Pretreatment: The Key to Unlocking Low Cost Cellulosic Ethanol

Charles E. Wyman
University of California
Riverside, California
and
Mascoma Corporation
Cambridge, Massachusetts

Biofuels and Bioenergy:
Challenges and Opportunities
IEA Bioenergy Meeting
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,

Mascoma Corporation

- Conceived in summer 2005
- Developing advanced technologies for conversion of cellulosic biomass to ethanol
  - Initially based on Dartmouth biological systems
- Forming partnerships to commercialize advanced cellulosic ethanol technologies

Mascoma Corporation

- Founders: Charles Wyman, Lee Lynd
- President: Colin South
- Chairman of Board: Vinod Khosla
- First round of capital from Khosla Ventures, Flagship Ventures
- More information: Mascoma.com

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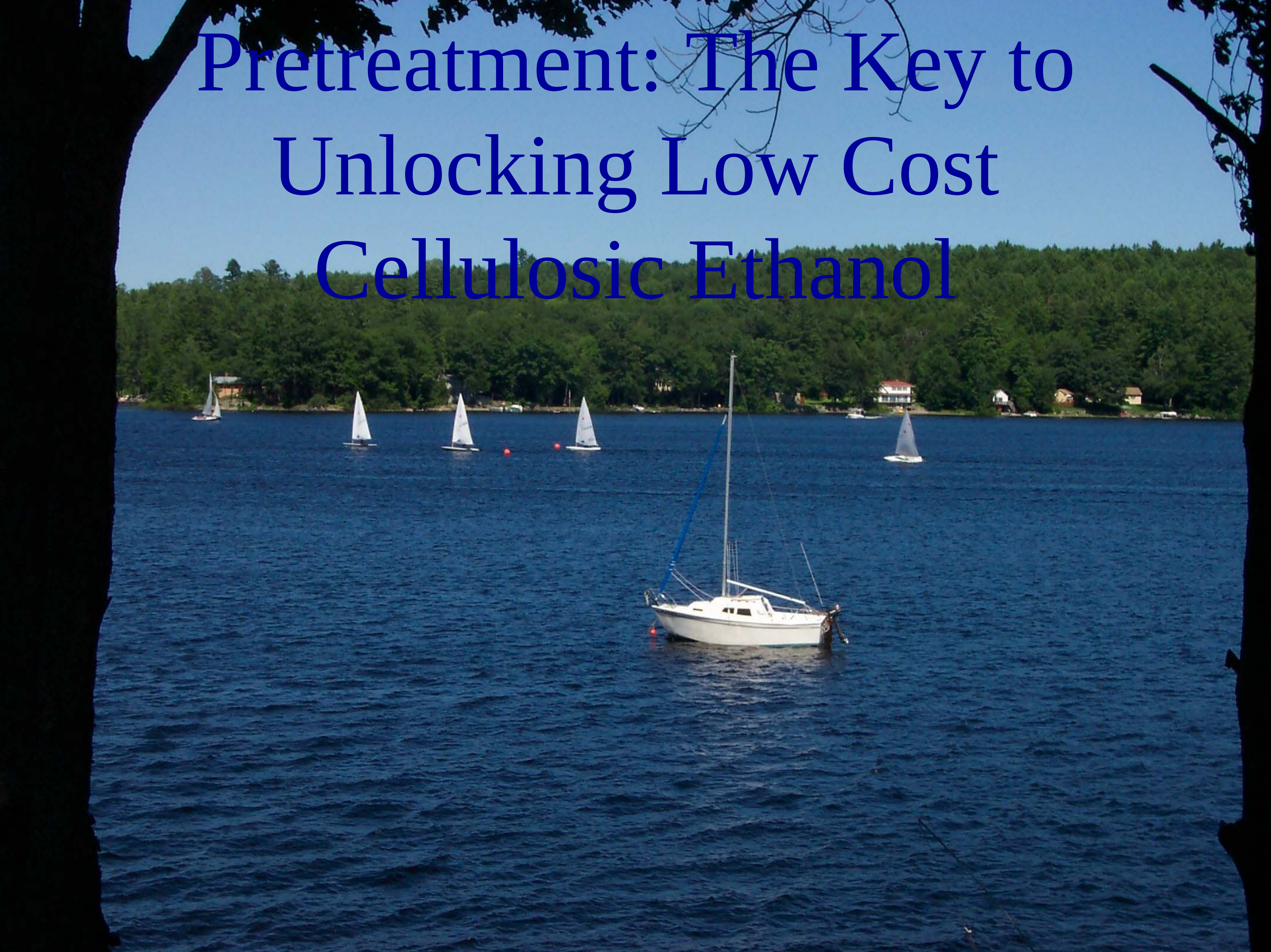


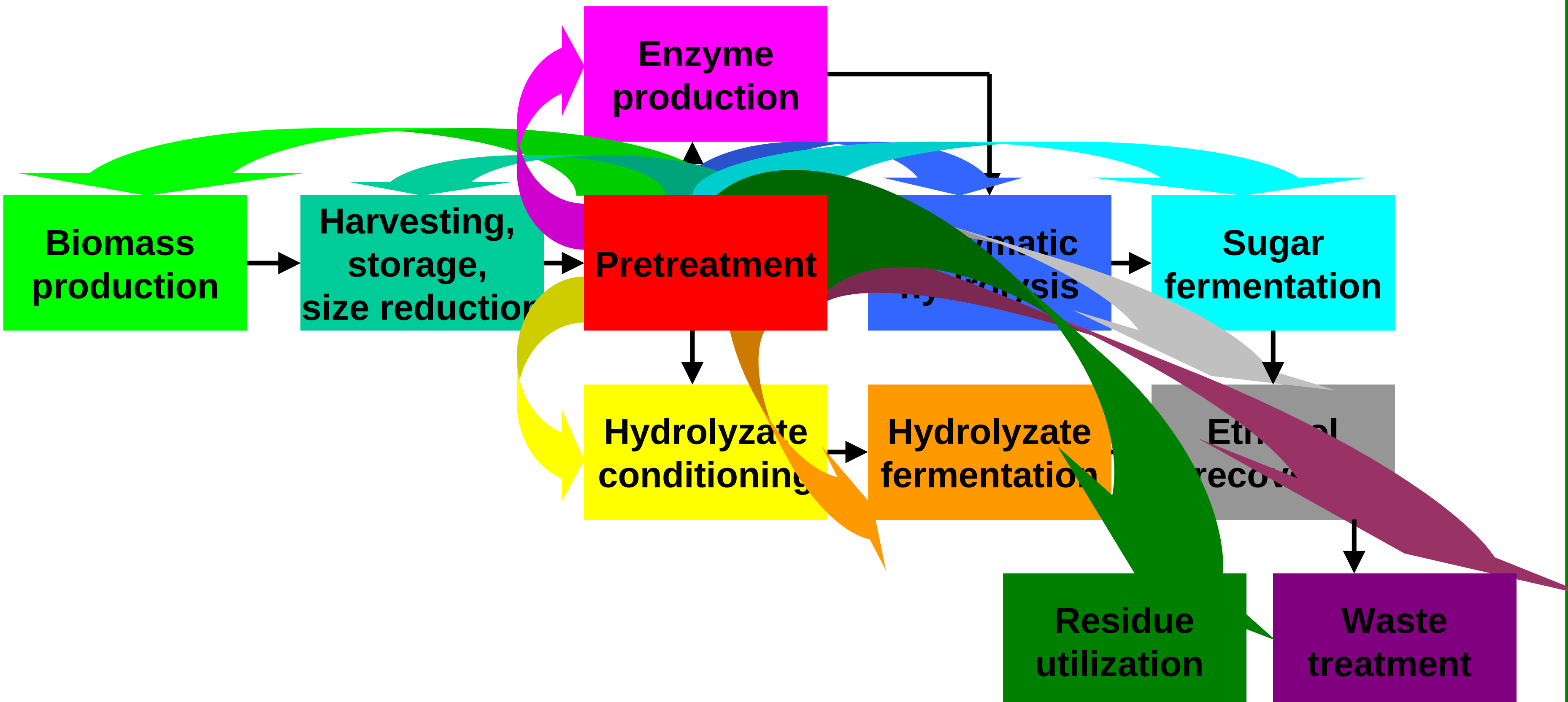
Overall Status of Cellulosic Ethanol

- Operating costs are low
- Technology is ready to be commercialized
- 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 are to improve ability to predict performance to support first uses and to advance technologies to reduce costs

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



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

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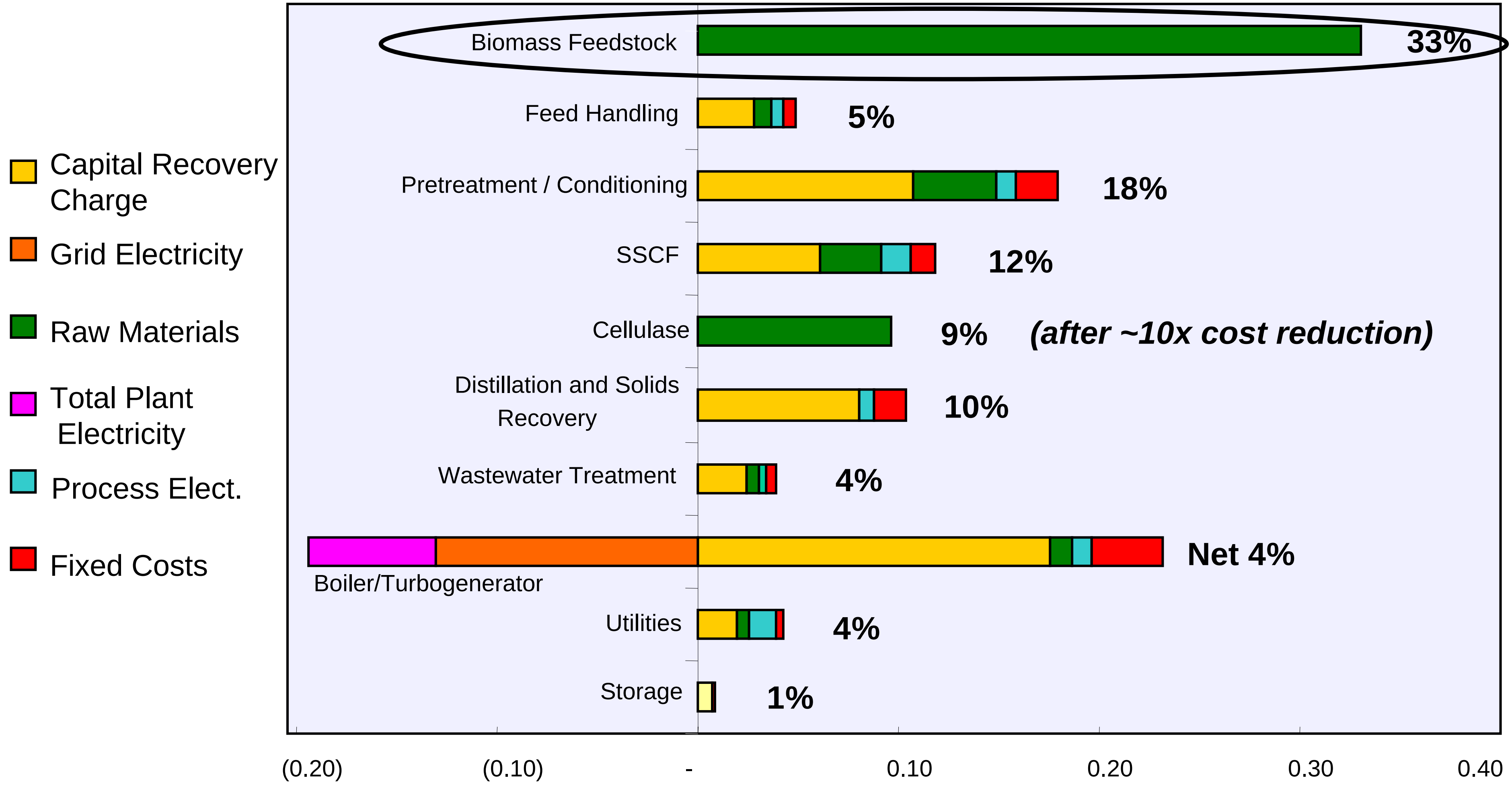
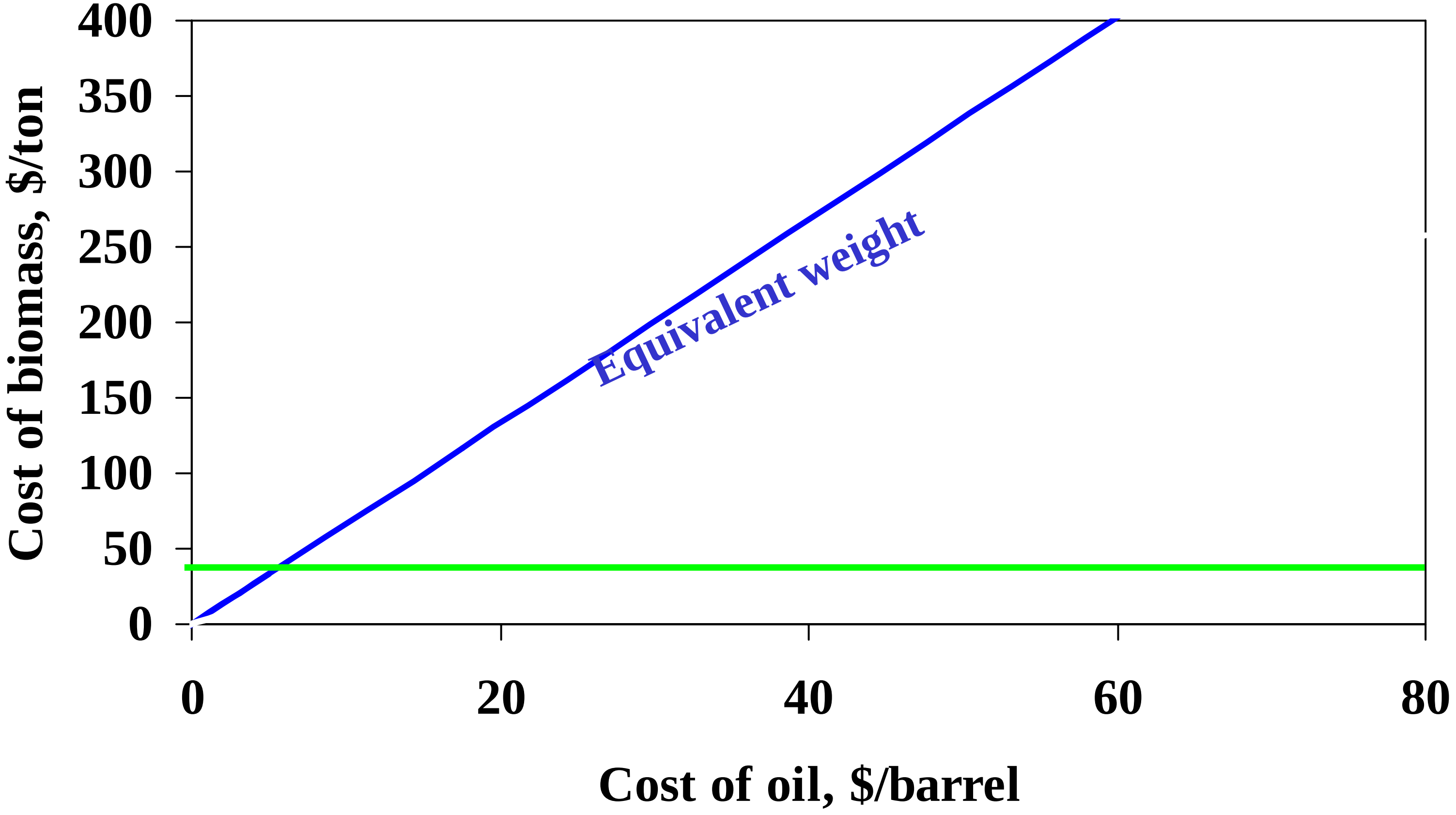
Key Processing Cost Elements



Cost of Cellulosic Biomass vs Petroleum



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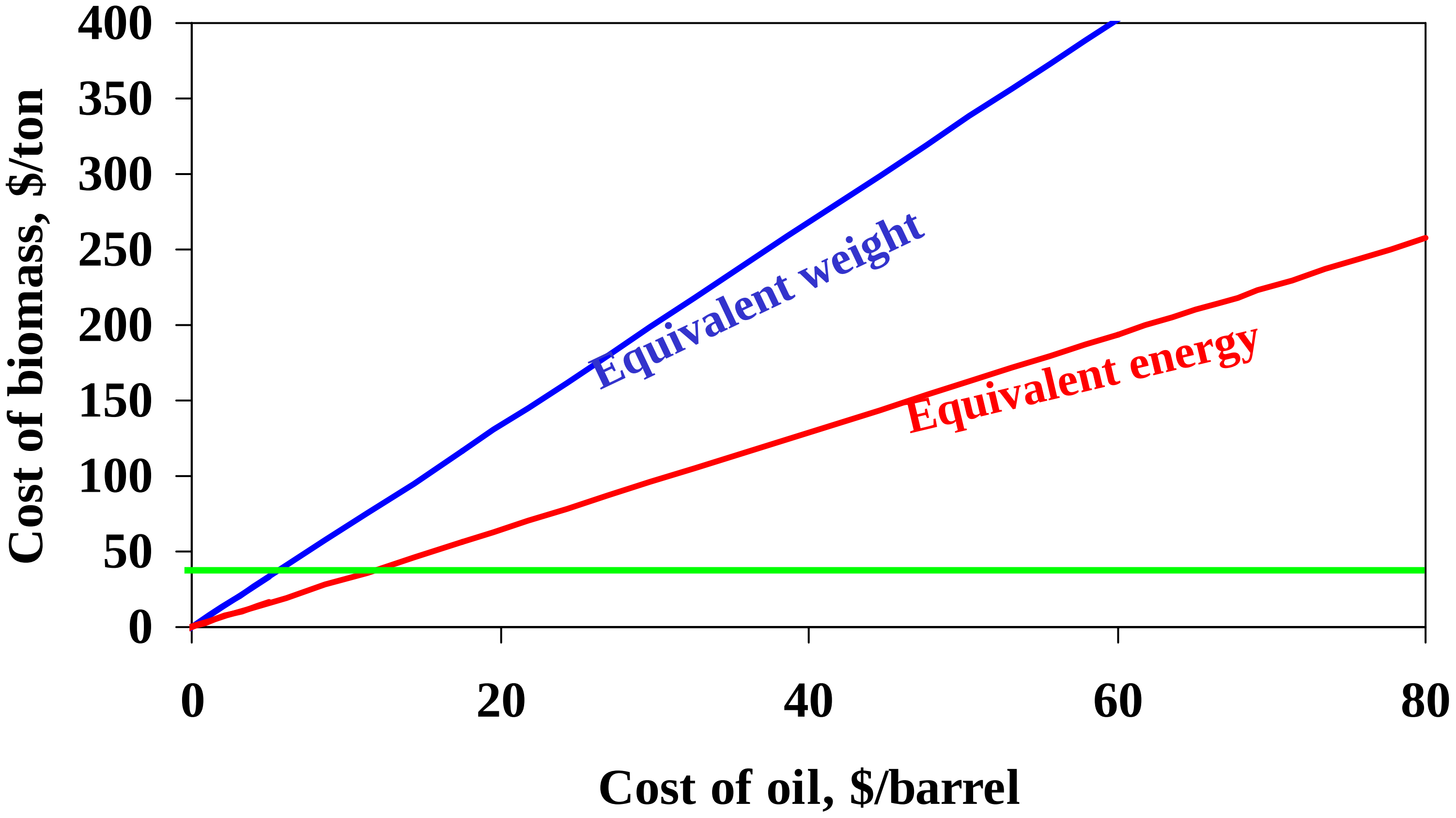

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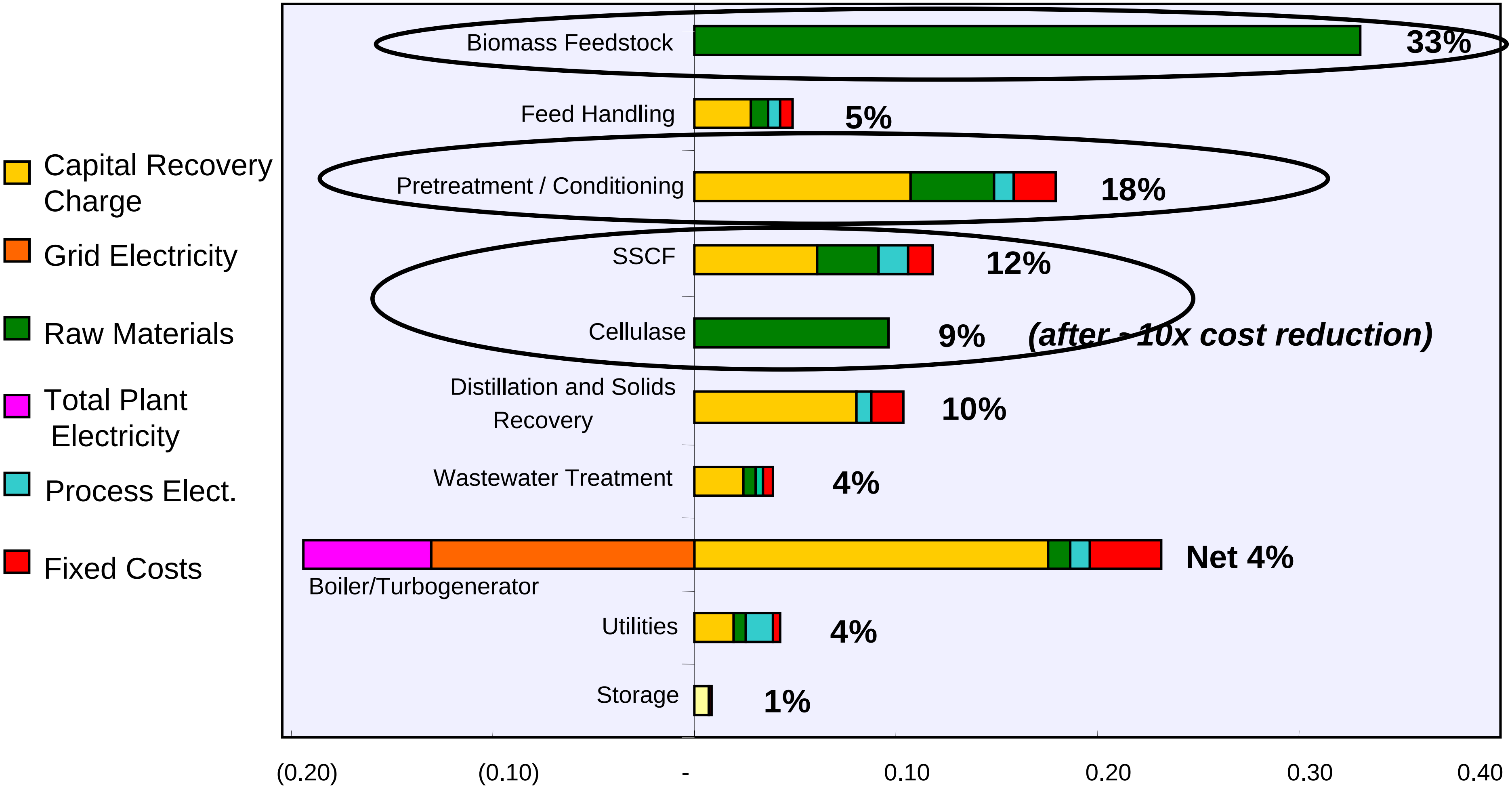

Importance of Pretreatment

- 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

Current and Goal Yields

Parameter	Current	Goal
Feedstock storage	97% +	99%
Xylan to xylose	63%*	95%
Pretreatment solids loading	30%*	50%
Pretreatment materials construction	Hastelloy	CS equiv’lt
Pretreatment pressure	100 psig	<30 psig
Conditioning	87-88%*	99%
Xylose to ethanol	95%	95%
Minor sugars to ethanol	92%	95%
Cellulase loading	15 FPU/g	5 FPU/g
Product recovery	99%	99%

* from NREL

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CAFI Background

- Biomass Refining Consortium for Applied Fundamentals and Innovation organized in late 1999 and 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.

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

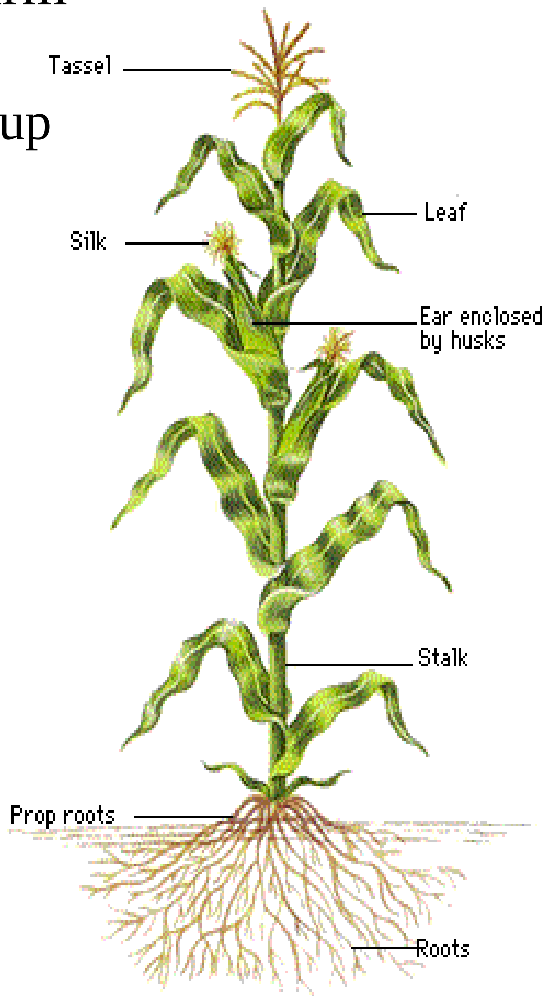
Tasks for the DOE OBP CAFI II Project

- Pretreat corn stover and poplar by leading technologies to improve cellulose accessibility to enzymes
- Enzymatically hydrolyze cellulose and hemicellulose in pretreated biomass, as appropriate, and develop models to understand the relationship between pretreated biomass features, advanced enzyme characteristics, and enzymatic digestion results
- Develop conditioning methods as needed to maximize fermentation yields by a recombinant yeast, determine the cause of inhibition, and model fermentations
- Estimate capital and operating costs for each integrated pretreatment, hydrolysis, and fermentation system and use to guide research

CAFI II Corn Stover

- Second pass harvested corn stover from Kramer farm (Wray, CO)
  - Collected using high rake setting to avoid soil pick-up
  - No washing
  - Milled to pass ¼ inch round screen
- Performed like CAFI I material for all pretreatments

Component	Composition (wt %)
Sucrose	2.2
Glucan	34.4
Xylan	22.8
Arabinan	4.2
Mannan	0.6
Galactan	1.4
Lignin	11.0
Protein	2.3
Acetyl	5.6
Ash	6.1
Uronic Acids	3.8
Extractives	8.5

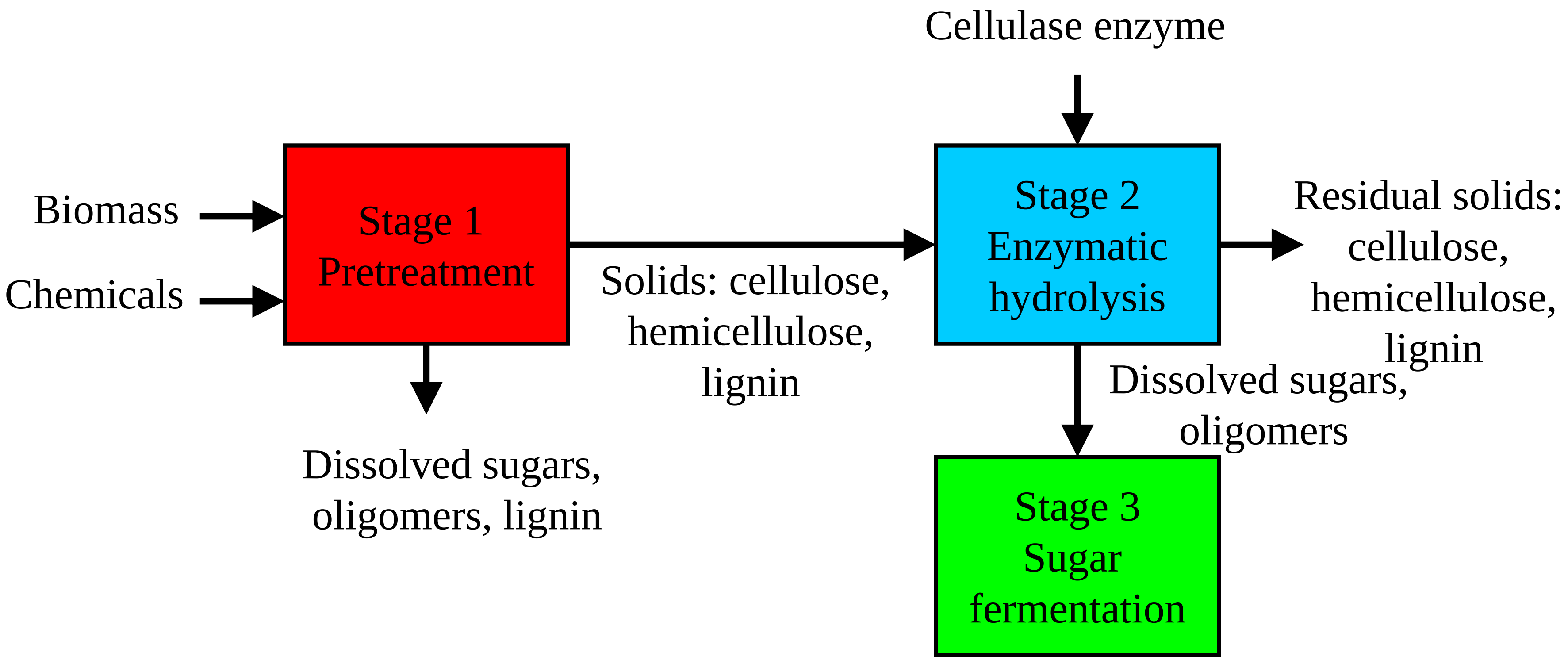


CAFI II Standard Poplar

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

CAFI II Hydrolysis Stages



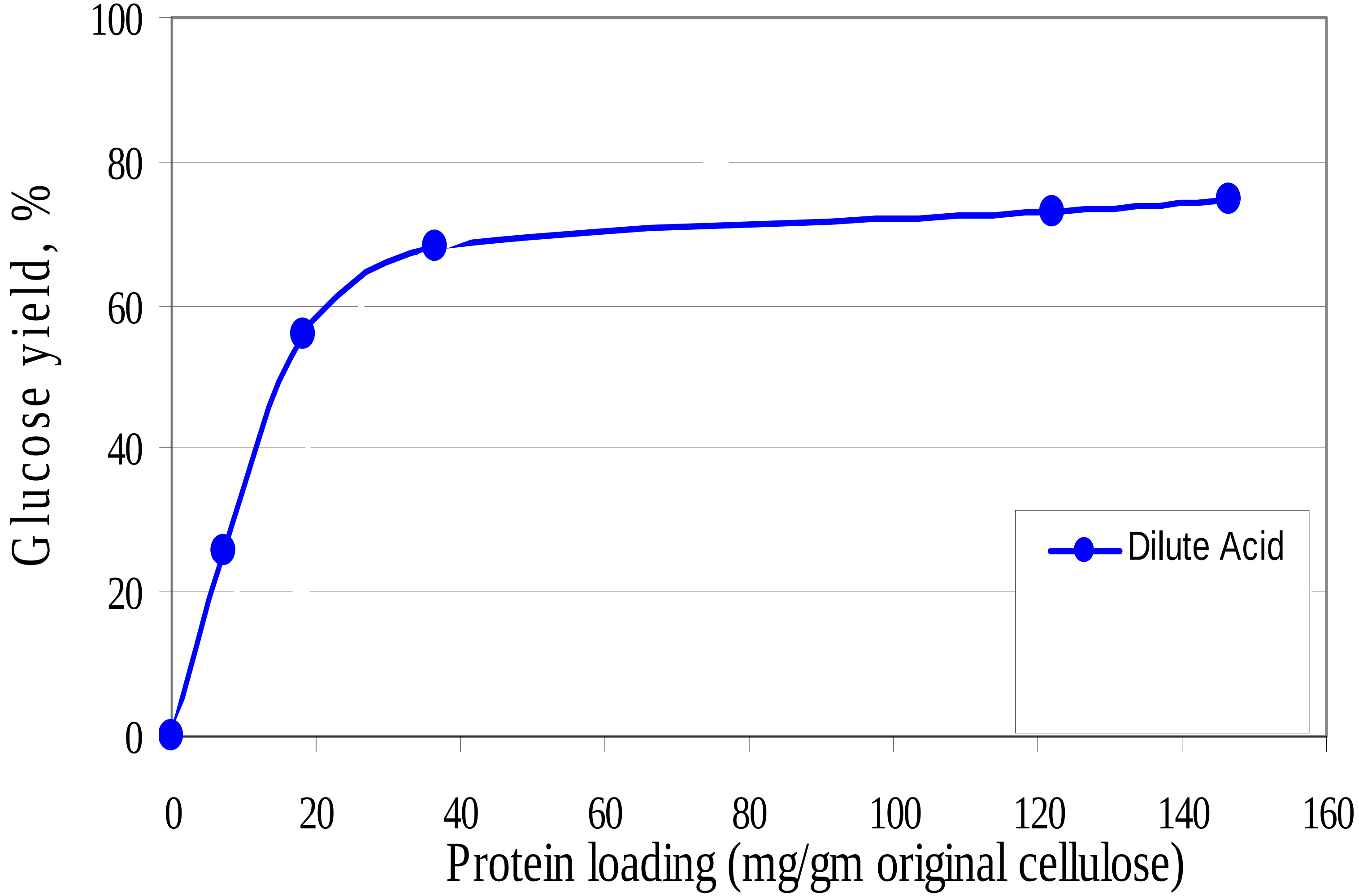
Overall Yields for Corn Stover at 15 FPU/g Glucan

Increasing pH

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

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

Effect of Protein Loadings on Cellulose Hydrolysis of Poplar Solids



Biomass Refining CAFI

Digestion time =72hr

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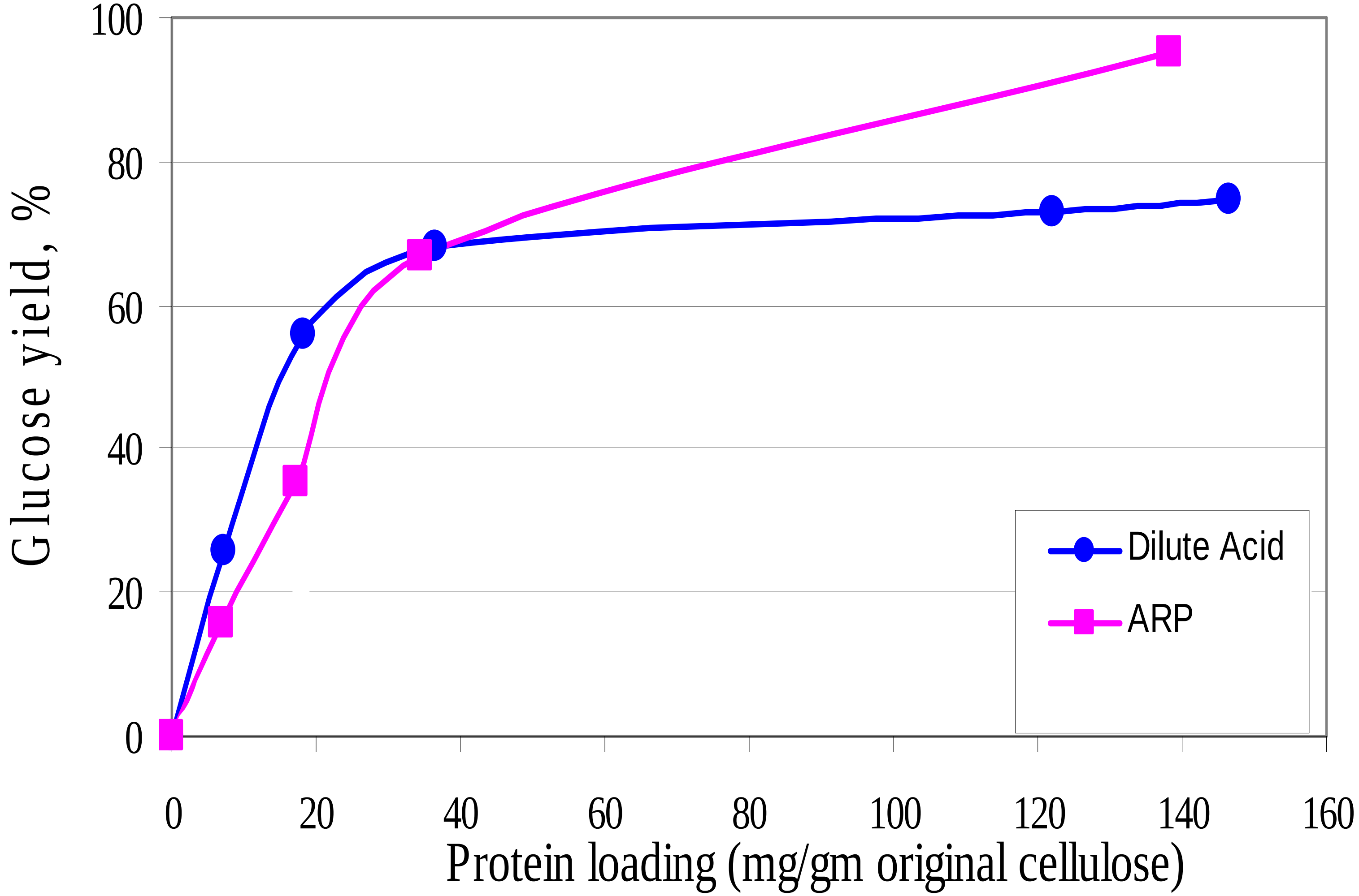

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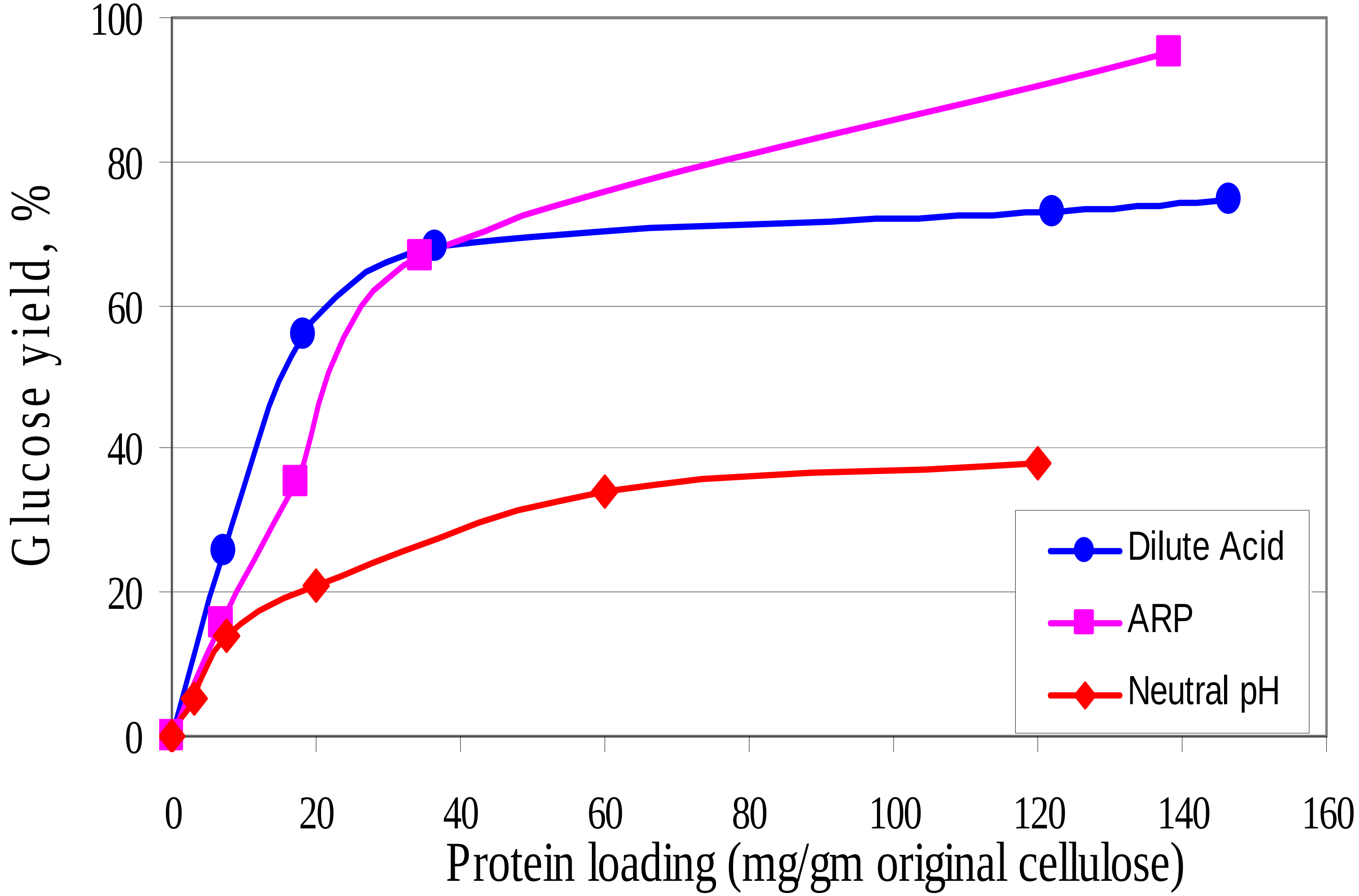

Biomass Refining CAFI

Digestion time =72hr

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

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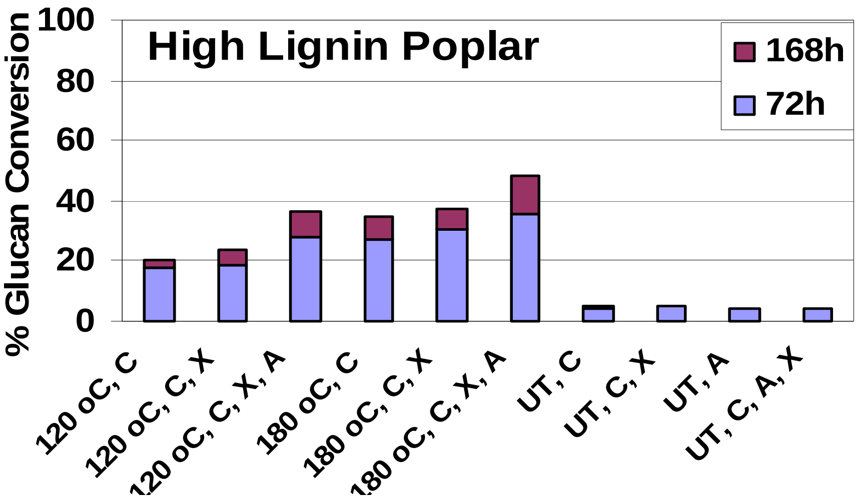
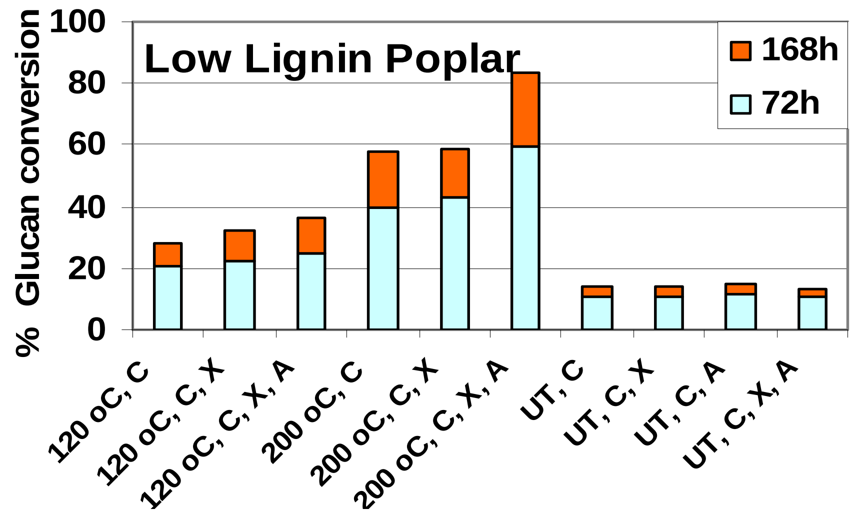
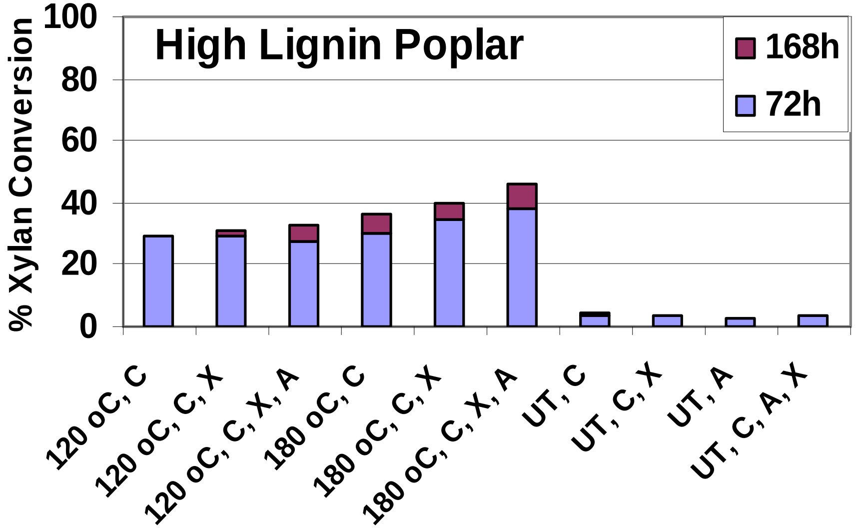
AFEX Optimization for High/Low Lignin Poplar

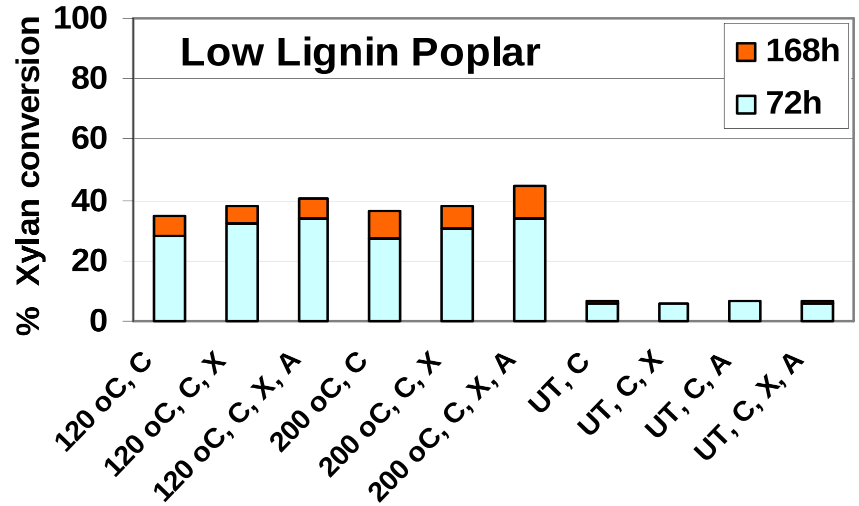
C - Cellulase
(31.3 mg/g glucan)
X - Xylanase
(3.1 mg/g glucan)
A - Additive
(0.35g/g glucan)

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









SO_2 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 SO_2 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

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

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

- Ford Motor Company and University of California for sponsoring this trip
- 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


V-Power
1,59
2,69
TOTAL A PAGAR
LITROS
PREÇO POR LITRO
Gilbarco
V-Power
Álcool Comum
anp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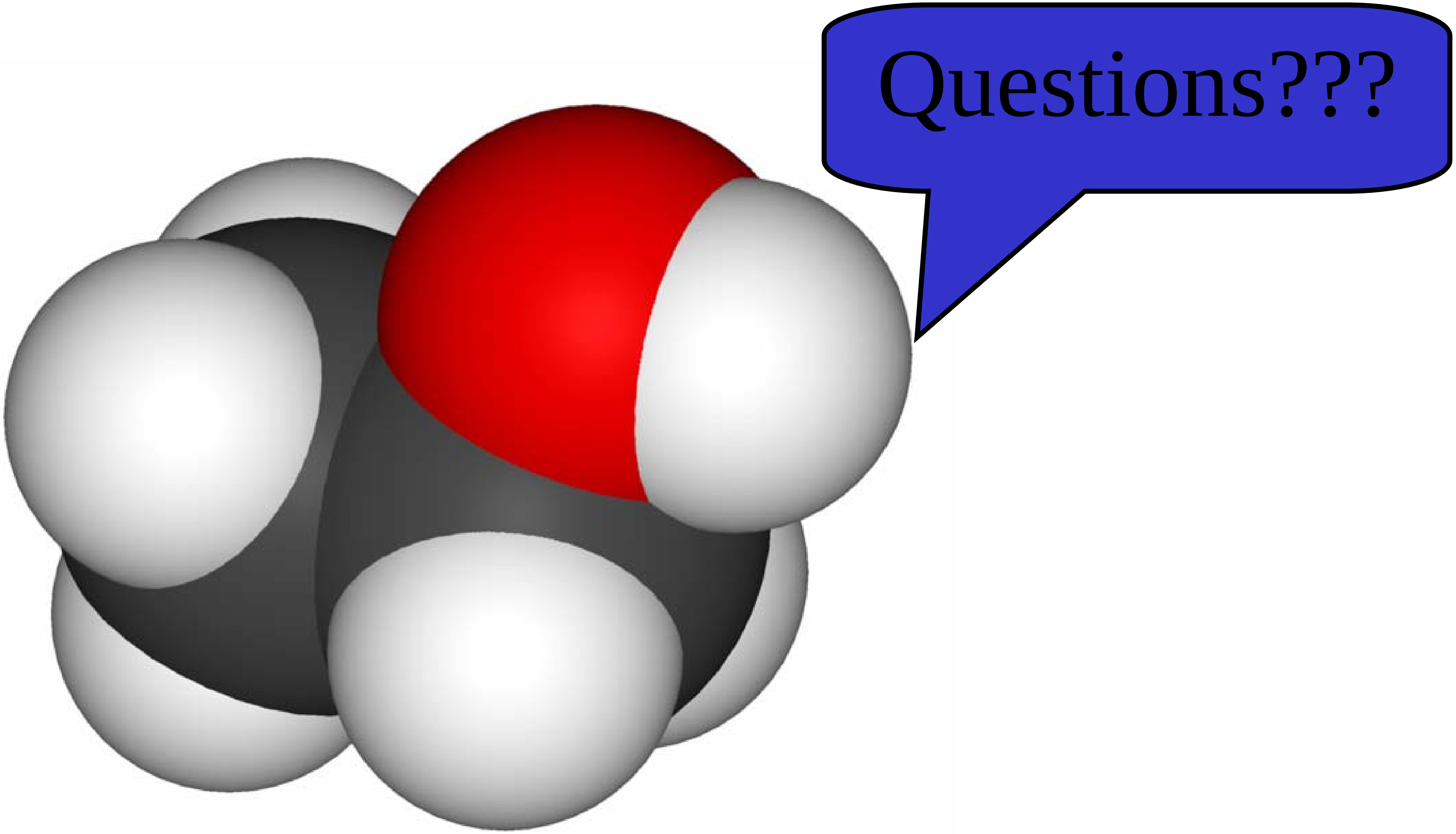
ConocoPhillips
Silco
Regular
$2.959 now
Diesel
309 9
E-85
Motor Fuel
1.99 9/10
Car Wash
For higher octane!


Questions???