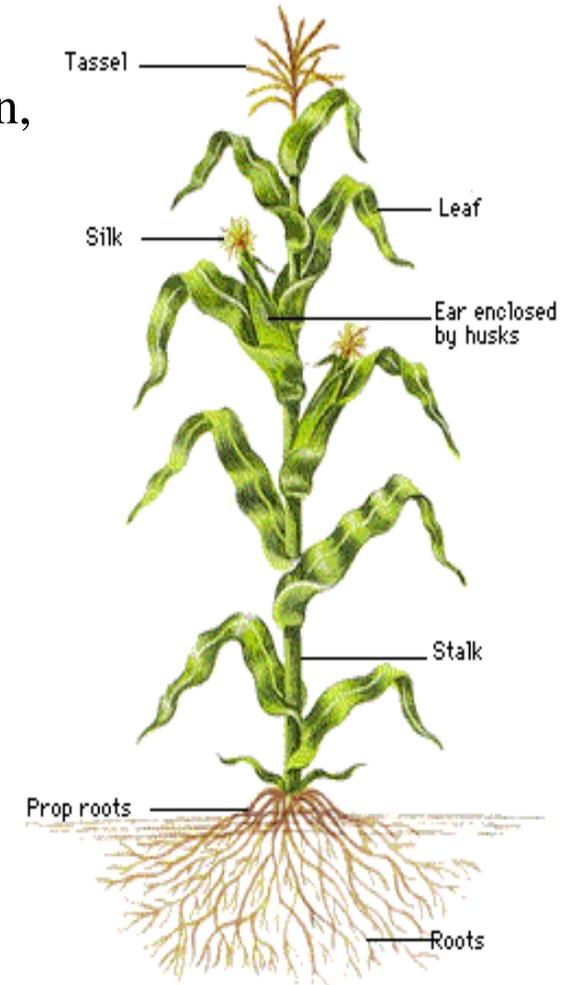
- Multi-institutional effort funded by USDA Initiative for Future Agriculture and Food Systems Program for \$1.2 million to develop comparative information on cellulosic biomass pretreatment by leading pretreatment options with common source of cellulosic biomass (corn stover) and identical analytical 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
- Completed in 2004

Biomass Refining CAFI

CAFI 1 Feedstock: Corn Stover

- 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 %



Overall Yields for Corn Stover at 15 FPU/g Glucan

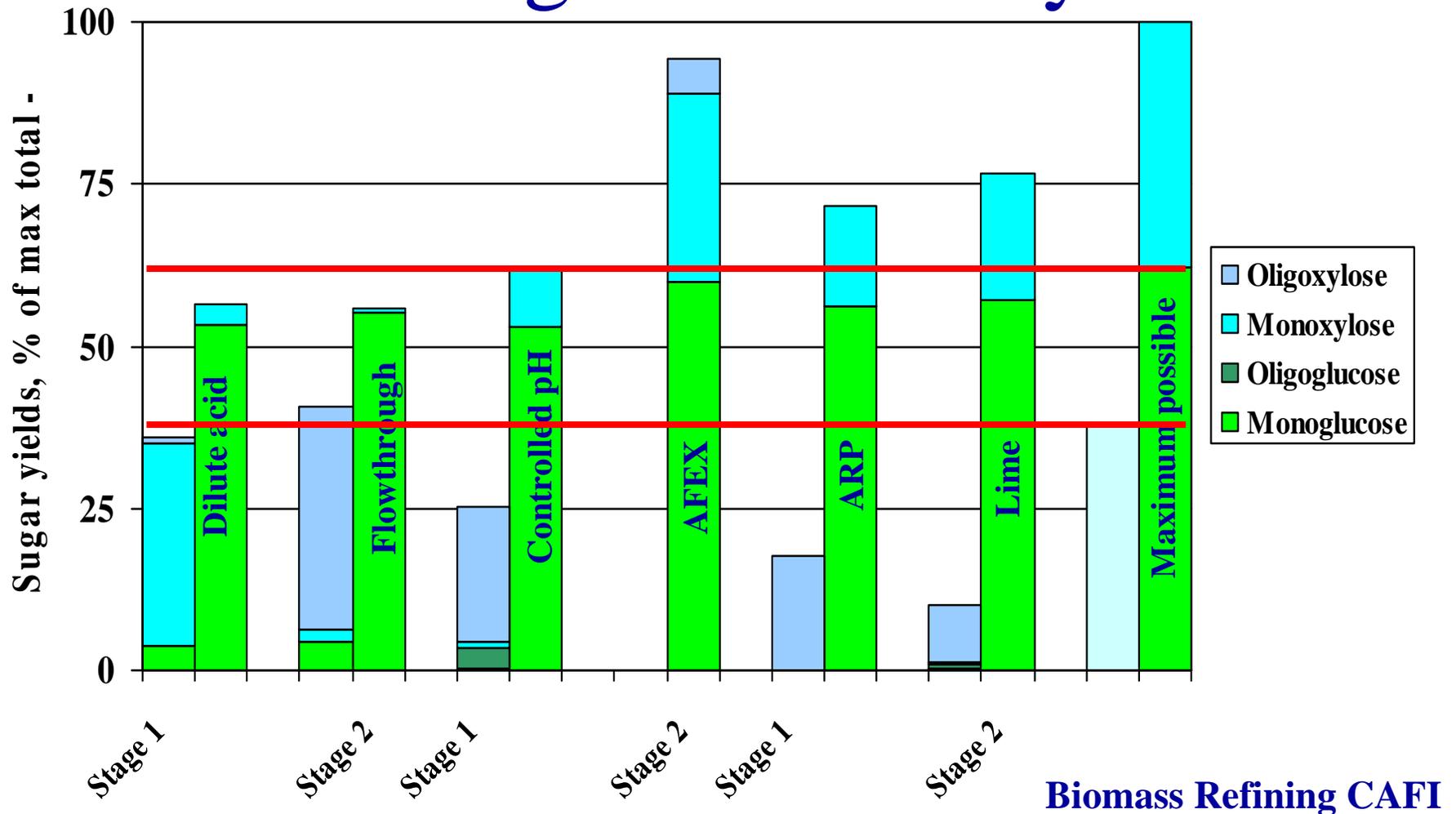
Pretreatment system	Xylose yields*			Glucose yields*			Total sugars*		
	Stage 1	Stage 2	Total xylose	Stage 1	Stage 2	Total glucose	Stage 1	Stage 2	Combined total
Maximum possible	37.7	37.7	37.7	62.3	62.3	62.3	100.0	100.0	100.0
Dilute acid	32.1/31.2	3.2	35.3/34.4	3.9	53.2	57.1	36.0/35.1	56.4	92.4/91.5
SO ₂ Steam explosion	14.7/1.0	20.0	34.7/21.0	2.5/0.8	56.7	59.2/57.5	17.2/1.8	76.7	93.9/78.5
Flowthrough	36.3/1.7	0.6/0.5	36.9/2.2	4.5/4.4	55.2	59.7/59.6	40.8/6.1	55.8/55.7	96.6/61.8
Controlled pH	21.8/0.9	9.0	30.8/9.9	3.5/0.2	52.9	56.4/53.1	25.3/1.1	61.9	87.2/63.0
AFEX		34.6/29.3	34.6/29.3		59.8	59.8		94.4/89.1	94.4/89.1
ARP	17.8/0	15.5	33.3/15.5		56.1	56.1	17.8/0	71.6	89.4/71.6
Lime	9.2/0.3	19.6	28.8/19.9	1.0/0.3	57.0	58.0/57.3	10.2/0.6	76.6	86.8/77.2

Increasing pH

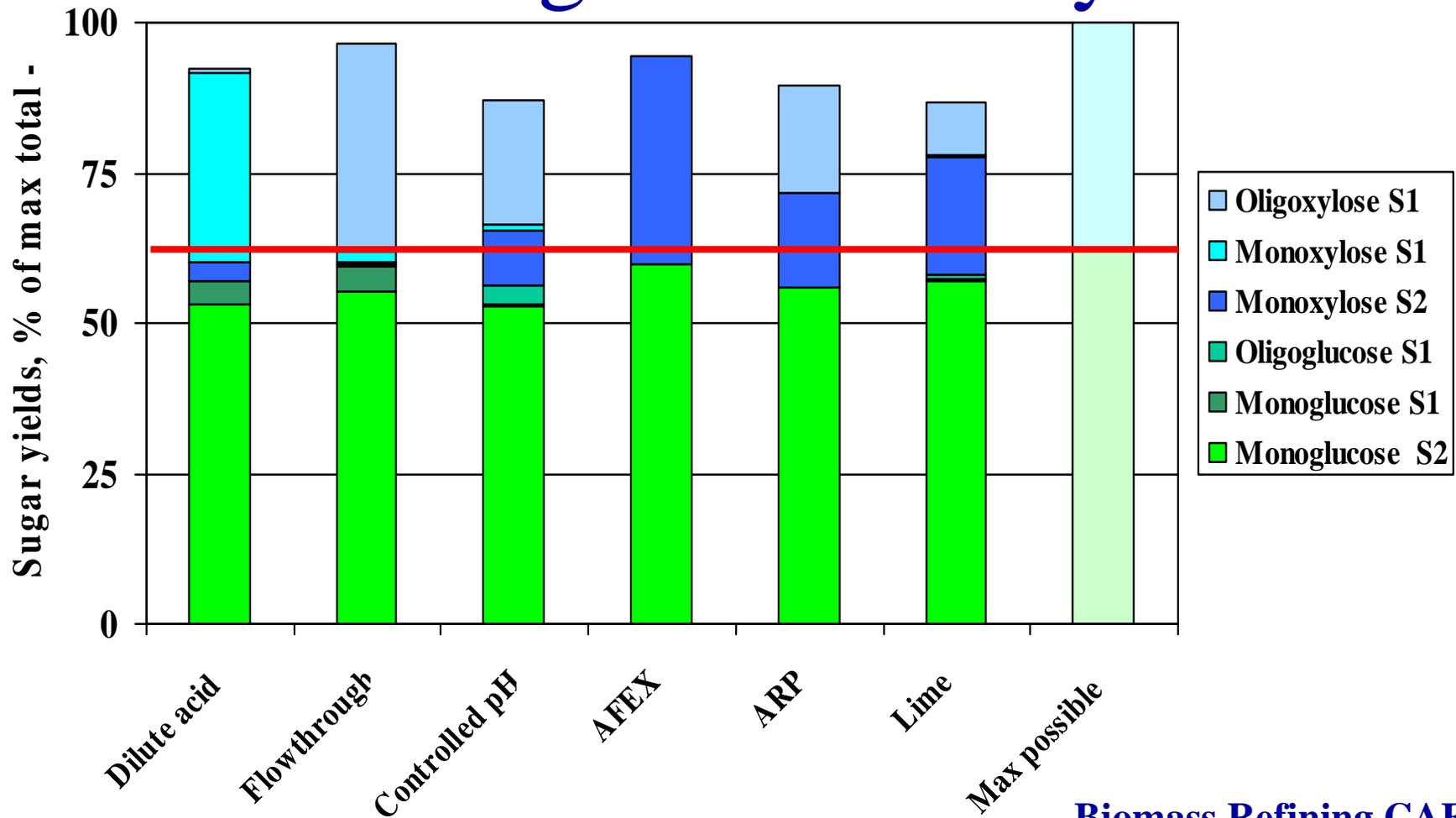


*Cumulative soluble sugars as total/monomers. Single number = just monomers.

Sugar Yields from Corn Stover at 15 FPU/g Glucan Enzyme



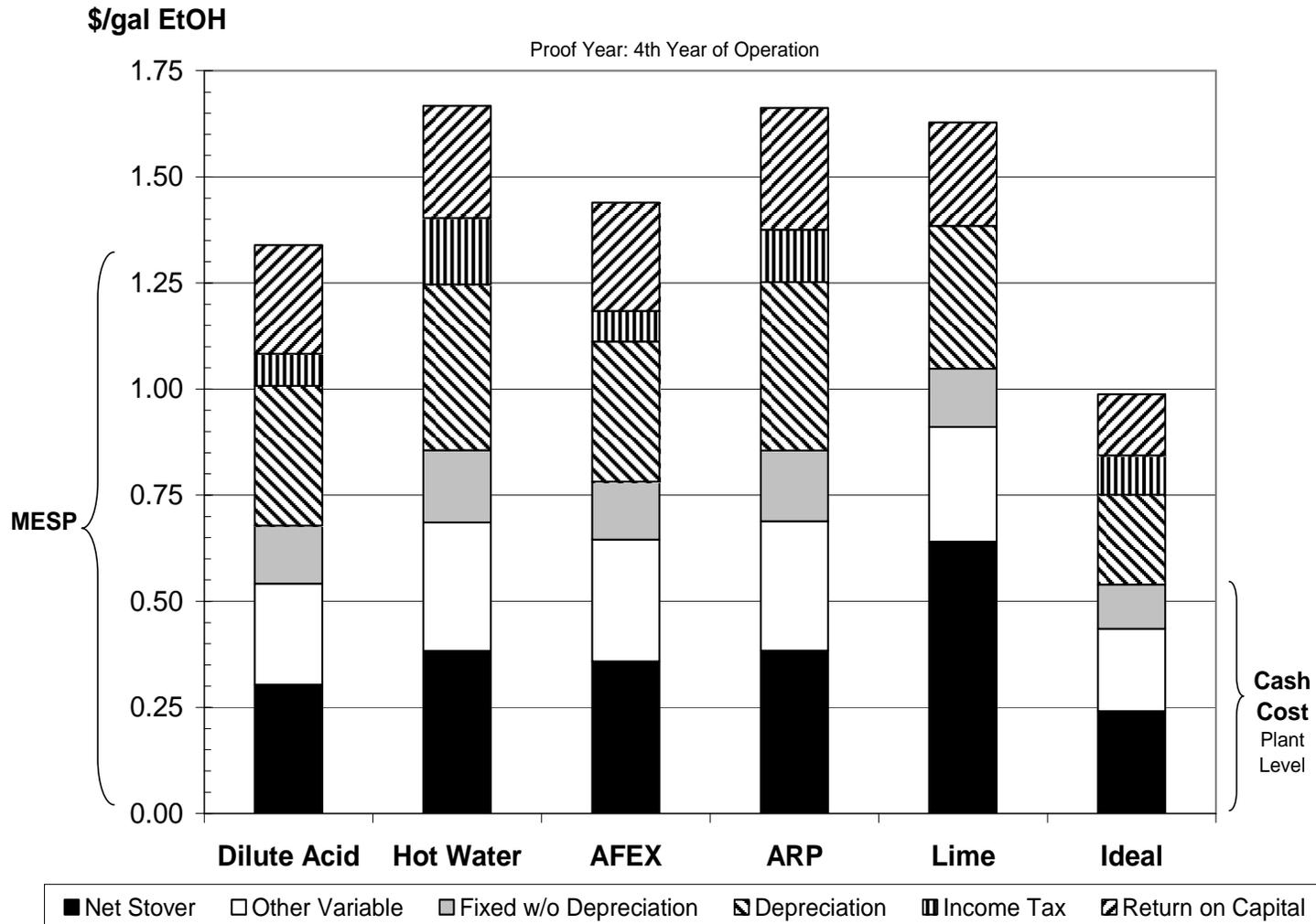
Sugar Yields from Corn Stover at 15 FPU/g Glucan Enzyme



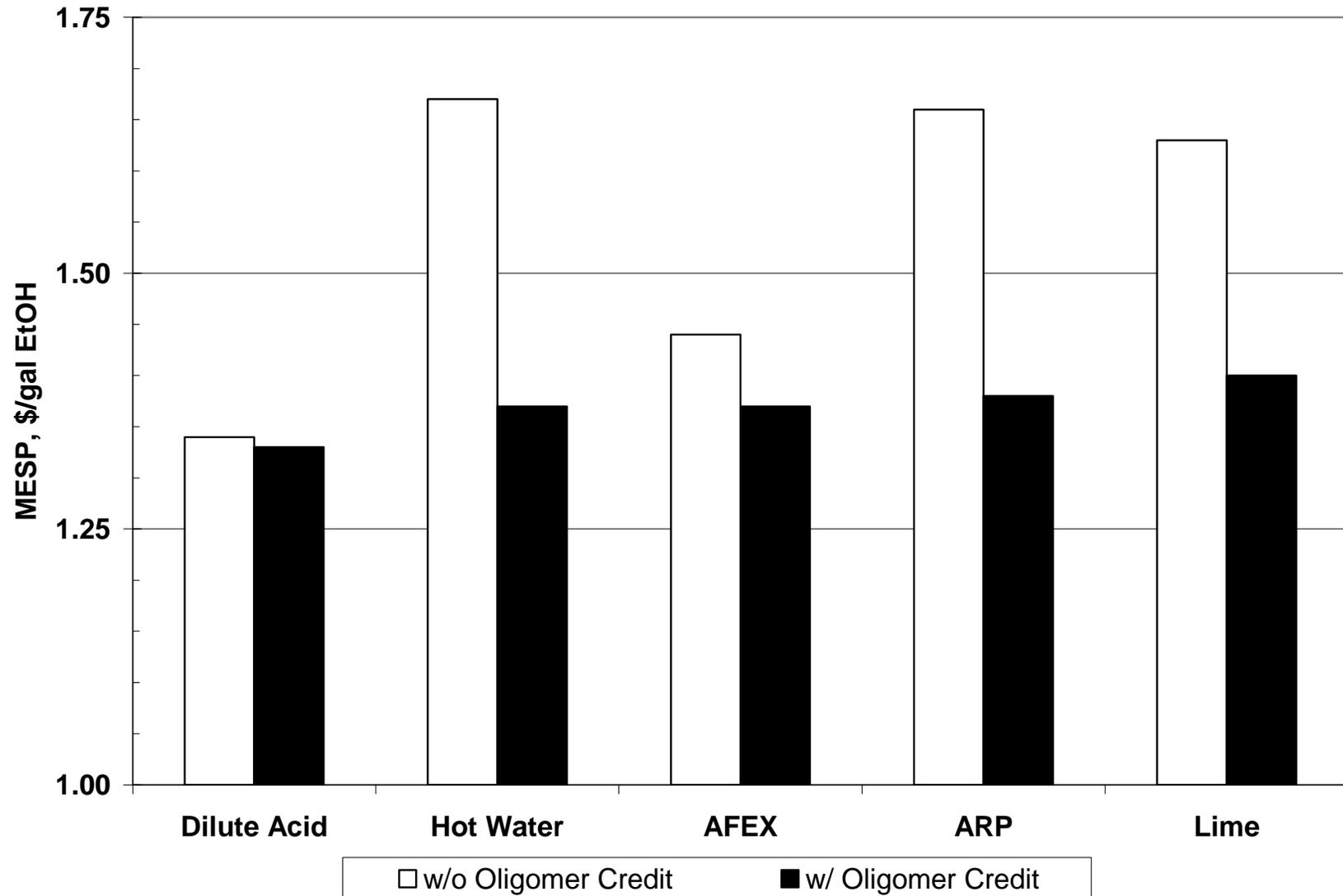
Biomass Refining CAFI

Minimum Ethanol Selling Price (MESP)

Assumptions: 2.5 years construction, 0.5 years start up, 20 year plant life, zero net present value when cash flows are discounted at 10% real after tax rate



Effect of Oligomer Conversion



DOE OBP Project: CAFI II

- Started in April 2004 after completion of USDA IFAFS funded CAFI I on corn stover
- Funded by DOE Office of the Biomass Program for \$1.88 million through a joint competitive solicitation with USDA
- Using identical analytical methods and feedstock sources to develop comparative data for corn stover and poplar
- Determining in depth information on
 - Enzymatic hydrolysis of cellulose and hemicellulose in solids
 - Conditioning and fermentation of pretreatment hydrolyzate liquids
 - Predictive models
- Evaluating AFEX, ARP, controlled pH, dilute acid, lime, sulfur dioxide pretreatments
- Genencor supplies commercial and advanced enzymes

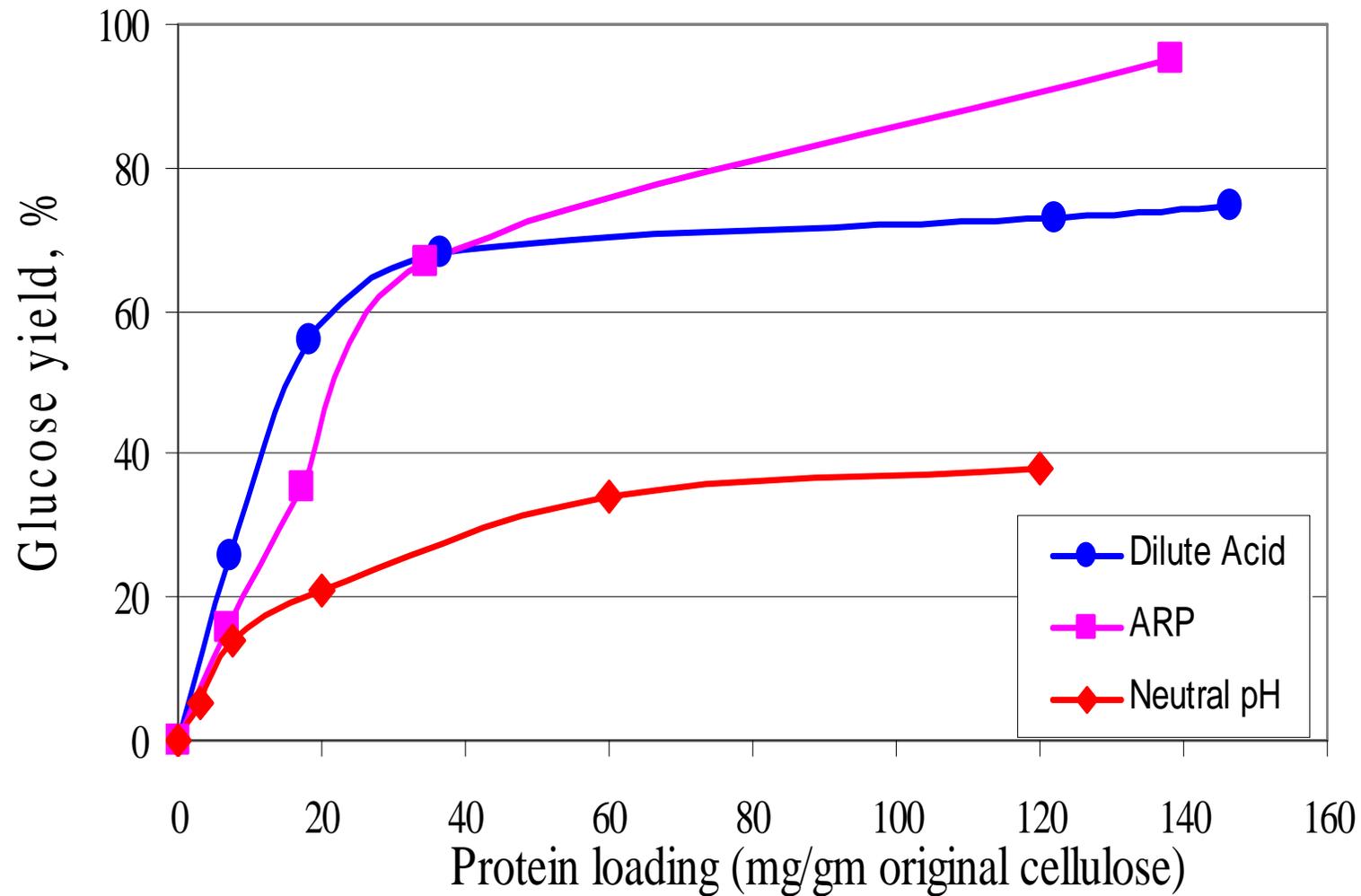
CAFI II Standard Poplar

Component	Composition (wt %)
Glucan	43.8
Xylan	14.9
Arabinan	0.6
Mannan	3.9
Galactan	1.0
Lignin	29.1
Protein	nd
Acetyl	3.6
Ash	1.1
Uronic Acids	nd
Extractives	3.6



1/4 inch Milled Poplar

Effect of Protein Loadings on Cellulose Hydrolysis of Poplar Solids



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Digestion time =72hr

CAFI II Initial Poplar

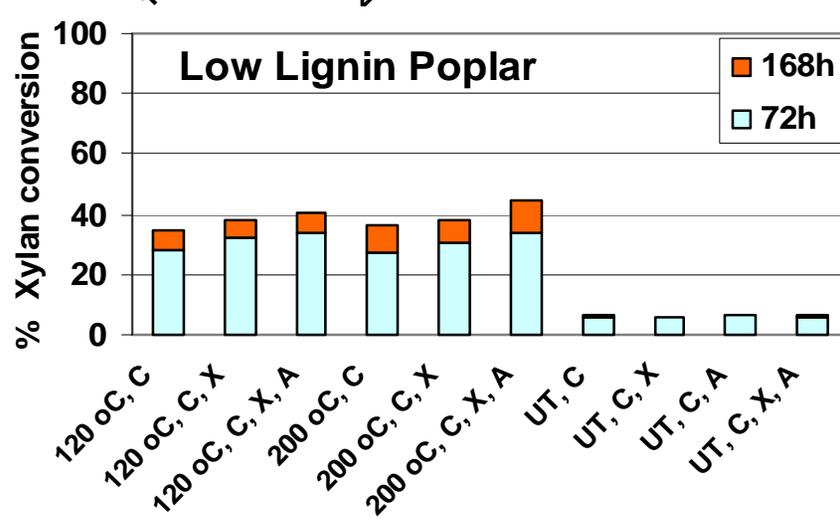
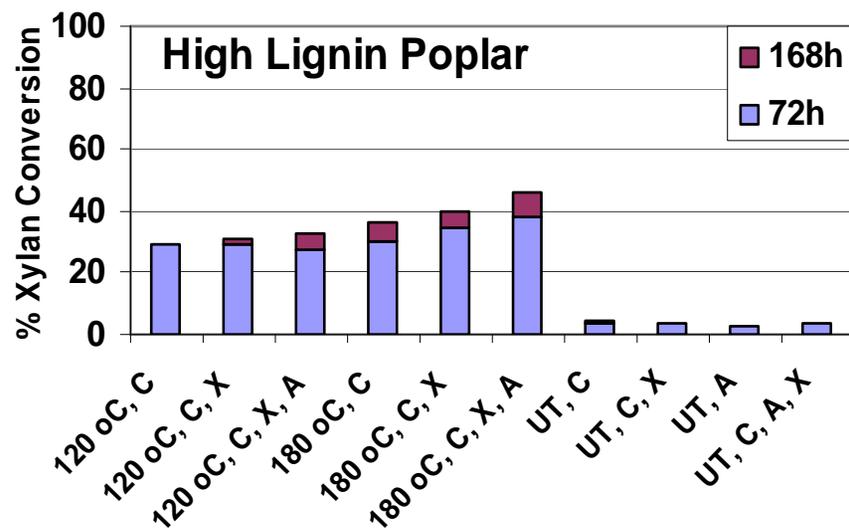
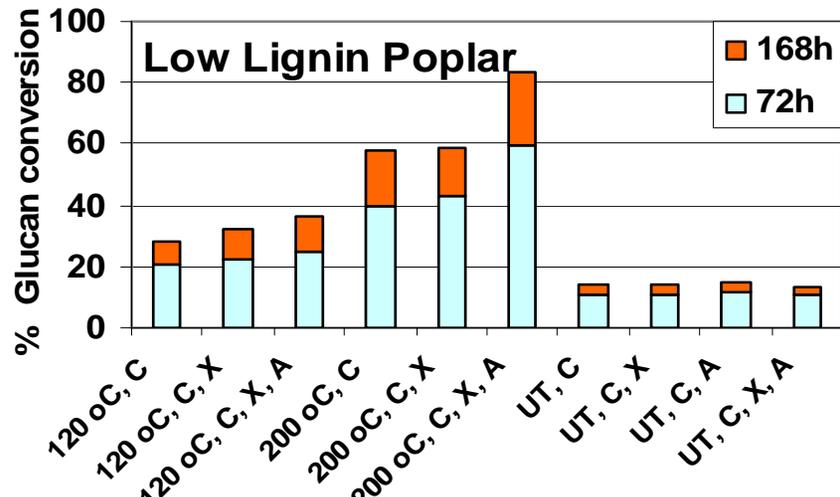
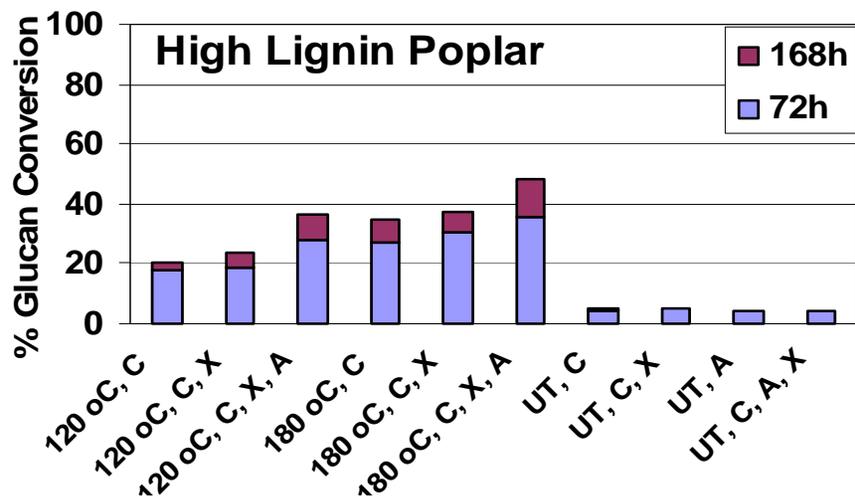
- Feedstock: USDA-supplied hybrid poplar (Arlington, WI)
 - Debarked, chipped, and milled to pass $\frac{1}{4}$ inch round screen
 - Not enough to meet needs

Component	Wt %
Glucan	45.1
Xylan	17.8
Arabinan	0.5
Mannan	1.7
Galactan	1.5
Lignin	21.4
Protein	nd
Acetyl	5.7
Ash	0.8
Uronic Acids	nd
Extractives	3.4

AFEX Optimization for High/Low Lignin Poplar

C - Cellulase
(31.3 mg/g glucan)
X - Xylanase
(3.1 mg/g glucan)
A - Additive
(0.35g/g glucan)

UT - Untreated
AFEX condition
 24 h water soaked
 1:1 (Poplar:NH3)
 10 min. res. time



SO₂ Overall Yields at 15 FPU/g of Glucan (148 hours hydrolysis)

Pretreatment conditions	Xylose yields*			Glucose yields*			Total sugars*		
	Stage 1	Stage 2	Total xylose	Stage 1	Stage 2	Total glucose	Stage 1	Stage 2	Combined total
Maximum possible	25.8	25.8	25.8	74.2	74.2	74.2	100	100	100
190°C,5min,3% SO ₂ (High lignin poplar)	20.3/13.7	2.7	23/16.4	1.5	69.9	71.4	21.8/15.2	72.6	94.4/87.8
200°C,5min,3% SO ₂ (High lignin poplar)	19.3/14.0	2.4	21.7/16.4	2.3	71.9	74.2	21.6/16.3	74.3	95.9/90.6
190°C,5min,3% SO ₂ (Low lignin poplar)	18.4/12.9	3.5	21.9/16.4	1.0	73.2	74.2	19.4/13.9	76.7	96.1/90.6

Why Is Variability Important?

- Impacts yields for all but SO₂ pretreatment
- Assumption is that all hardwoods of same type behave similarly
- Woody crops proponents plan to use standing forest to “store” wood, but harvest season may affect yields
- Important to understand what causes this and whether it impacts other feedstocks such as herbaceous crops or agricultural residues

Differences Among Poplar Species*

Original Poplar - Low Lignin	Poplar Standard - High Lignin
<ul style="list-style-type: none">•Arlington, WI near Madison•Very rich, loamy soil•Demonstrated some of best growth rates•Harvested and shipped in February 17, 2004•Planted in 1995, probably in spring but possibly in fall	<ul style="list-style-type: none">•Alexandria, Minnesota•Lower growth rate than Arlington•Slightly shorter growing season•Harvested and shipped in August 2004•Planted in spring 1994

* Based on information provided by Adam Wiese, USDA Rheinlander, WI

Closing Thoughts

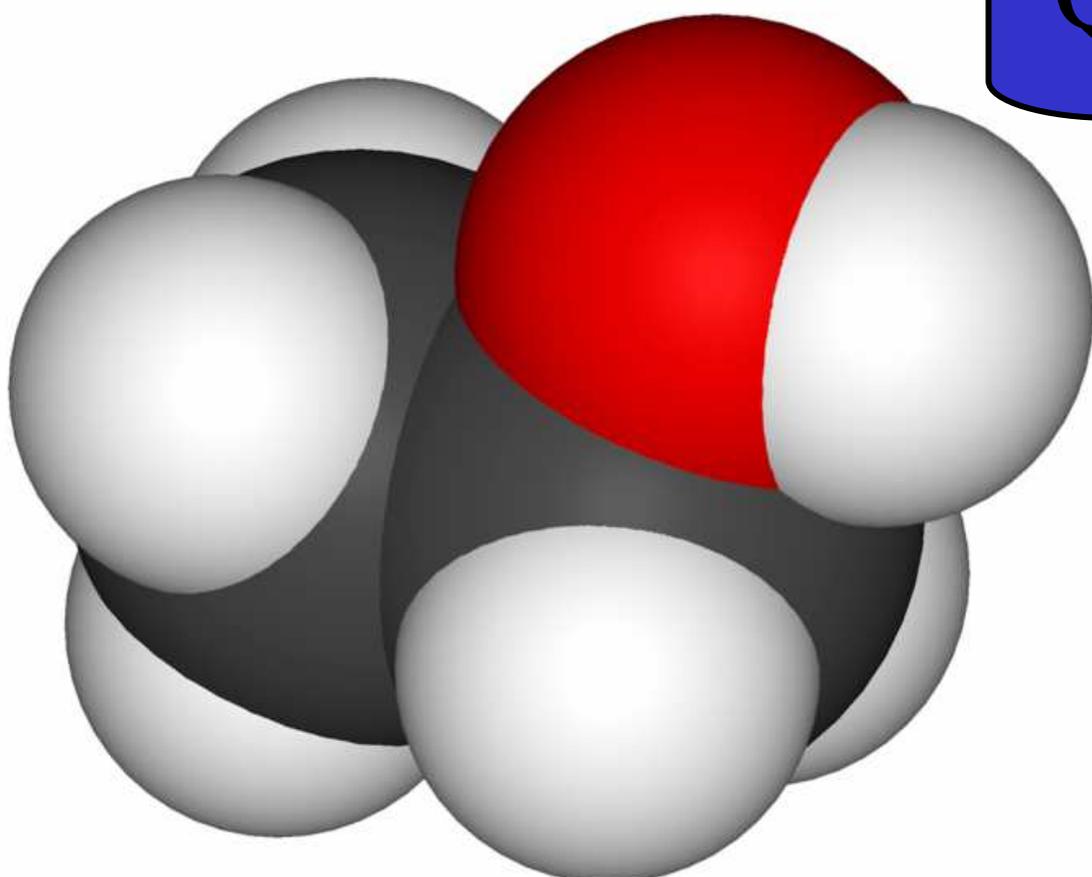
- Biology provides a powerful platform for low cost fuels and chemicals from biomass
 - Can benefit both crop production and conversion systems
- The resistance of one biological system (cellulosic biomass) to the other (biological conversion) requires a pretreatment interface
- Advanced pretreatment systems are critical to enhancing yields and lowering costs
- Not all pretreatments are equally effective on all feedstocks
- Focus on 2 biologies - plants and biological conversion - without integrating their interface – pretreatment – will not significantly lower costs

Acknowledgments

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- Natural Resources Canada
- All of the CAFI Team members, students, and others who have been so cooperative
- Ford Motor Company and University of California at Riverside

Today's Speakers and Topics

- Thomas Foust, National Renewable Energy Laboratory: "DOE and NREL Perspectives on Cellulosic Ethanol - Budget, Research Objectives, Research Achievements"
- Val Tiangco, California Energy Commission: "Potential of Cellulosic Ethanol in California including Feedstock Availability, Research Objectives, Promising Approaches"
- Larry Gross, Altra: "The Current Ethanol Industry: Growth and Challenges"
- Douglas Cameron, Khosla Ventures: "Growth of Ethanol in the USA including Regional Feedstock Availability"
- Michael Ladisch, Purdue University: "Current and Emerging Technologies for Production of Cellulosic Ethanol"
- Bruce Dale, Michigan State University: "Energy Balance and Greenhouse Gas Emission Implications for Large Scale Production of Cellulosic Ethanol"



Questions???