Advancing Cellulosic Ethanol Technology

Bin Yang and Charles E. Wyman

Bourns College of Engineering
Center for Environmental Research and Technology
University of California
Riverside, CA 92507

Advanced Bioenergy Technologies and Biofuels from Municipal Wastes
California Biomass Collaborative Forum
Sacramento, California. March 28, 2007

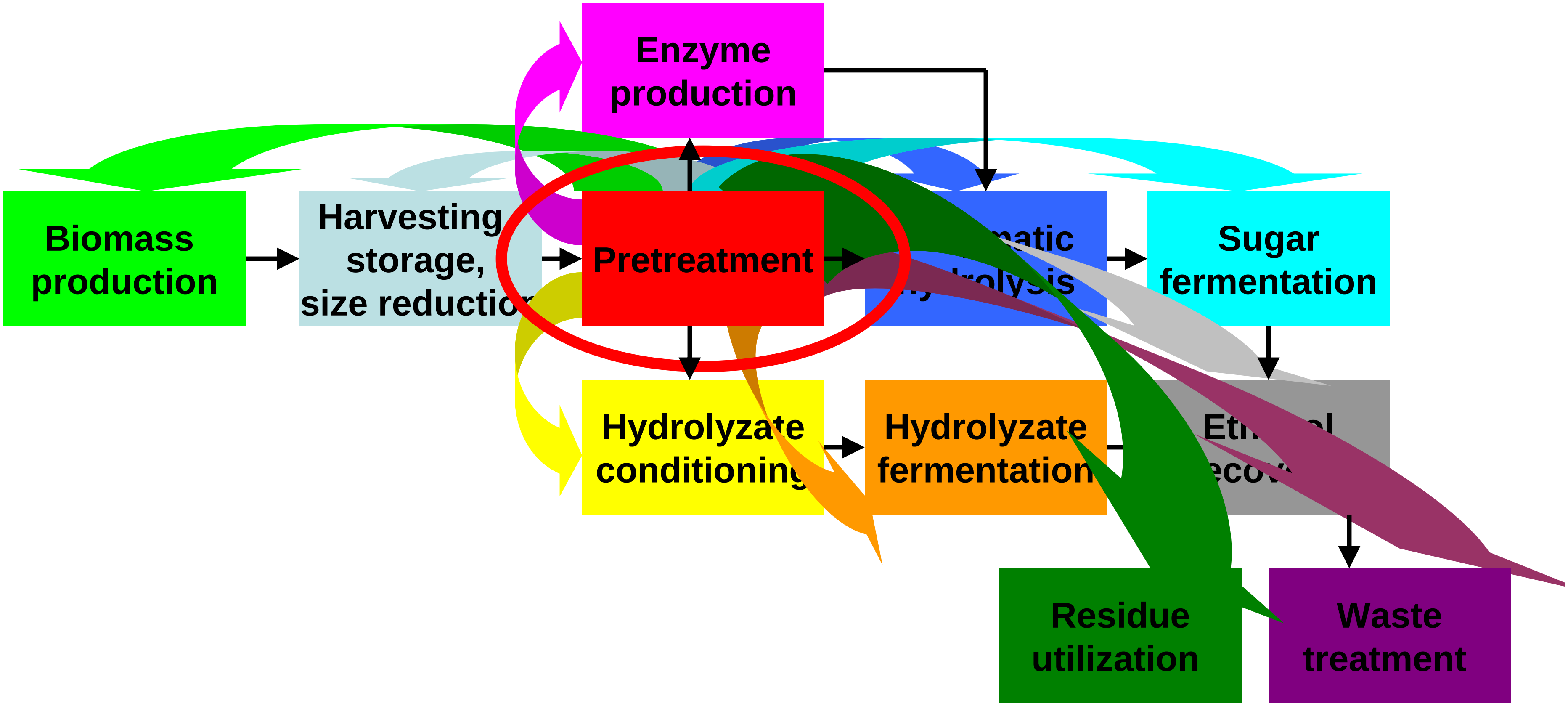
Overall Status of Cellulosic Ethanol

- Technology is ready to be commercialized
- Operating costs are low
- Capital costs are high
- The cost of capital is high – particularly for new technologies
- The technology is not proven at large scale
- Ethanol is a commodity product with low returns
- Challenges: 1) commercialize soon and 2) significantly advance technologies to reduce costs
- Improving quality of performance data and ability to predict performance vital to success

Biological Processing of 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

Central Role and Pervasive Impact of Pretreatment for Biological Processing



Enzyme production

Biomass production

Harvesting storage, size reductio

Pretreatment

matic
rolysis

Sugar fermentation

Hydrolyzate conditionin

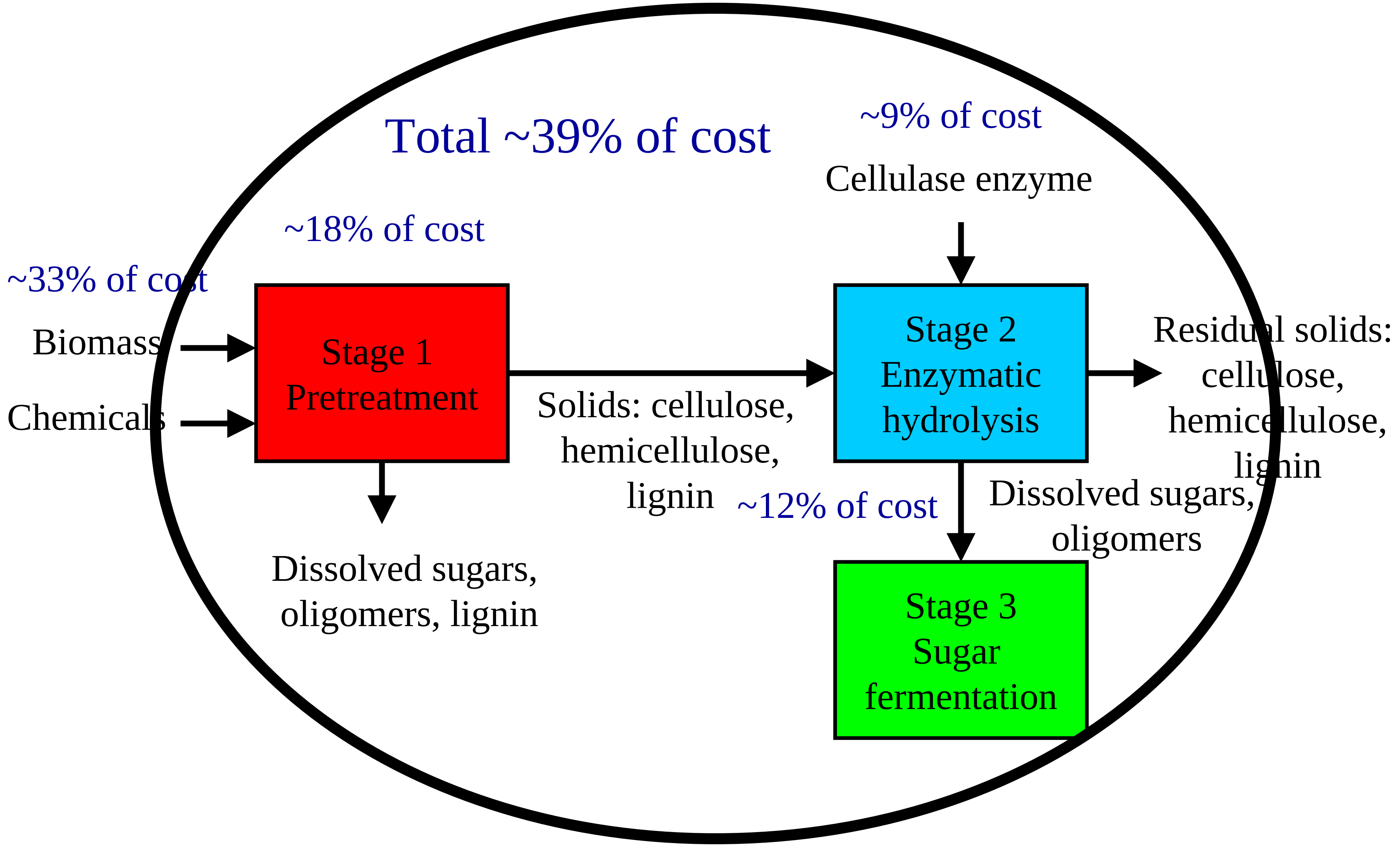
Hydrolyzate fermentation

Eth l
ecov

Residue utilization

Waste treatment

Key Processing Cost Elements



Total ~39% of cost

~9% of cost

Cellulase enzyme

~18% of cost

~33% of cost

Biomass

Chemicals

Stage 1
Pretreatment

Solids: cellulose,
hemicellulose,
lignin

Stage 2
Enzymatic
hydrolysis

Residual solids:
cellulose,
hemicellulose,
lignin

~12% of cost

Dissolved sugars,
oligomers

Dissolved sugars,
oligomers, lignin

Stage 3
Sugar
fermentation

Opportunity/Impact for Advances

Operation	Enhance yield	Reduce costs
Biomass production	M	M
Harvesting/Storage	L	M
Size reduction	L	L
Pretreatment	H	H
Enzyme production	H	M
Enzymatic hydrolysis	H	H
Glucose fermentation	L	M
Hydrolyzate conditioning	H	H
Hydrolyzate fermentation	L	M
Ethanol recovery	L	M
Residue utilization	M	H
Waste treatment	L	L

Opportunity/Impact for Advances

Operation	Enhance yield	Reduce costs
Biomass production	M	M
Harvesting/Storage	L	M
Size reduction	L	L
Pretreatment	H	H
Enzyme production	H	M
Enzymatic hydrolysis	H	H
Glucose fermentation	L	M
Hydrolyzate conditioning	H	H
Hydrolyzate fermentation	L	M
Ethanol recovery	L	M
Residue utilization	M	H
Waste treatment	L	L

UCRIVERSIDE UNIVERSITY OF CALIFORNIA | CE-CERT

Opportunity/Impact for Advances

Operation	Enhance yield	Reduce costs
Biomass production	M	M
Harvesting/Storage	L	M
Size reduction	L	L
Pretreatment	H	H
Enzyme production	H	M
Enzymatic hydrolysis	H	H
Glucose fermentation	L	M
Hydrolyzate conditioning	H	H
Hydrolyzate fermentation	L	M
Ethanol recovery	L	M
Residue utilization	M	H
Waste treatment	L	L

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

Key Pretreatment Needs

- Achieve high yields for multiple crops, sites, ages, harvest times
- Achieve very high total sugar yields
- Reduce chemical use for pretreatment and post treatment
- Lower cost of materials of construction
  - Less corrosive chemicals
  - Lower pressure
- Eliminate hydrolyzate conditioning and its losses
- Reduce enzyme (cellulase and hemicellulase) use
- Minimize heat and power requirements
- Achieve high sugar concentrations

Mission of Our Research Team

- Improve the understanding of biomass fractionation, pretreatment, and cellulose hydrolysis to support applications and foster advances in biomass conversion technologies for production of low cost commodity products

Current Research Topics

- Effect of different pretreatments on enzymatic hydrolysis of biomass – US DOE
  - Consortium with Auburn, Michigan State, NREL, Purdue, Texas A&M, U. British Columbia, and Genencor
- Use of proteins to reduce non productive cellulase adsorption on lignin – USDA
- Continuous fermentations of pretreated biomass and sugar mixtures - NIST
- CFD simulations of fermentation systems for scale up – NIST
- Protein extraction from biomass - NIST

Example Experimental Systems

Pretreatment tubes

Pretreatment reactor

Batch fermentor

Pretreatment steam gun

Oligomer separations

Continuous fermentation train

Consortium for Applied Fundamentals and Innovation (CAFI) Pretreatment Technologies

- Aqueous ammonia recycle pretreatment - Auburn University
- Water only and dilute acid hydrolysis by co-current and flowthrough systems - Dartmouth College
- Ammonia fiber explosion (AFEX) - Michigan State University
- Controlled pH pretreatment - Purdue University
- Lime pretreatment - Texas A&M University
- Logistical support and economic analysis - NREL through DOE Biomass Program funding

Partners and Collaborators

- YY Lee, Auburn University
- Bruce Dale, Michigan State University
- Rick Elander, National Renewable Energy Laboratory
- Michael Ladisch, Purdue University
- Mark Holtzapple, Texas A&M University
- Jack Saddler, University of British Columbia
- Colin Mitchinson, Genencor International

CAFI DOE Project Agricultural and Industrial Advisory Board

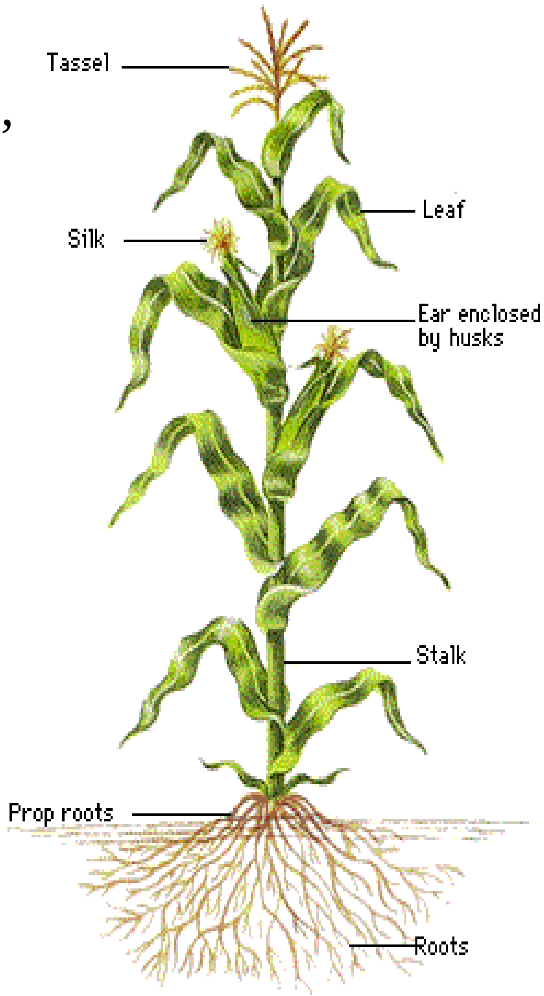
Quang Nguyen, Abengoa Bioenergy
Gary Welch, Aventinerei
Mohammed Moniruzzaman, BioEnergy International
Mark Stowers, Broin
Paris Tsobanakis, Cargill
James Hettenhaus, CEA
Steve Thomas, CERES
Lyman Young, ChevronTexaco
Kevin Gray, Diversa
Paul Roessler, Dow
Julie Friend, DuPont
Mike Knauf, Ethanol Technology
Jack Huttner, Genencor
Don Johnson, GPC (Retired)

Dale Monceaux, Katzen Engineers
Kendall Pye, Lignol
Lee Lynd, Mascoma
Farzaneh Teymouri, MBI
Richard Glass, National Corn Growers Association
Bill Cruickshank, Natural Resources Canada
David Glassner, NatureWorks
Robert Goldberg, NIST
Joel Cherry, Novozymes
Ron Reinsfelder, Shell
Carl Miller, Syngenta
Carmela Bailey, USDA
Don Riemenschneider, USDA

CAFI 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 %**



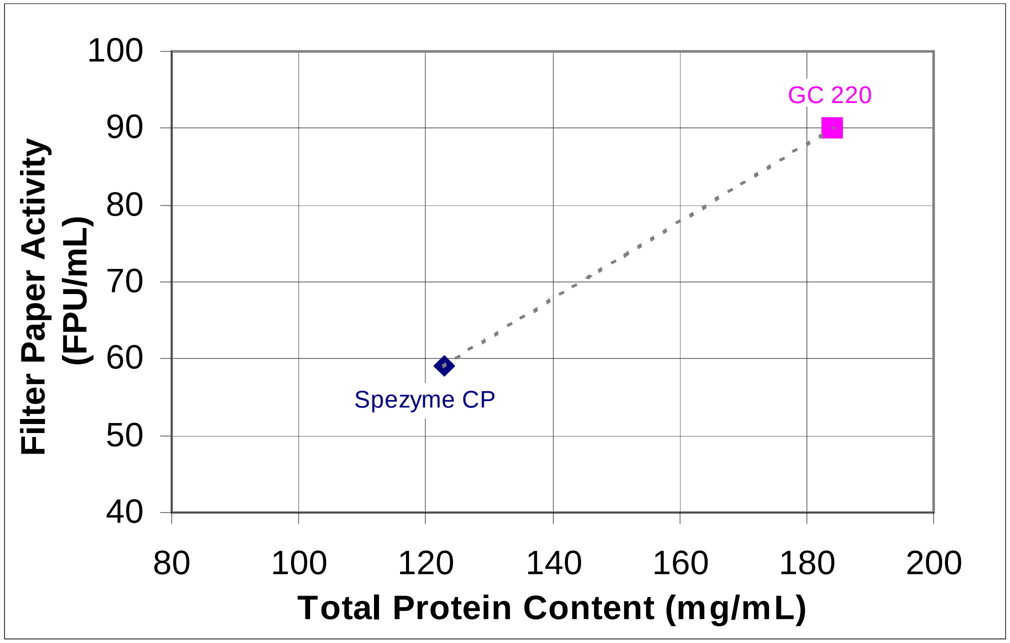
Key Features of CAFI Pretreatments for Corn Stover

Pretreatment system	Temperature, ºC	Reaction time, minutes	Chemical agent used	Percent chemical used	Other notes
Dilute acid	160	20	Sulfuric acid	0.49	25% solids concentration during run in batch tubes
Flowthrough	200	24	none	0	Continuously flow just hot water at 10mL/min for 24minutes
Partial flow pretreatment	200	24	none	0	Flow hot water at 10mL/min from 4-8 minutes, batch otherwise
Controlled pH	190	15	none	0	16% corn residue slurry in water
AFEX	90	5	Anhydrous ammonia	100	62.5% solids in reactor (60% moisture dry weight basis), 5 minutes at temperature
ARP	170	10	ammonia	15	Flow aqueous ammonia at 5 mL/min without presoaking
Lime	55	4 weeks	lime	0.08 g CaO/g biomass	Purged with air.

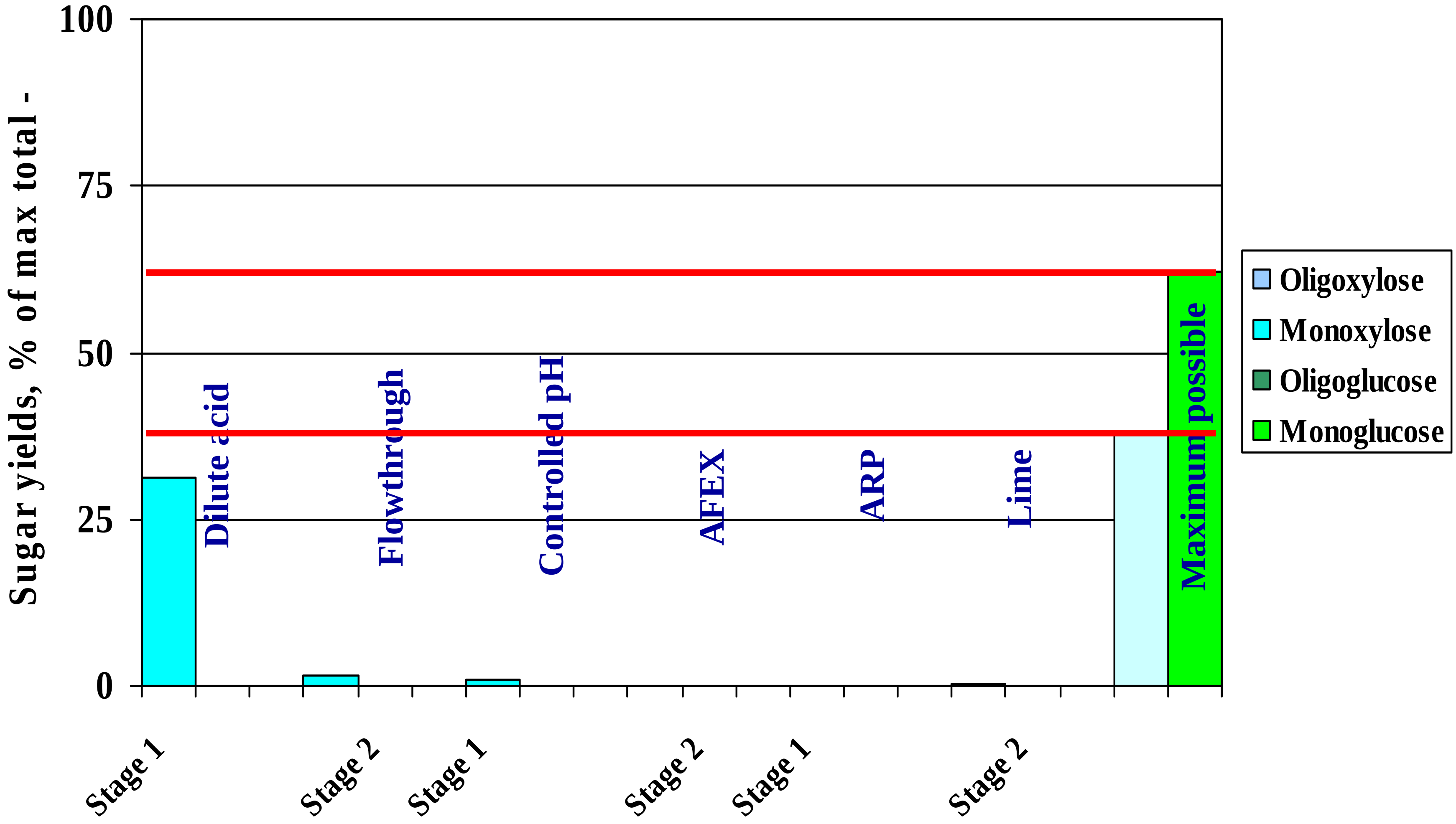
Relationship Between Total Protein Content and Filter Paper Activity for Genencor CAFI Enzymes

Enzyme	Lot #:	Total Protein Content (mg/mL)	Filter Paper Activity (FPU/mL)	Ratio of Protein Content to FPU Activity
Spezyme CP	301-04075-054	123	59	2.1
GC 220	301-04232-162	184	90	2.0
Multifect Xylanase	301-04021-015	42	N/A	N/A
Multifect Pectinase FE	A21-03356-001	82	N/A	N/A

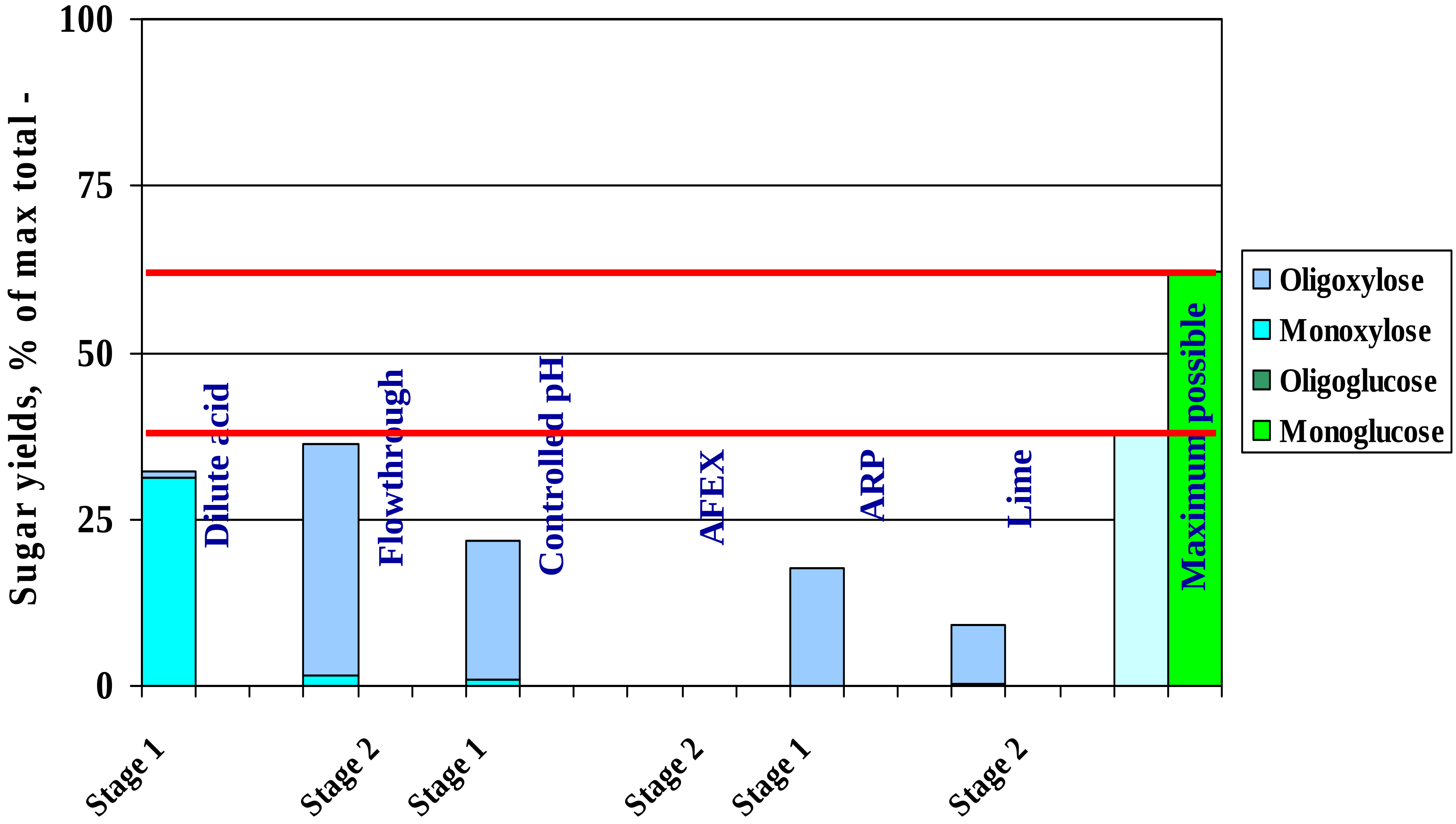
Average deviation: ± 5%
N/A - negligible activity on filter paper was detected



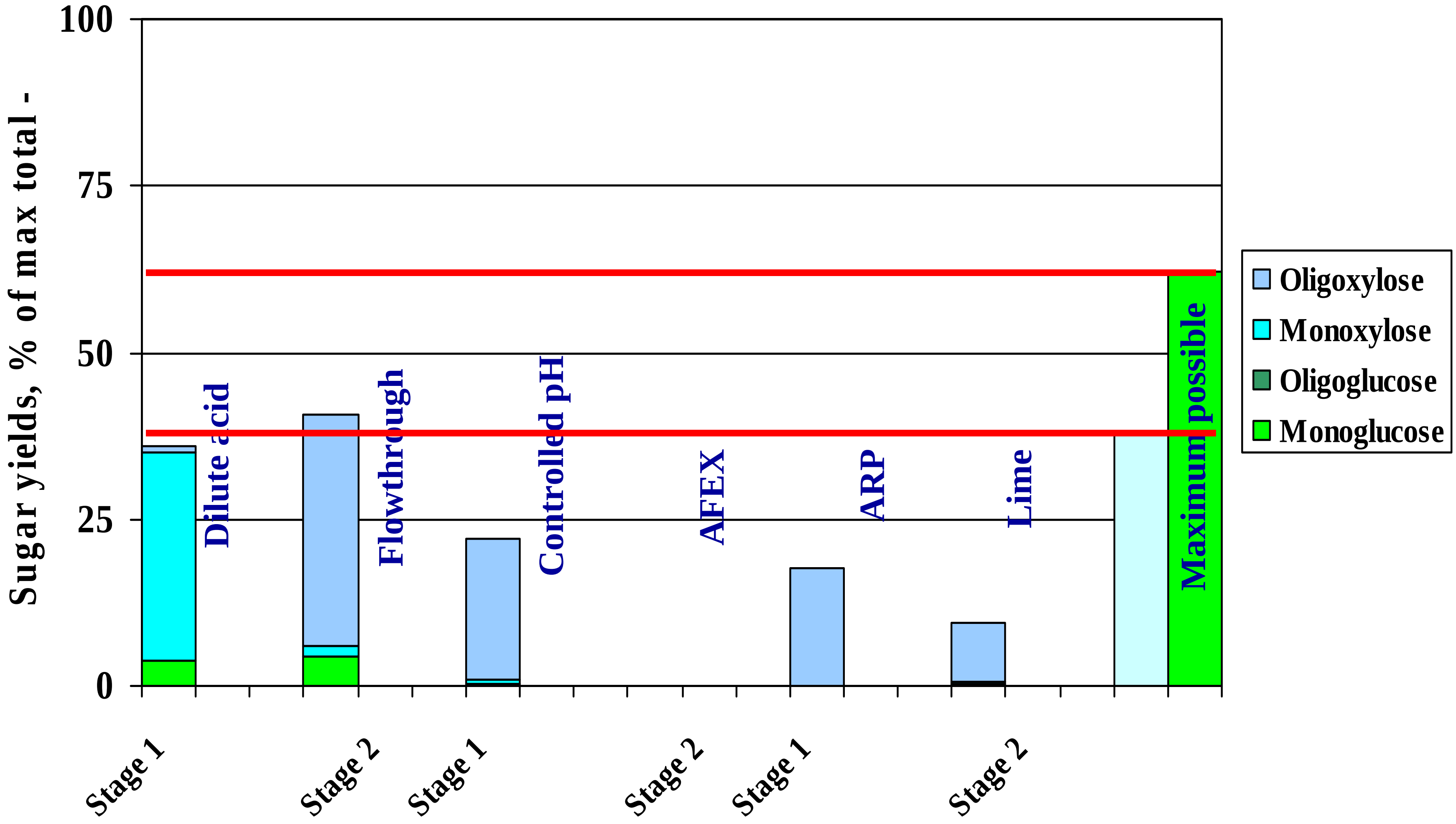
Previous Sugar Yields from Corn Stover at 15 FPU/g Glucan Enzyme



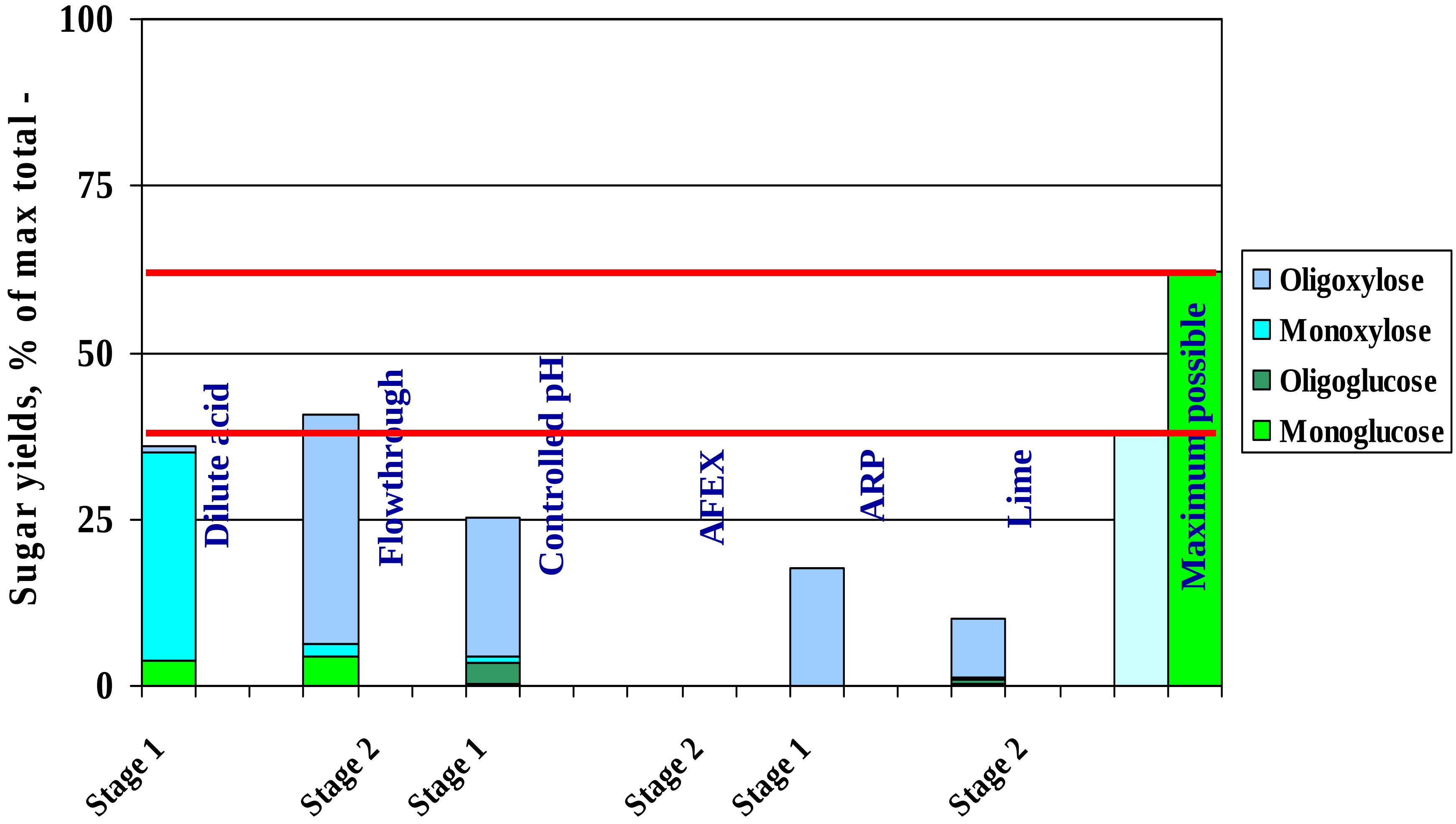
Previous Sugar Yields from Corn Stover at 15 FPU/g Glucan Enzyme



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

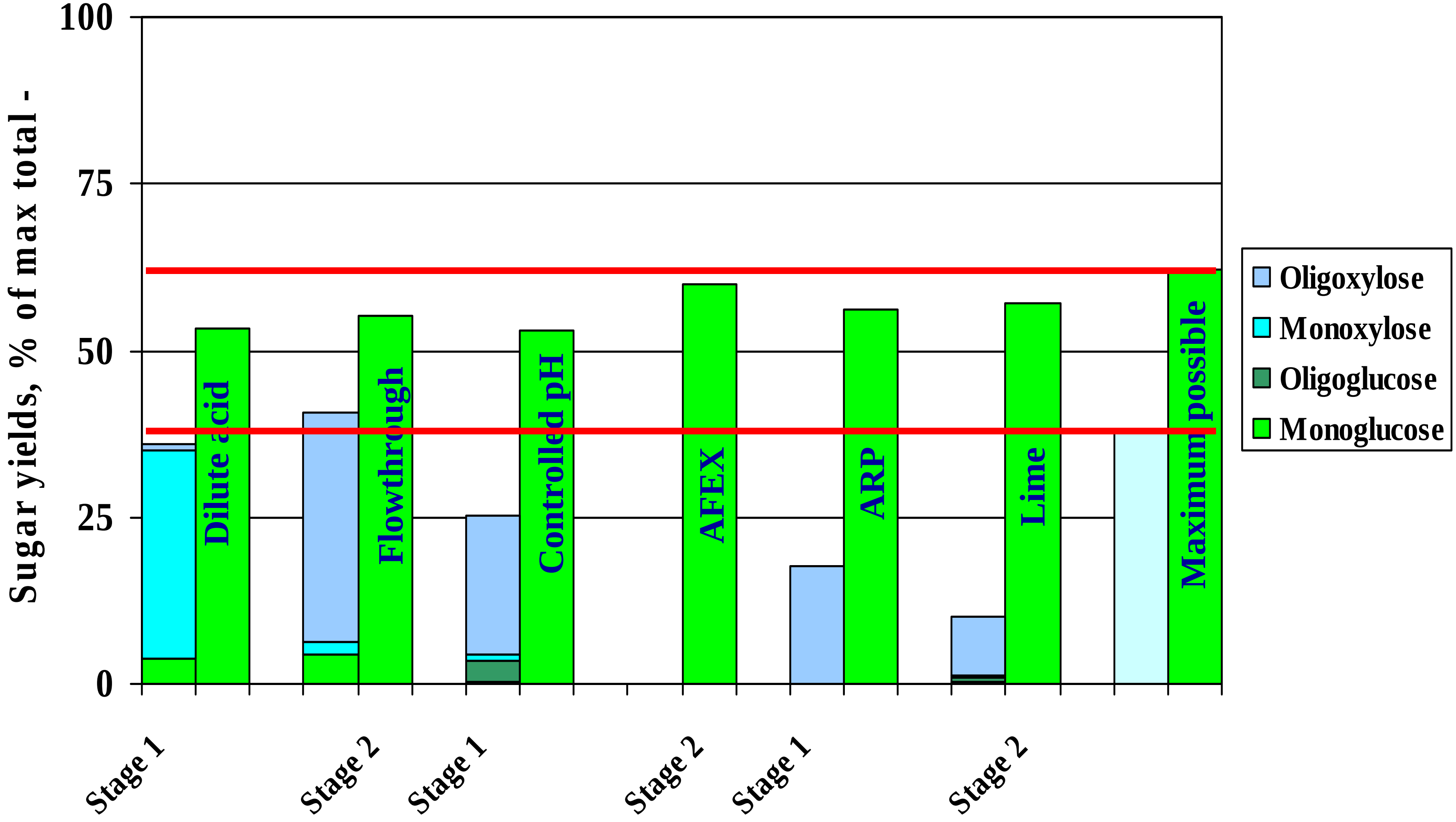


Previous Sugar Yields from Corn Stover at 15 FPU/g Glucan Enzyme

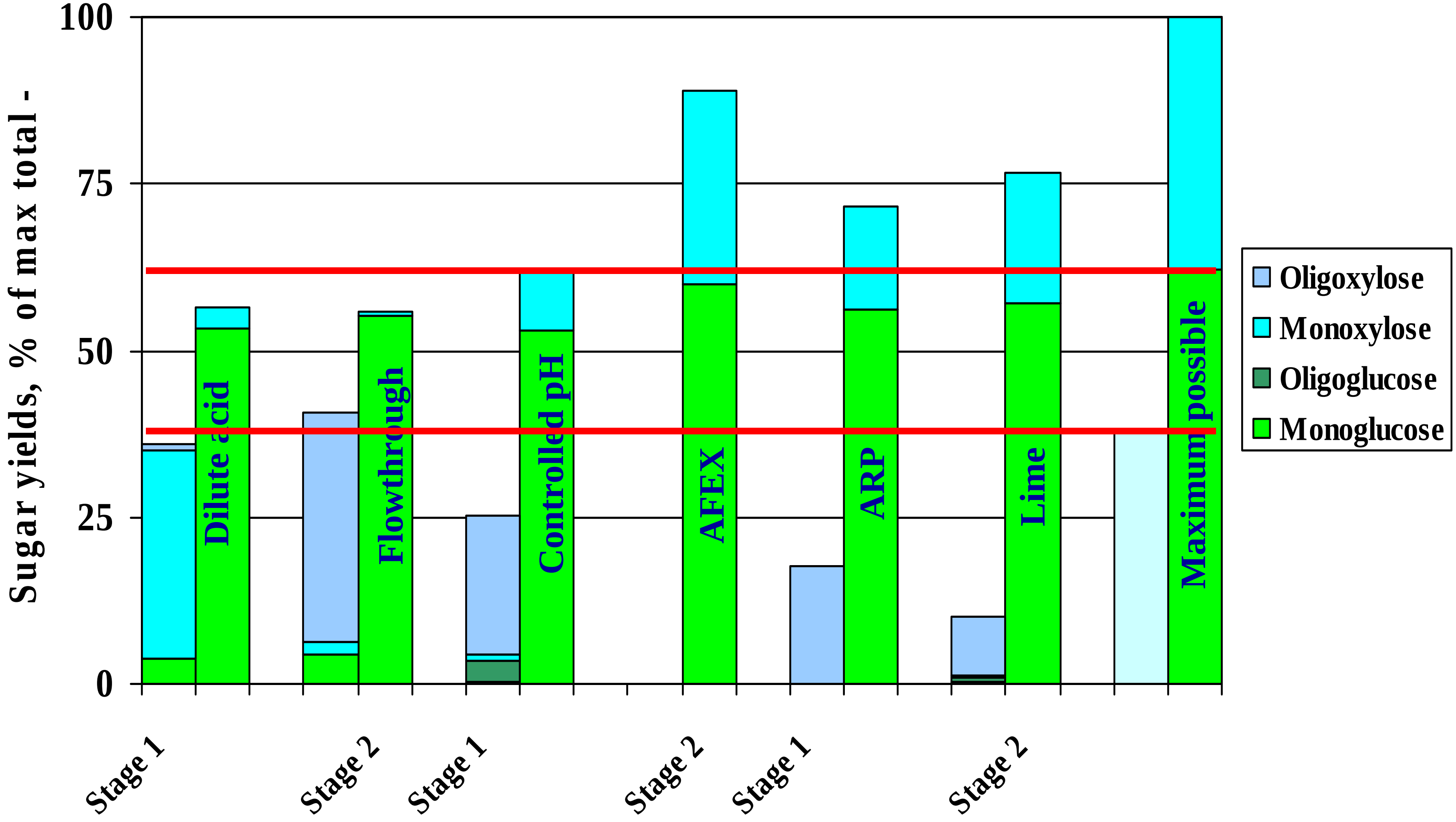


UC RIVERSIDE | CE-CERT

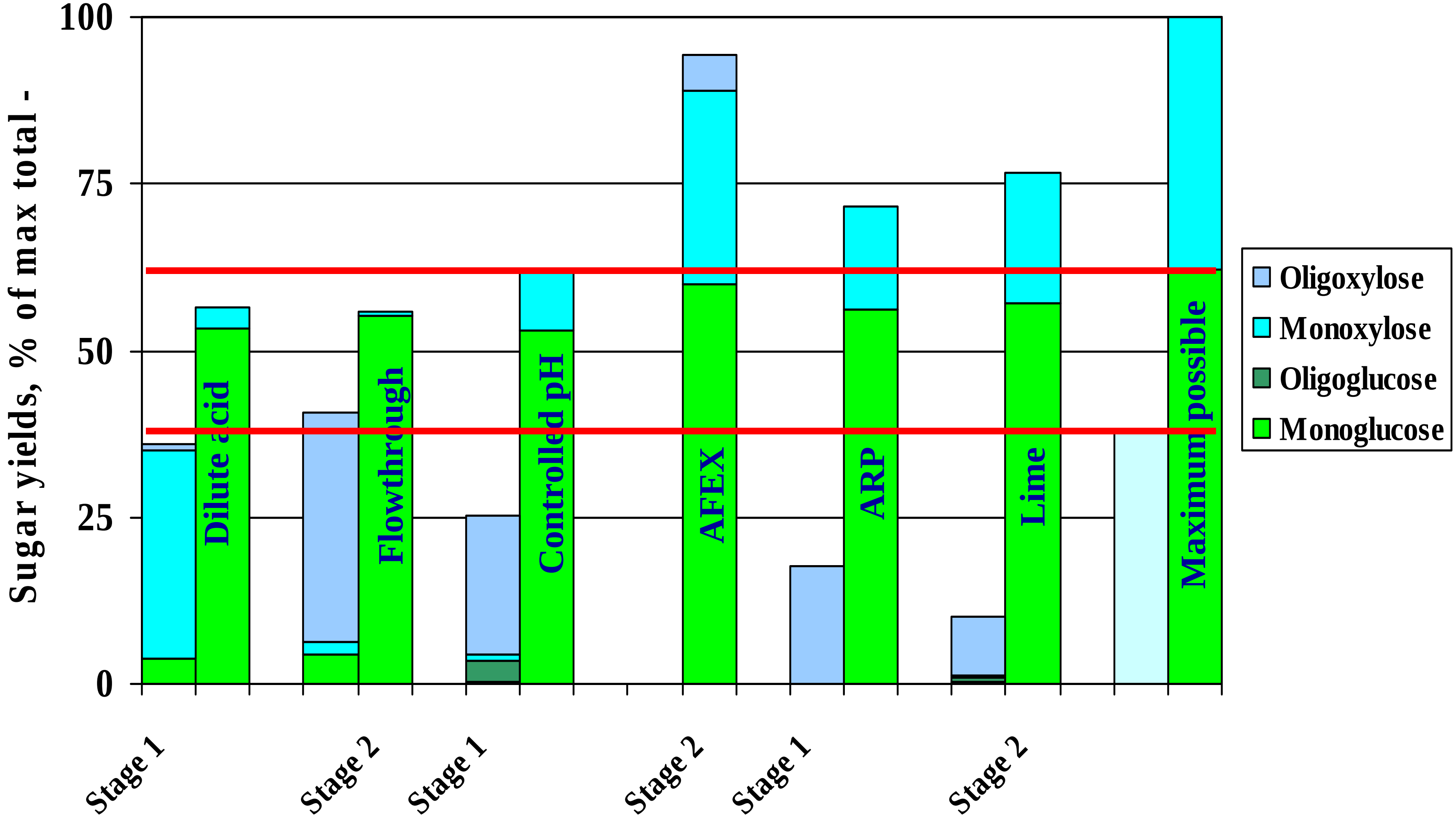
Previous Sugar Yields from Corn Stover at 15 FPU/g Glucan Enzyme



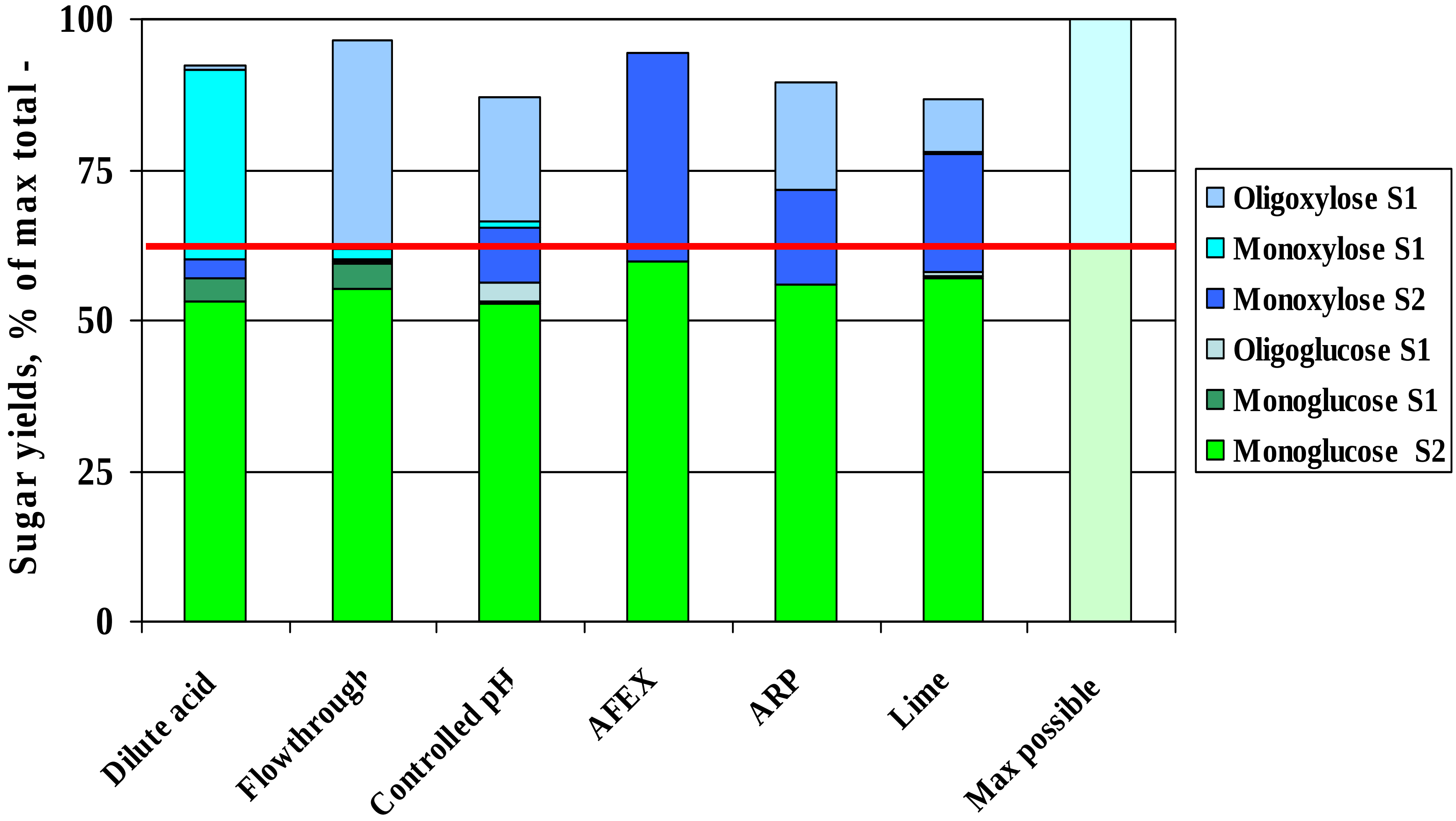
Previous Sugar Yields from Corn Stover at 15 FPU/g Glucan Enzyme



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



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



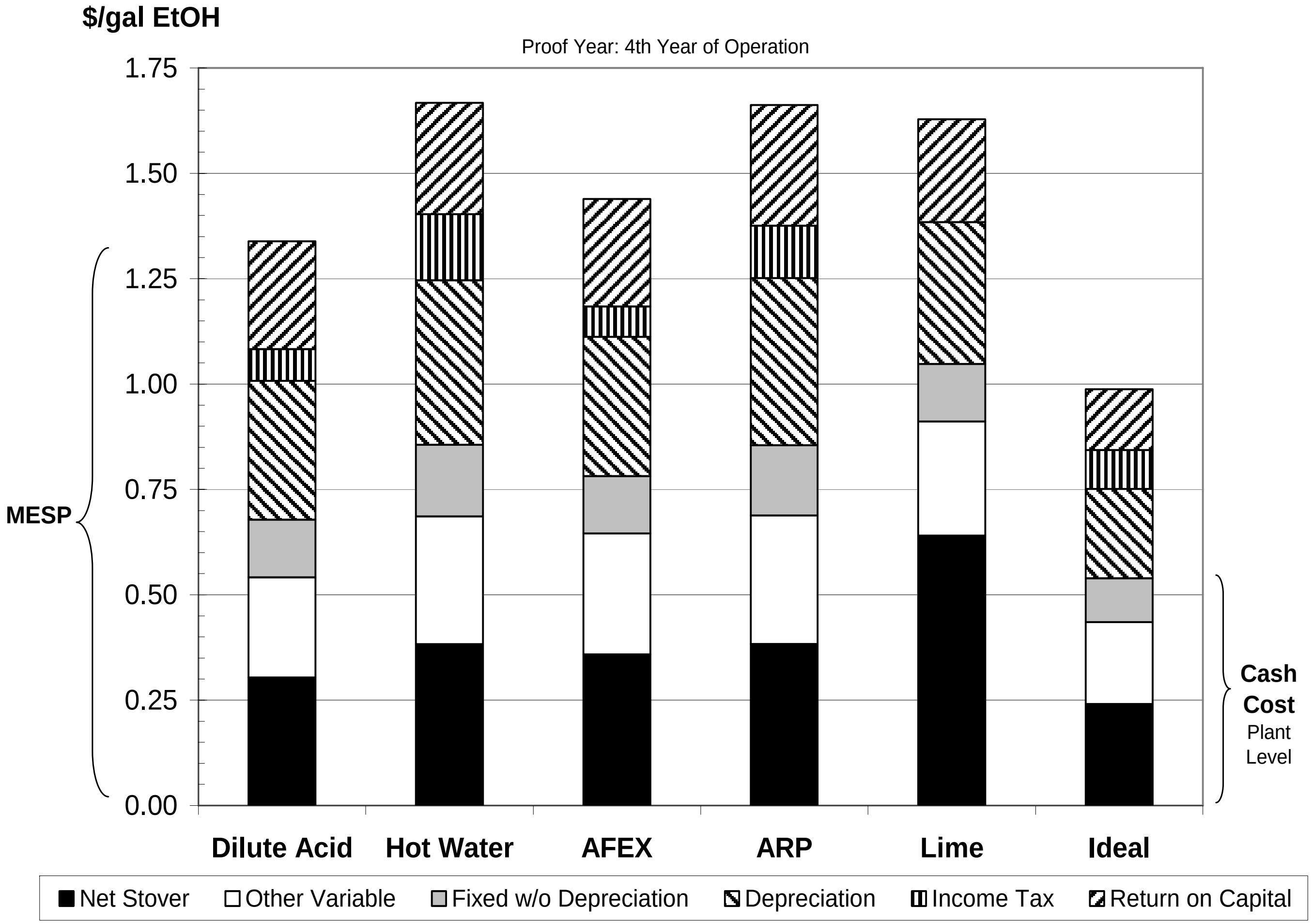
Capital Cost Estimates

Basis: 2000 metric tons (dry basis) corn stover/day, assumes only monomers fermented

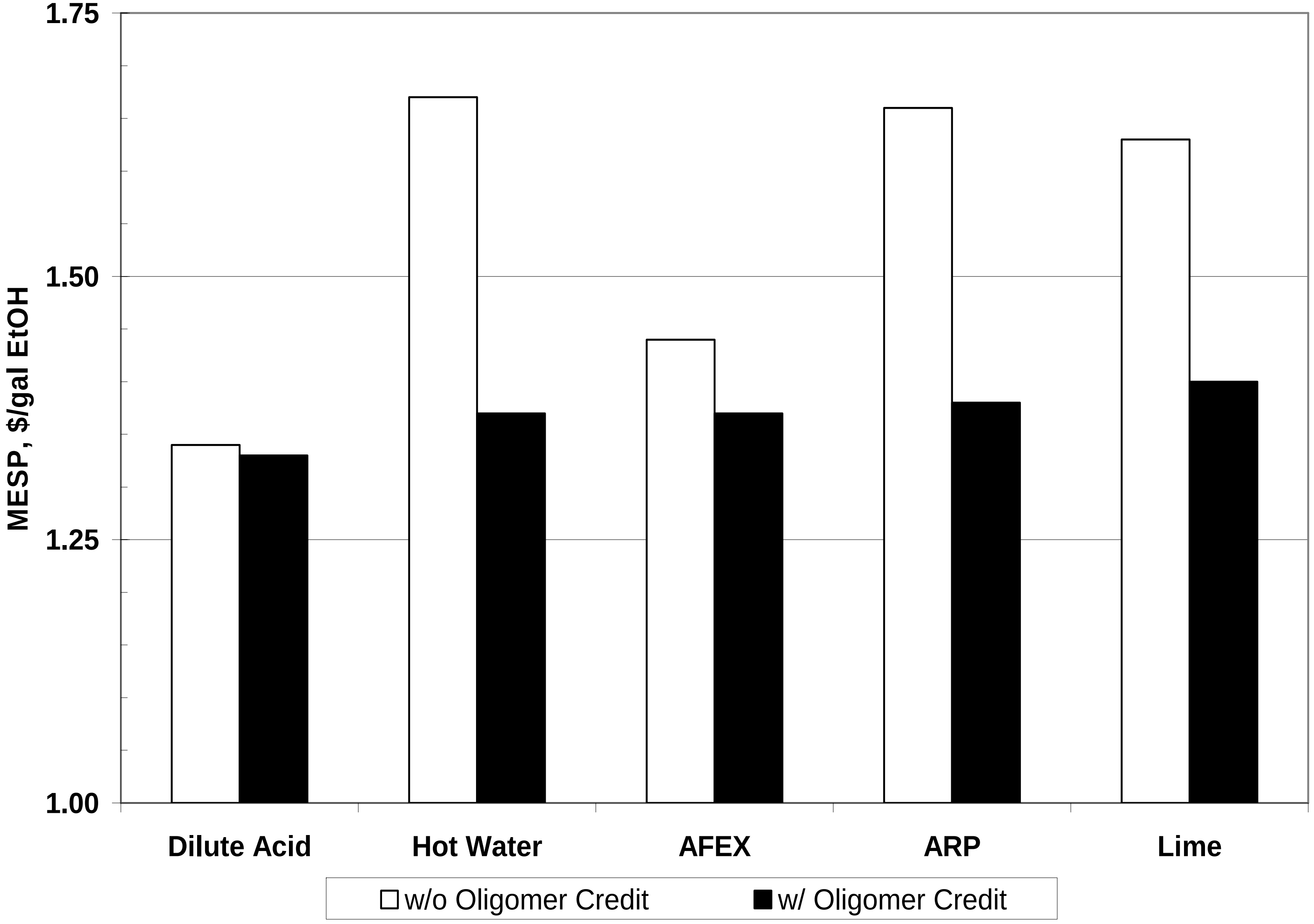
Pretreatment System	Pretreatment Direct Fixed Capital ($MM)	Pretreatment Breakdown, (% Reactor/ % Other)	Total Fixed Capital ($MM)	Ethanol Production (MM gal/yr)	Total Fixed Capital ($/gal Annual Capacity)
Dilute Acid	25.0	64/36	208.6	56.1	3.72
Controlled pH Hot Water	4.5	100/0	200.9	44.0	4.57
AFEX	25.7	26/74	211.5	56.8	3.72
ARP	28.3	25/75	210.9	46.3	4.56
Lime	22.3	19/81	163.6	48.9	3.35
No Pretreatment	0	-	200.3	9.0	22.26
Ideal Pretreatment	0	-	162.5	64.7	2.51

Minimum Ethanol Selling Price (MESP)

<u>Assumptions</u>: 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



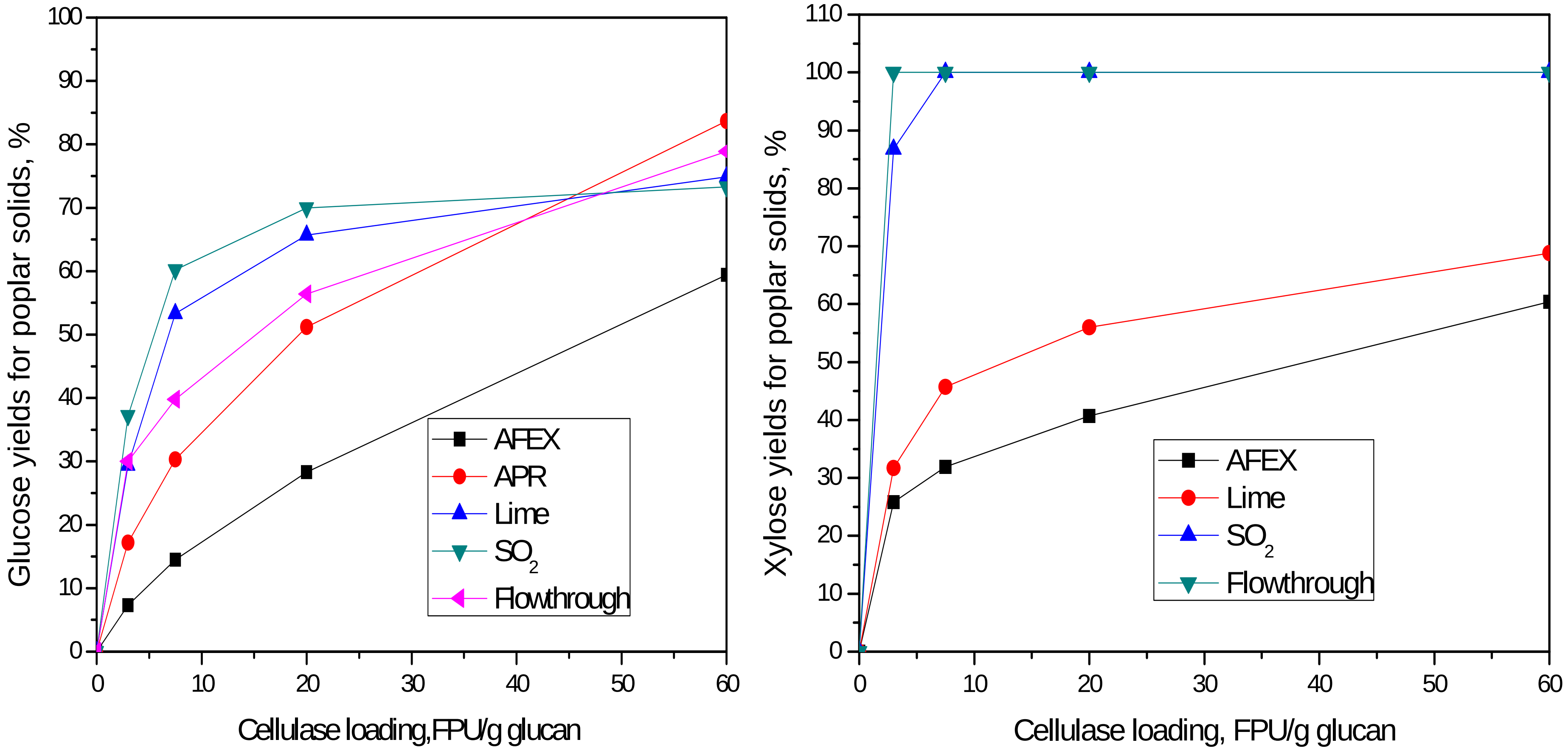
Effect of Oligomer Conversion



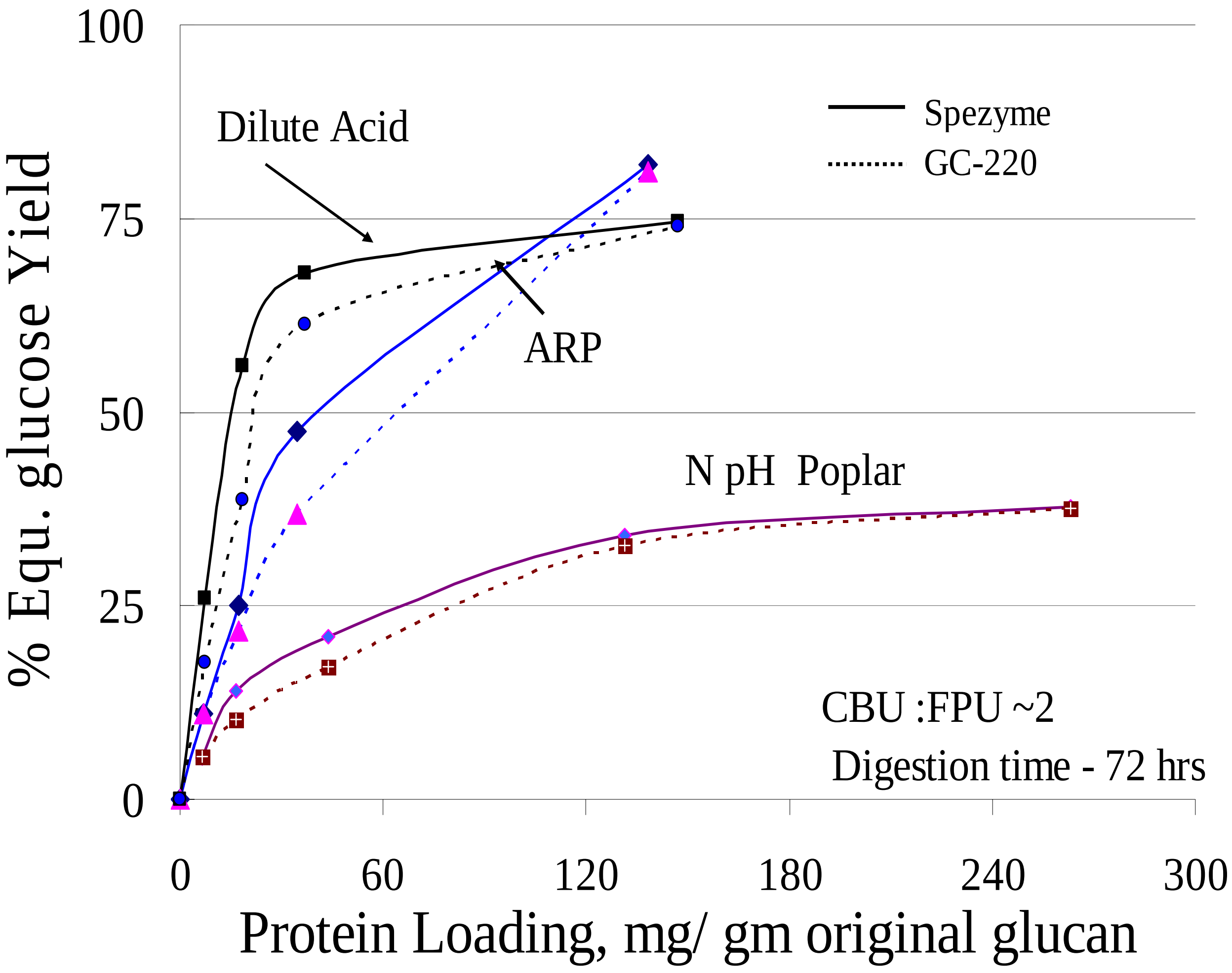
CAFI Poplar

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

Glucose and Xylose Yields for Poplar Solids



Enzymatic Hydrolysis of Standard Poplar



CAFI II Initial Poplar

- Feedstock: USDA-supplied hybrid poplar (Arlington, WI)
  - Debarked, chipped, and milled to pass ¼ 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

CAFI II Initial Poplar

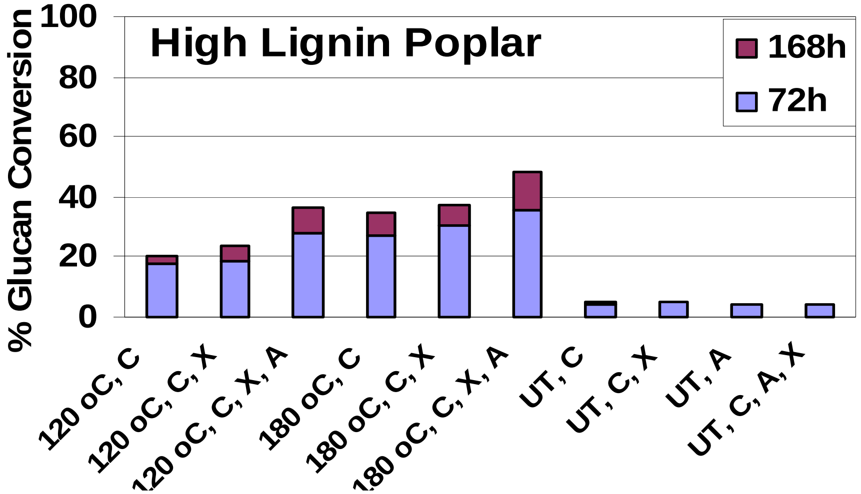
- Feedstock: USDA-supplied hybrid poplar (Arlington, WI)
  - Debarked, chipped, and milled to pass ¼ inch round screen
  - Not enough to meet needs

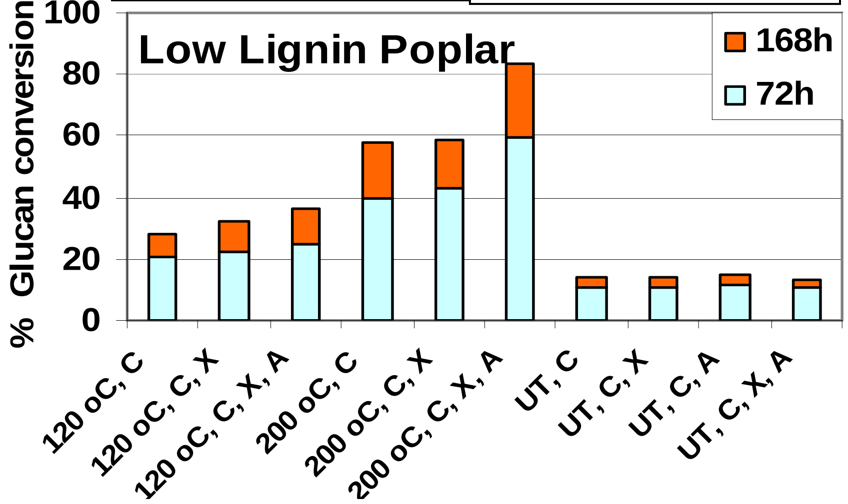
Component	Wt %
Glucan	45.1
Xylan	17.8
Arabinan	0.5
Mannan	1.7
Galactan	1.5
Lignin	21.4
Protein	nd
Acetyl	5.7
Ash	0.8
Uronic Acids	nd
Extractives	3.4

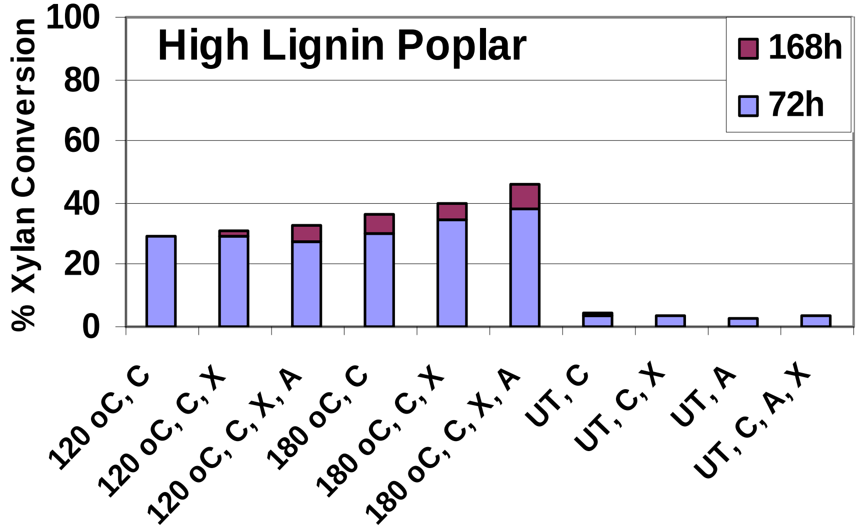
AFEX Optimization for High/Low Lignin Poplar

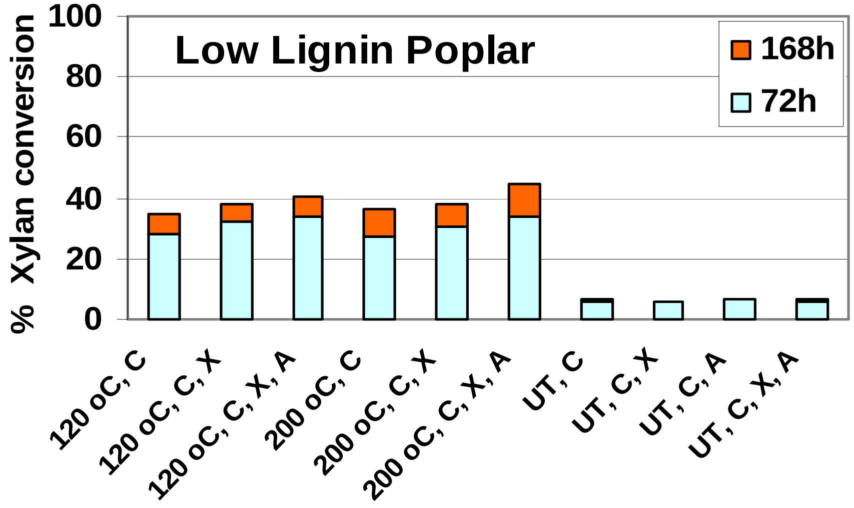
C - Cellulase
(31.3 mg/g glucan)
X - Xylanase
(3.1 mg/g glucan)
A - Additive
(0.35g/g glucan)

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









Why Is Variability Important?

- Impacts yields for most of 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
▪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	▪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

- US Department of Agriculture Initiative for Future Agricultural and Food Systems Program, Contract 00-52104-9663
- US Department of Energy Office of the Biomass Program, Contract DE-FG36-04GO14017
- Natural Resources Canada
- All of the CAFI Team members, students, and others who have been so cooperative
- University of California at Riverside

Questions???