Title

Advancing Cellulosic Ethanol for Large Scale Sustainable Transportation

Author
Wyman, C

Publication Date
2007

Peer reviewed

Advancing Cellulosic Ethanol for Large Scale Sustainable Transportation

Charles E. Wyman
Ford Motor Company Chair in Environmental Engineering
Chemical and Environmental Engineering Department and Center for Environmental Research and Technology
Bourns College of Engineering
University of California, Riverside
and
Mascoma Corporation
Cambridge, Massachusetts

CFANS Solution Driven Science Symposium
St Paul, Minnesota
September 19, 2007

Acknowledgments

- Ford Motor Company
- Bourns College of Engineering at the University of California, Riverside
- USDA National Research Initiative Competitive Grants Program, contract 2004-35504-14668
- US Department of Energy Office of the Biomass Program, contract DE-FG36-04GO14017
- Natural Resources Canada for supporting partners
- CAFI Partners from Auburn, Michigan State, Purdue, and Texas A&M Universities; the University of British Columbia; the National Renewable Energy Laboratory; and Genencor International

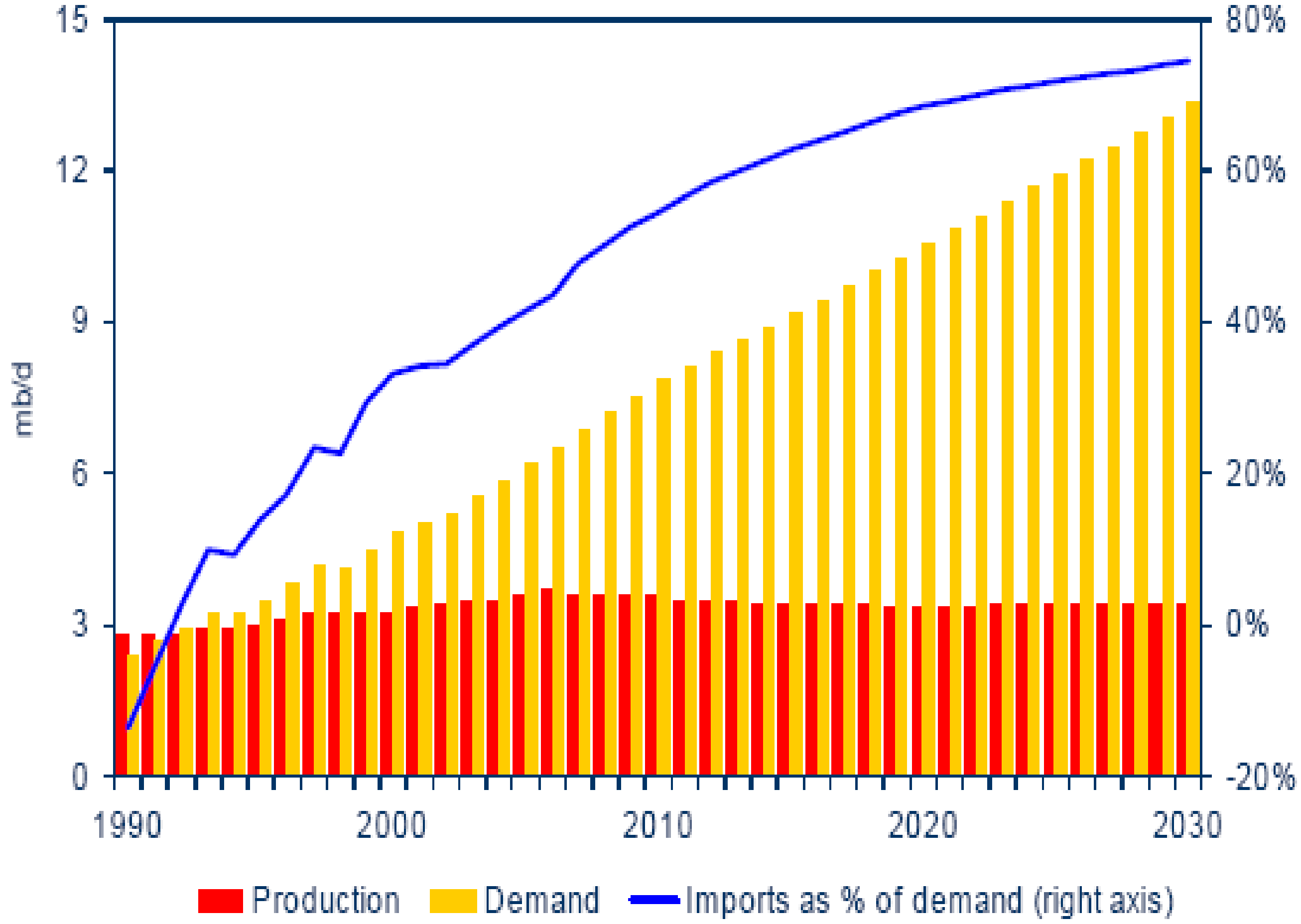
Where is a New Energy Source Needed in United States?

- U.S. energy production and demand are nearly balanced for all but one energy source: petroleum
  - We use more petroleum than we produce – >70% imported
- Petroleum is single largest energy source in U.S. supplying ~40% of total energy

Similar Issues Are Building Around the World

- China is increasing petroleum use extremely rapidly
- India is also consuming considerably more oil
- The vast majority of petroleum reserves are in unstable regions of the world

China's Oil Production and Demand: Actual and Forecasts thru 2030

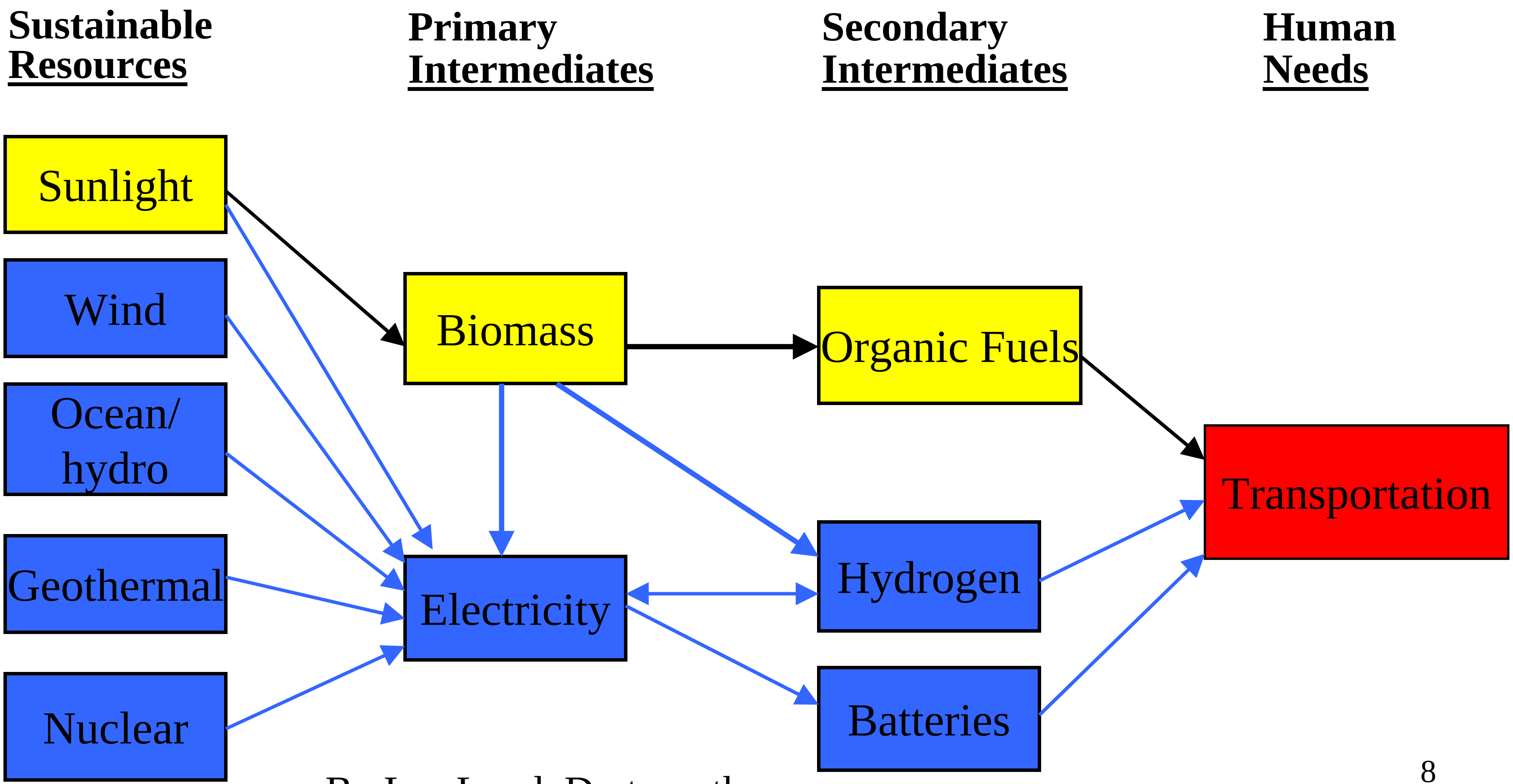


Source: World Energy Outlook 2004, IEA.

Petroleum and Transportation

- Over 70% of U.S. petroleum goes to transportation
- Transportation is almost totally dependent on petroleum (~96%)
- The largest source of U.S. carbon dioxide emissions comes from transportation (~33%)
- Need to find alternatives to petroleum for transportation
- Should seek sustainable fuels to avoid future transitions and reduce greenhouse gases

Sustainable Alternatives for Transportation



By Lee Lynd, Dartmouth

Ethanol

- Ethanol, ethyl alcohol, fermentation ethanol, or just “alcohol”
- Ethanol is one of the broader alcohol family of chemical form ROH in with R for ethanol has two carbon atoms:

$$C_2H_5OH$$

- Beverage alcohol (mixed ethanol/water) referred to in Sumerian language in Mesopotamia in about 2500BC
- Used in beverages, solvents, medicines, lotions, tonics, cologne, rubbing compounds, organic synthesis
- Clear, colorless, volatile, flammable liquid that is completely miscible with water
- Excellent fuel properties for SI engines
  - High octane – 98 (RON + MON)/2
  - High heat of vaporization

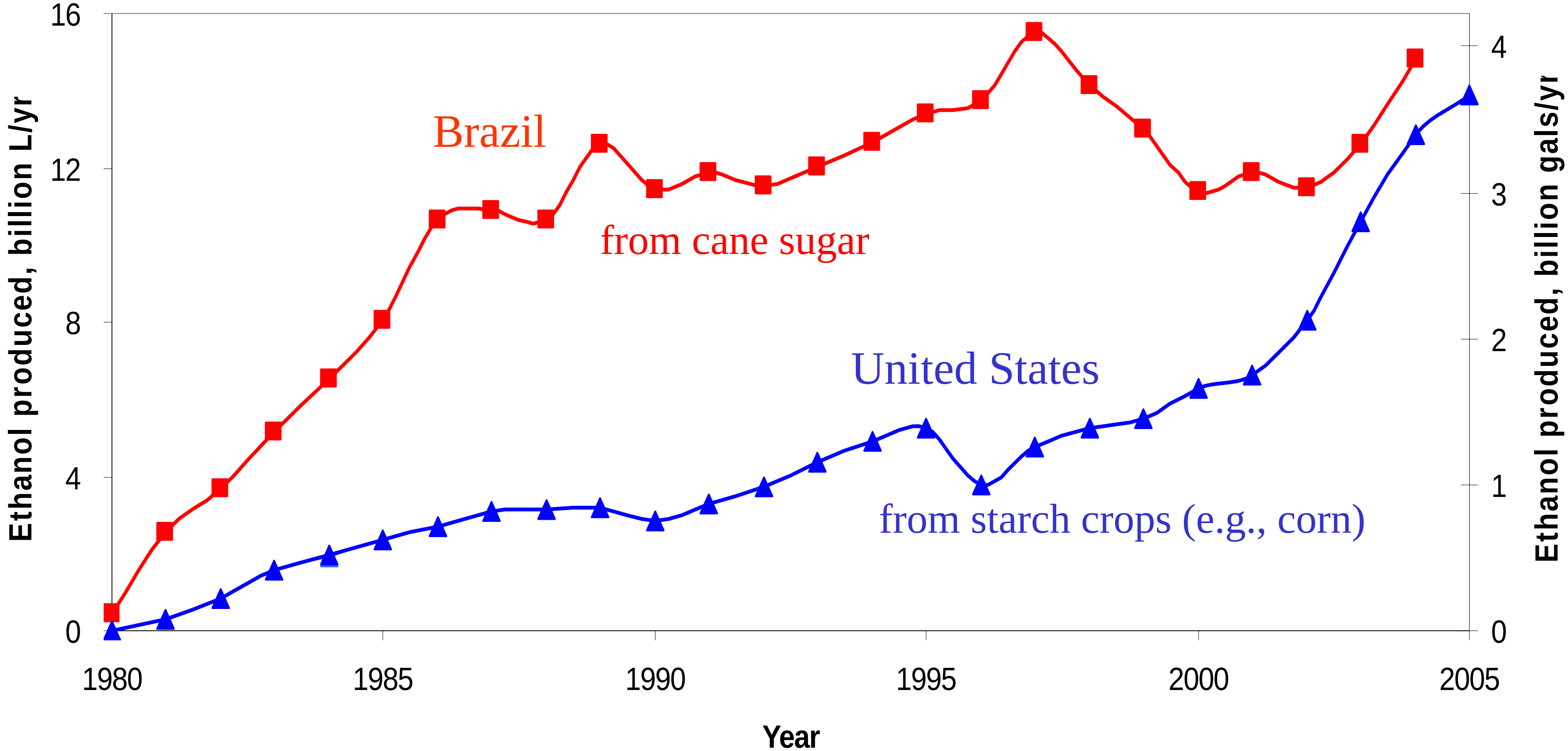
Ethanol

- Ethanol, ethyl alcohol, fermentation ethanol, or just “alcohol”
- Ethanol is one of the broader alcohol family of chemical form ROH in with R for ethanol has two carbon atoms:

$$C_2H_5OH$$

- Beverage alcohol (mixed ethanol/water) referred to in Sumerian language in Mesopotamia in about 2500BC
- Used in beverages, solvents, medicines, lotions, tonics, cologne, rubbing compounds, organic synthesis
- Clear, colorless, volatile, flammable liquid that is completely miscible with water
- **Excellent fuel properties for SI engines**
  - **High octane – 98 (RON + MON)/2**
  - **High heat of vaporization**

Ethanol Production in Brazil and the United States



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

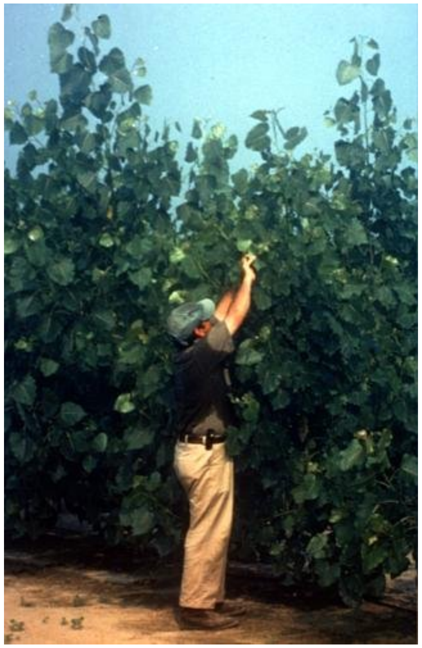
Sugarcane

Sugarcane Bagasse

Louisiana Rice Hulls Pile

Energy Crops

Switchgrass harvested annually or biannually



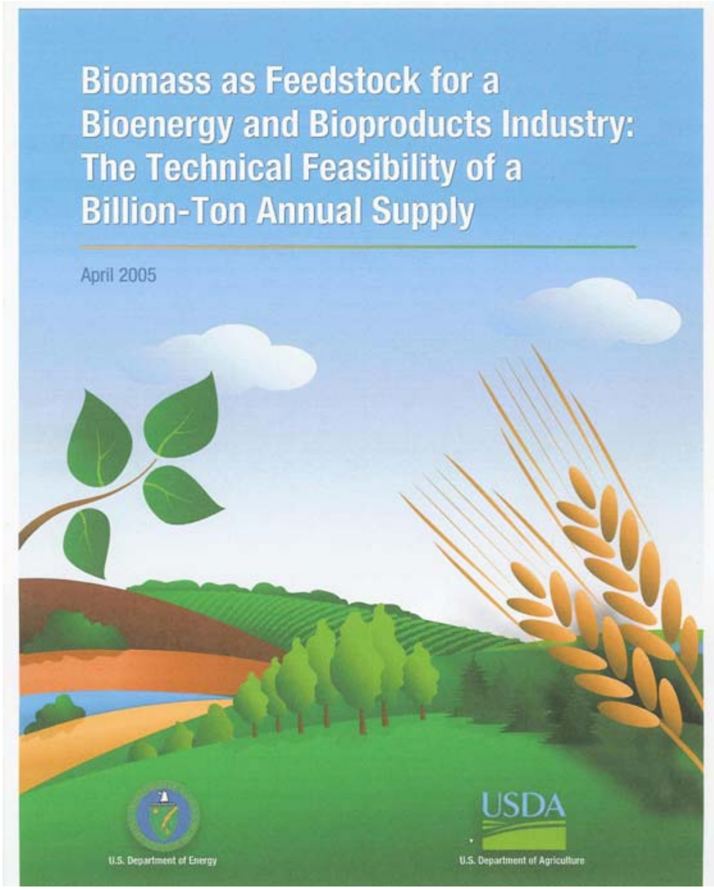
Hybrid Poplar harvested at age 5 to 10

Willow coppice harvested at age 3 or 4

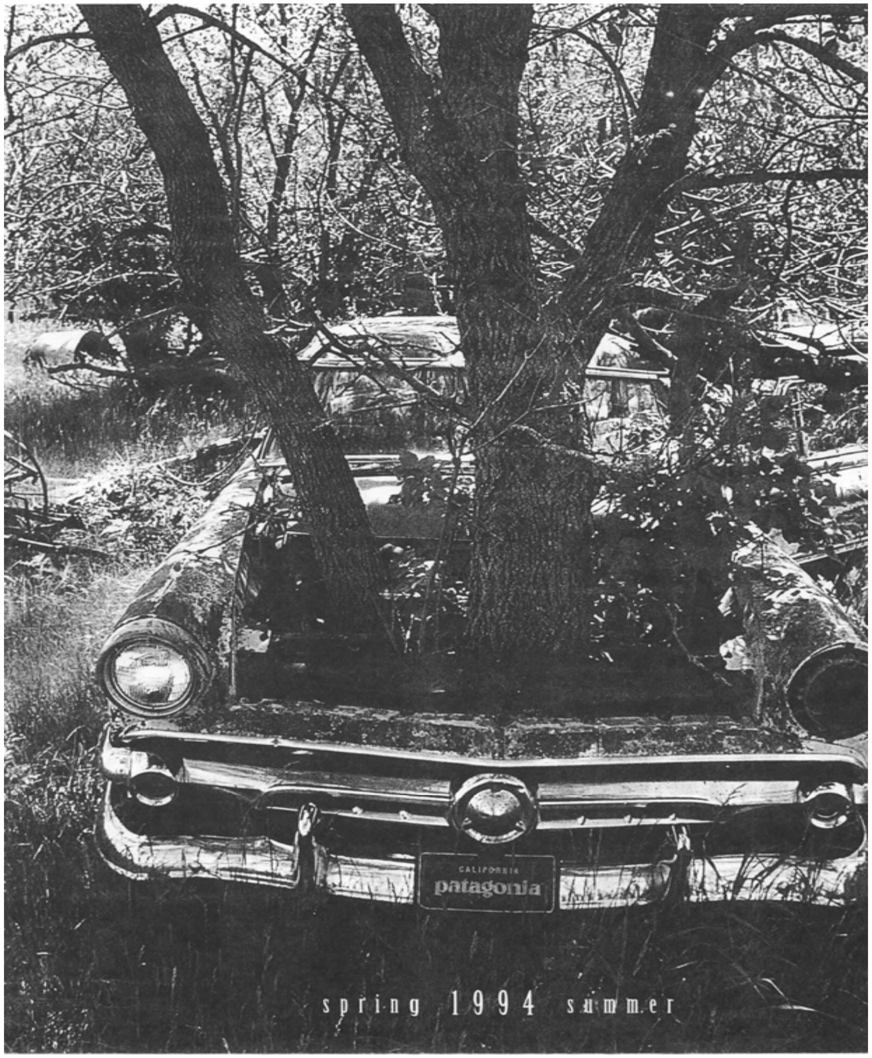
Courtesy of L. Wright, ORNL

Billion Ton Supply of Cellulosic Biomass

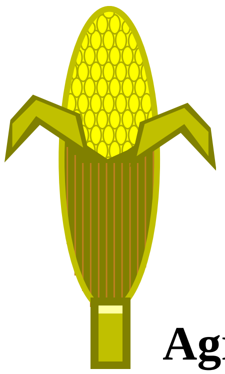
- DOE and USDA recently estimated 1.3 billion tons of cellulosic biomass could be available
- Includes 368 million dry tons from forests and 998 million dry tons from agriculture



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

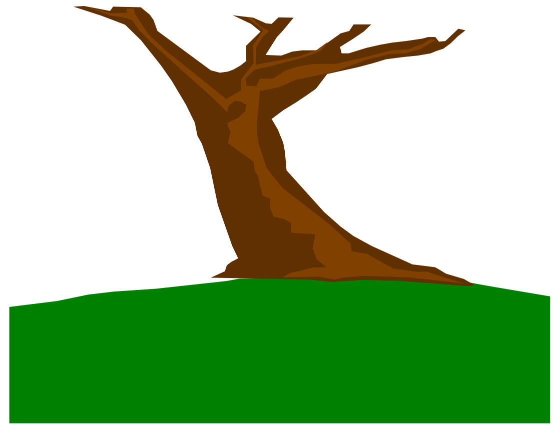


Cellulosic Biomass Composition



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

Agricultural Residues



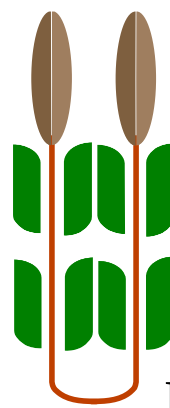
Cellulose 45%
Hemicellulose 25%
Lignin 22%
Extractives 5%
Ash 3%

Woody Crops

Cellulose 45%

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

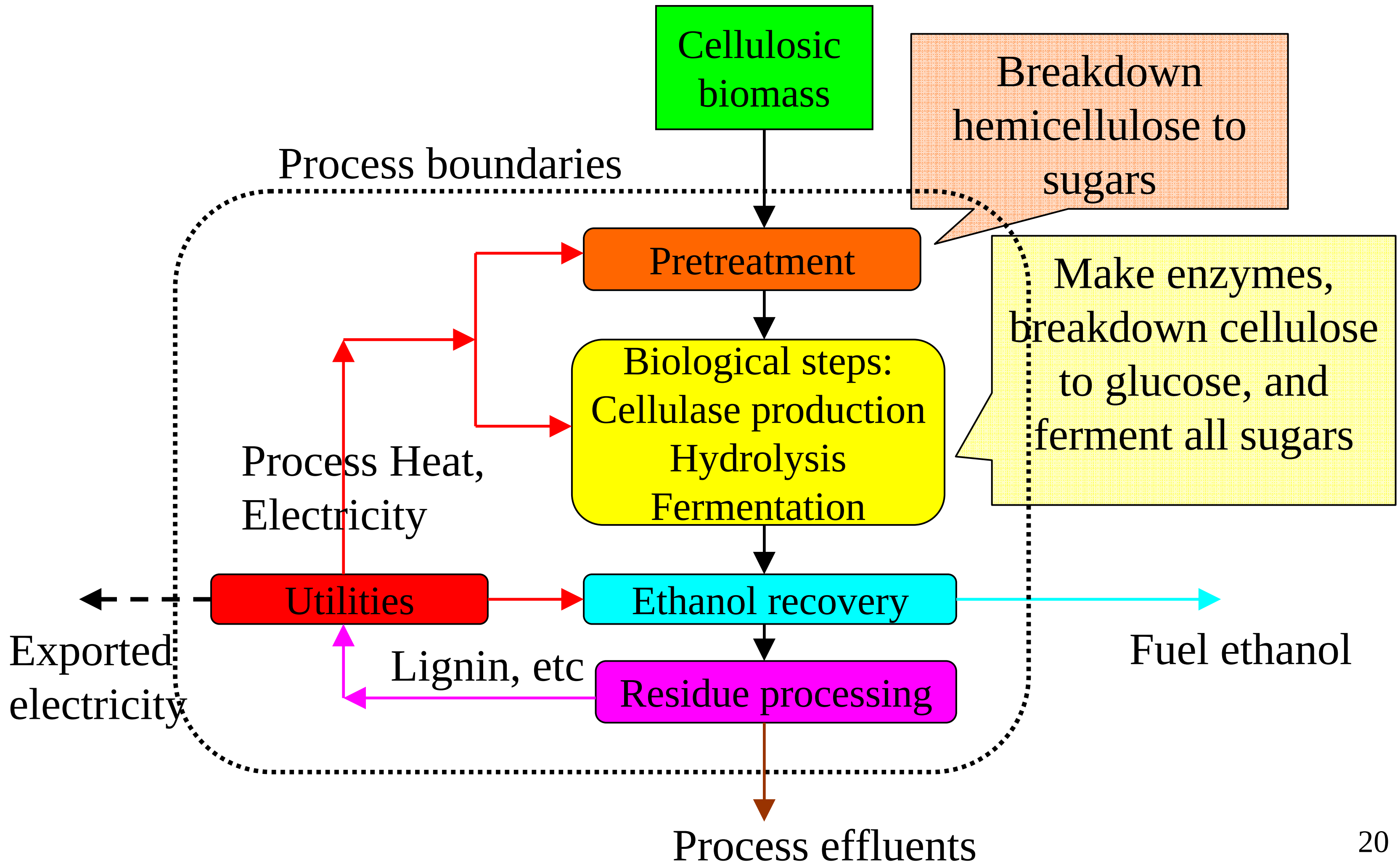
Municipal Solid Waste



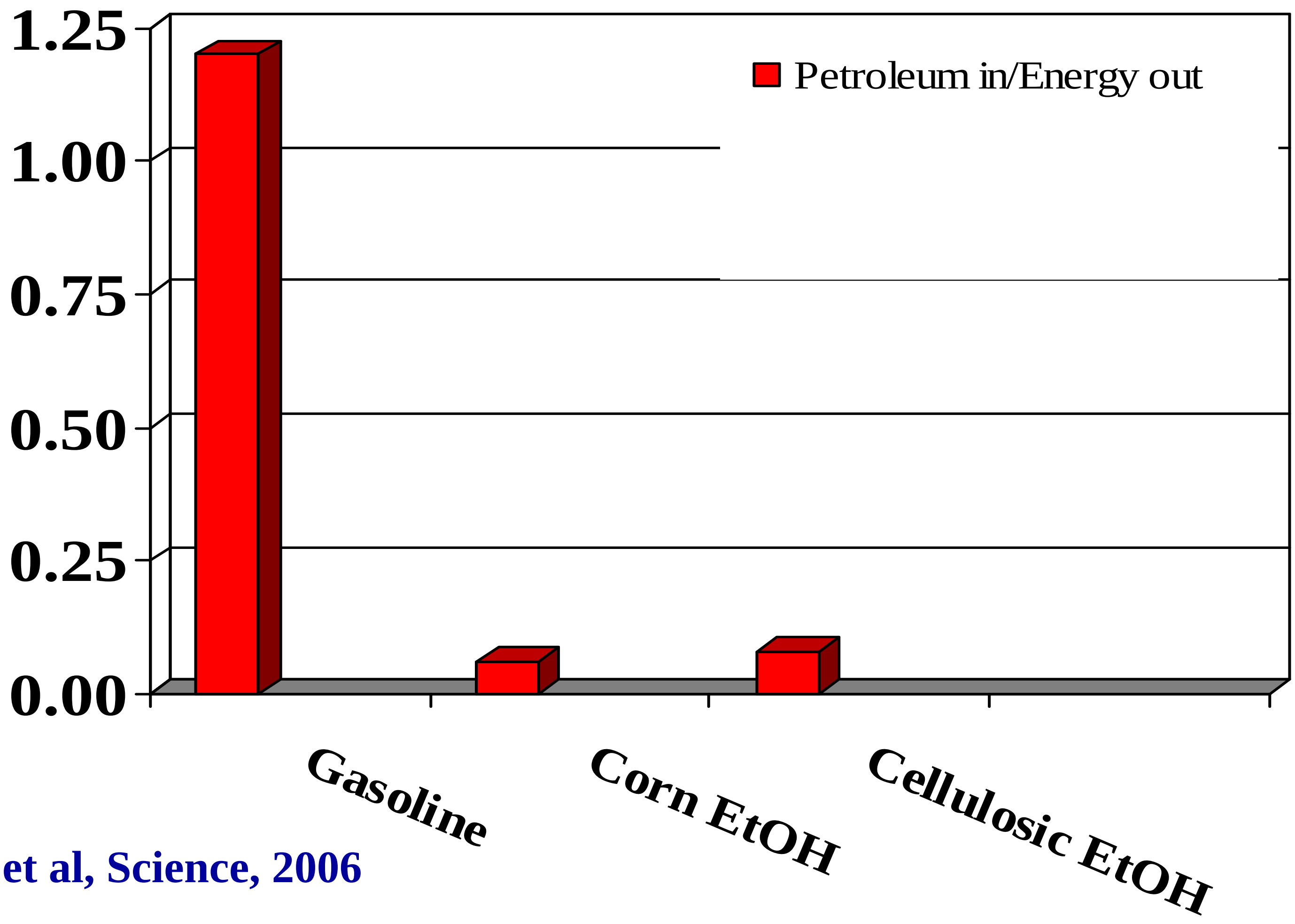
Cellulose 45%
Hemicellulose 30%
Lignin 15%
Other 10%

Herbaceous Energy Crops

Enzymatic Conversion of Cellulosic Biomass to Ethanol

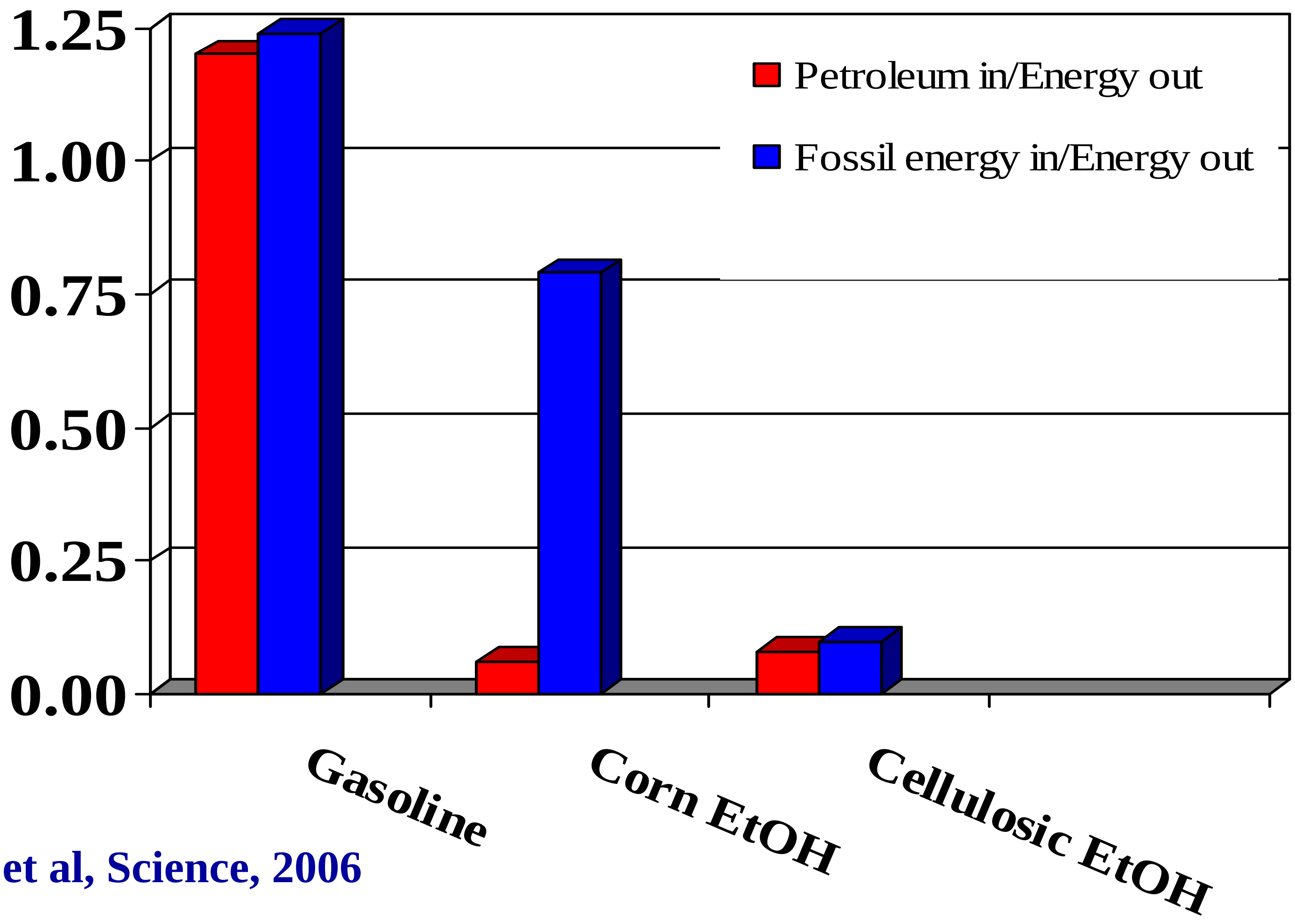


Relative Metrics for Ethanol



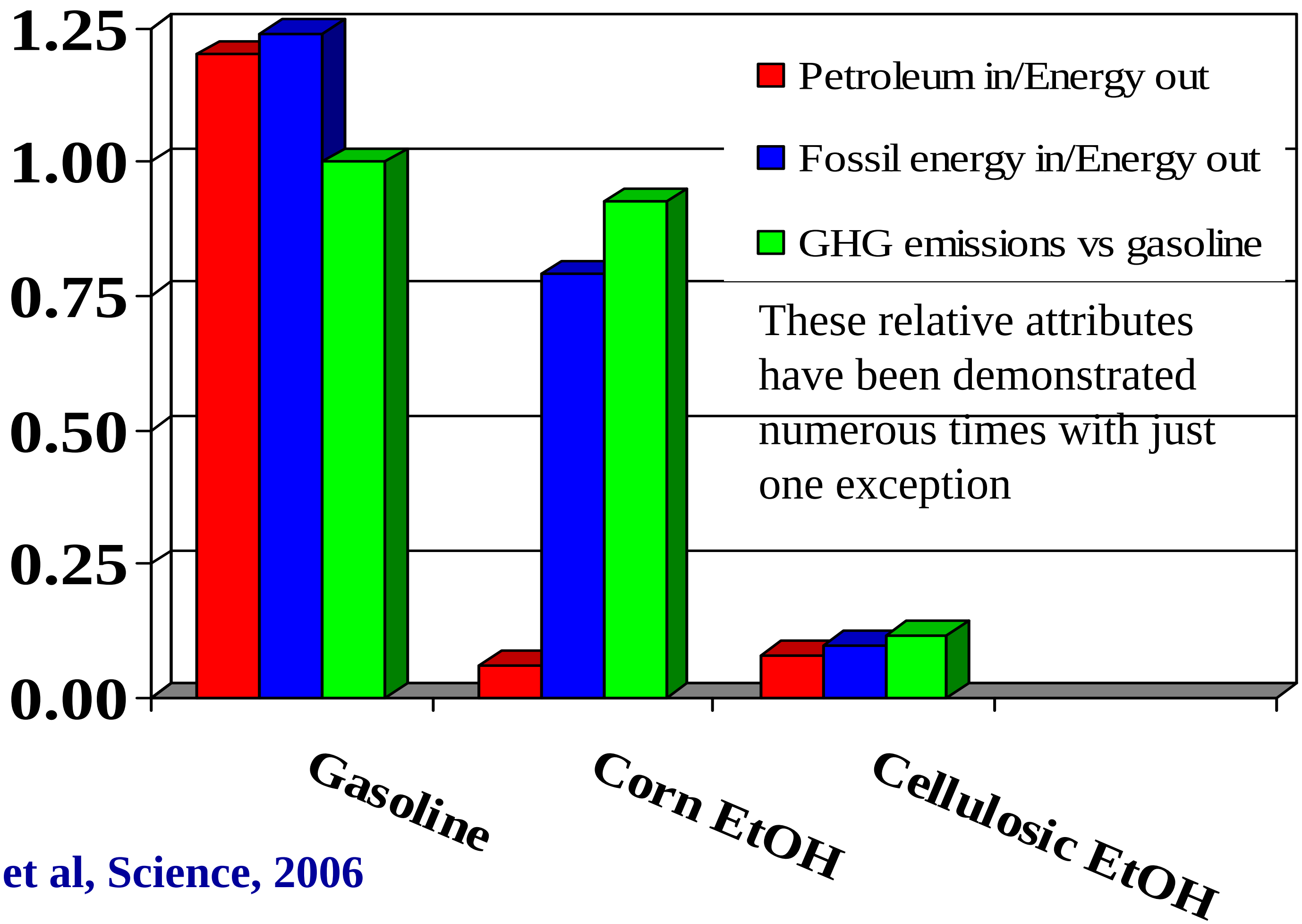
***Farrell et al, Science, 2006**

Relative Metrics for Ethanol



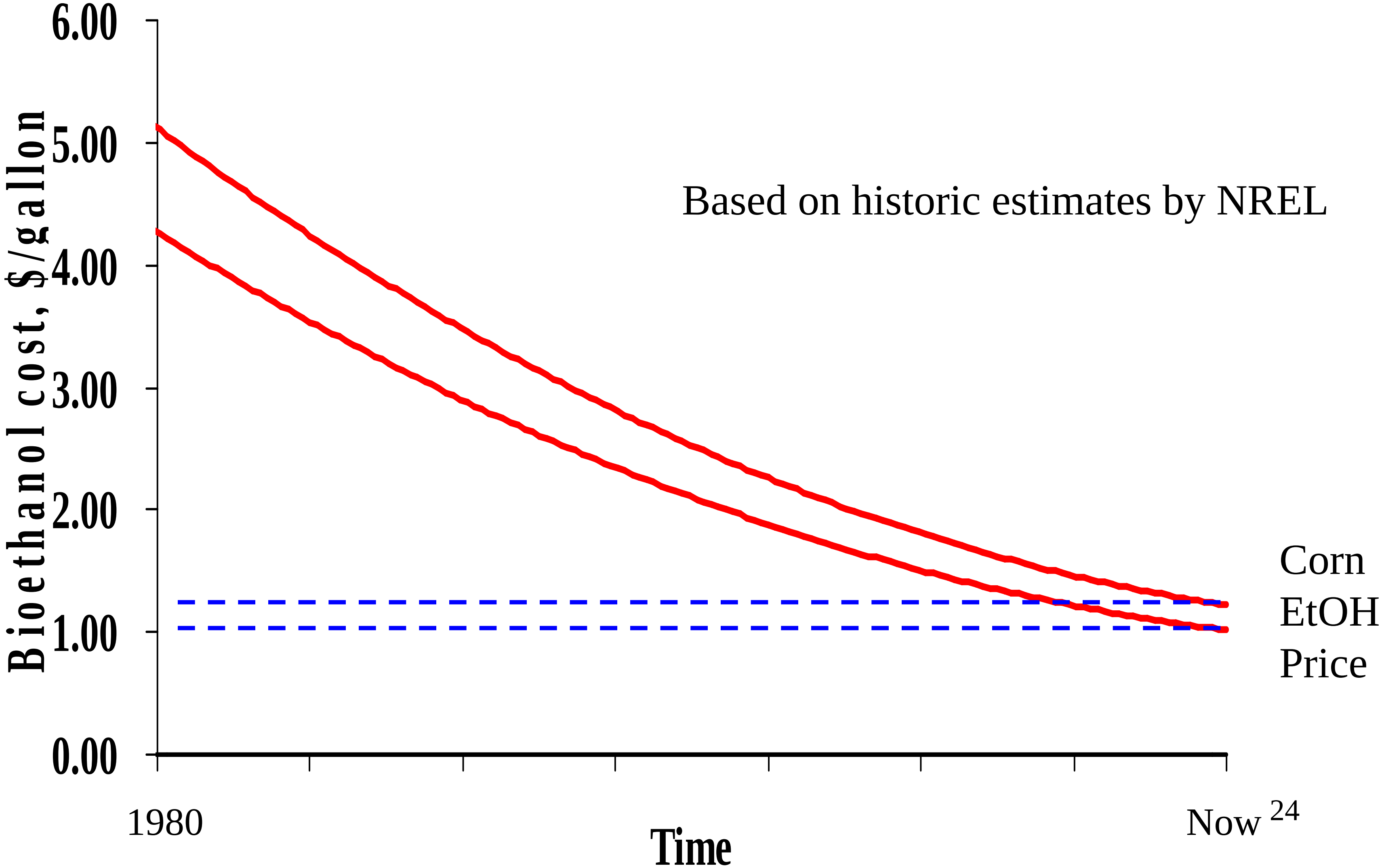
***Farrell et al, Science, 2006**

Relative Metrics for Ethanol



***Farrell et al, Science, 2006**

Significant Progress in Enzyme Based Cellulosic Ethanol Technology



Key to Advances To Date in Cellulosic Ethanol Technology

- Overcoming the recalcitrance of cellulosics
  - Improved pretreatment to increase yields from hemicellulose and cellulose
  - Improved cellulase enzymes to increase rates from cellulose, reduce enzyme use
  - Integrated systems to improve rates, yields, concentrations of ethanol (SSF)
- Overcoming the diversity of sugars
  - Recombinant organisms ferment all five sugars to ethanol at high yields

Benefits of Cellulosic Ethanol Technology

- Environmental
  - Little if any net carbon dioxide emissions
  - Solid waste disposal
  - Low impact biomass crops
  - Can improve air quality
- Economic
  - Abundant, inexpensive, domestic feedstock
  - Low cost potential without subsidies
  - Agricultural and rural manufacturing employment
  - Provides synergies for emergence of biorefining
- Energy
  - Secure resource available for most countries

Commercial Status of Cellulosic Ethanol

- Operating costs are low
- Technology is ready to be commercialized
- Lower costs are foreseeable through learning curve and leap forward advances
- The economic, environmental, and strategic benefits of cellulosic ethanol could be huge
- HOWEVER, NO biological processes for cellulosic biomass conversion are commercial
- The vital goal: Commercialize cellulosic ethanol to realize its benefits

Several Companies Seek to Commercialize Cellulosic Ethanol

- Abengoa – enzymes
- BlueFire - concentrated acid
- Dupont - enzymes
- HFTA - nitric acid
- Iogen - enzymes
- Mascoma – advanced enzymes
- Poet (Broin) – enzymes
- Range Fuels - gasification
- SWAN Biomass - enzymes
- Verenium (BCI/Celunol plus Diversa) – enzymes

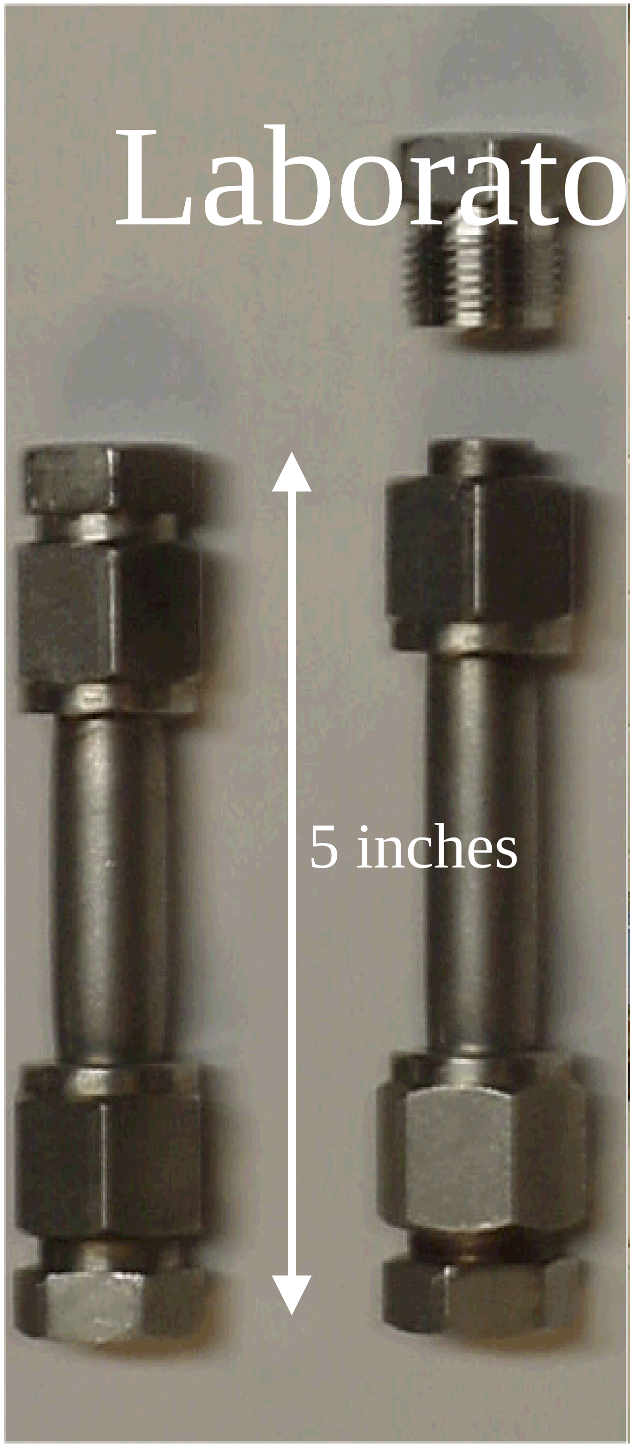
What is Holding Back Cellulosic Ethanol?

- 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

Basis of My Perspectives – Led Development of BCI Technology

- Responsible for defining technology in concert with engineers and constructors through ~weekly trips to AL, LA, etc
- Worked with internal and numerous outside researchers
- Evaluated equipment with vendors
- Explained technology to investors
- Worked with independent engineers, market analysts, etc
- Achieved process guarantees and project financing for first-of-a-kind technology and $100 million process
- Fell just short on portion of equity funds
- Founded Mascoma Corporation, Cambridge, MA

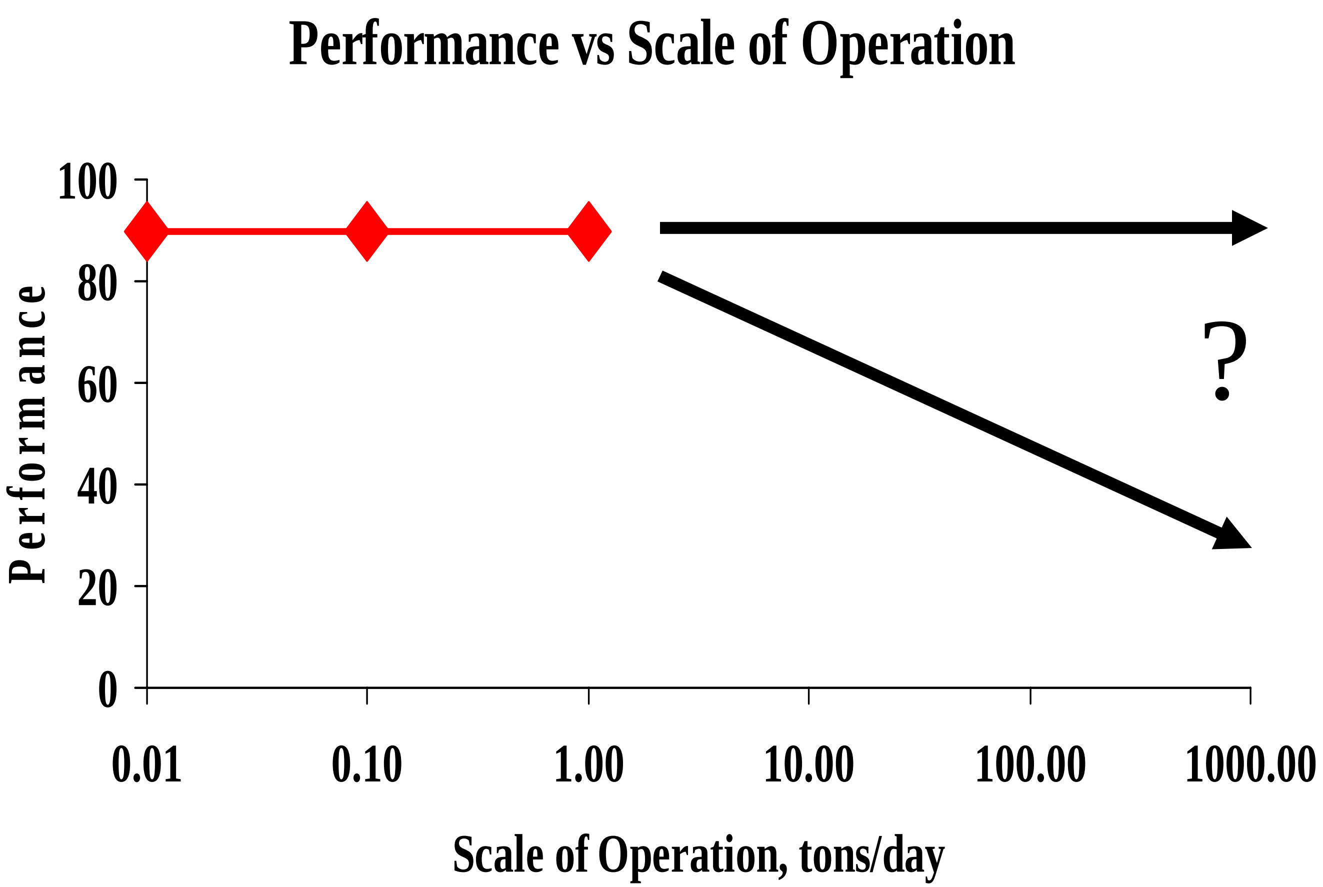
Laboratory Reaction Systems



NREL Bench Systems

Commercial Dilute Acid Hydrolysis

First-of-a-Kind Technology Scale-Up/Extrapolation



Mascoma Corporation

- Conceived in summer 2005 in meeting on my back porch on Lake Mascoma, NH
- Developing advanced technologies for conversion of cellulosic biomass to ethanol
  - Initially based on Dartmouth biological systems
- Forming partnerships to commercialize advanced cellulosic ethanol technologies

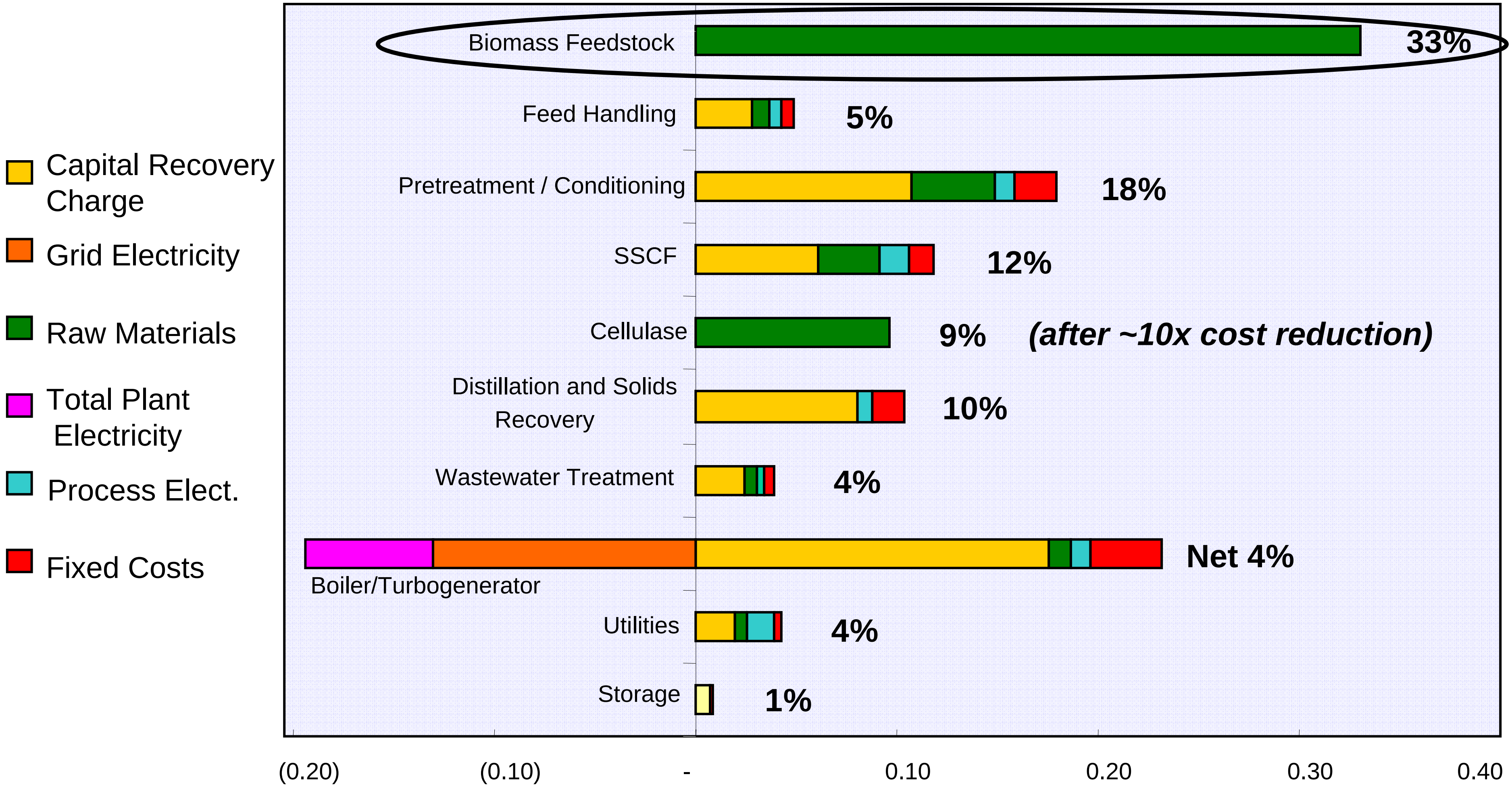
Mascoma Corporation

- Founders: Charles Wyman, Bob Johnsen, Lee Lynd
- CEO: Bruce Jamerson
- President: Colin South
- Chairman of Board: Samir Kaul

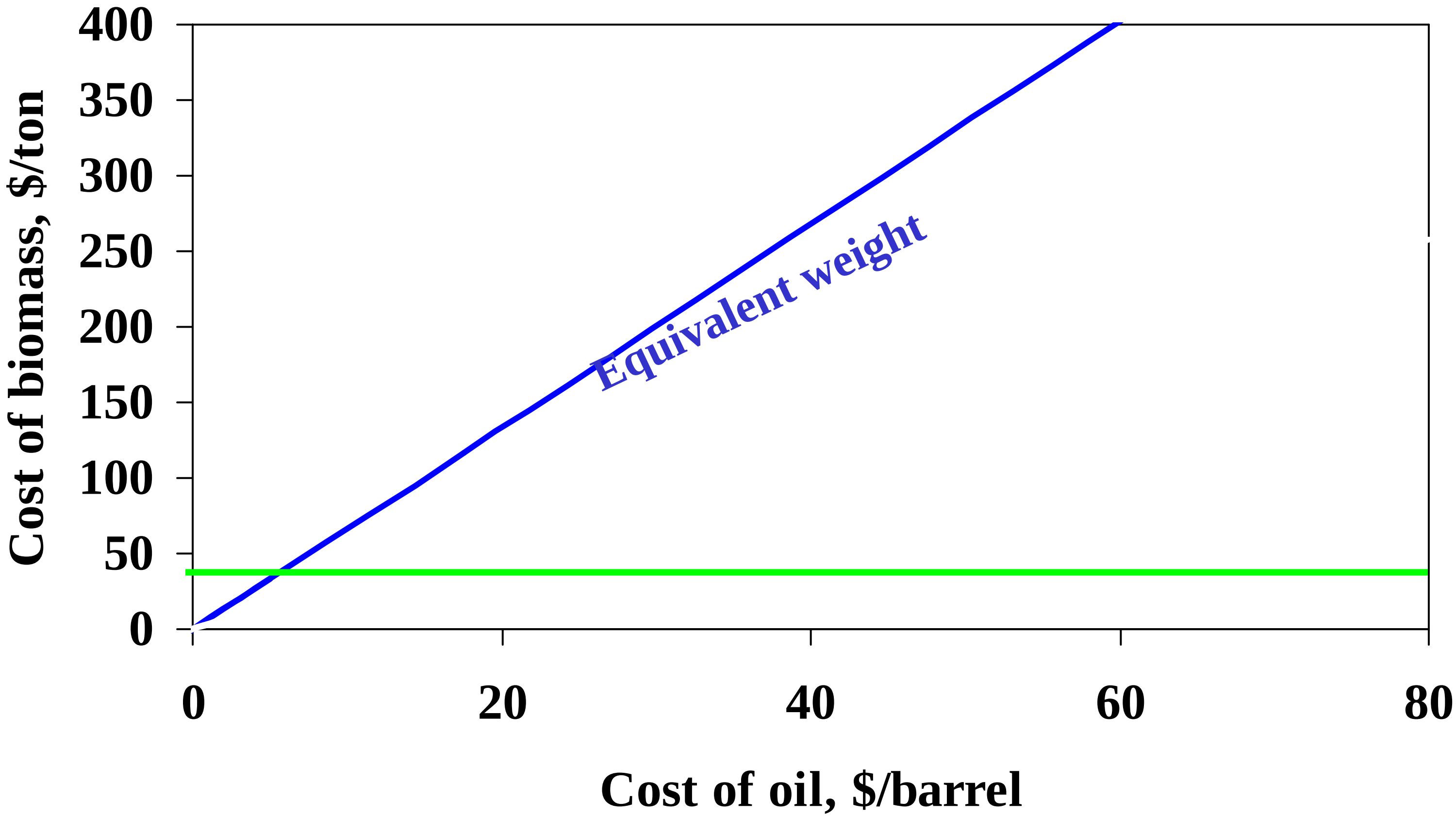
Mascoma Corporation

- First round of capital from Khosla Ventures, Flagship Ventures
- Raised about $39 million in Series A and B rounds
- Awarded about $19 million in NY and US contracts
- More information: Mascoma.com

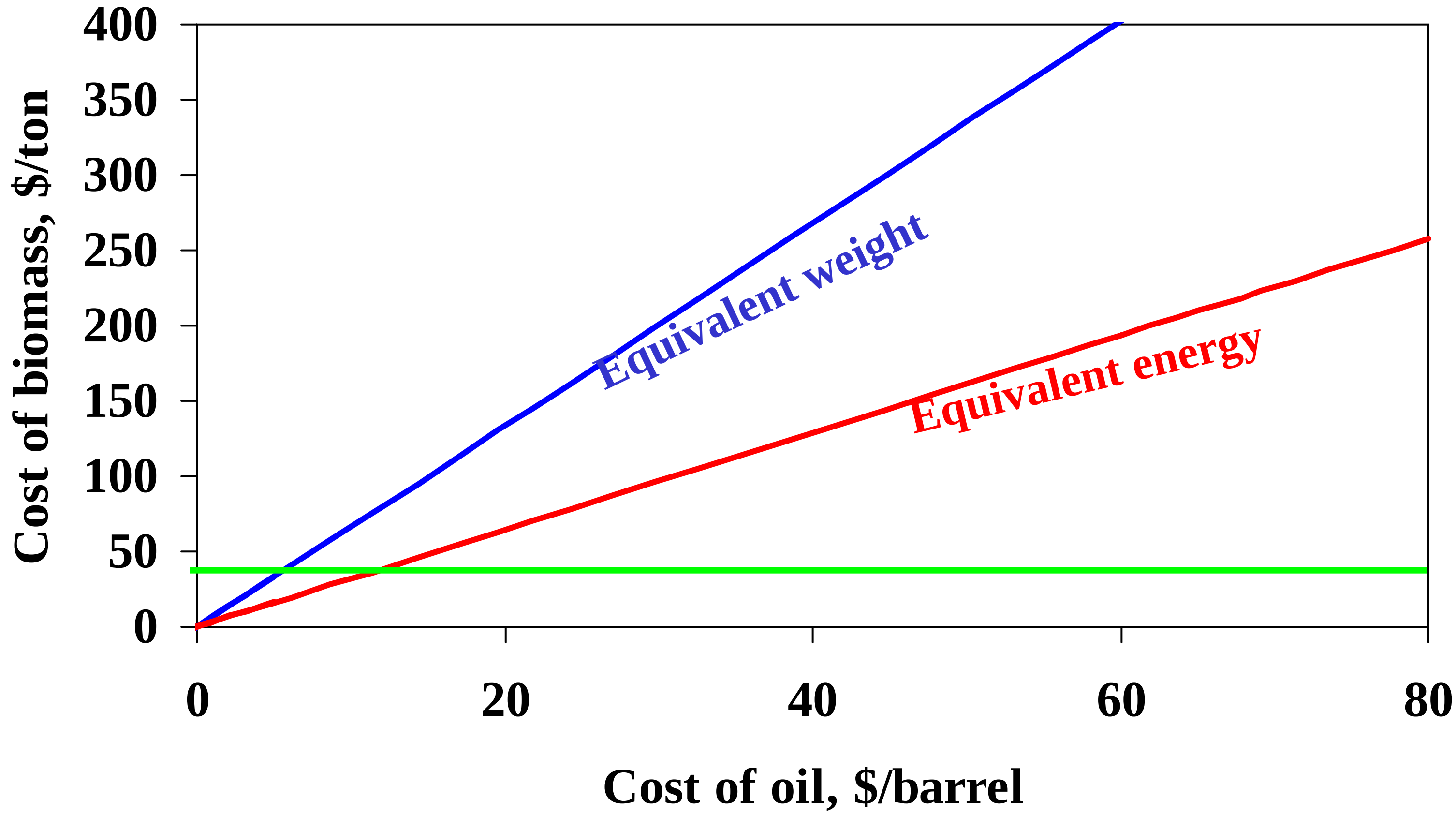
Key Processing Cost Elements



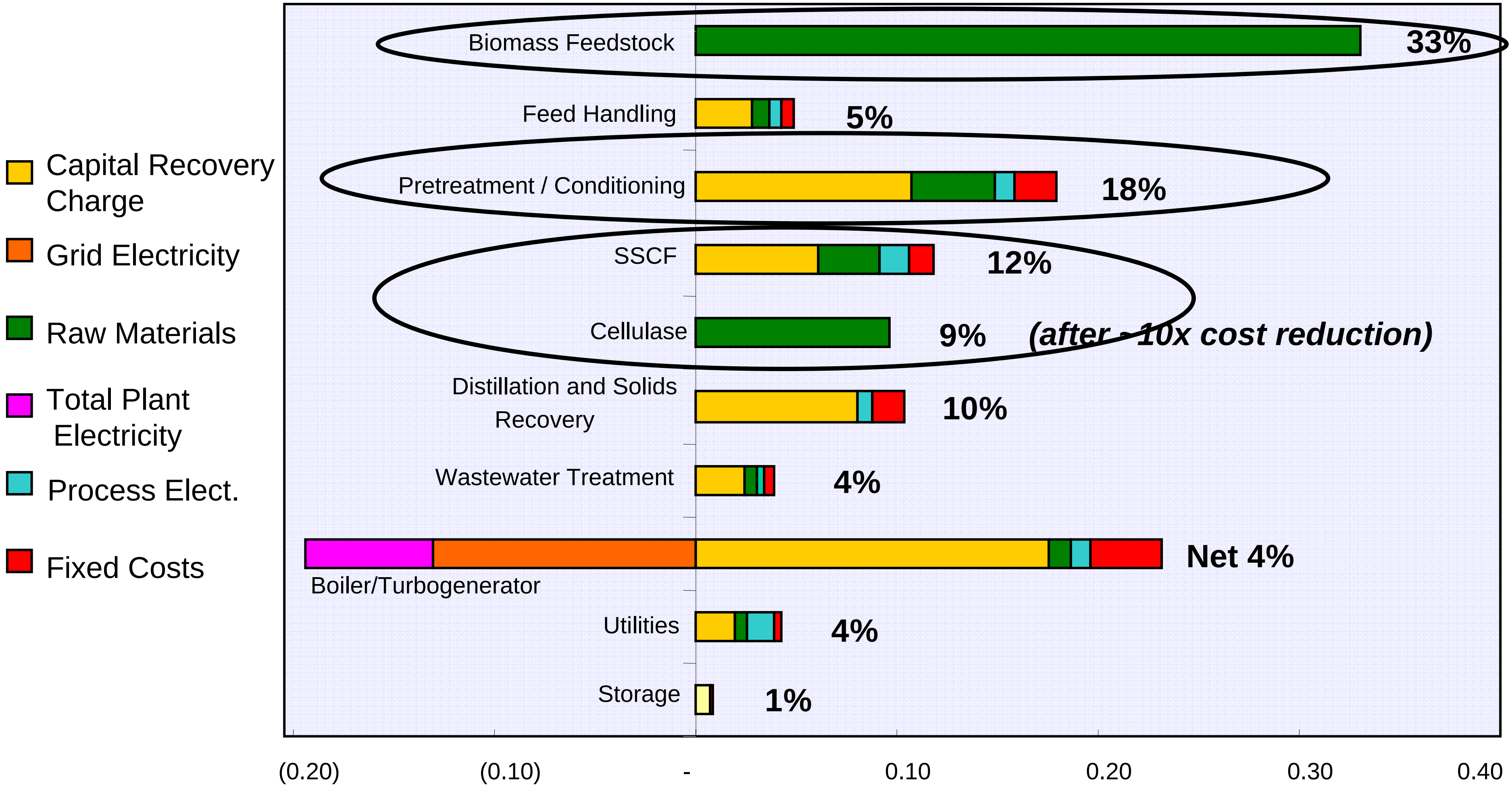
Cost of Cellulosic Biomass vs Petroleum



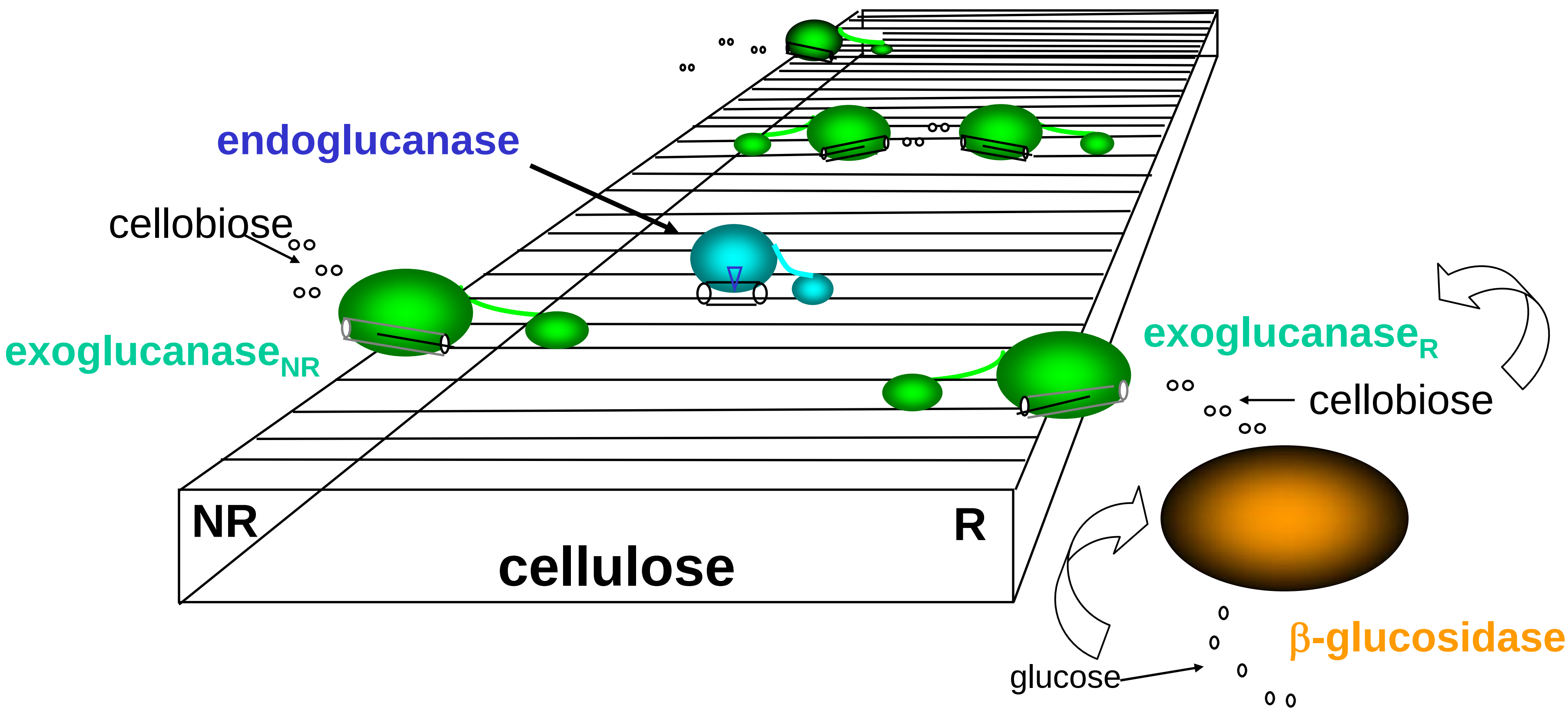
Cost of Cellulosic Biomass vs Petroleum



Key Processing Cost Elements



Fungal Cellulases Include Many Different Components



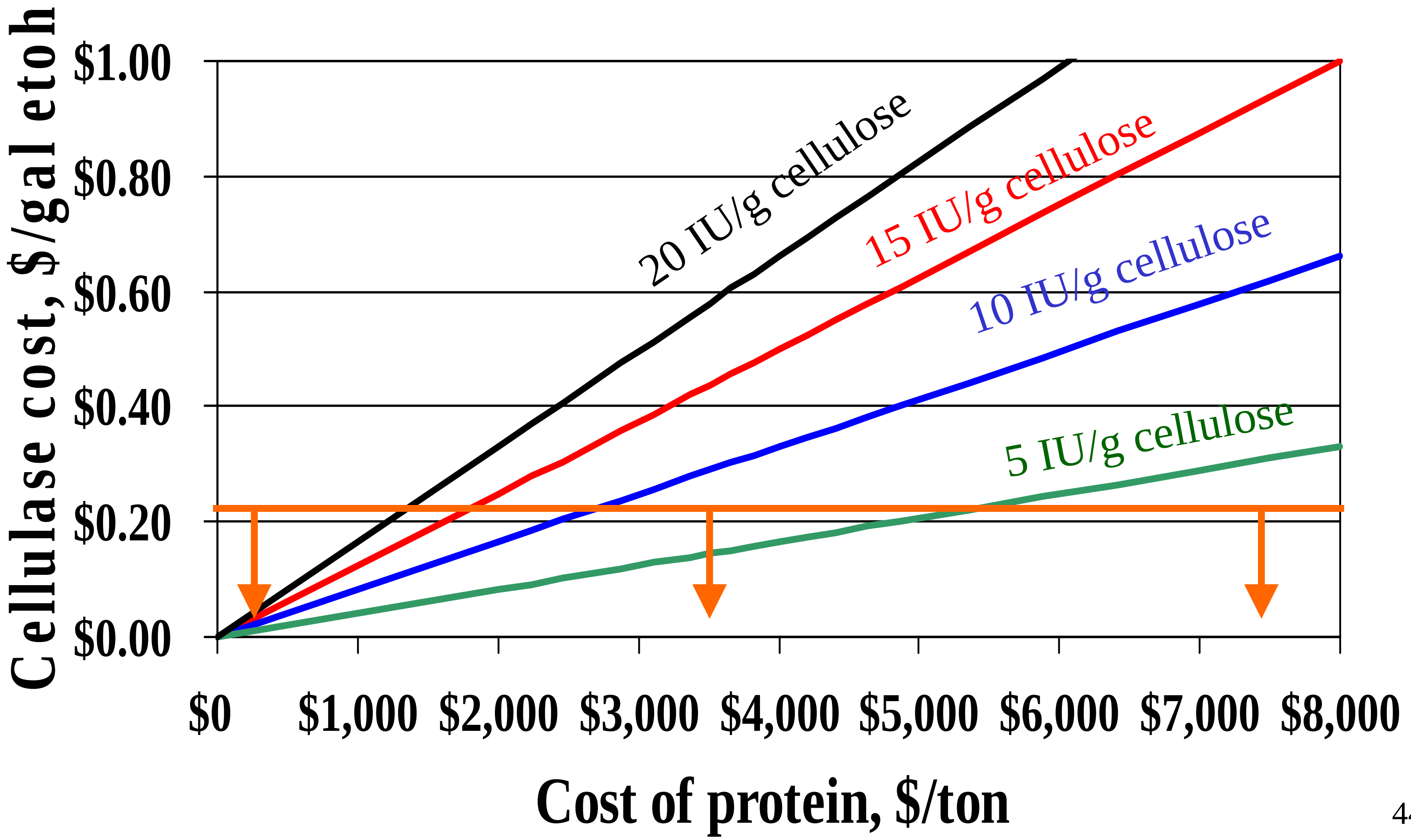
Courtesy of M. Himmel, NREL

Key Question: How Much Does Cellulase Cost?

- Typically require about 15 IU/g cellulose to hydrolyze
- At a specific activity of 0.5 IU/mg protein, this translates into about 0.25 lbs of protein or more per gallon of ethanol
  - Includes ethanol produced from hemicellulose fraction, most of which can actually be released during many pretreatments
- What does a pound of protein cost?

Cost of Cellulase vs Cost of Protein

Specific Activity = 0.5 IU/mg protein



How Can We Reduce Cellulase Costs?

- Reduce protein production costs
- Improve specific activity – double activity would cut cost in half
  - Thermophilic operation
- Reduce protein loadings
  - "Better" pretreatment
  - Reduce non productive binding to lignin
- Reduce inhibition by sugars, oligomers

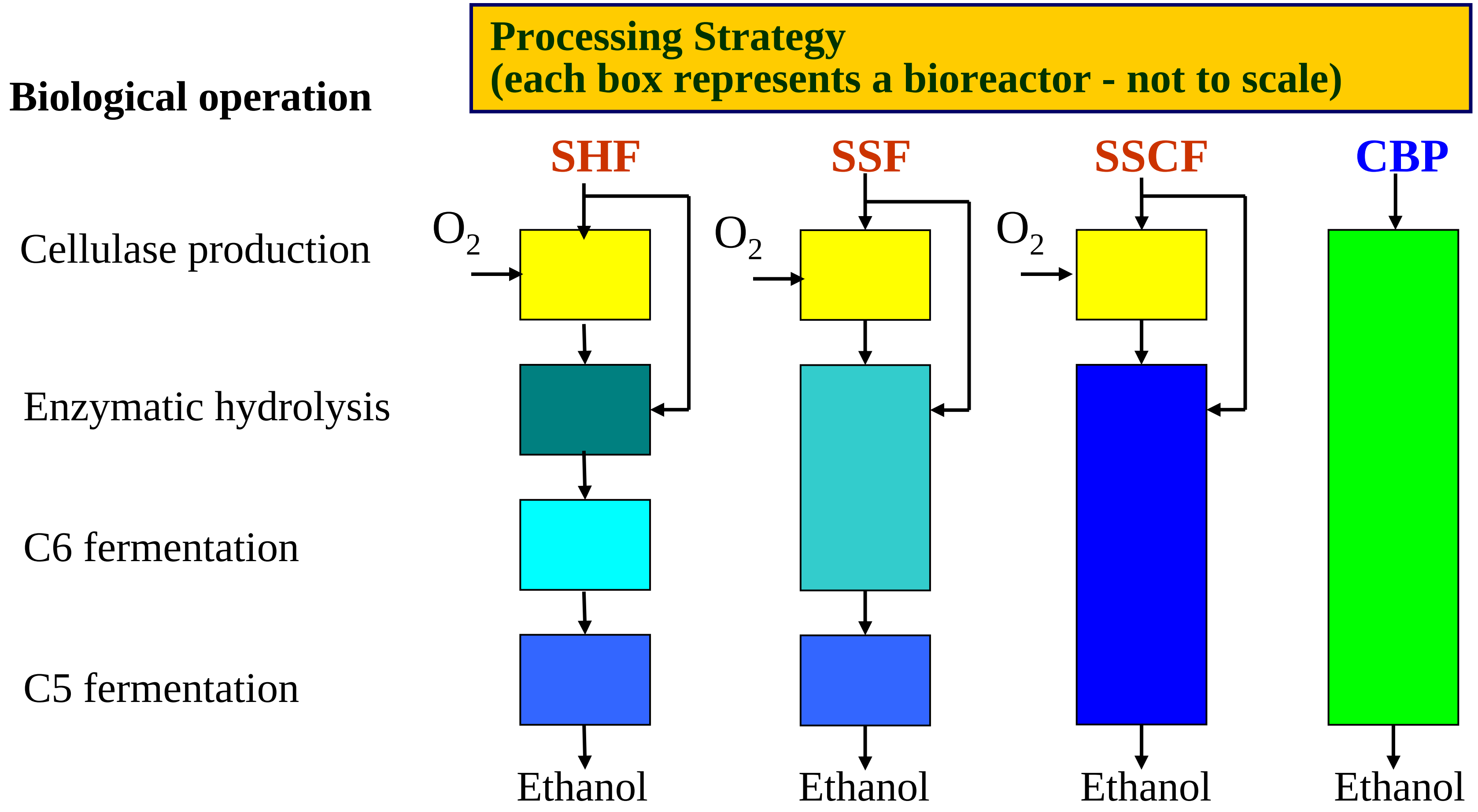
Advancing Cellulosic Ethanol Technology

- Paper by Lee Lynd of Dartmouth, Rick Elander of NREL, and Charles Wyman 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

Basis for Lower Cost Scenarios

- Larger scale operation - 2.74 million tons/yr feedstock
- Feedstock cost - $38.60/dry ton
- Advances in pretreatment
- High yields from consolidated bioprocessing

Evolution of Biomass Processing Featuring Enzymatic Hydrolysis



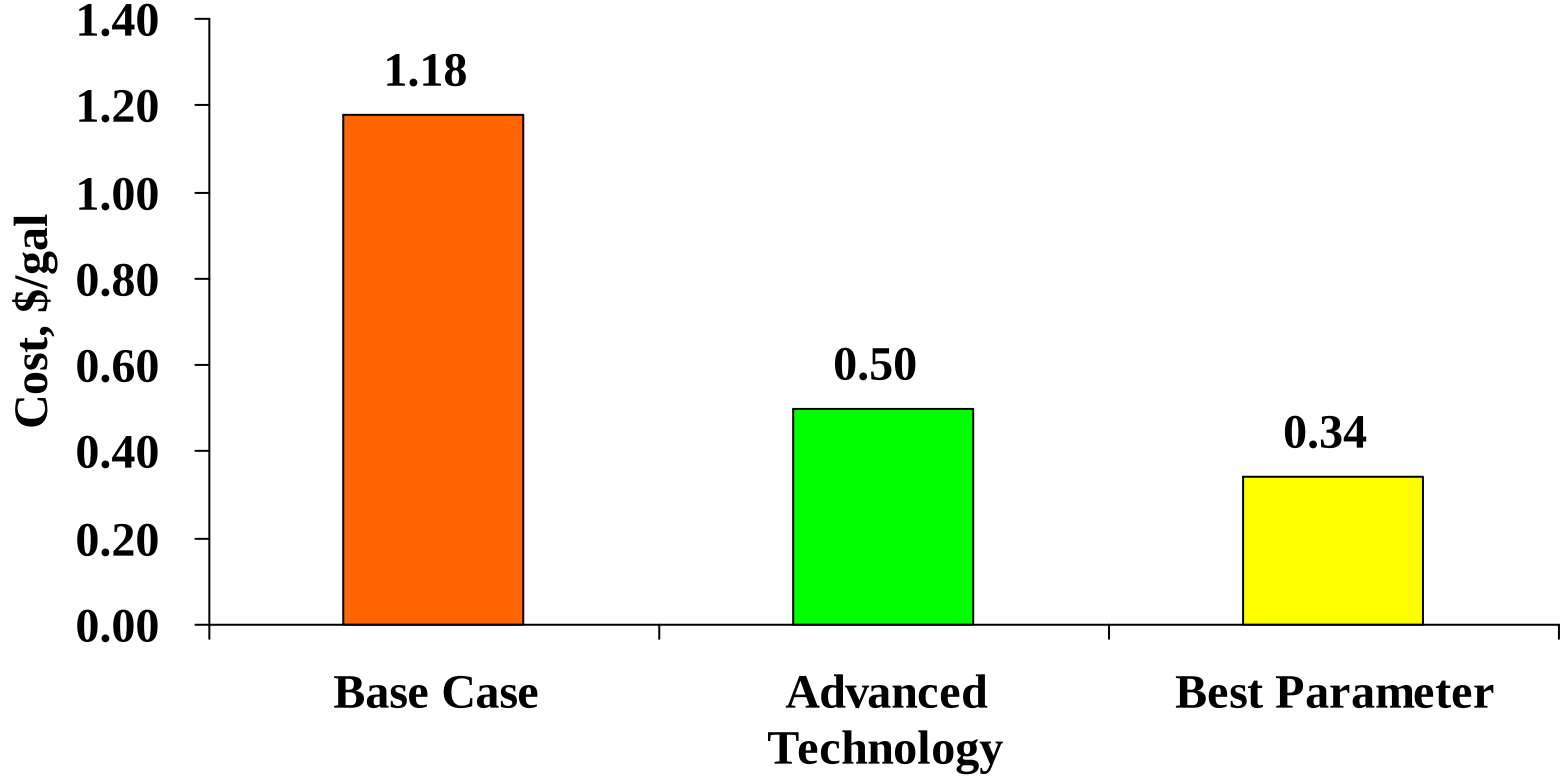
SHF: Separate hydrolysis & fermentation **SSCF: Simultaneous saccharification & co-fermentation**

SSF: Simultaneous saccharification & fermentation **CBP: Consolidated bioprocessing - TBD**

Pretreatment Advances

- Liquid hot water-like technology
- Limited chemical use
- Reduced milling: Use chips not sawdust
- Low cost materials of construction
- High hemicellulose yields
- High yields of glucose from cellulose

Projected Cellulosic Ethanol Costs



Another Viewpoint

- Should realize over 100 gals/ton with mature technology
- For a feedstock cost of $40/ton, this amounts to about $0.40/gal
- Generally expect feedstock cost to represent over 2/3 of overall conversion costs for mature process
- In this scenario, ethanol cost would be less than $0.60/gal

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
  - $375 million over 5 years for 3 DOE Bioenergy Research Centers

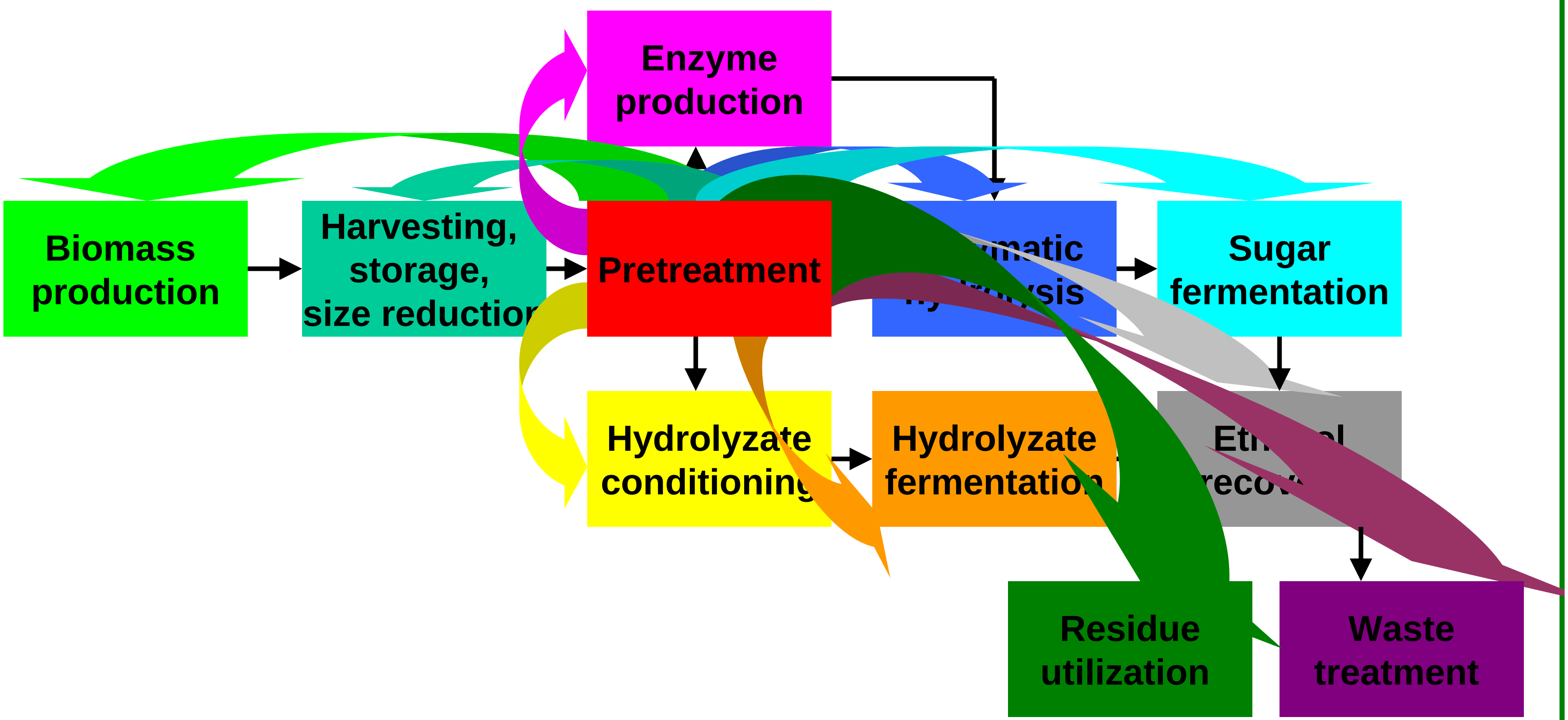
Importance of Pretreatment

- 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

Importance of Pretreatment

- 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

Pretreatment Can Also Affect All Biological Processing Operations



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 UCR Ethanol Research

- 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
- Develop advanced technologies that will dramatically reduce the cost of production

Current Research Topics

- Effect of different pretreatments on enzymatic hydrolysis of biomass – US DOE
  - Lead 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

Consortium for Applied Fundamentals and Innovation (CAFI)

- Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI) 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.

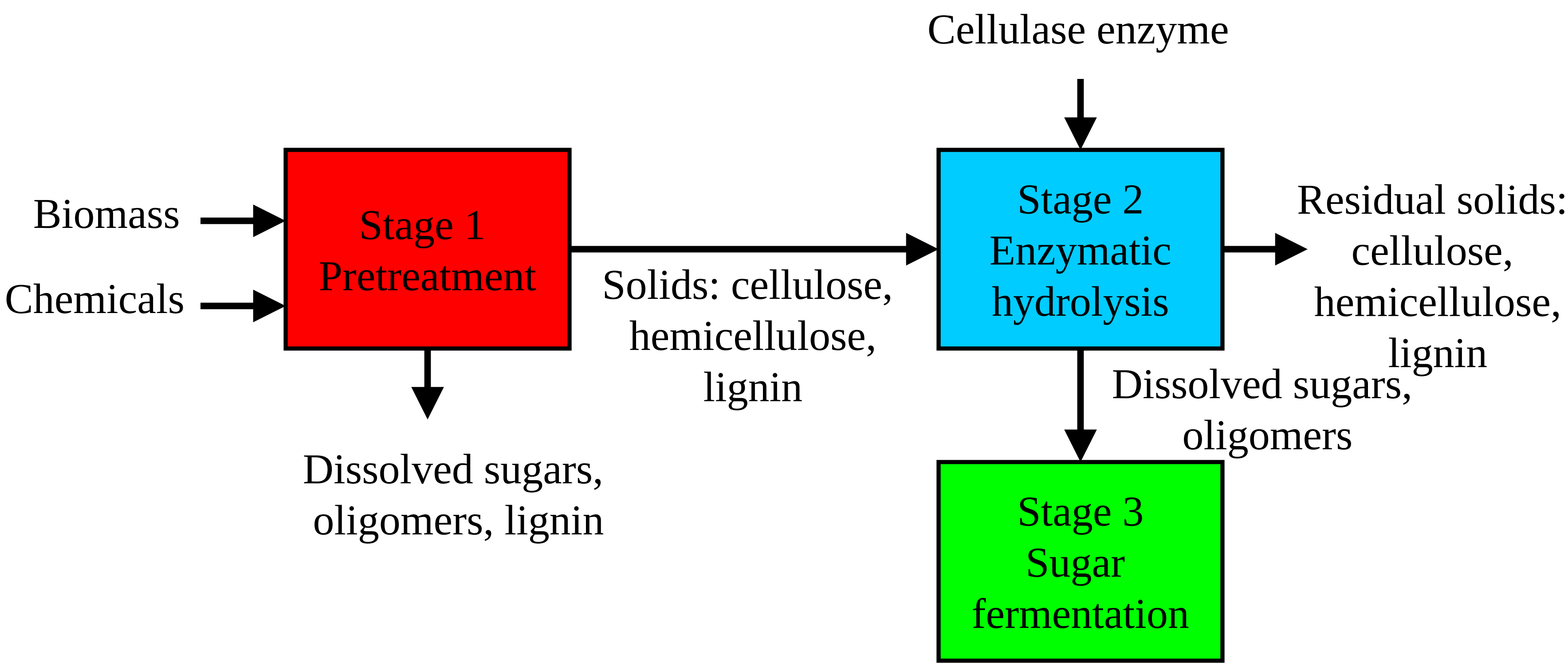
CAFI Projects

- USDA IFAFS Program first funded CAFI through competitive solicitation starting in September 2000 for corn stover
- DOE Office of the Biomass Program selected CAFI for $1.88 million through a joint competitive solicitation with USDA with project funding started in April 2004 for poplar wood
- Use identical analytical methods, feedstock sources, enzymes, analytical methods, and material balance protocols 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

CAFI Pretreatment Technologies

- **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 expansion (AFEX)** - Bruce Dale, Michigan State University
- **Controlled pH pretreatment** - Mike Ladisch, Purdue University
- **Lime pretreatment** - Mark Holtzapple, Texas A&M University
- **Sulfur dioxide pretreatment** – Jack Saddler, University of British Columbia
- **Logistical support and economic analysis** - Rick Elander/Tim Eggeman, NREL through DOE Biomass Program funding
- **Commercial and advanced ezymes** – Colin Mitchinson, Genencor

CAFI Hydrolysis Stages



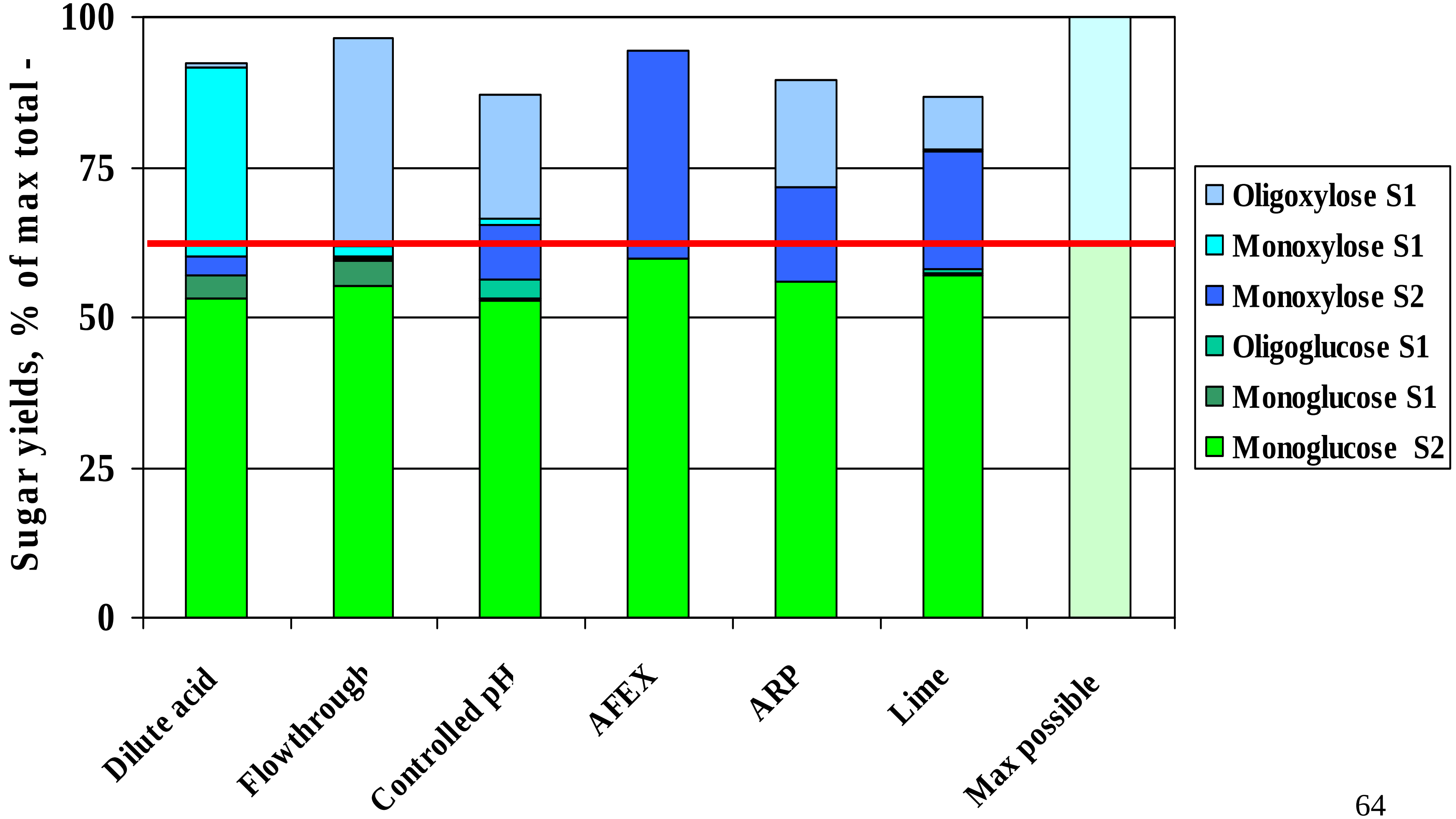
Overall Yields for Corn Stover at 15 IU/g Glucan

Increasing pH

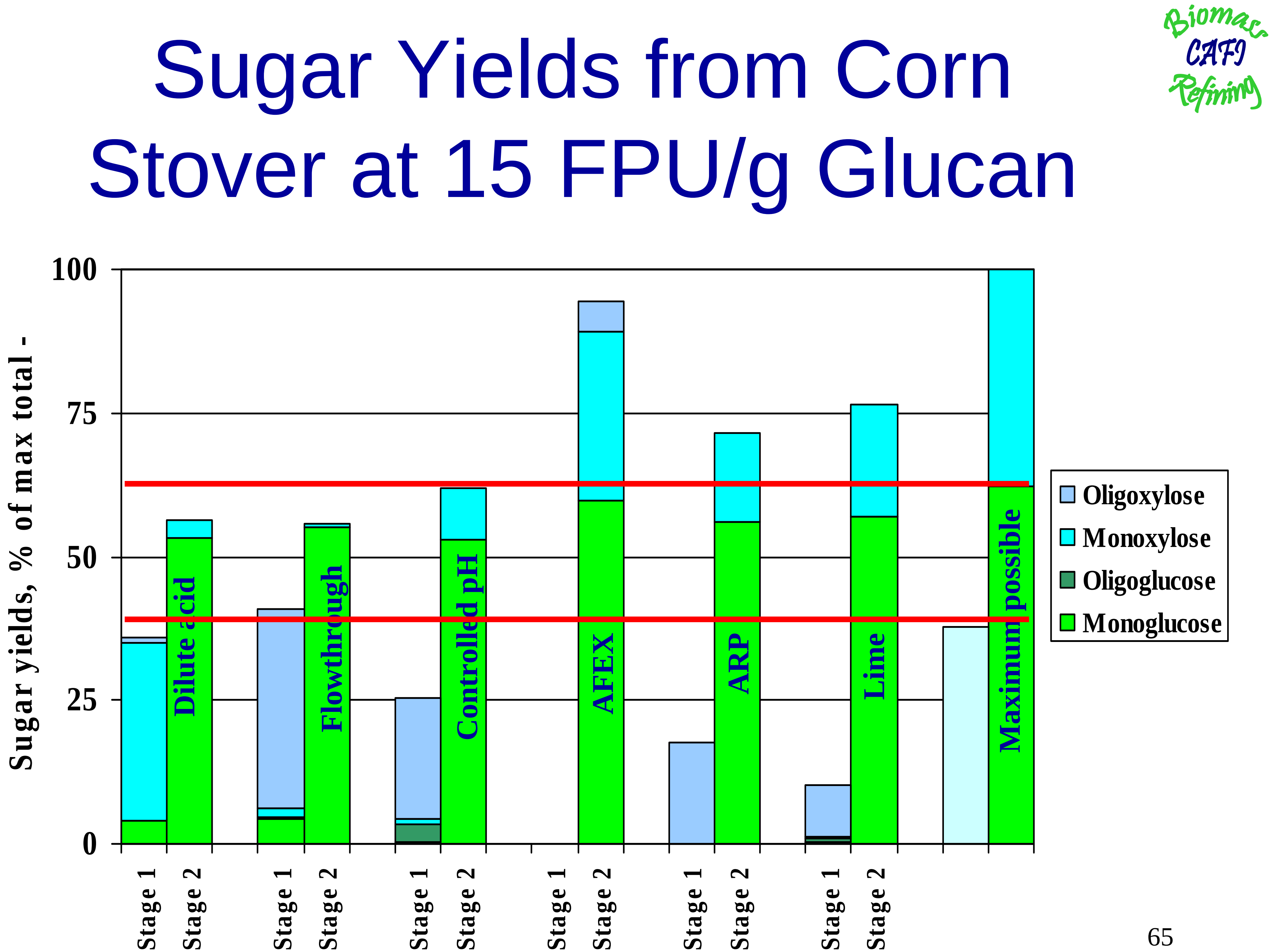
Pretreatment system	Xylose yields*			Glucose yields*			Total sugars*		
	Stage 1	Stage 2	Total xylose	Stage 1	Stage 2	Total glucose	Stage 1	Stage 2	Combined total
Maximum possible	37.7	37.7	37.7	62.3	62.3	62.3	100.0	100.0	100.0
Dilute acid	32.1/31.2	3.2	35.3/34.4	3.9	53.2	57.1	36.0/35.1	56.4	92.4/91.5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

Sugar Yields from Corn Stover at 15 FPU/g Glucan



Sugar Yields from Corn Stover at 15 FPU/g Glucan



CAFI Standard Poplar

- Feedstock: USDA-supplied hybrid poplar (Alexandria, MN)
  - Debarked, chipped, and milled to pass ¼ inch round screen

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 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

1/4 inch Milled Poplar

CAFI Initial Poplar

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

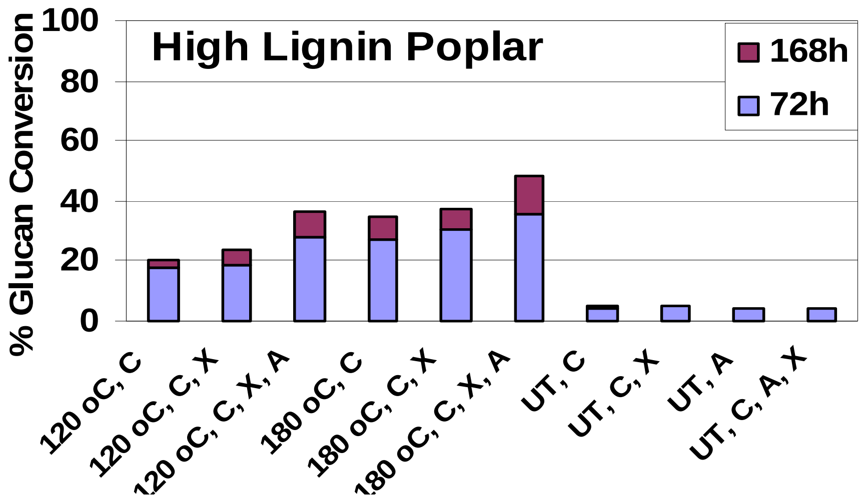
Component	Wt %
Glucan	45.1
Xylan	17.8
Arabinan	0.5
Mannan	1.7
Galactan	1.5
Lignin	21.4
Protein	nd
Acetyl	5.7
Ash	0.8
Uronic Acids	nd
Extractives	3.4

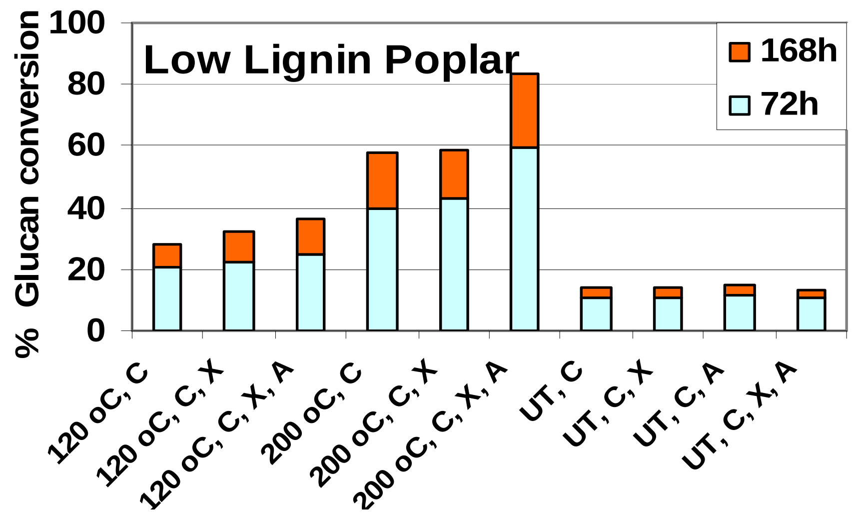
1/4 inch Milled Poplar

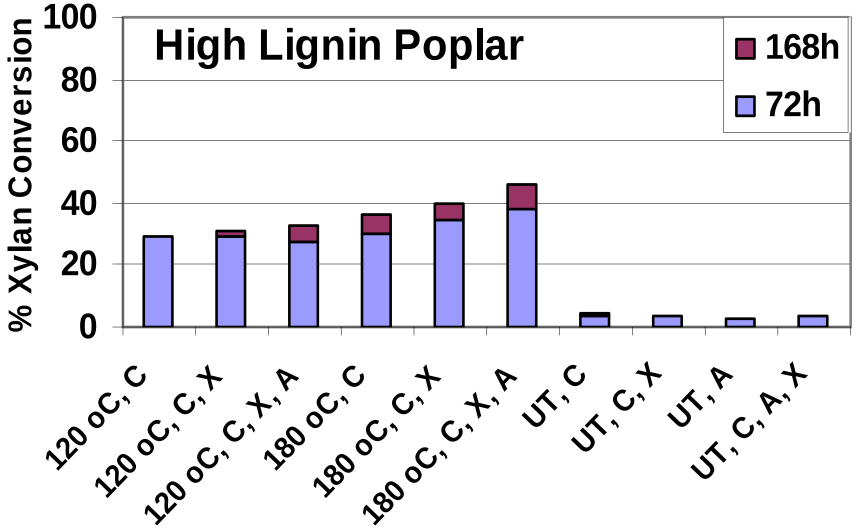
AFEX Optimization for High/Low Lignin Poplar

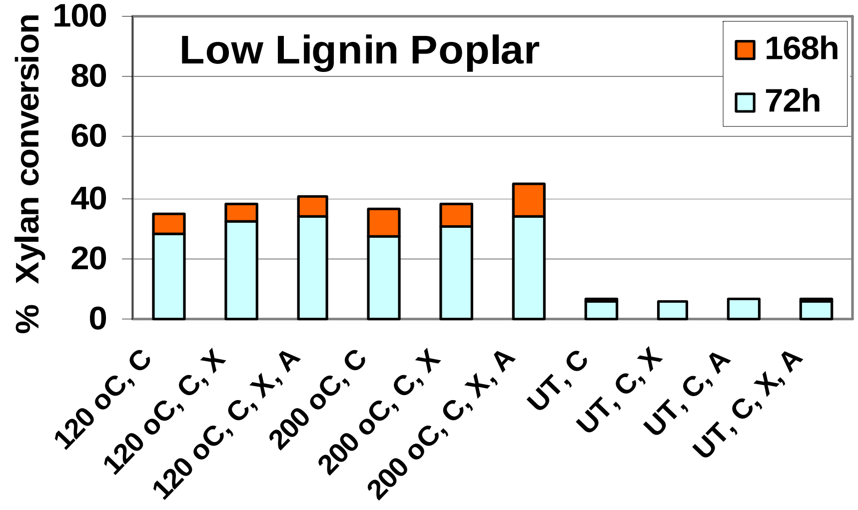
C - Cellulase
(31.3 mg/g glucan)
X - Xylanase
(3.1 mg/g glucan)
A - Additive
(0.35g/g glucan)

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







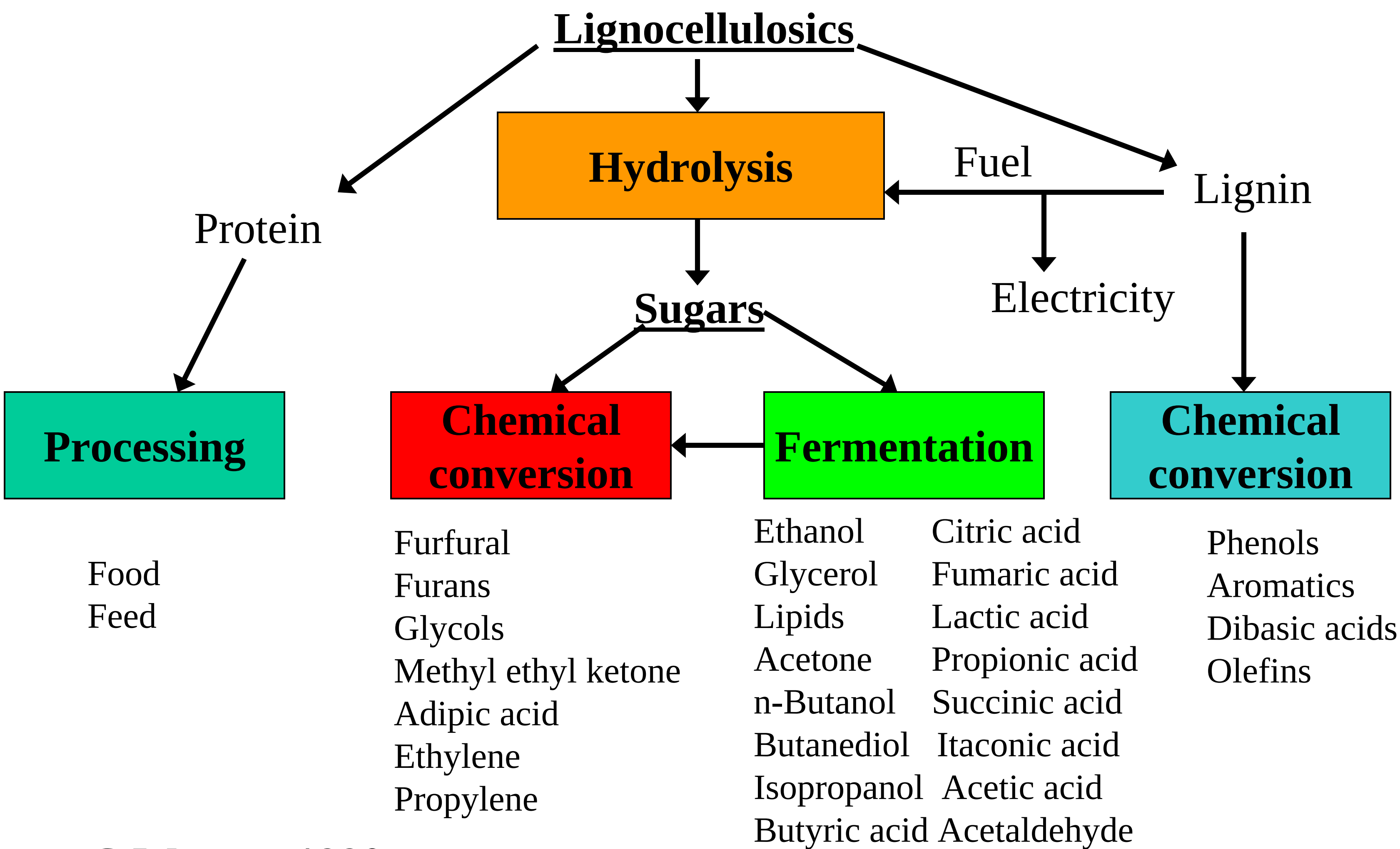


SO_2 Overall Yields at 15 FPU/g of Glucan (148 hours hydrolysis)

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
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

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

Refinery for Cellulosic Biomass to Fuels,Chemicals, Power, Food, and Feed



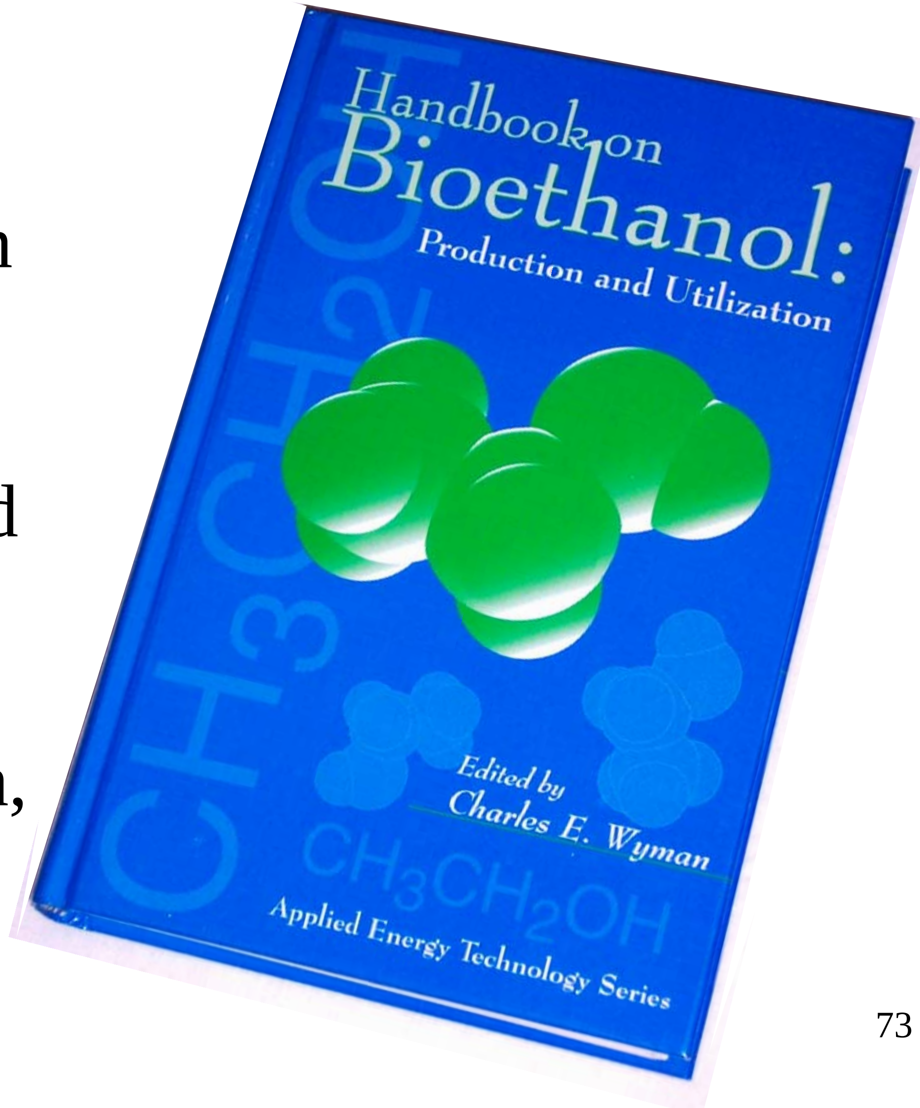
From C Wyman 1990

Feedstock Wish List

- High productivity to
  - Maximize impact on fuel use
  - Reduce land requirements
  - Reduce transportation costs
- High carbohydrate content to maximize yields
- Low fertilizer needs to reduce costs and environmental impacts
- Draught tolerance to avoid irrigation
- Easily fractionated to major components
- Easily hydrolyzed to minimize enzyme and chemical use

For More Information on Ethanol

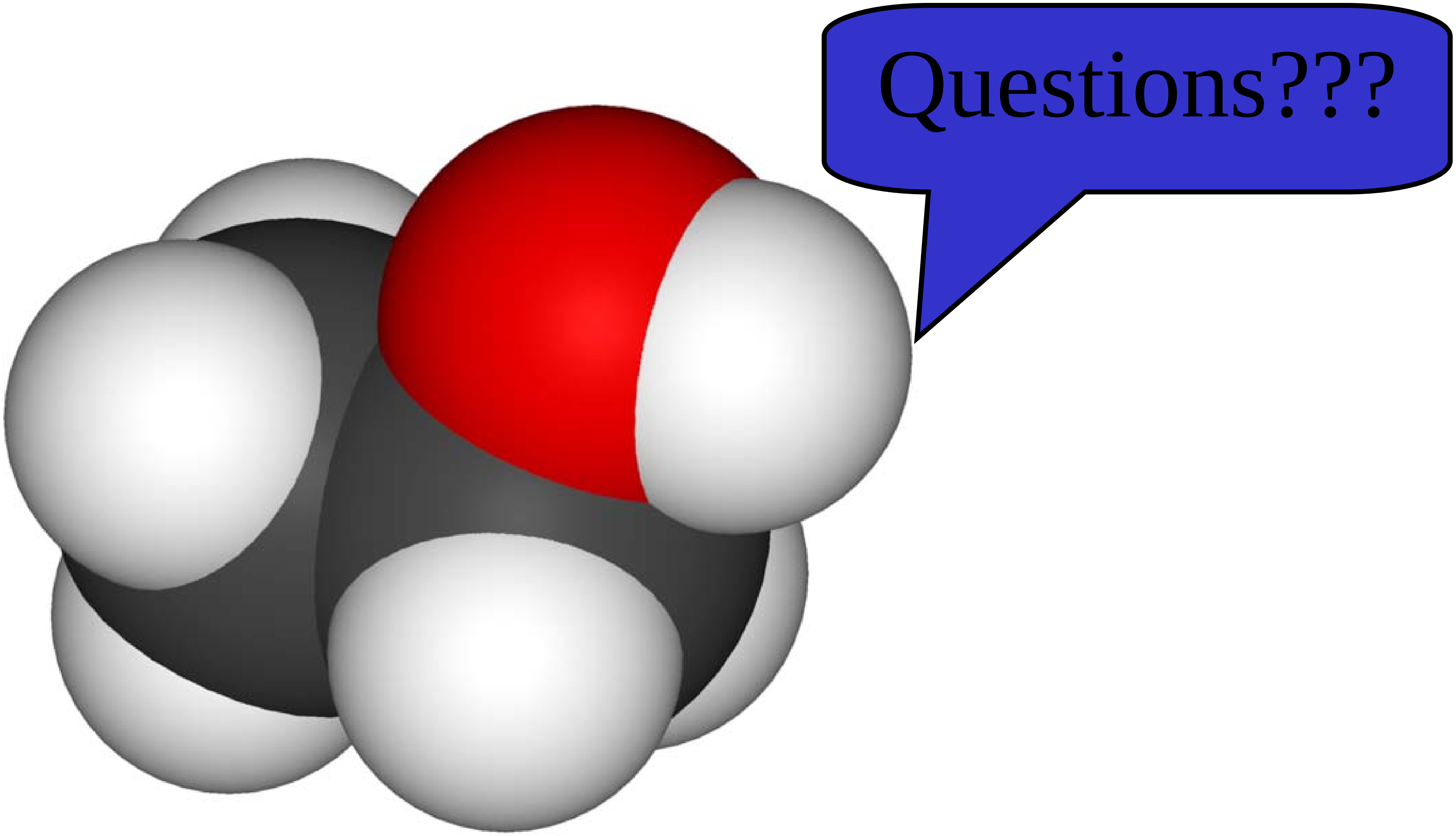
Wyman CE, Editor. 1996. "Handbook on Bioethanol: Production and Utilization," Applied Energy Technology Series, Taylor and Francis, Washington, DC, 424 pages.



Closing Thoughts

- Cellulosic ethanol offers significant environmental, economic, and strategic benefits
- Tremendous progress has been made in improving the technology so it is ready to be commercialized
- Leap forward advances in pretreatment and biological conversion steps can realize cellulosic ethanol that is competitive as a pure fuel
- Immediate challenge is to overcome perceived risk of initial commercial applications if we are to realize these benefits and capitalize on learning curve to reduce costs
- In longer term, seek to diversify the product slate from biomass through cellulosic refinery concept that could produce a number of products including butanol if sugar costs are low enough
- Advances in feedstock could enhance conversion and extend impact of cellulosic biomass

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


Questions???