Cellulosic Ethanol for Sustainable Transportation

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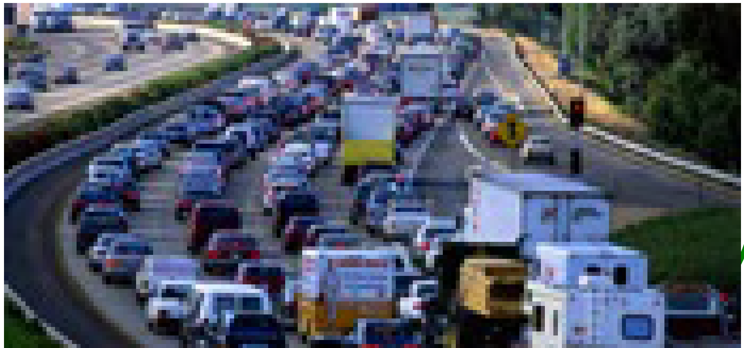
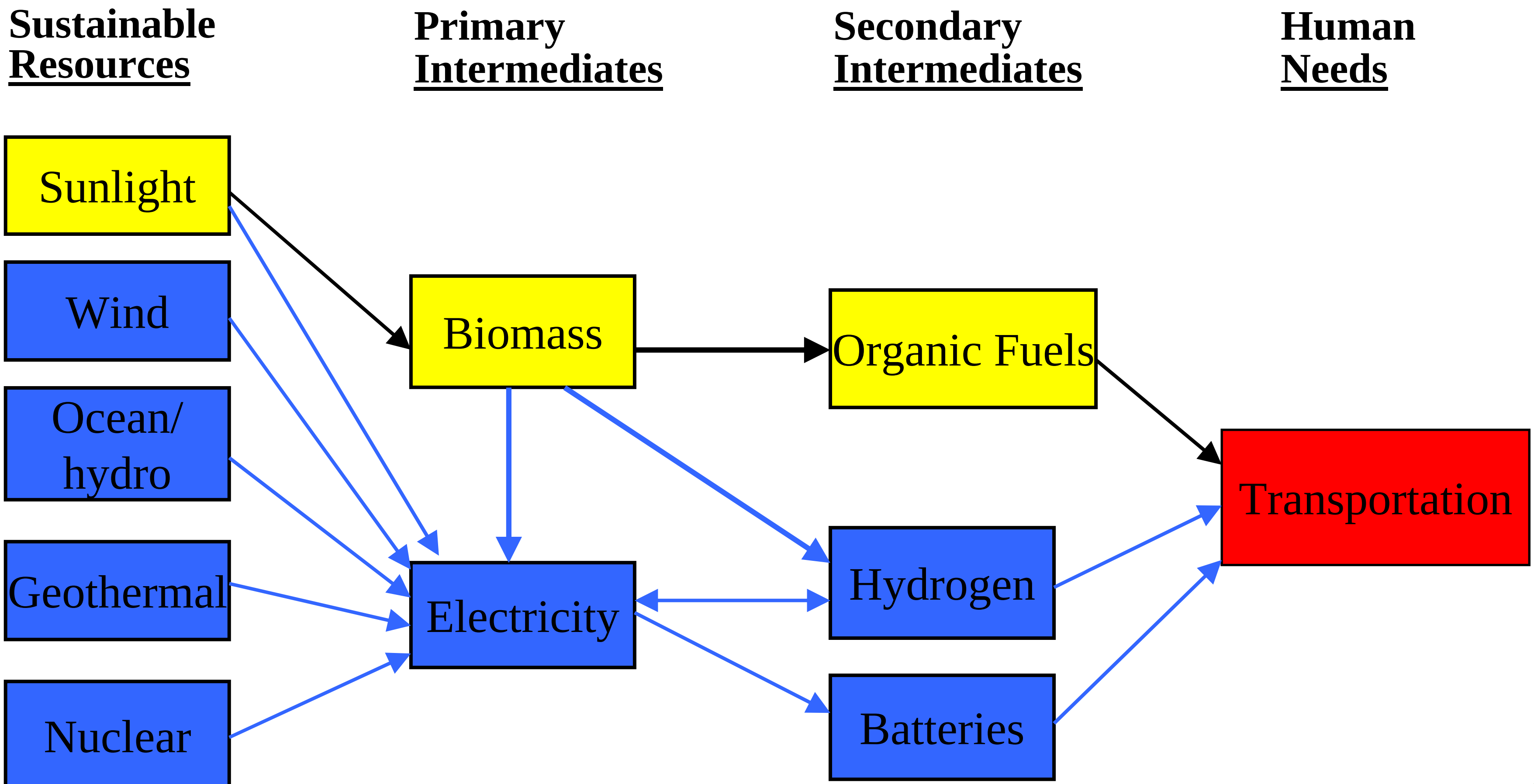
The Need: Reduce Petroleum Use

- Petroleum is largest source of energy in U.S. and the world
- About 2/3 of petroleum is imported to U.S.
- Nearing point where half of total world petroleum has been consumed
- M. King Hubbert of Shell predicted production declines when half of oil is gone – in 1956, he predicted 1970 peak in US production
- Largest fraction (~2/3) of petroleum used for transportation

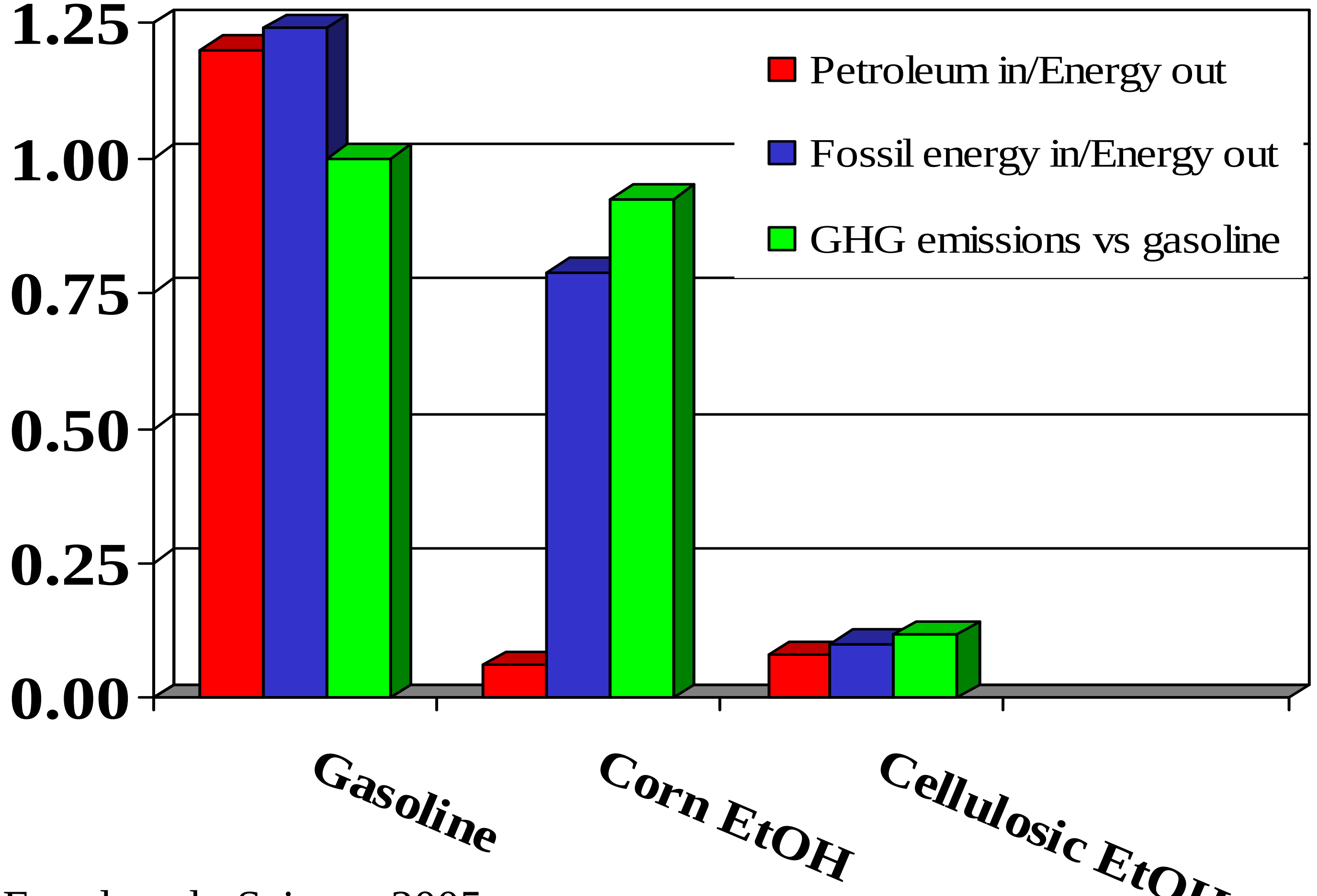


Sustainable Alternatives for Transportation



By Lee Lynd, Dartmouth

Relative Metrics for Ethanol



from Farrel et al., Science 2005

Focus: Cellulosic Biomass - Abundant, Inexpensive

- Existing resources
  - Agricultural wastes
    - Sugar cane bagasse
    - Corn stover and fiber
  - Forestry wastes
    - Sawdust
  - Municipal wastes
    - Waste paper
    - Yard waste
  - Industrial waste
    - Pulp/paper sludge

- Future resources
  - Dedicated crops
    - Herbaceous
    - Woody

- Not sugar or starch crops such as used for making ethanol in Brazil and the U.S. respectively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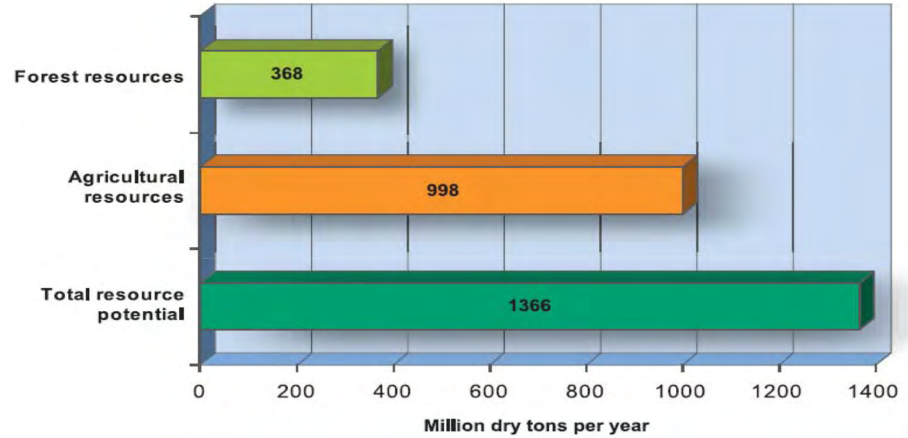
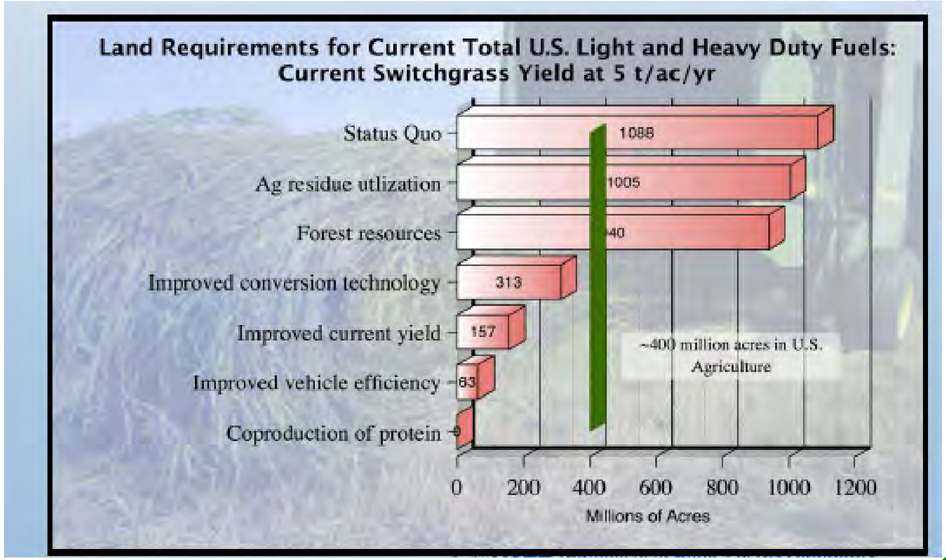
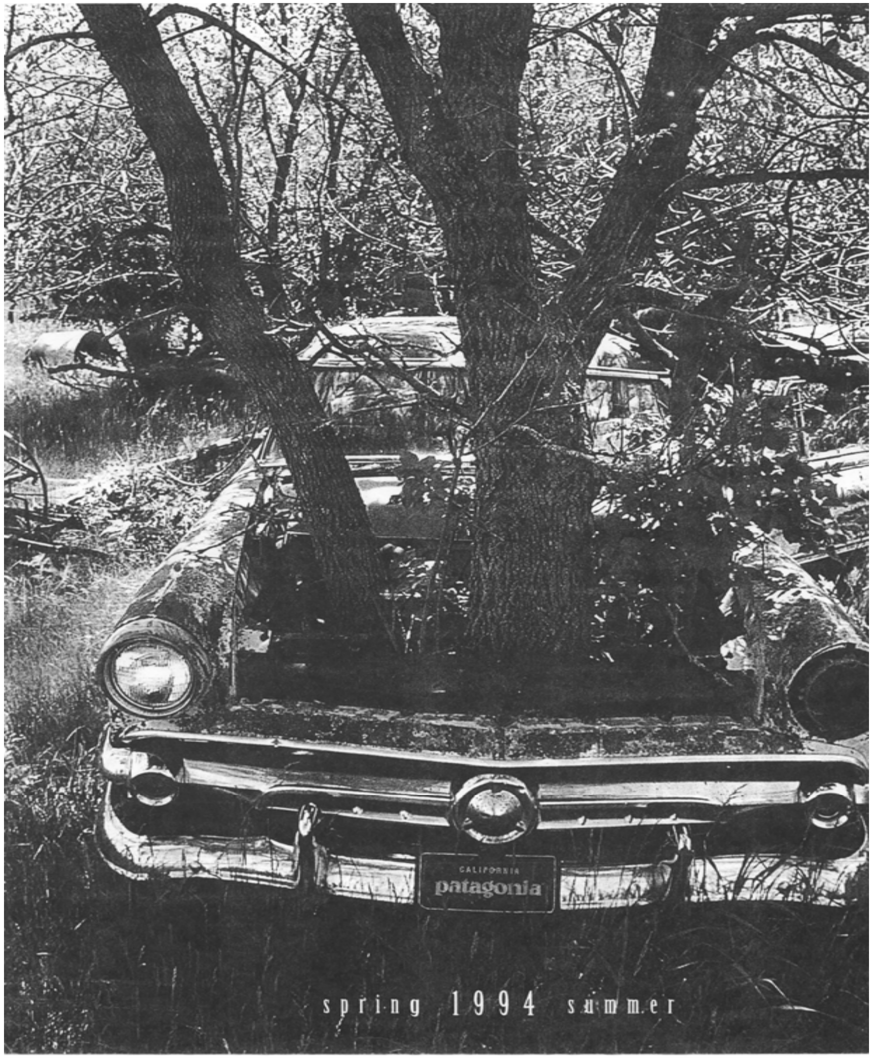
Cellulosic Biomass as a Major Energy Supply

- DOE and USDA recently estimated 1.3 billion tons of cellulosic biomass could be available
- Includes 368 million dry tons from forests and 998 million dry tons from agriculture
- “Role of Biomass Study” demonstrates the ability to meet current US light duty and heavy duty transportation fuel demand by using less than 16% of current agricultural land

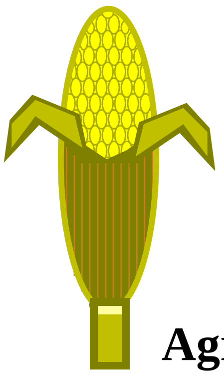




Challenge: How Do You Put Low Cost Biomass in Your Car?

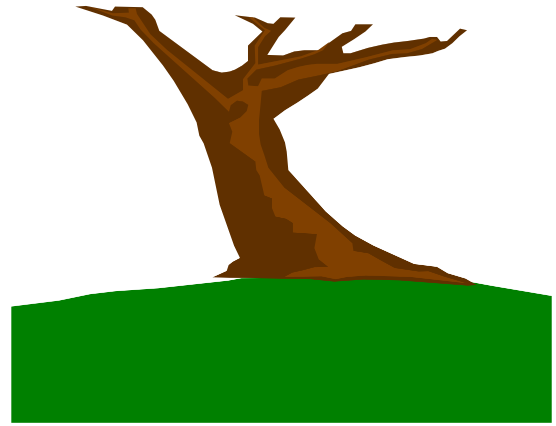


Cellulosic Biomass Composition



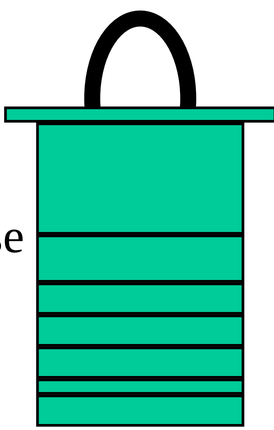
Cellulose 43%
Hemicellulose 27%
Lignin 17%
Other 13%

Agricultural Residues



Cellulose 45%
Hemicellulose 25%
Lignin 22%
Extractives 5%
Ash 3%

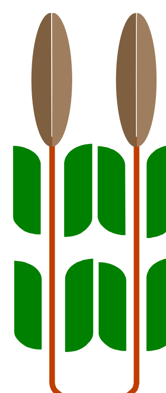
Woody Crops



Cellulose 45%

Ash 15%
Lignin 10%
Hemicellulose 9%
Other carbohydrates 9%
Protein 3%
Other 9%

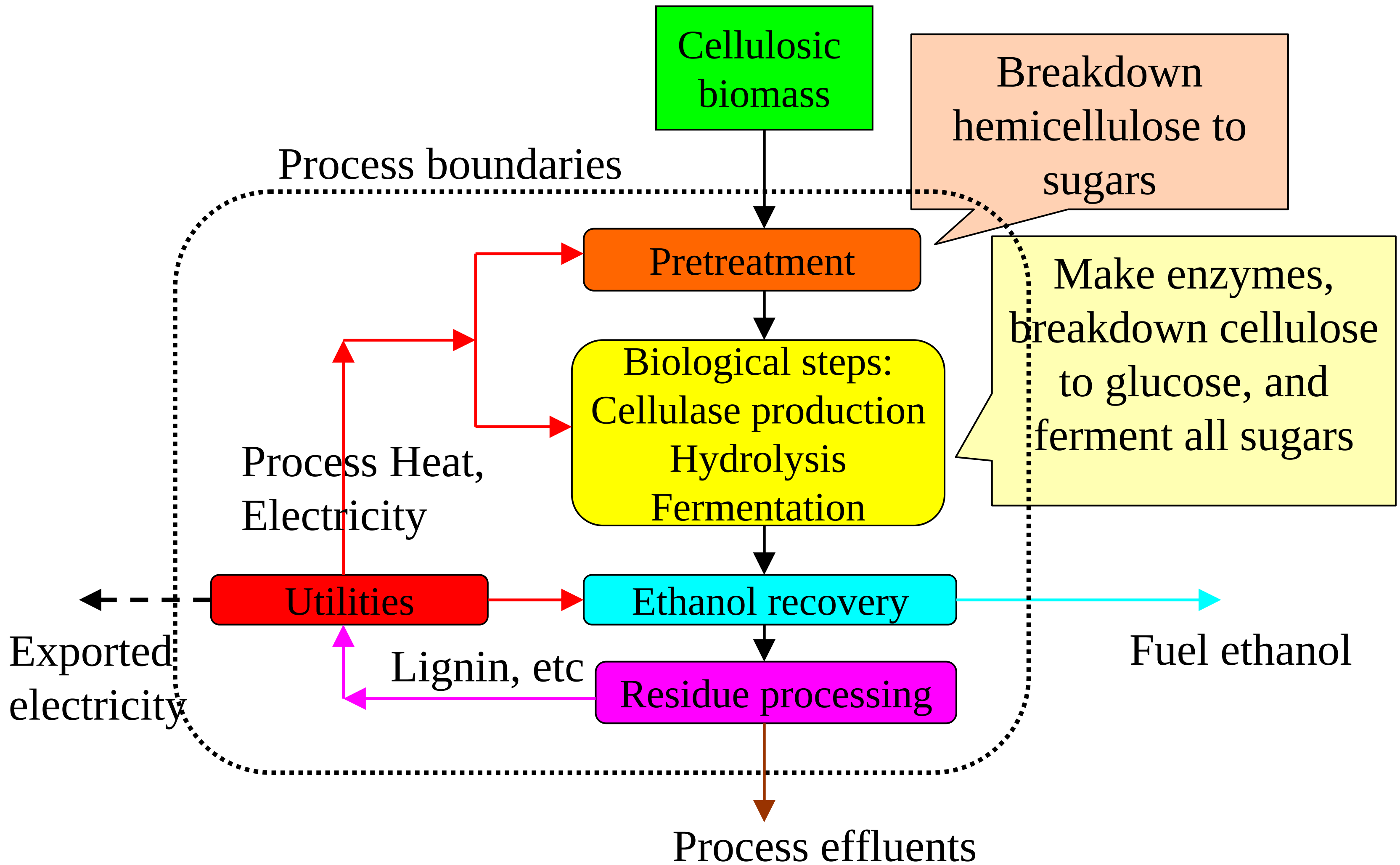
Municipal Solid Waste



Cellulose 45%
Hemicellulose 30%
Lignin 15%
Other 10%

Herbaceous Energy Crops

Enzymatic Conversion of Cellulosic Biomass to Ethanol



Cellulosic Biomass Pretreatment

- Need to open up structure to make cellulose accessible to enzymes - high digestibility
- High sugar yields from hemicellulose are also vital
- Low capital cost – pressure, materials of construction
- Low energy cost
- Low degradation
- Low cost and/or recoverable chemicals
- A large number of pretreatment technologies have been studied to improve cellulose digestion, but only a few show promise

CAFI 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

∗CAFI - Consortium for Applied Fundamentals and Innovation

CAFI DOE Project Advisory Board

1. Quang Nguyen, Abengoa Bioenergy
2. Mat Peabody, Applied CarboChemicals
3. Gary Welch, Aventinerei
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19. Joel Cherry, Novozymes
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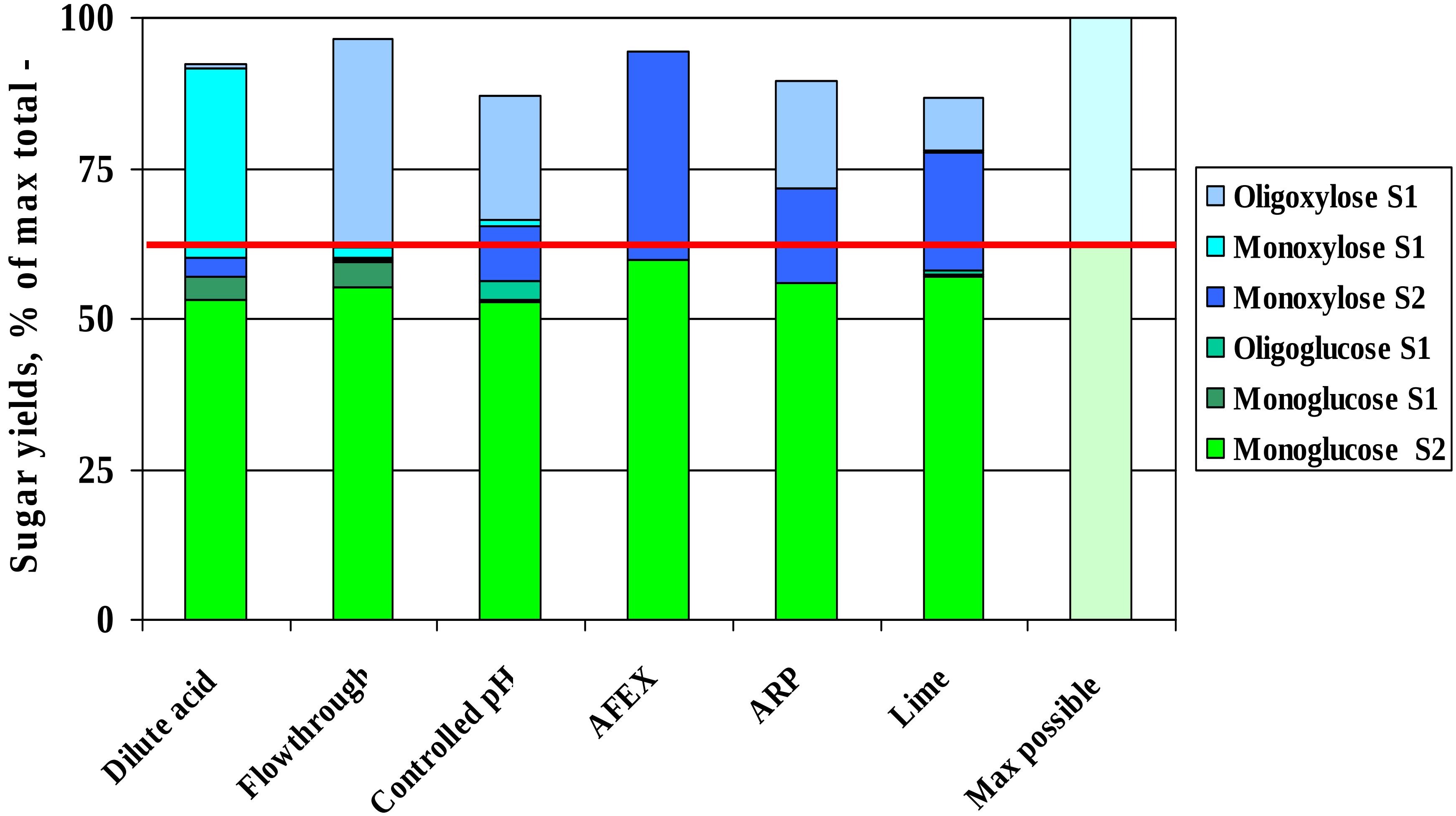
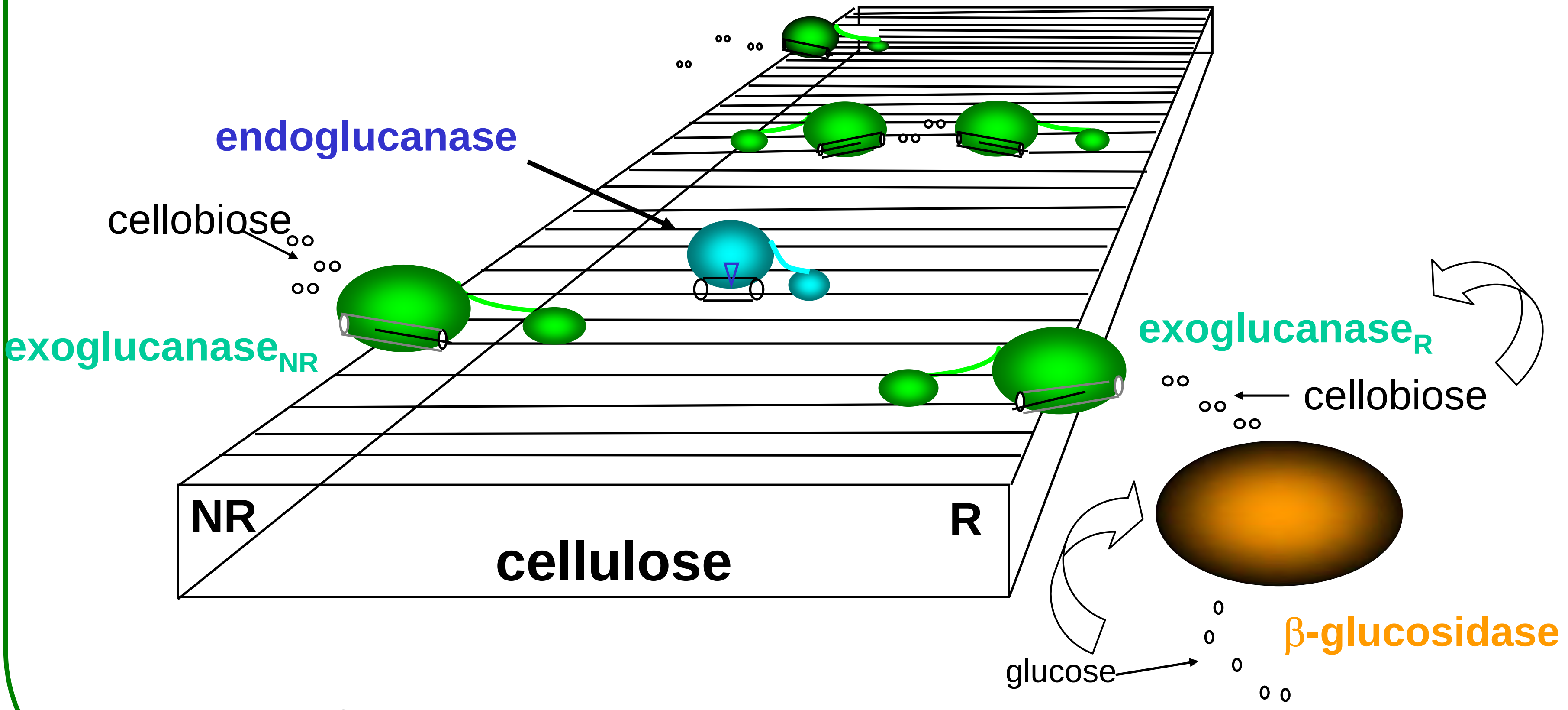
21. Carl Miller, Syngenta
22. Carmela Bailey, USDA
23. Don Riemenschneider, USDA

Total Yields at 15 FPU/g Glucan



Synergies and Inhibitions of Fungal Cellulases



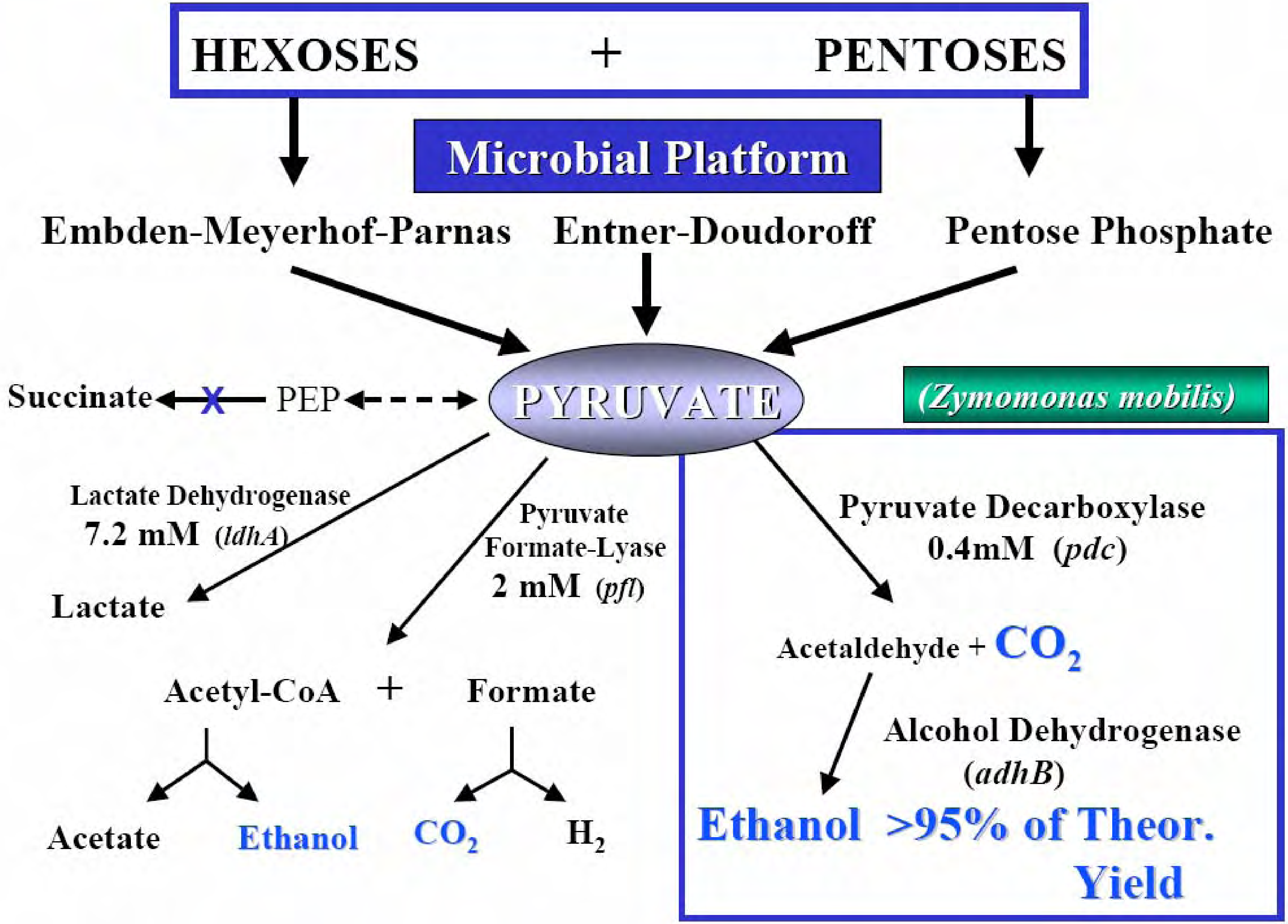
Courtesy of M. Himmel, NREL

Cellulase Enzymes

- Cellulase is expensive, particularly if purchased
- Need to reduce costs to about $0.05/gal of ethanol made
- Also need to take advantage of process integration to avoid cellulase purification and concentration
- DOE has funded Genencor and Novozymes to reduce cellulase cost
- Enzyme cost for corn stover to ethanol reduced to $0.10-$0.20 per gallon in laboratory trials by 2005

Full Sugar Utilization: The Historic Problem

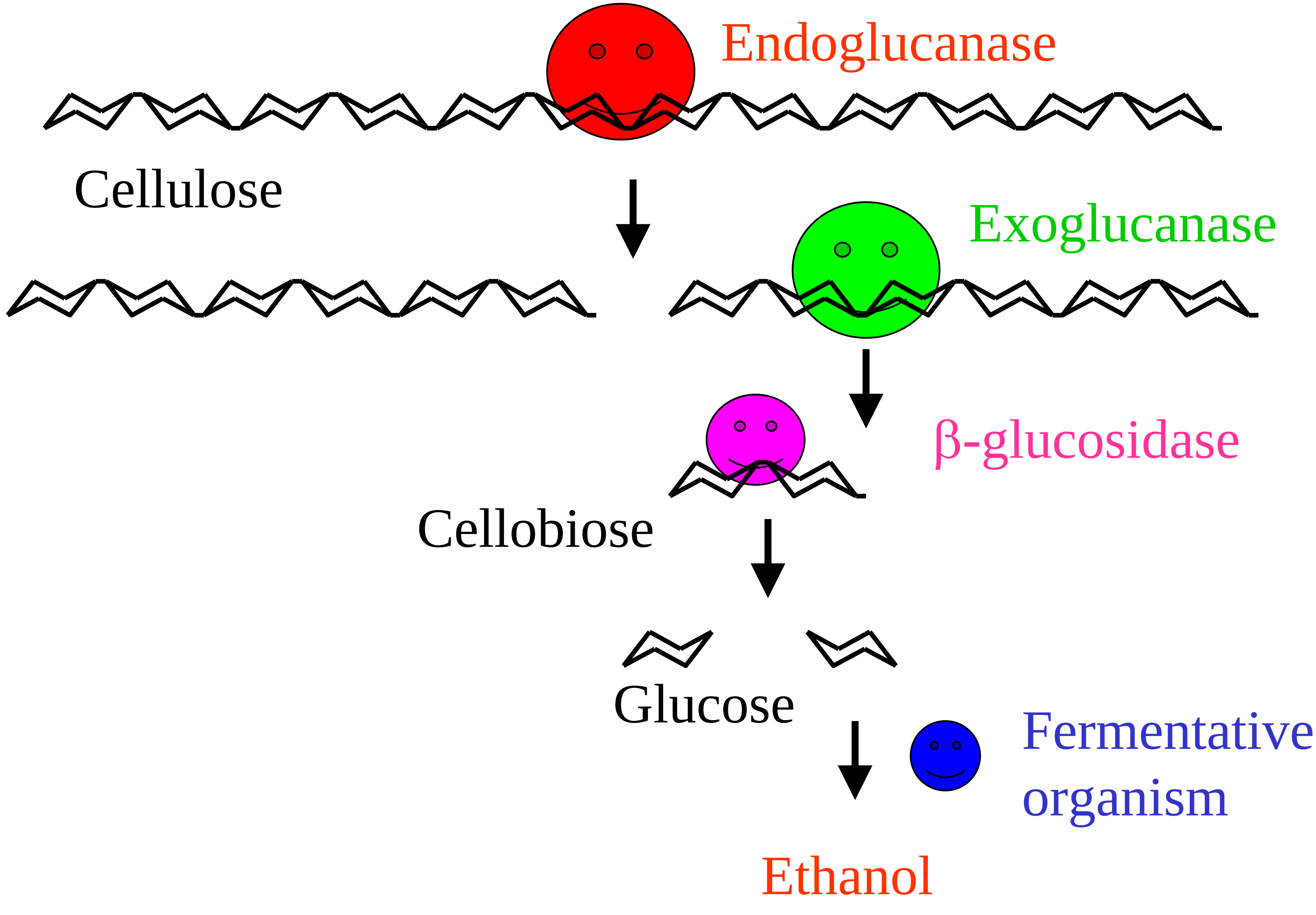
- Native organisms cannot ferment 5 carbon sugars to ethanol at high yields
- This results in a loss of about one quarter to one third or more of yield and revenue for most biomass sources
- Could not make cellulosic ethanol economically without a compatible large scale use for all the sugars - a BIG obstacle to success. Furfural, other markets too small
- U Florida researchers inserted *Zymomonas mobilis* bacterium genes into several bacteria that naturally use all sugars, e.g., *E. coli*, *Klebsiella oxytoca*, to make ethanol
- Landmark invention awarded patent 5,000,000 in March 1991 following 2-3 years search for milestone patent


HEXOSES + PENTOSES
Microbial Platform
Embden-Meyerhof-Parnas
Entner-Doudoroff
Pentose Phosphate
Succinate
X
PEP
PYRUVATE
(Zymomonas mobilis)
Lactate Dehydrogenase
7.2 mM (ldhA)
Lactate
Pyruvate
Formate-Lyase
2 mM (pfl)
Acetyl-CoA + Formate
Acetate
Ethanol
CO_2
H_2
Pyruvate Decarboxylase
0.4mM (pdc)
Acetaldehyde + CO_2
Alcohol Dehydrogenase
(adhB)
Ethanol >95% of Theor. Yield

Integration of Cellulose Hydrolysis and Fermentation

- Takagi et al found that combining cellulose hydrolysis and glucose fermentation in one vessel improved rates, yields, concentrations - Simultaneous Saccharification and Fermentation (SSF)
- Follow on work at NREL and by others improved combinations of organisms and enzymes
- Reducing glucose and cellobiose inhibition enhances performance more than slight drop in temperature from optimum for cellulase (about 45^{o}C) hurts
- Adding whole cellulase broth further enhances performance by utilizing cell bound enzymes and simplifies process
- High β-glucosidase activity in cellulase and cellobiose fermenting organisms keys to good rates and yields

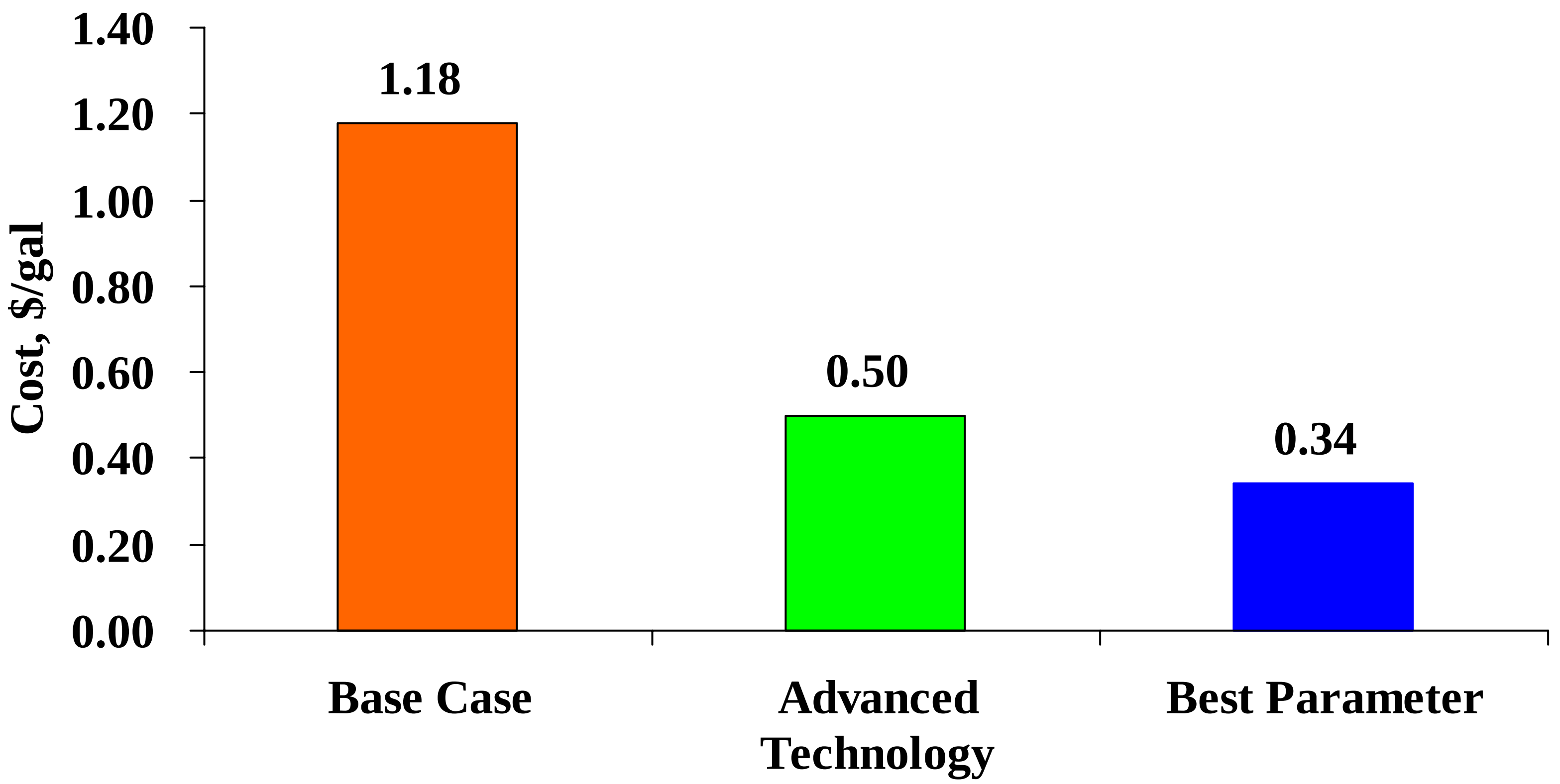
SSF Process


Endoglucanase
Cellulose
Exoglucanase
β-glucosidase
Cellobiose
Glucose
Fermentative organism
Ethanol

Advancing Cellulosic Ethanol Technology

- Biomass is a low cost abundant feedstock that is competitive in price with petroleum
- The challenge is to reduce processing costs to be competitive without subsidies
- Biotechnology offers potential for lower cost processing
- Considered three scenarios
  - NREL“current” technology
  - Advanced technology - judged to have most likely features for mature technology
  - Best parameter technology - represents ultimate potential for R&D driven advances

Projected Cellulosic Ethanol Costs

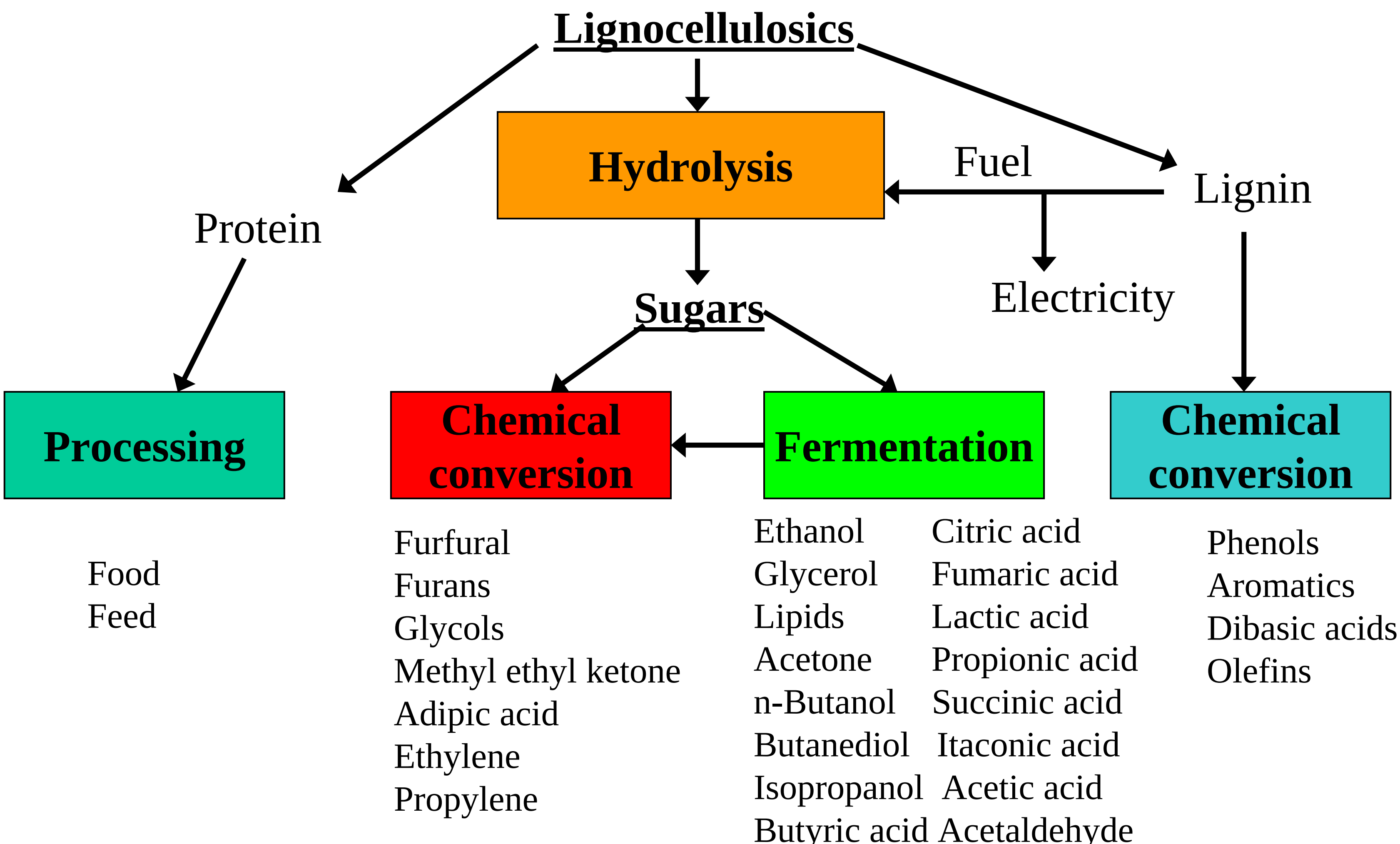


from Lynd, Elander, Wyman, 1996

Implications

- Cost of ethanol production has potential to be competitive without tax incentives
- Achieving competitiveness requires advanced process configurations for
  - Pretreatment
  - Biological processing – e.g., Consolidated BioProcessing (CBP)
  - Overall: Overcoming the recalcitrance of cellulosic biomass at low cost
- Key is to focus on advanced technology configurations to overcome the recalcitrance of biomass

Cellulosic Refinery for Renewable Feedstocks to Fuels,Chemicals, Power, Food, and Feed



From C Wyman 1990

Status of Biological Conversion for Cellulosic Ethanol

- The economic, environmental, and strategic benefits could be huge
- Lower costs are foreseeable
- HOWEVER, NO biological processes for cellulosic biomass conversion are commercial
- The vital goal: Commercialize biological processing of cellulosic biomass to realize these benefits
- What is slowing us down: CAPITAL RISK vs REWARDS

Commercialization of Fuels and Chemicals from Biomass

- Several companies seeking to commercialize cellulosic ethanol technologies
  - Abengoa - enzymes
  - Arkenol - concentrated acid
  - BC International - dilute acid then enzymes
  - HFTA - nitric acid
  - Iogen - enzymes only now
  - Masada - concentrated acid
  - SWAN Biomass - enzymes
- Others seeking to make chemicals from biomass - currently glucose from corn starch
  - Nature Works – polylactic acid
  - Dupont – 1,3-propanediol

Success in Three Very Diverse Directions Now Vital

- Successfully commercialize cellulosic ethanol technology
  - Only way to realize benefits soon
  - Must deal with risk of first-of-a-kind technology with high capital costs
- Develop leap forward pretreatment and biological conversion advances that overcome biomass recalcitrance and realize low cost cellulosic ethanol that is competitive as a pure fuel
  - Key to large scale impact
- Diversify the product slate from biomass through refinery concept
  - Make fuels, chemicals, and power from cellulosics in one process

Mission of Wyman Research Team

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

Acknowledgements

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- USDA National Research Initiative Competitive Grants Program
- US Department of Energy Office of the Biomass Program
- Natural Resources Canada for supporting partners

Partners and Collaborators

- Professor YY Lee, Auburn
- Professor Bruce Dale, Michigan State
- Mr. Rick Elander, NREL
- Professor Michael Ladisch, Purdue
- Professor Mark Holtzapple, Texas A&M
- Dean Jack Saddler, University of British Columbia
- Professor Esteban Chornet, University of Sherbrooke
- Professor Joseph Norbeck, UCR

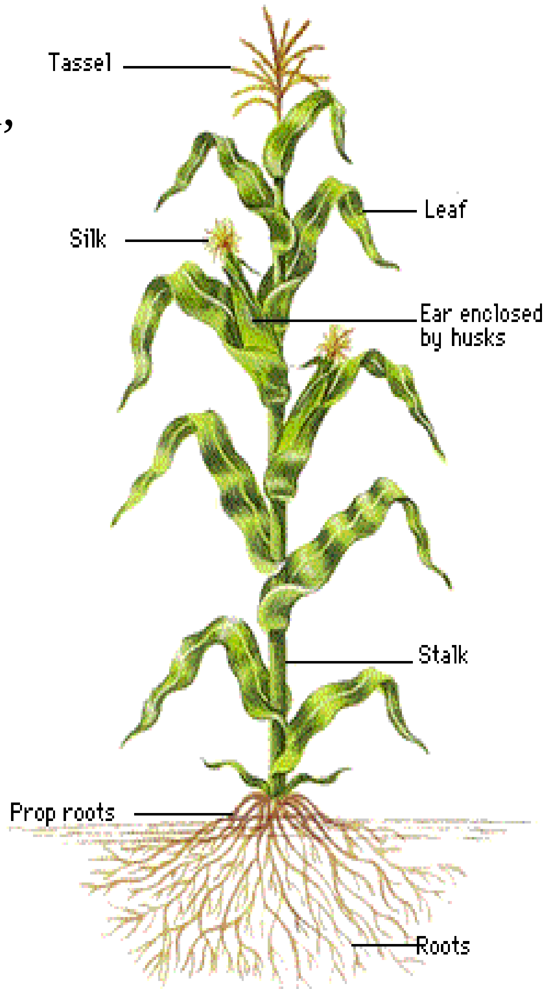
Insanity is doing what you always have always been doing and expecting different results

Questions?

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 %**



Calculation of Sugar Yields

- Comparing the amount of each sugar monomer or oligomer released to the maximum potential amount for that sugar would give yield of each
- However, most cellulosic biomass is richer in glucose than xylose
- Consequently, glucose yields have a greater impact than for xylose
- Sugar yields in this project were defined by dividing the amount of xylose or glucose or the sum of the two recovered in each stage by the maximum potential amount of both sugars
  - The maximum xylose yield is 24.3/64.4 or 37.7%
  - The maximum glucose yield is 40.1/64.4 or 62.3%
  - The maximum amount of total xylose and glucose is 100%.

Overall Yields at 60 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	3.3	35.4/34.5	3.9	53.3	57.2	36.0/35.1	56.6	92.6/91.7
Flowthrough	36.3/1.7	0.8/0.7	37.1/2.4	4.5/4.4	57.0	61.5/61.4	40.8/6.1	57.8/57.7	98.6/63.8
Controlled pH	21.8/0.9	9.0	30.7	3.5/0.2	54.7	58.2	25.3/1.1	63.6	88.9
AFEX		ND/30.2	ND/30.2		61.8	61.8		ND/92.0	ND/92.0
ARP	17.8/0	17.0	34.8/17.0		59.4	59.4	17.8/0	76.4	94.2/76.4
Lime	9.2/0.3	20.2	29.4/20.5	1.0/0.3	59.5	60.5/59.8	10.2/0.6	79.7	89.9/80.3

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

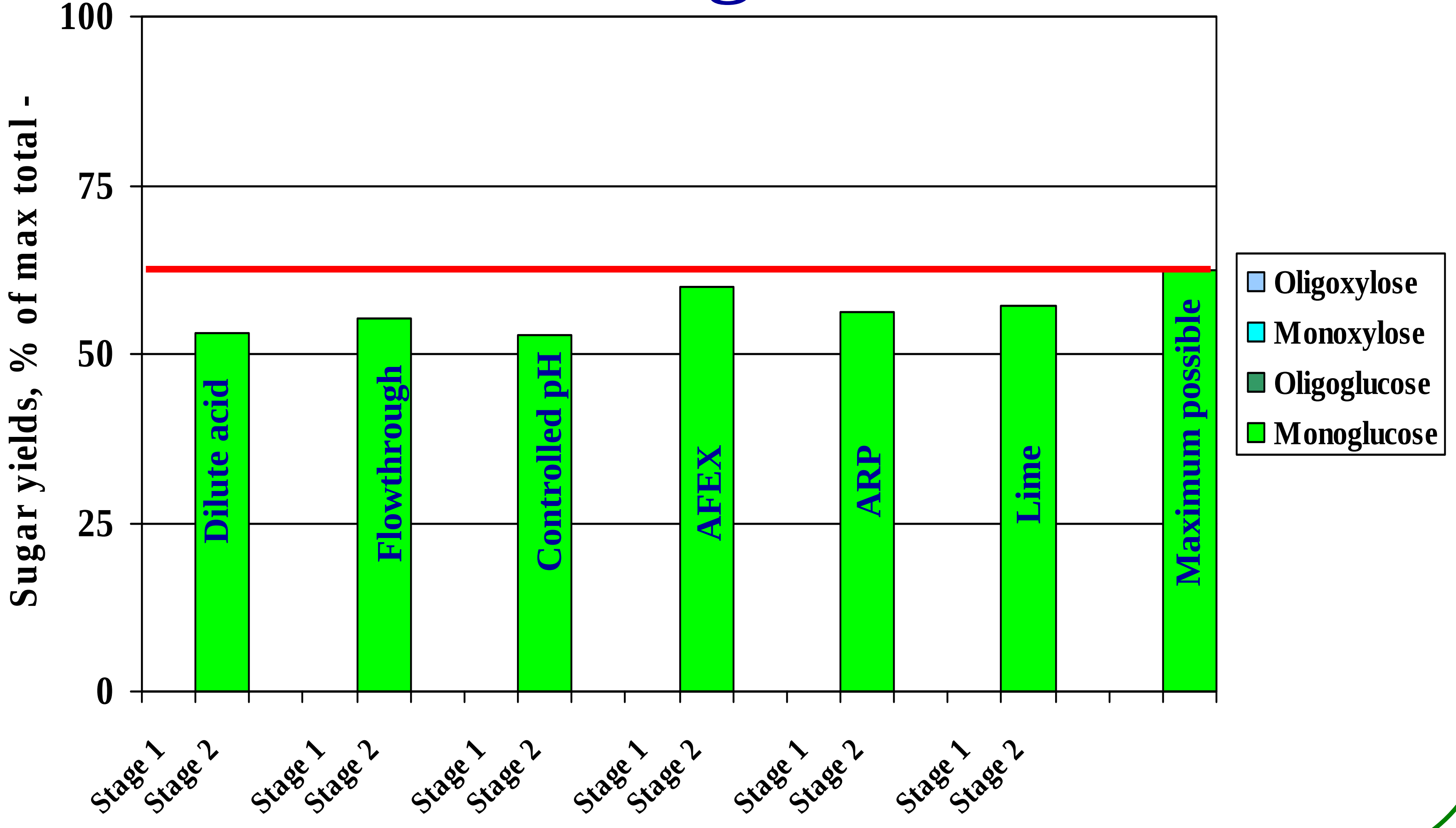
Overall Yields at 15 FPU/g Glucan

Increasing pH

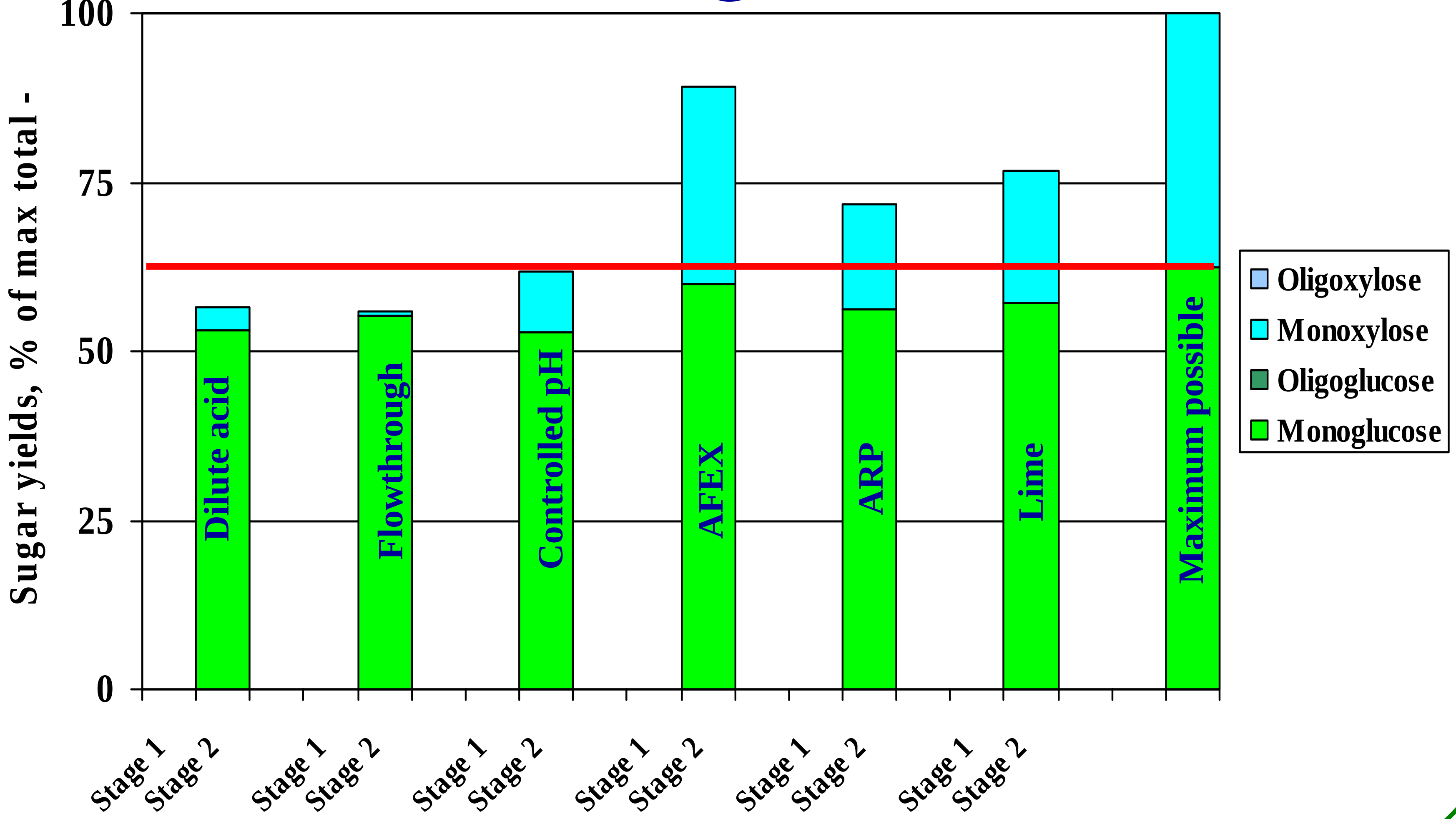
Pretreatment system	Xylose yields*			Glucose yields*			Total sugars*		
	Stage 1	Stage 2	Total xylose	Stage 1	Stage 2	Total glucose	Stage 1	Stage 2	Combined total
Maximum possible	37.7	37.7	37.7	62.3	62.3	62.3	100.0	100.0	100.0
Dilute acid	32.1/31.2	3.2	35.3/34.4	3.9	53.2	57.1	36.0/35.1	56.4	92.4/91.5
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.

Overall Yields at 15 FPU/g Glucan



Overall Yields at 15 FPU/g Glucan



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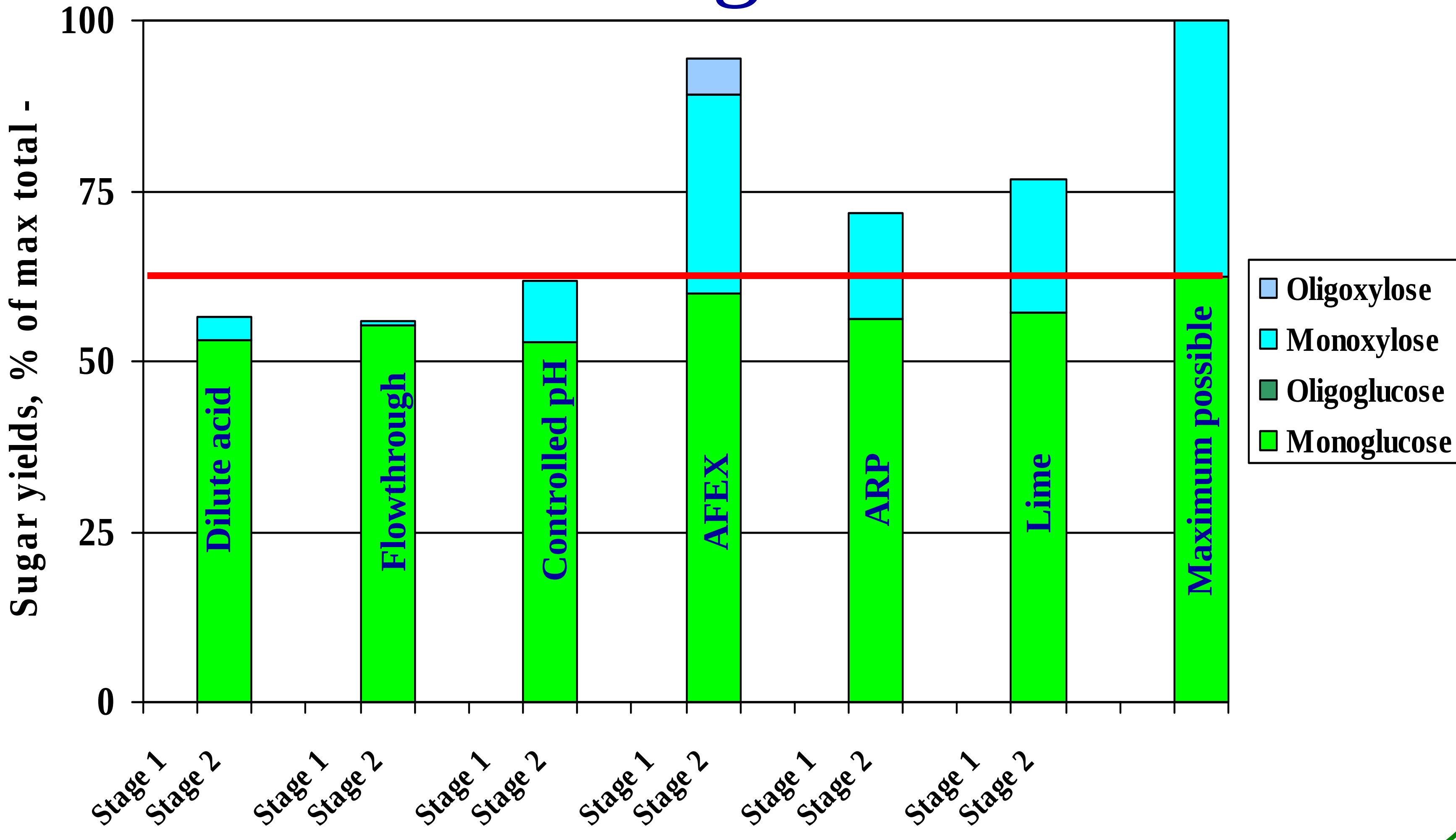

Overall Yields at 15 FPU/g Glucan