

*Innovation for Our Energy Future*

# Biochemical Conversion of Cellulosic Feedstocks



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Biomass to Chemicals and Fuels:  
Science, Technology and Public Policy  
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# The Biomass Opportunity: Large-scale Petroleum Displacement and Bioindustry Enablement

- Move beyond grains to grains plus cellulosic crops
  - Key to achieving substantial petroleum displacement and greatly expanding the bioenergy industry

- USDA/DOE's "Billion Ton Vision"

*[http://feedstockreview.ornl.gov/pdf/billion\\_ton\\_vision.pdf](http://feedstockreview.ornl.gov/pdf/billion_ton_vision.pdf)*

- More than 1.3 billion tons of cellulosic biomass (dry basis) is sustainably available domestically
- This amount can provide abundant cheap sugars for commodity biofuels (and bioproducts)
  - Sufficient to displace 30% of current gasoline demand

# Outline

- **Composition of Cellulosic Feedstocks**
- **Biochemical Conversion Routes**
- **Enzymatic Cellulose Hydrolysis Pathway**
- **Remaining Technical Barriers/R&D Foci**
- **Outlook**



# Corn Grain vs. Cellulosics

## Corn Stover and Beyond

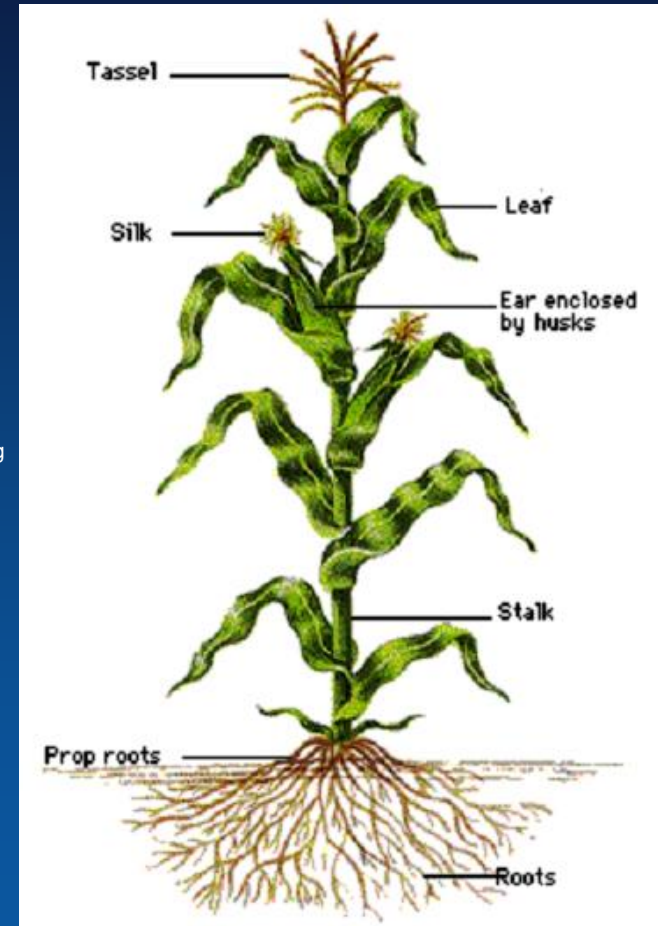


<http://maize.agron.iastate.edu/corngrows.html>



<http://www.bisonfarm.com/images/fsp-corn.jpg>

## SWITCHGRASS



## GRAIN



<http://amica.csustan.edu/key/corn.jpg>

## STOVER



# Composition: Grain vs. Cellulosics

Component	Corn Grain	Corn Stover	Switch-grass	Poplar
Starch	72-73	Trace	Trace	0
Cellulose/Hemicellulose	10-12	63-74	60	73
Lignin	0	14-18	10	21
Other Sugars	1-2	3-5	6	3
Protein	8-10	1-3	5	0
Oil/Other Extractives	4-5	2	13	3
Ash	1-2	6-8	6	0.5
Total	96-104	90-110	100	100

Constituent levels can vary by roughly  $\pm 5\%$  dry weight due to environmental and genetic factors

# Cellulosic Biomass: Major Constituents

## Lignin: 15%–25%

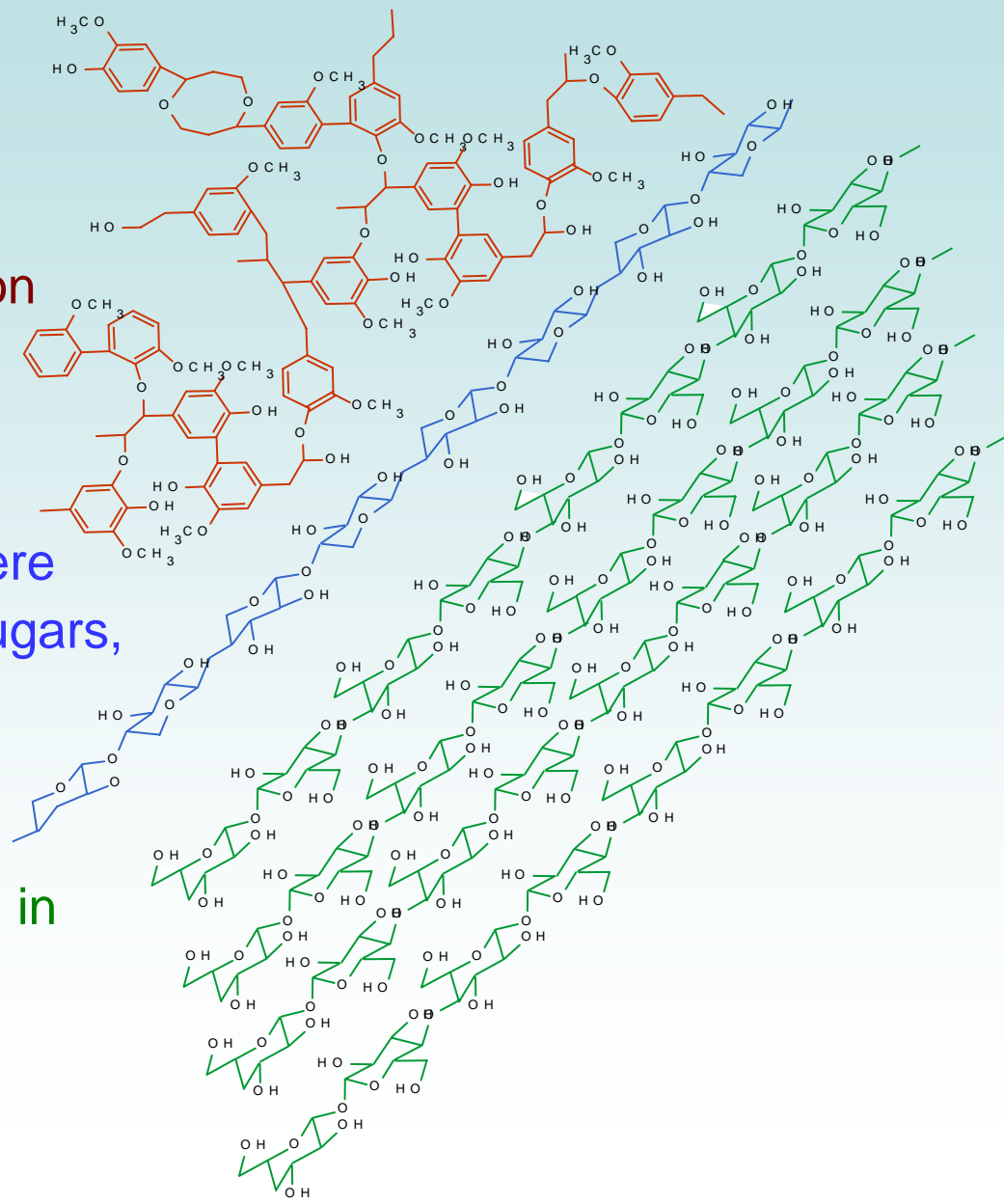
- Complex aromatic structure
- High energy content
- Resists biochemical conversion

## Hemicellulose: 23%–32%

- Xylose is the second most abundant sugar in the biosphere
- Polymer of 5- and 6-carbon sugars, marginal biochemical feed

## Cellulose: 38%–50%

- Most abundant form of carbon in biosphere
- Polymer of glucose, good biochemical feedstock



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# Routes to Biofuels



**Bio/chemical  
transformation  
of natural  
compounds**

- Ethanol  
from sugars
- Biodiesel from renewable oils

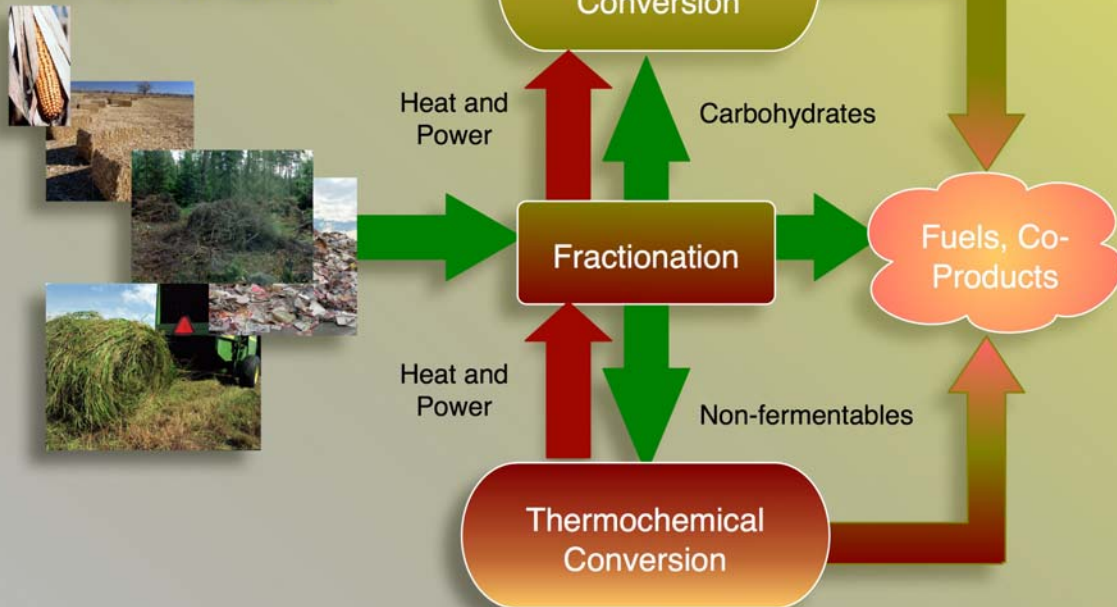
**Thermal reduction  
to “syngas”  
(H<sub>2</sub>, CO) chemical  
building blocks**

- Traditional chemistry
- Fischer-Tropsch diesel, gasoline
- Methanol,  
other alcohols  
(bio/catalytic)

# The USDOE Biomass Program

## Organized Around an Evolving Biorefinery Vision

The Integrated Biorefinery  
The right tool for the right job  
Biological processing of carbohydrates  
Thermochemical processing of non fermentables

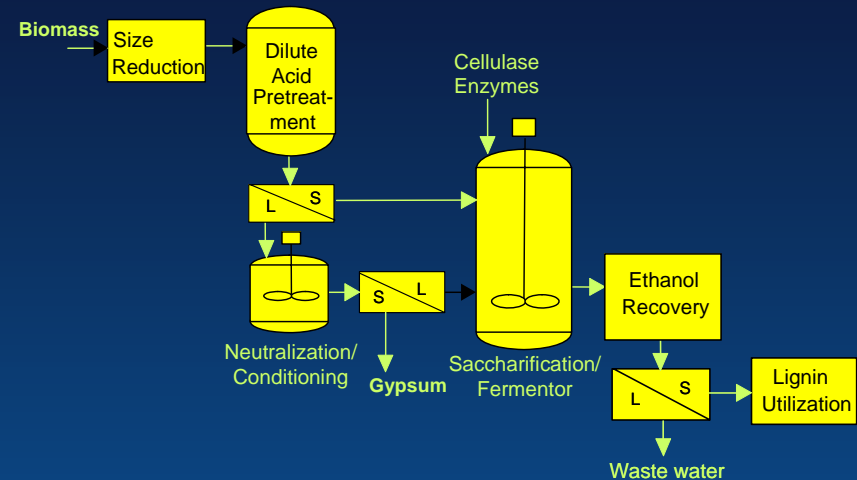


Biomass as  
“*The New Petroleum*”—  
and beyond:  
Source of food,  
feed, fiber, *and*  
*fuels (and*  
*chemicals)*

# Biochemical Conversion Pathways

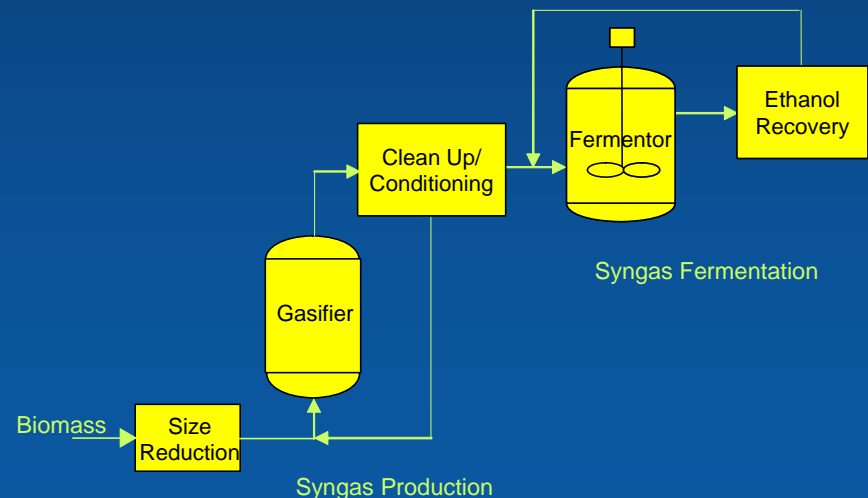
- Hydrolysis/Sugar Fermentation  
Categorize based on method for breaking down cellulose

- Dilute acid hydrolysis
- Concentrated acid hydrolysis
- Enzymatic hydrolysis
  - After using any of a variety of different primary fractionation or “pretreatment” methods



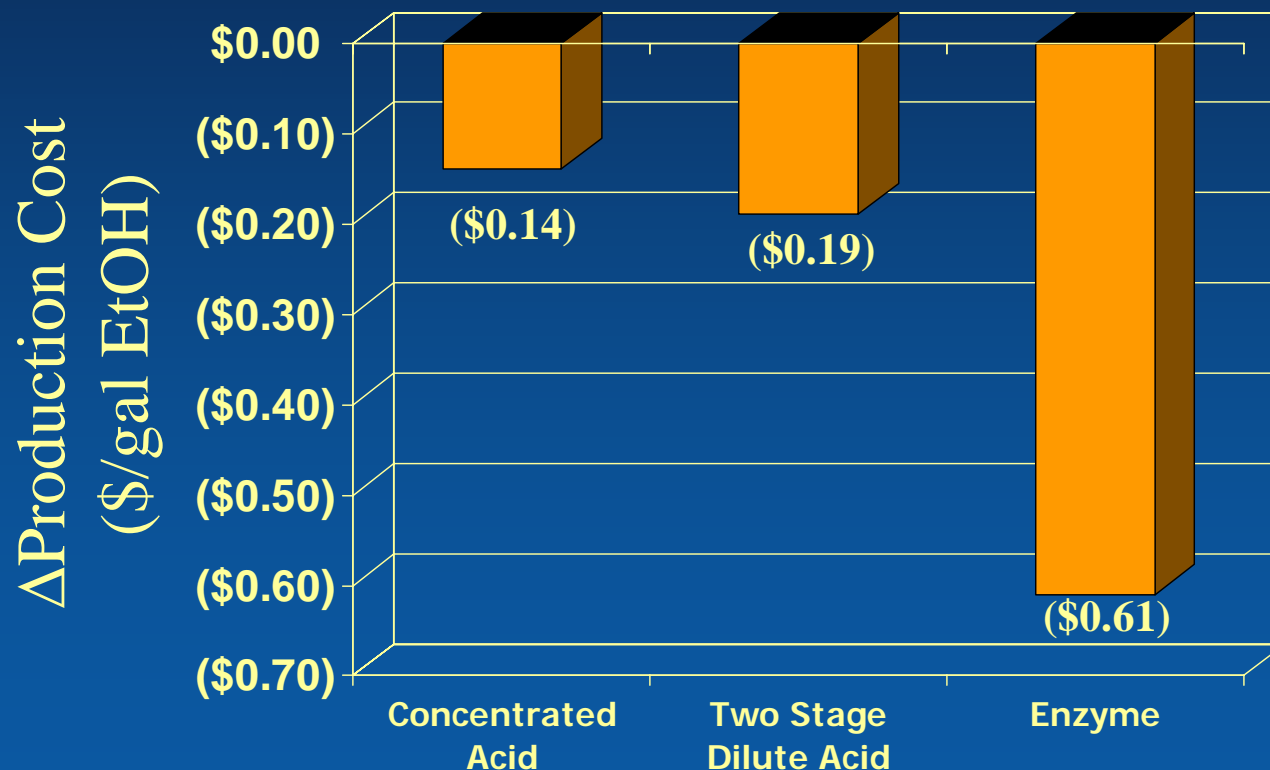
- Gasification/Synthesis Gas Fermentation

- Thermochemical gasification followed by fermentative conversion of (cleaned up) syngas



# Why Emphasize Enzymatic Route?

- Commercial processes based on enzymatic hydrolysis of cellulose don't yet exist, but are believed to offer the best long-term potential for minimizing ethanol production costs

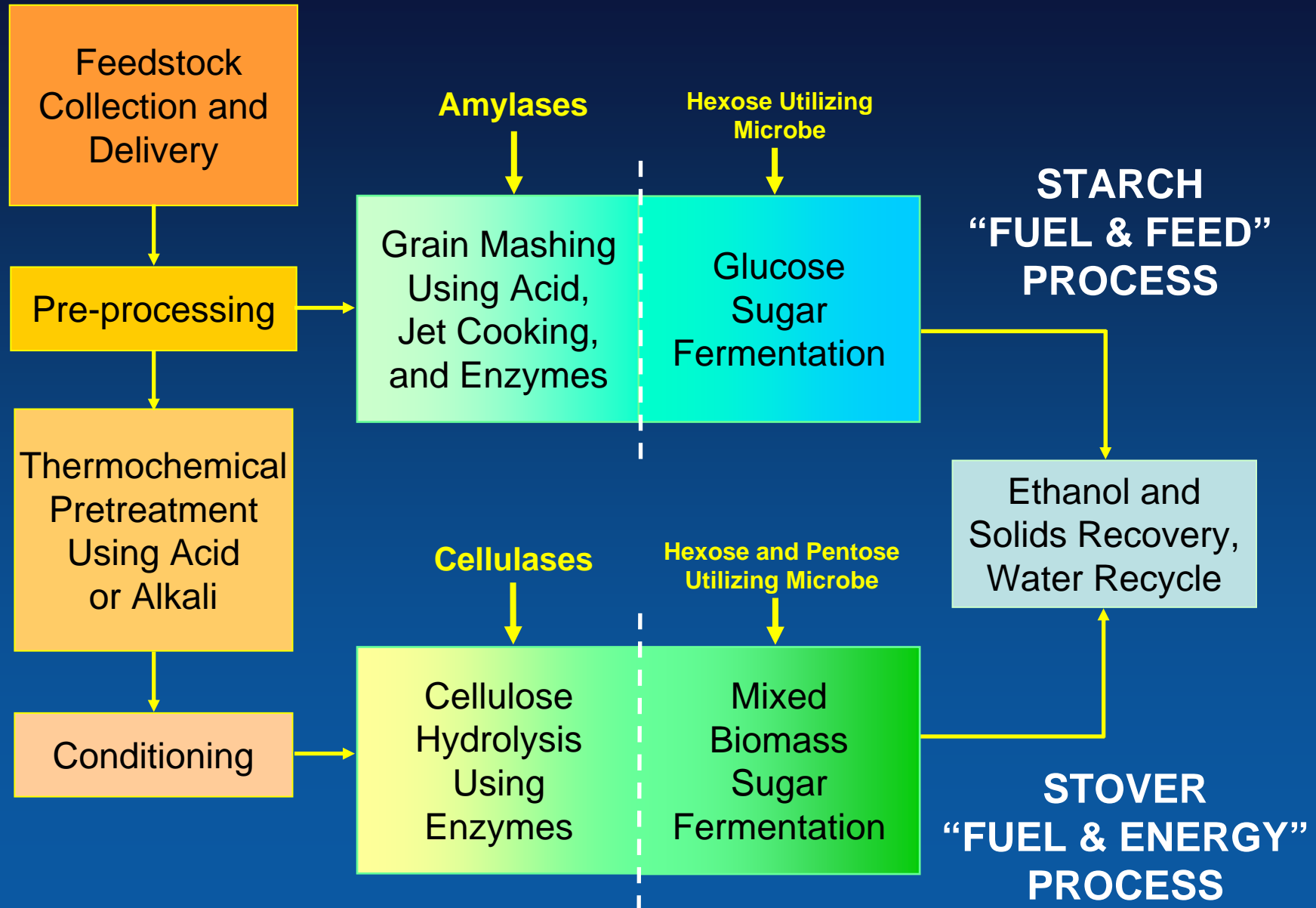


# Outline

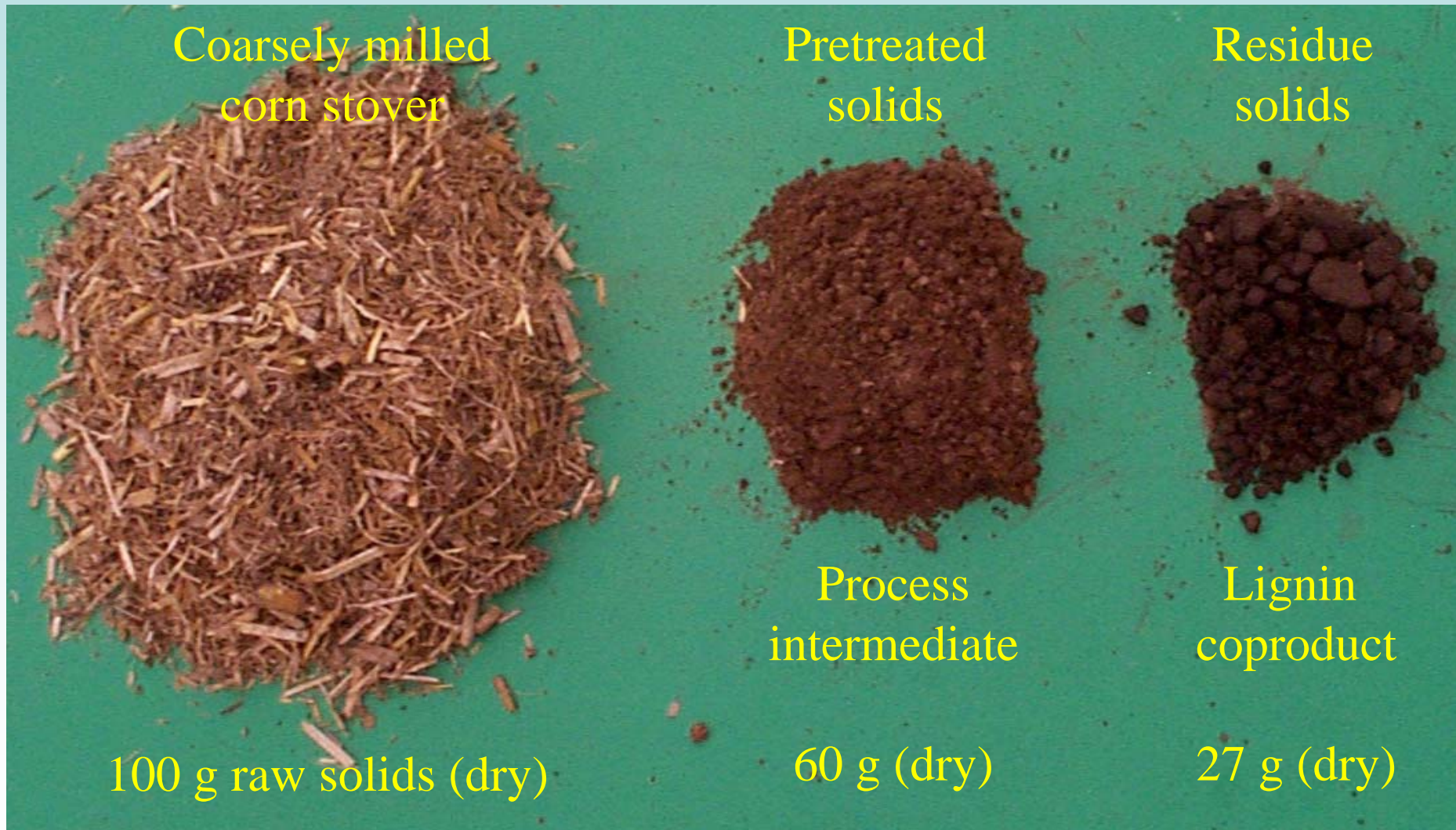
- Composition of Cellulosic Feedstocks
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# Carbohydrate Conversion Steps

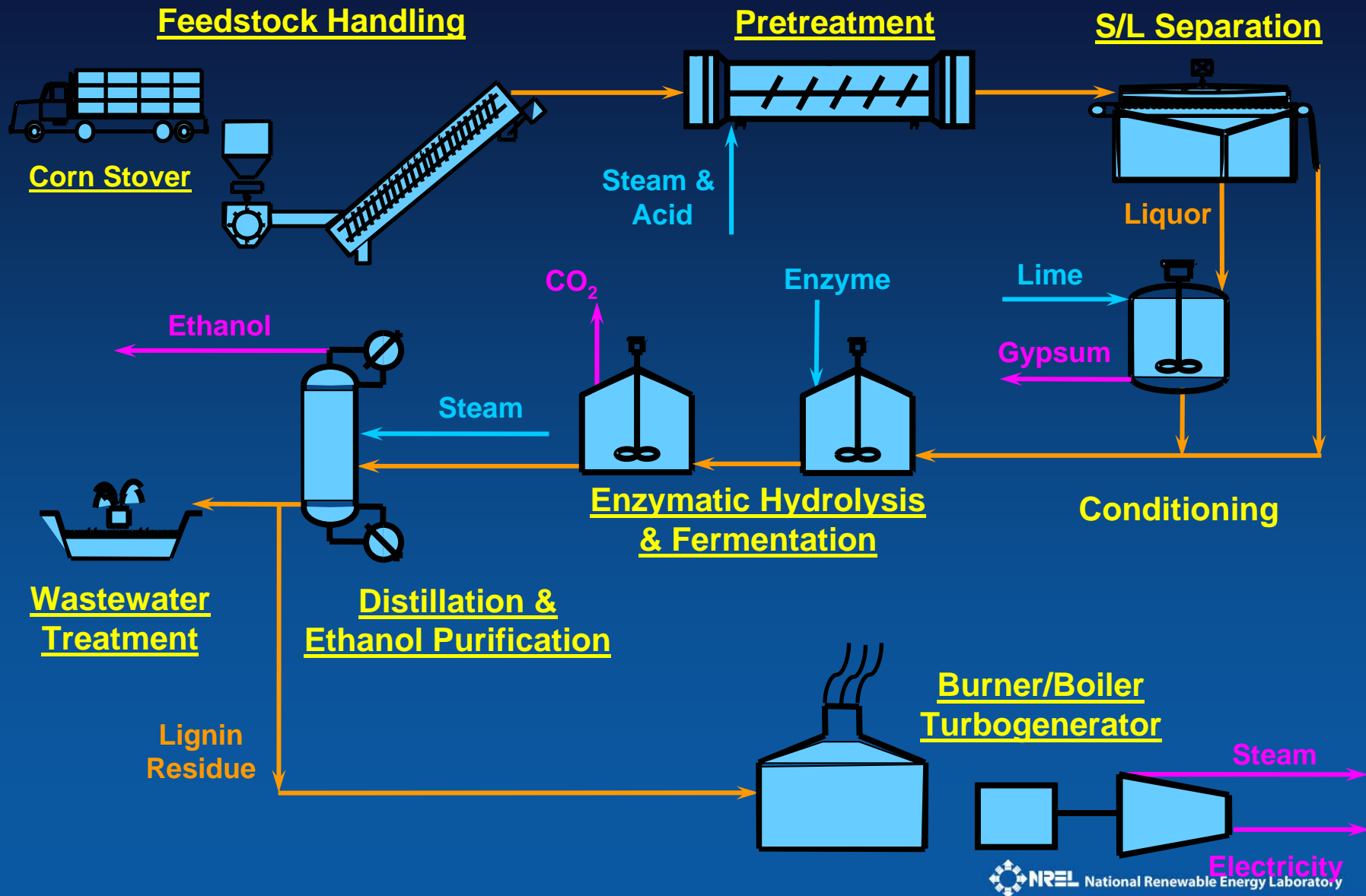


# Conversion is Technically Feasible...



***...the Challenge is Making it Economical!***

# Conceptual Stover-to-Ethanol Process





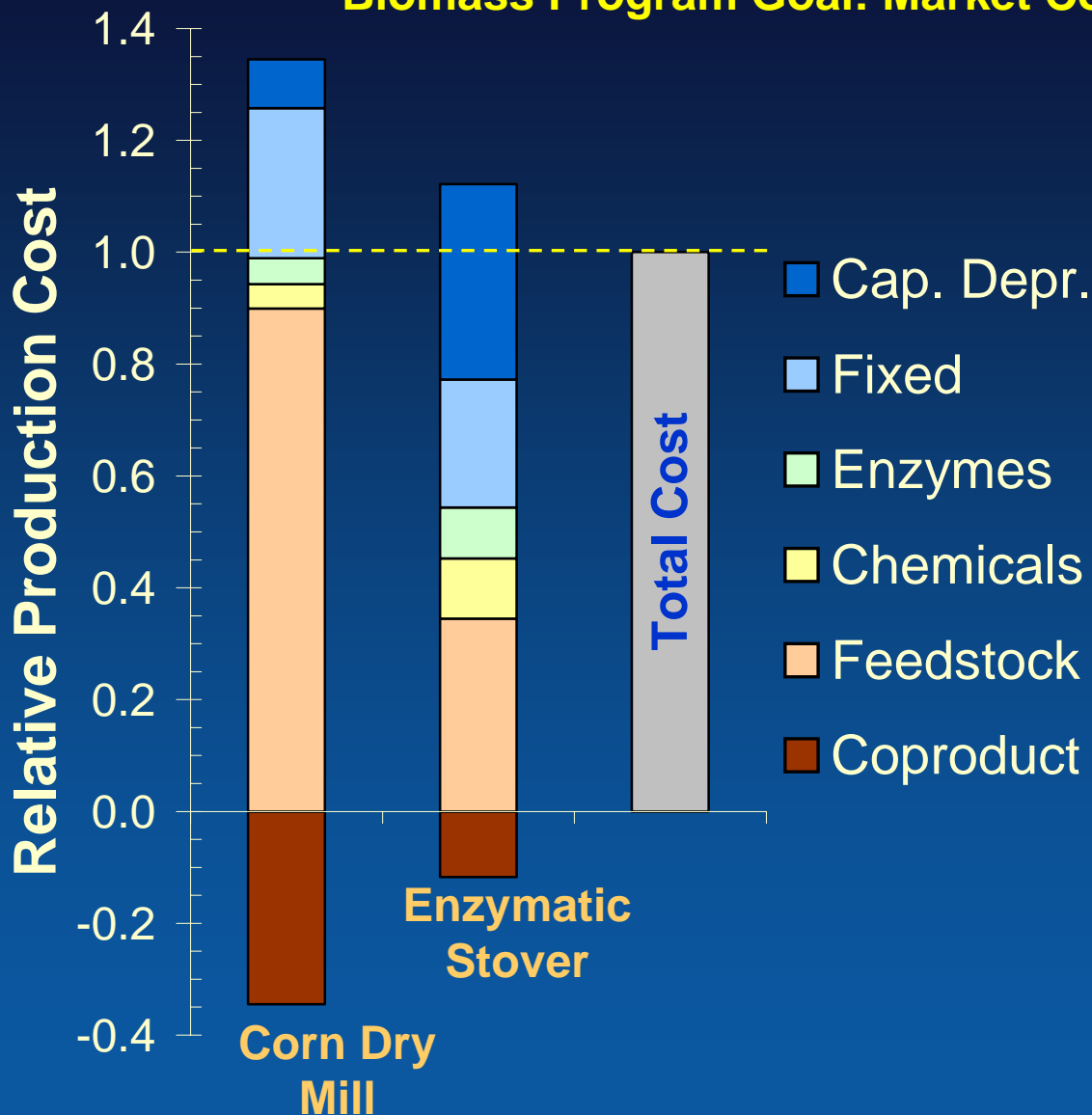
# Cellulosics Must Compete with Starch

## Corn Grain is King in America!



# Comparative Economics

Biomass Program Goal: Market Competitiveness



## Costs driven by

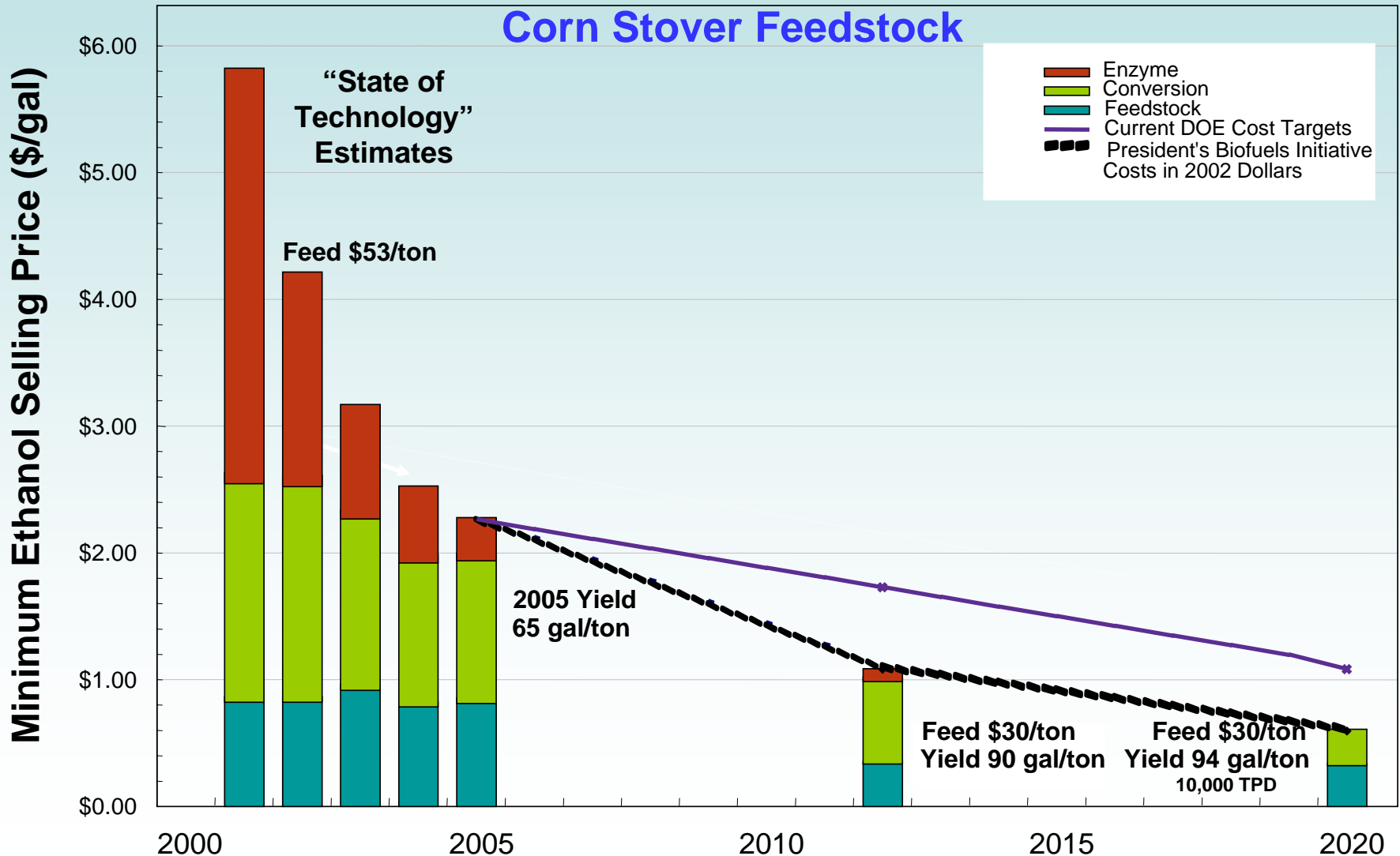
- Feedstock
- Coproduct value
- Utilities prices
- Capital equipment
  - Pretreatment
  - Enzyme Production
  - Distillation
  - Boiler/Combined Heat and Power



# Opportunities and Challenges

- Lower operating cost
  - Operating cost potentially 20-40% lower processing cellulosics (highly feedstock cost dependent)
  - Diversifying feedstock options hedges against rising grain or utilities prices
- Higher capital cost
  - \$2.5-4.0/annual gal for cellulosics vs. \$1.0-1.5 for grain
- Potential for novel higher value coproducts
  - Opportunity: New process streams provide opportunities
  - Challenge: Disparate scales of fuels and coproducts markets

# Cellulosic Ethanol Cost Reduction Progress and Goals



# Outline

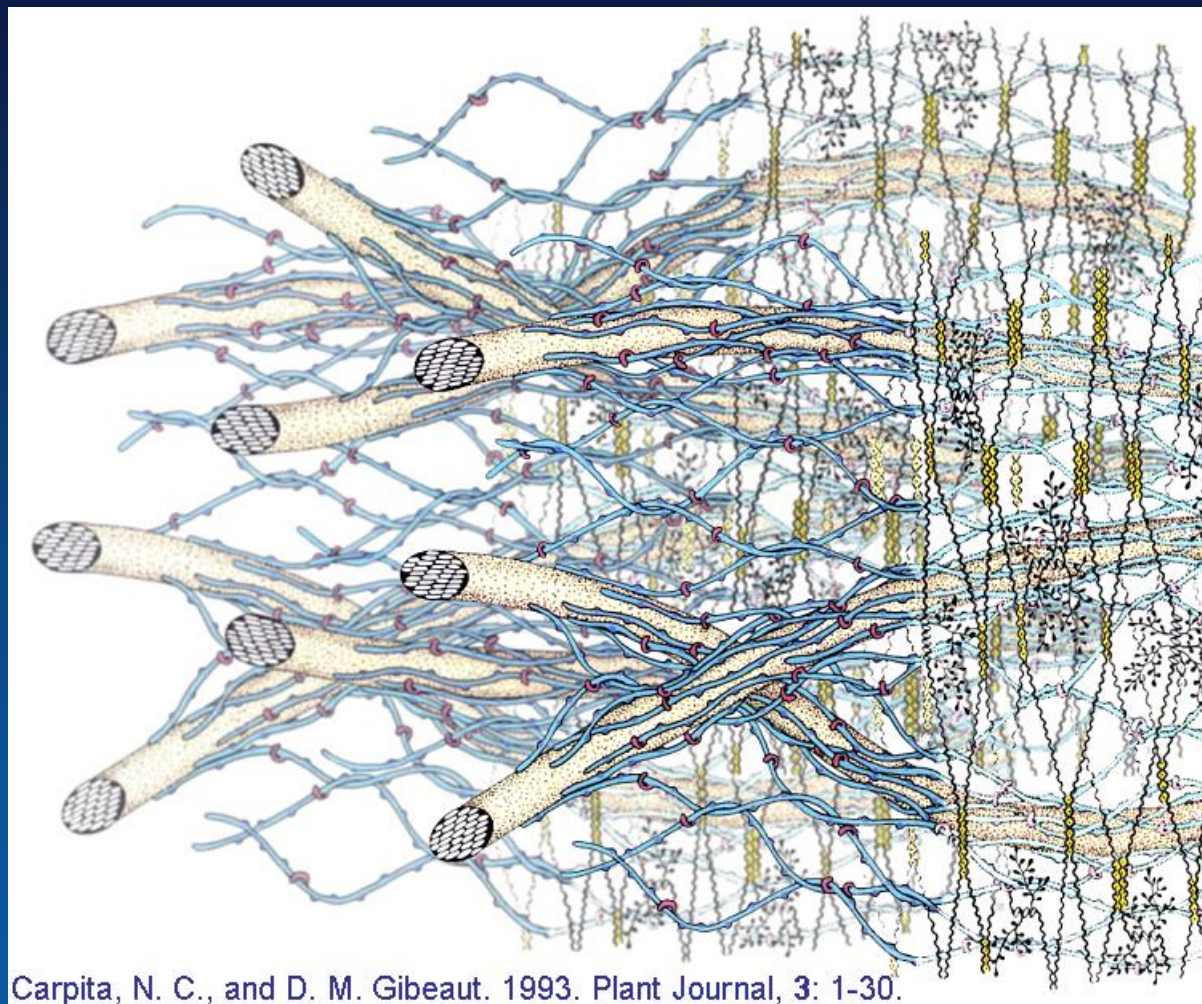
- Composition of Cellulosic Feedstocks
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# Techno-economic Barriers Directing Research and Development

- Feedstock Valuation and Delivery
  - Analytical methods/sensors
  - Sustainable supply systems
- Biomass Recalcitrance to Conversion
  - Pretreatment and enzymatic hydrolysis
  - Pentose and/or mixed sugar fermentation
- Biorefinery Integration
  - Depolymerization chemistry and process interactions
  - Solids and non-Newtonian slurry handling

# 1st R&D Barrier: Cell Wall Recalcitrance

- Lignocellulose cell walls contain *intermeshed* carbohydrate and lignin polymers and other minor constituents
  - The major structural polymers – cellulose, hemicellulose, and lignin – exhibit differential reactivity to thermal, chemical, and biological processing
  - By natural design, cell wall polysaccharides are more difficult to break down than storage carbohydrates like starch

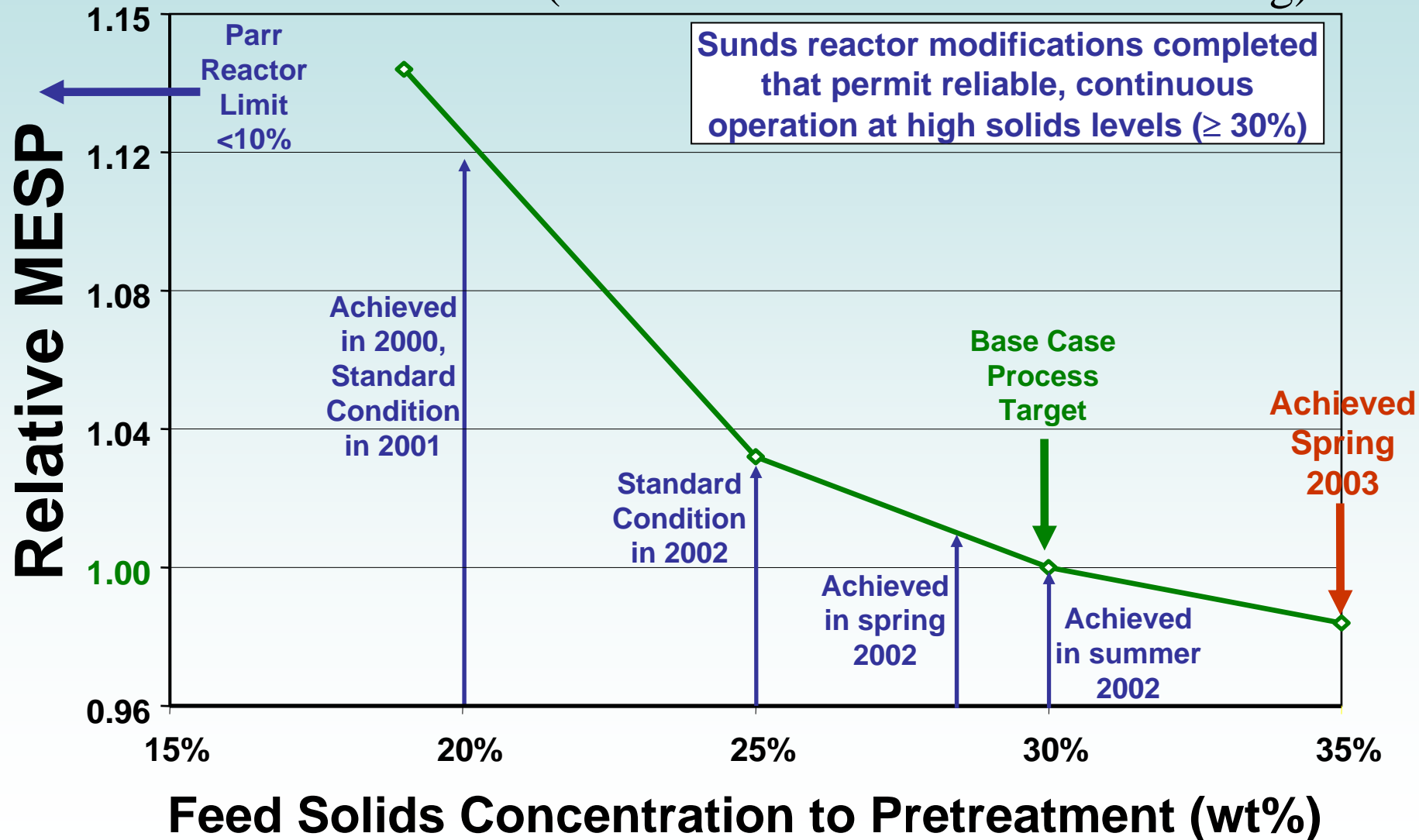


Carpita, N. C., and D. M. Gibeaut. 1993. Plant Journal, 3: 1-30.



# High Solids Pretreatment Demonstrated Key to High Sugar Concentrations and Lower Cost

Relative Cost =  $f(\text{Pretreatment Reactor Solids Loading})$



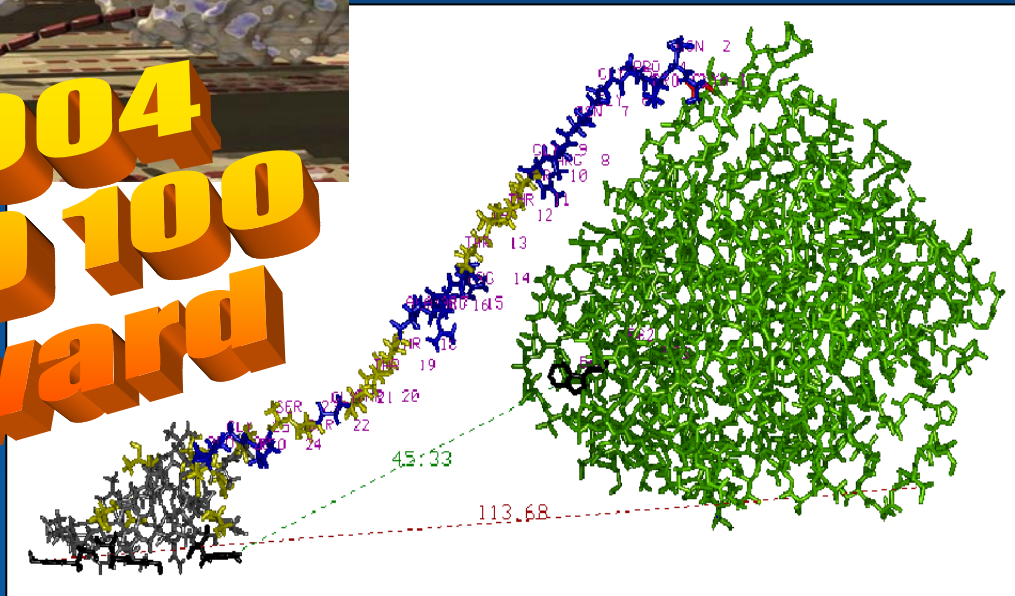
# Enzyme Costs Have Fallen Sharply

- DOE Subcontracts to Genencor and Novozymes (cost-shared)  
Focus: lower production cost, increase enzyme system efficacy
  - Enzyme cost (\$/gallon EtOH) = Prod. Cost (\$/kg) x Usage Req. (kg/gallon EtOH)
  - Cellulase cost reduced to below \$0.20/gal EtOH (by subcontract metric)

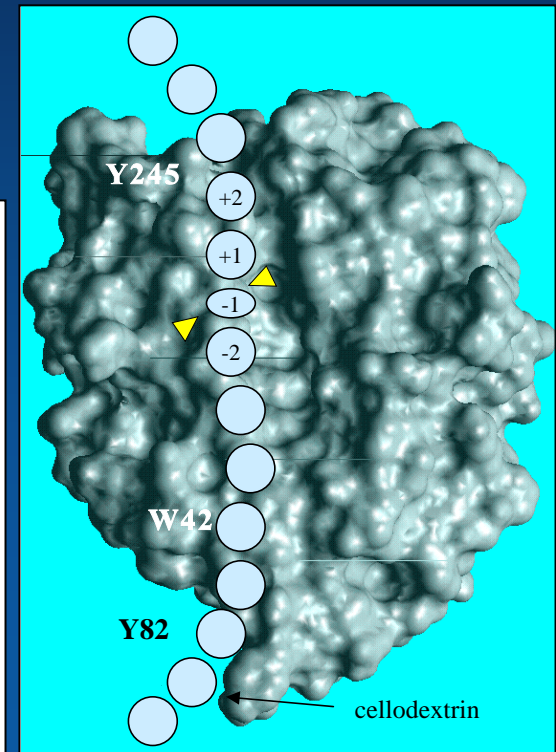


**2004  
R&D 100  
Award**

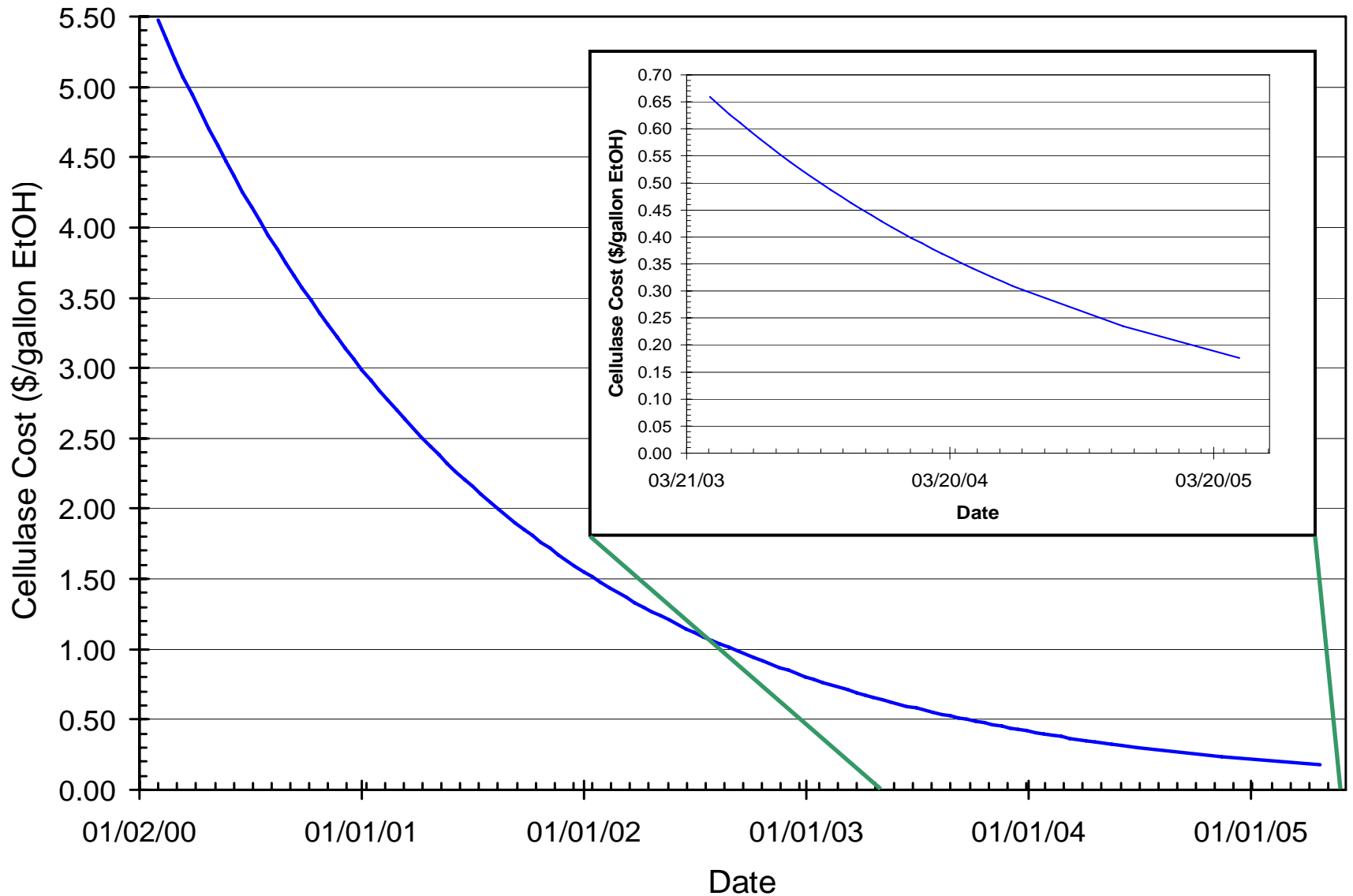
CBH1 from *T. reesei*



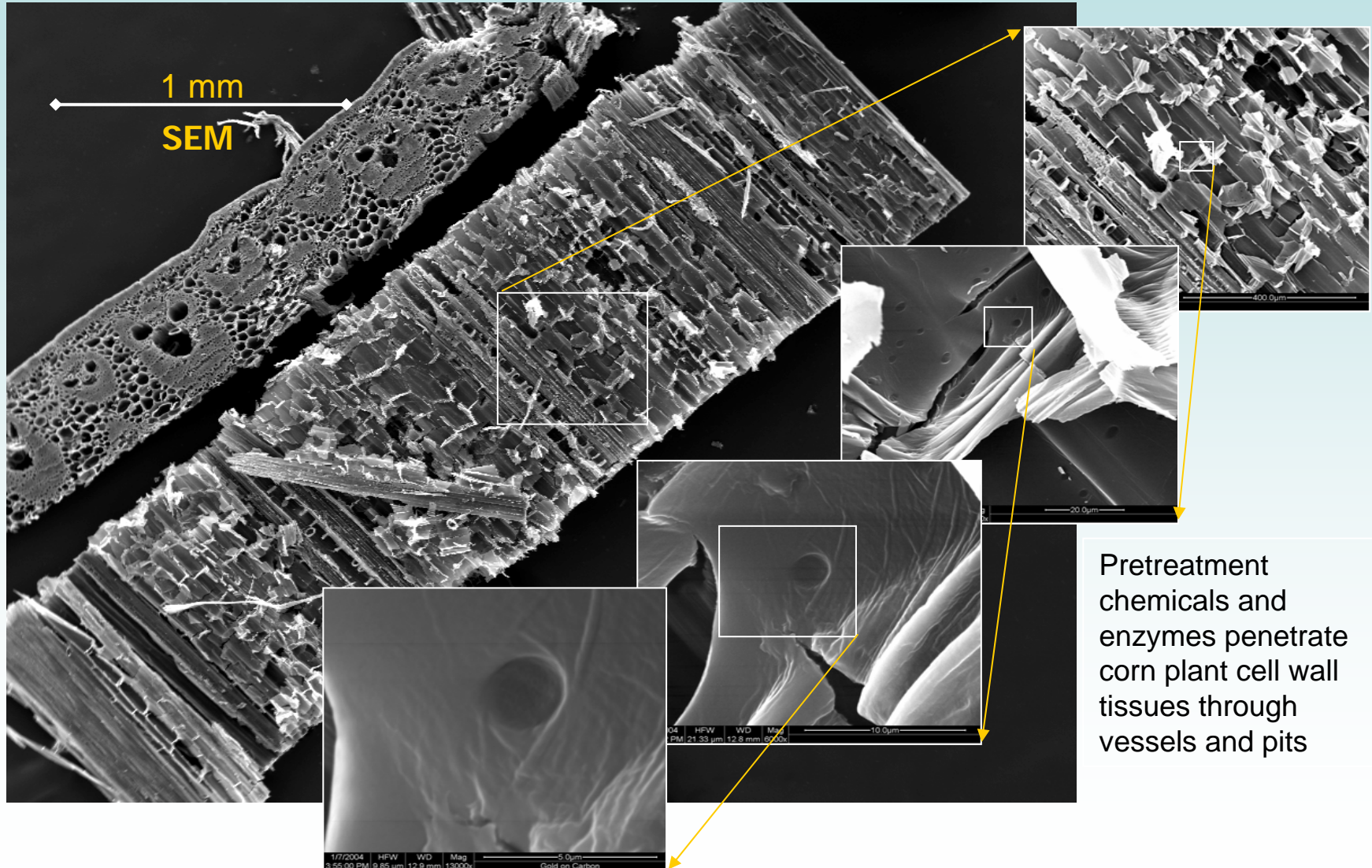
E1 from *A. cellulotiticus*



# Enzyme Cost No Longer Showstopper



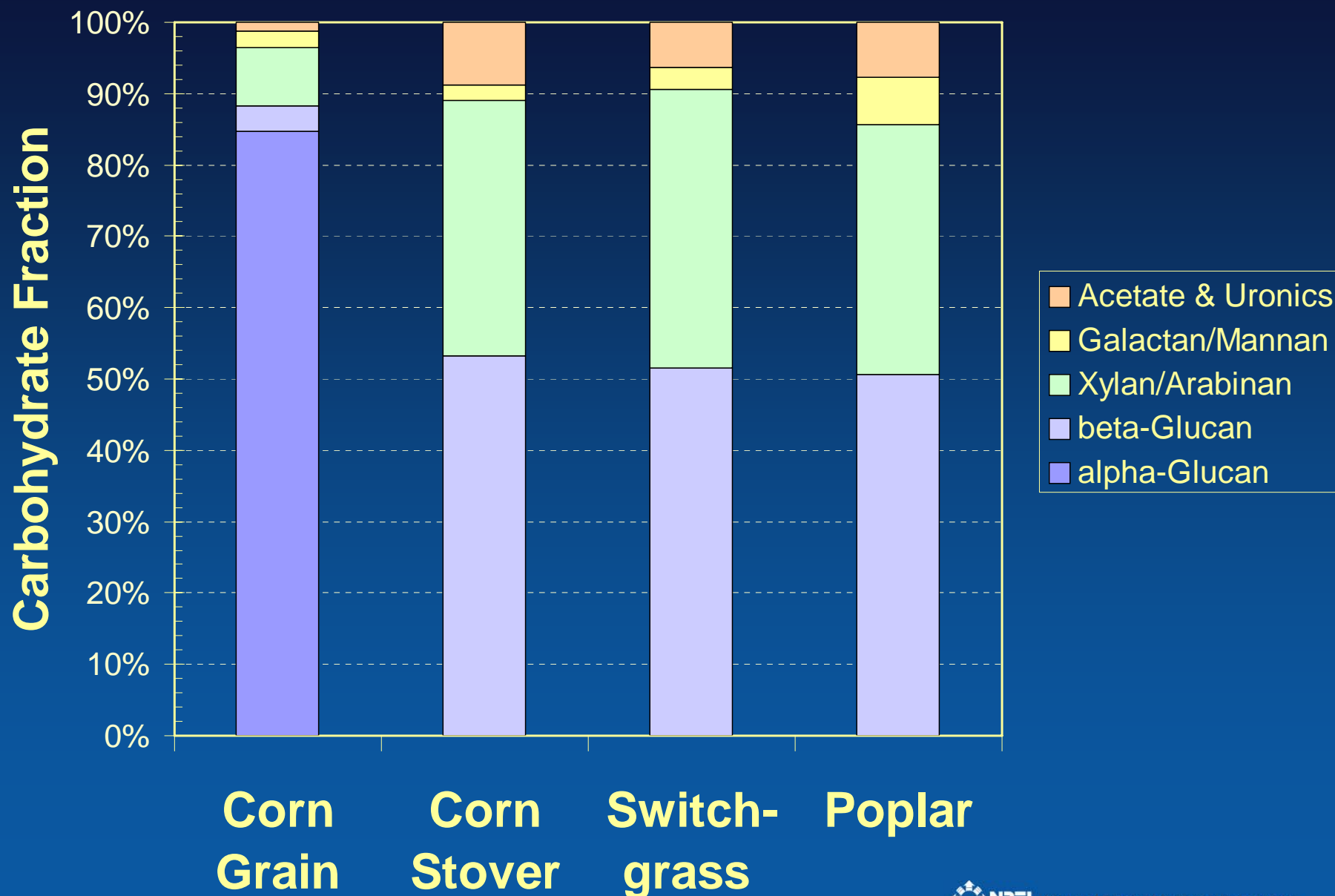
# Learning How Molecules Move in Biomass Through Imaging at Scale of Cell Wall Ultrastructure



Source: M. Himmel et al. (NREL, 2004) in collaboration with Colorado School of Mines EM Facility



# 2<sup>nd</sup> R&D Barrier: Pentosan Utilization





# Cofermentation Pathway in Engineered

## *Zymomonas mobilis* (putative)

D-Xylose<sub>EXT</sub>

D-Glucose<sub>EXT</sub>

Pentose Metabolism Pathway

Entner Doudoroff Pathway

XYL Transport

GLUC Transport

D-Xylose<sub>INT</sub>

D-Glucose<sub>INT</sub>

Xylose isomerase

D-Xylulose

Xylulokinase

D-Xylulose-5-P

Ribulose-5-P

Ribose-5-P

Transketolase

Sedoheptulose-7-P

Glyceraldehyde-3-P

Transaldolase

Erythrose-4-P

Fructose-6-P

Transketolase

18-1

16-1

13

1  
ATP  
ADP

Glucose-6-P

2

Gluconolactone-6-P

3

6-P-Gluconate

4

2-Keto-3-deoxy-6-P-Gluconate

5

Glyceraldehyde-3-P

6

1,3-P-Glycerate

7  
ADP  
ATP

3-P-Glycerate

8

2-P-Glycerate

9

Phosphoenolpyruvate

10  
ADP  
ATP

Pyruvate

11

Acetaldehyde + CO<sub>2</sub>

12

Ethanol<sub>INT</sub>

ETOH Transport

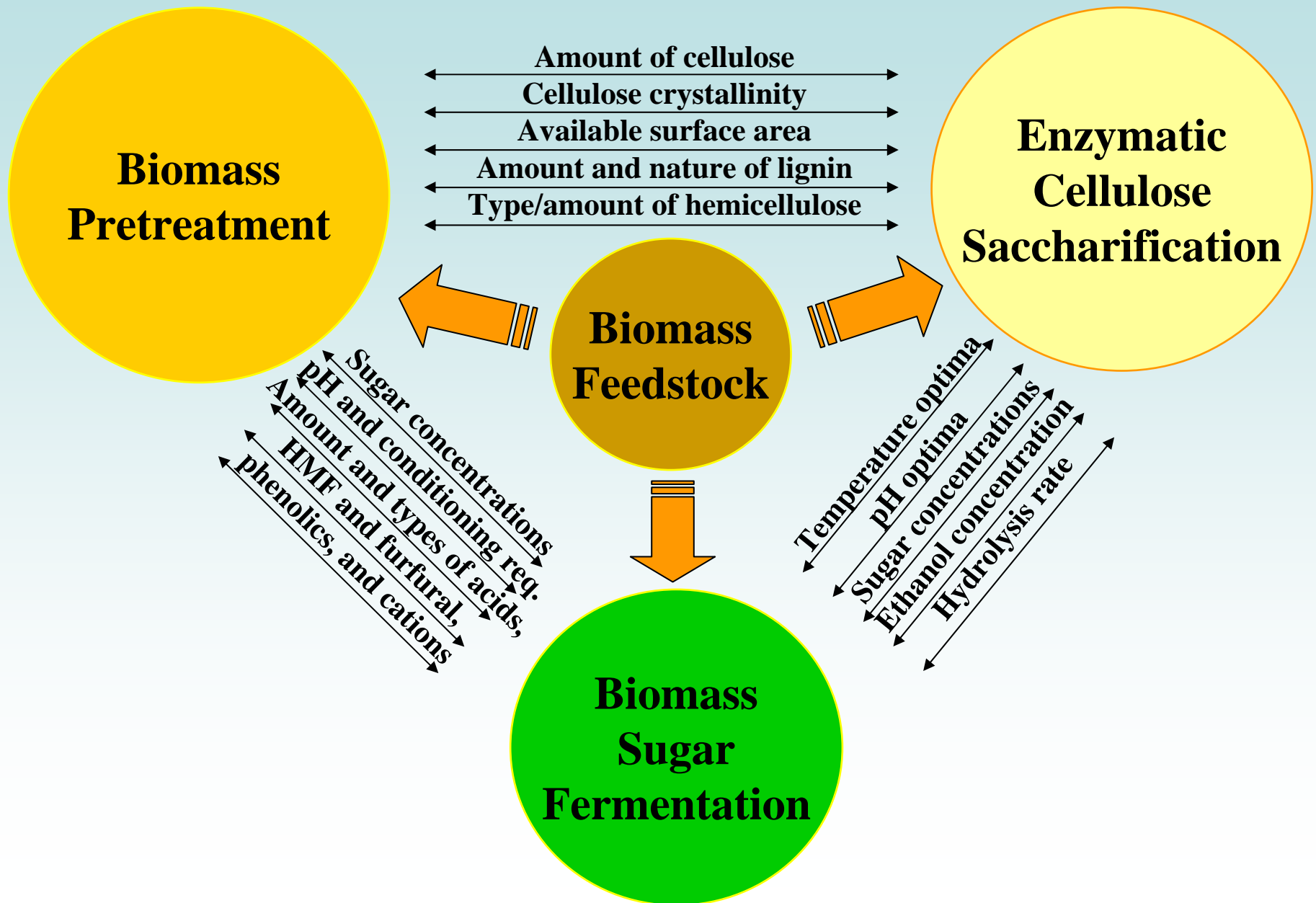
Ethanol<sub>EXT</sub>

(1) GK, (2) GPD, (3) PGLS, (4) PGD, (5) KDPGA, (6) GAPD, (7) G3PK, (8) GPM, (9) ENO, (10) PYRK, (11) PYRD, (12) ALD, (13) PGI, (14) XI, (15) XK, (16) TKT, (17) TAL, (18) TKT, (19) RPE, (20) RPI

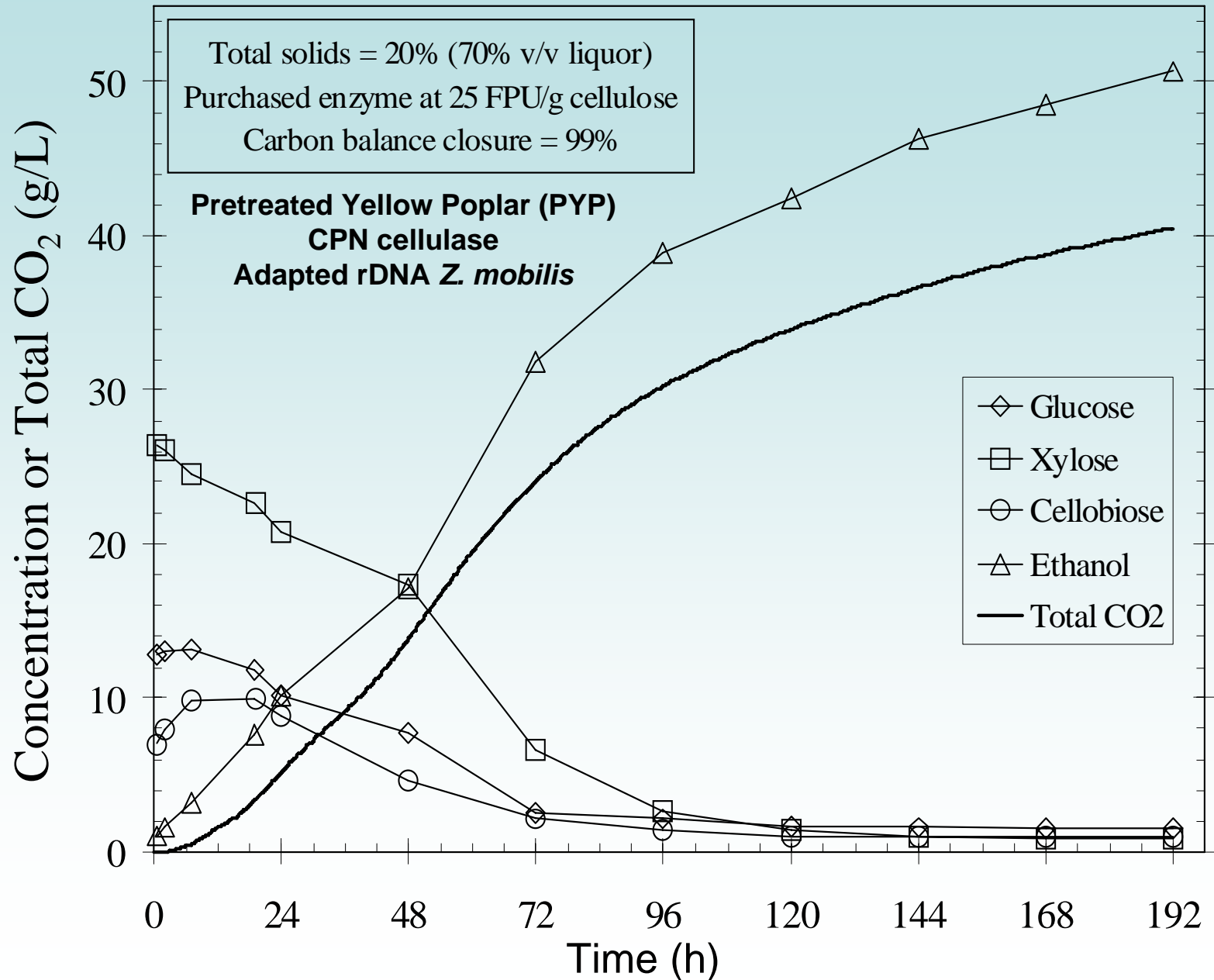
Xylose  
Utilization  
Enzymes

Pentose  
Phosphate  
Pathway  
Enzymes

# 3<sup>rd</sup> R&D Barrier: Process Integration

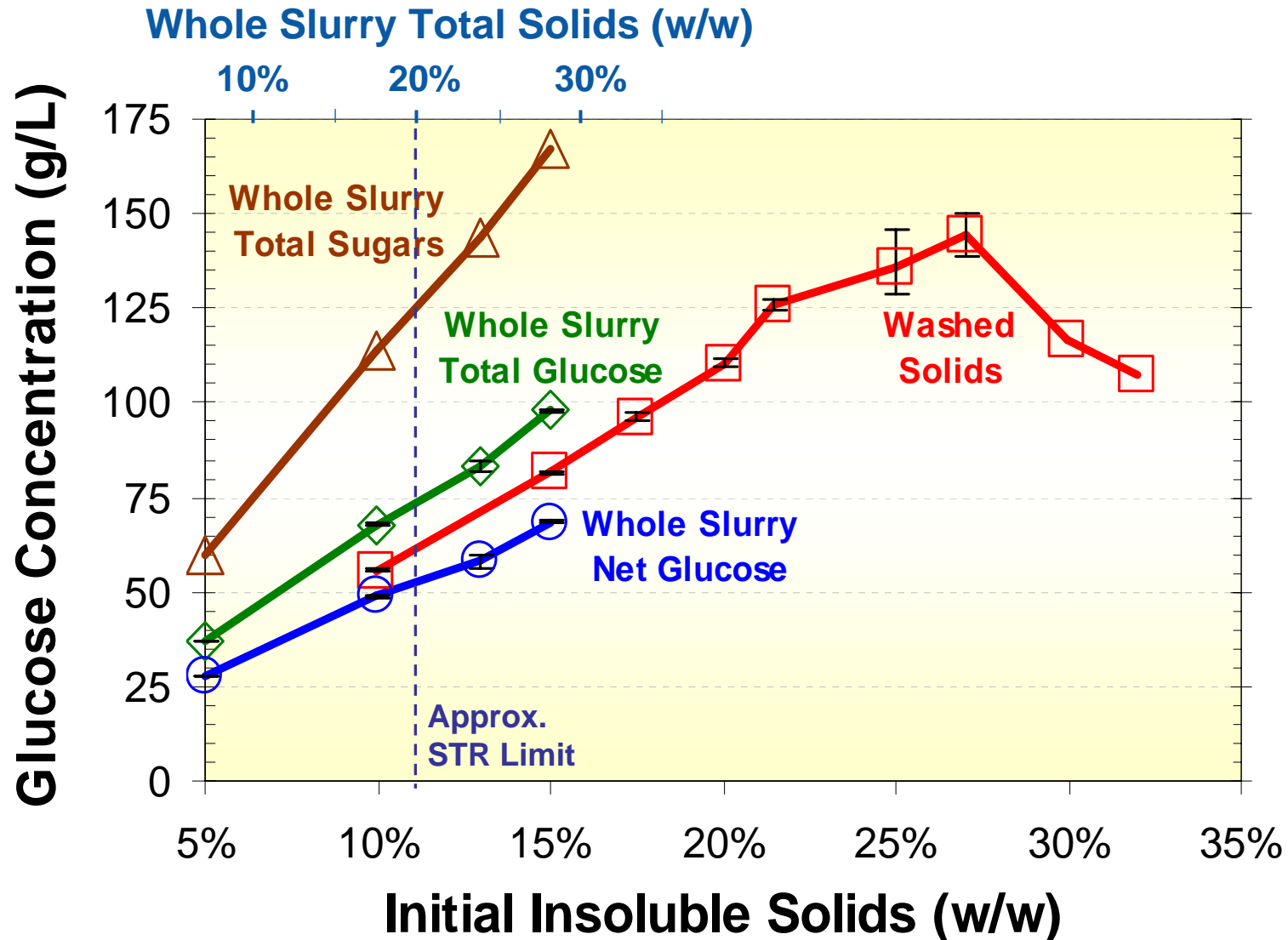


# Mini-pilot Scale Integrated SSCF



# Intensified Processing Key to High Titrers

## Example: Glucose Production from Whole Slurry



# High Solids Enzymatic Saccharification

Pretreated corn stover, 45°C, 20 mg cellulase/g cellulose, 25% initial insoluble solids loading  
Video shows how slurry rheology changes over 7 days of enzymatic cellulose hydrolysis



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## ➤ ***Outlook***



# Outlook

- Major progress being made
  - Compelling operating costs within reach
  - High solids processing promising to decrease capital hurdle
  - Industry investments in R&D reducing commercialization risks
- More needed to achieve market competitiveness, especially for more costly feedstocks
  - Sustainable feedstock supply systems must be developed
  - Process(es) must be proved at scale
  - Societal/Environmental benefits must be rigorously validated
- Breakthroughs will spur deployment – key to achieving leap forward economics
  - Overcoming recalcitrance
  - Robust ethanologens (>10% ethanol on pentoses/mixed sugars)
  - New value-added commodity coproducts
  - Supportive legislation/policies`

# More Information

- The National Renewable Energy Laboratory:  
<http://www.nrel.gov>
- DOE's Biomass Program:  
<http://www.eere.energy.gov/biomass/>
- DOE-USDA Biomass R&D Initiative:  
<http://www.biomass.govtools.us/>
- Alternative Fuels:  
<http://www.afdc.doe.gov>

# Acknowledgments



- Funding
  - USDOE's EERE's Office of the Biomass Program
- Comparative economics from NREL and NREL-USDA joint study
  - USDOE/NREL: Kelly Ibsen, John Jechura, Robert Wallace
  - USDA ARS: Andrew McAloon, Frank Taylor, Winnie Yee
- Enzyme cost reduction progress
  - Genencor, Novozymes, and NREL (each with large teams!)
- High solids enzymatic saccharification (NREL)
  - Jody Farmer, David Hodge, Dan Schell
- Electron micrographs (NREL)
  - Mike Himmel, Todd Vinzant