Biochemical Conversion of Cellulosic Feedstocks

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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
  - 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

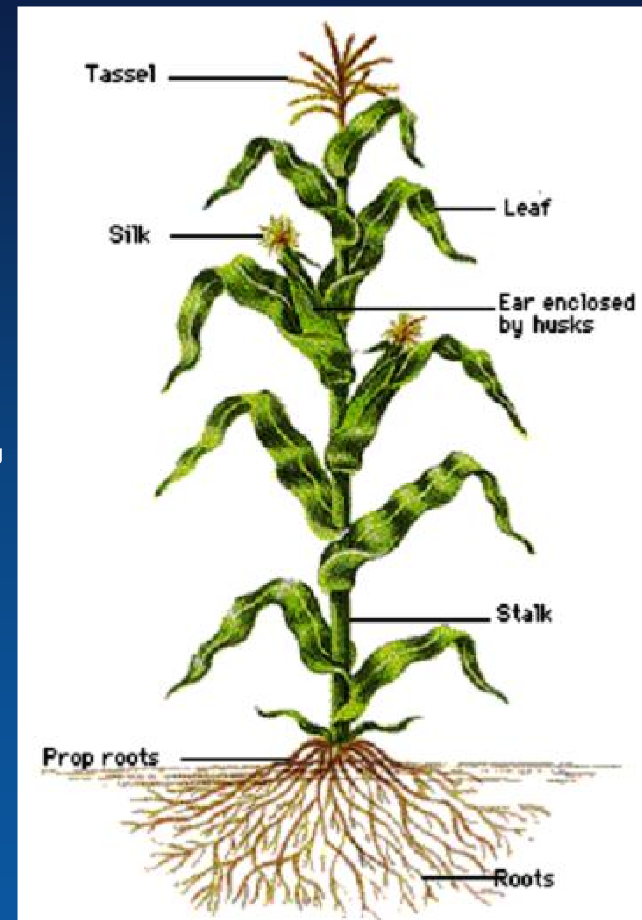
Corn Grain vs. Cellulosics

Corn Stover and Beyond

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

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

SWITCHGRASS



GRAIN

http://arnica.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

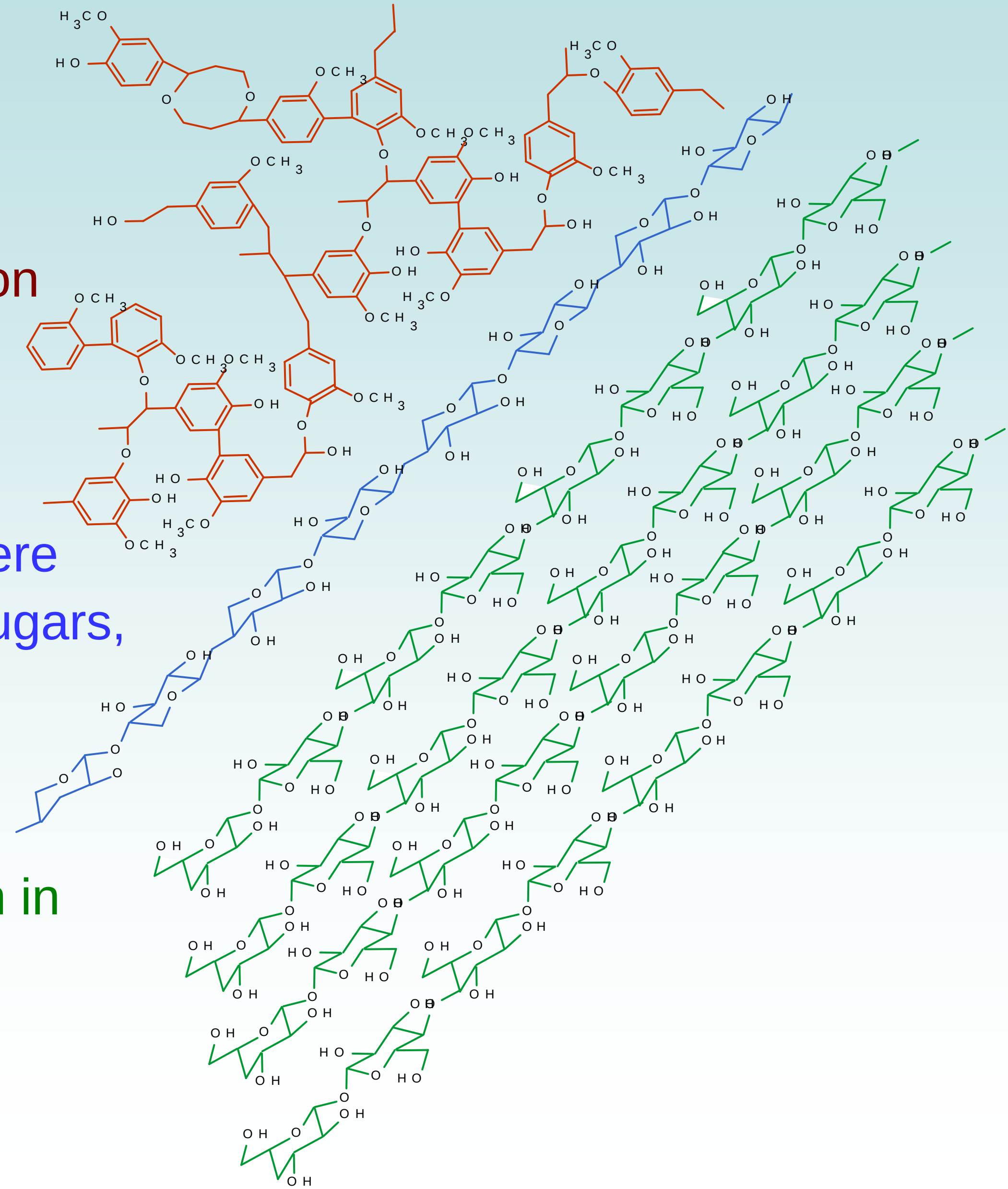
Constituent levels can vary by roughly ± 5% dry weight due to environmental and genetic factors

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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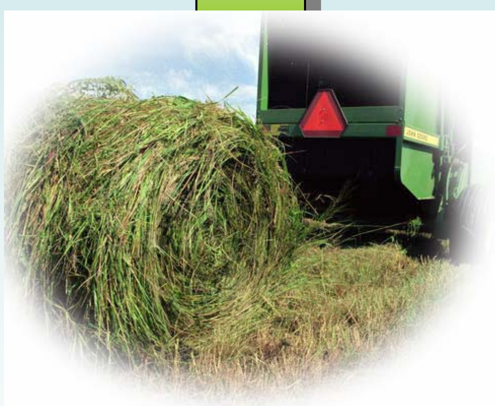
Routes to Biofuels



Bio/chemical transformation of natural compounds

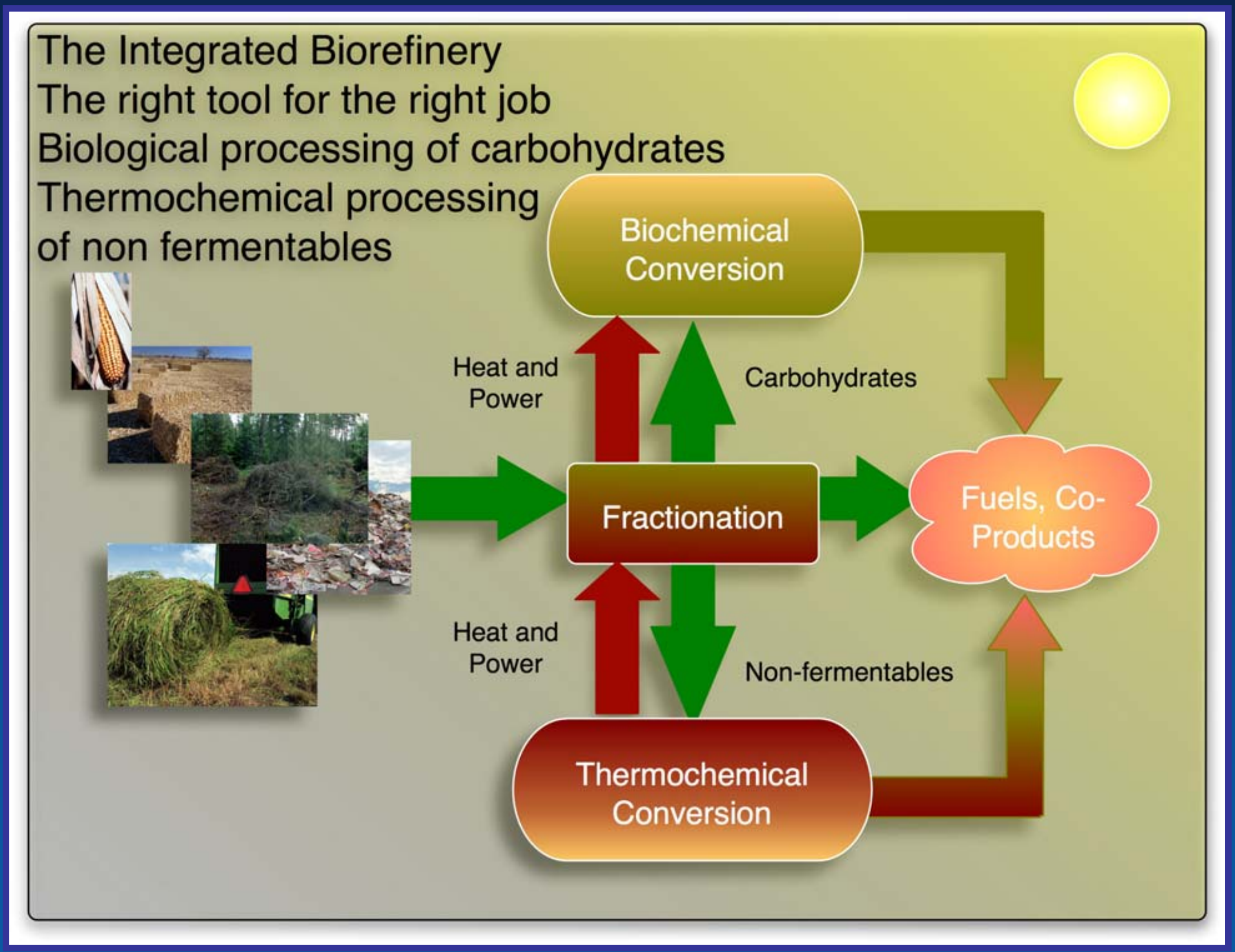
- ***Ethanol from sugars***
- **Biodiesel from renewable oils**

Thermal reduction to "syngas" (H_2, 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



Biomass as "*The New Petroleum*"—and beyond:

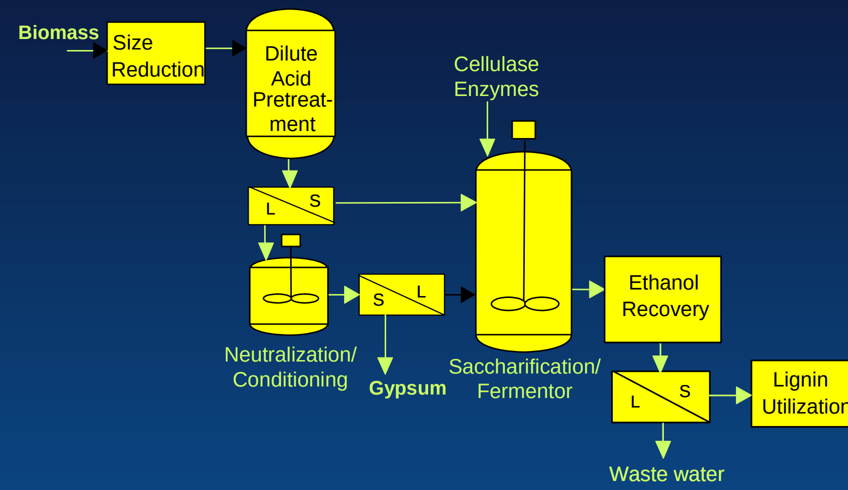
Source of food, feed, fiber, ***and fuels (and chemicals)***

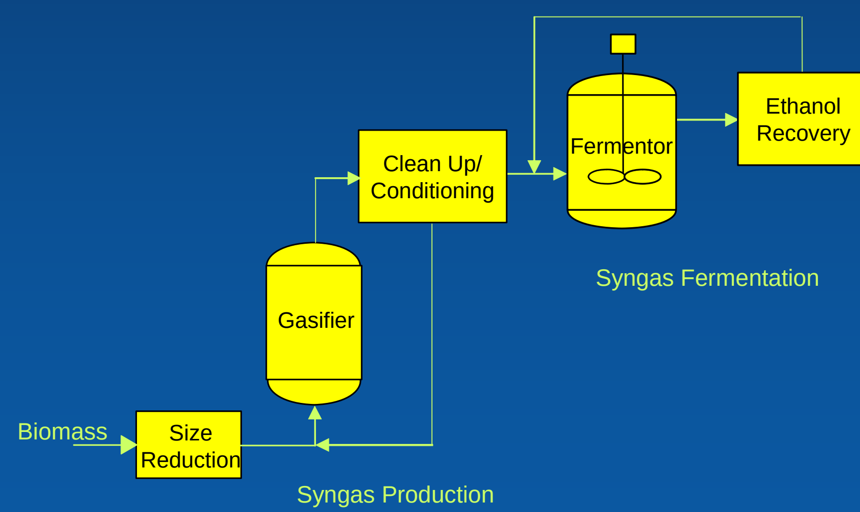
Biochemical Conversion Pathways

- 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

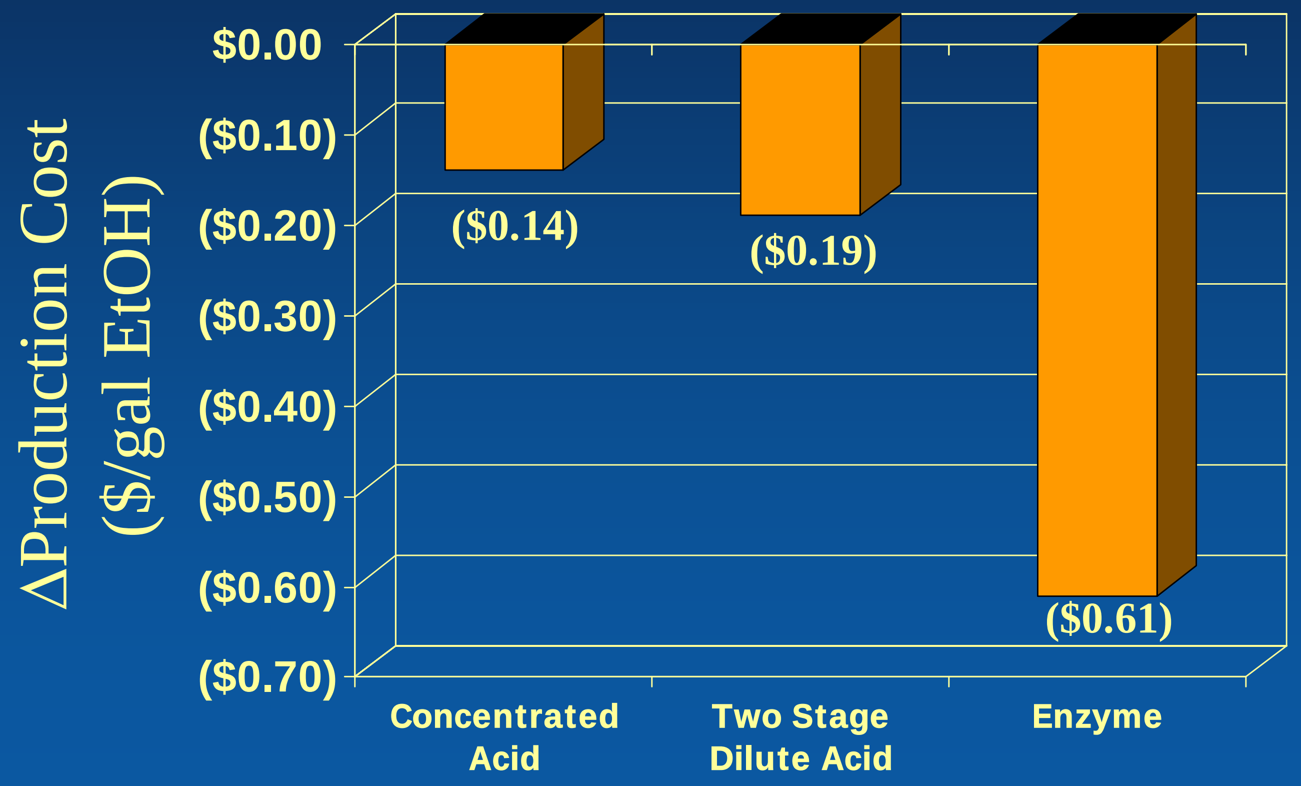
- Gasification/Synthesis Gas Fermentation
  - Thermochemical gasification followed by fermentative conversion of (cleaned up) syngas





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



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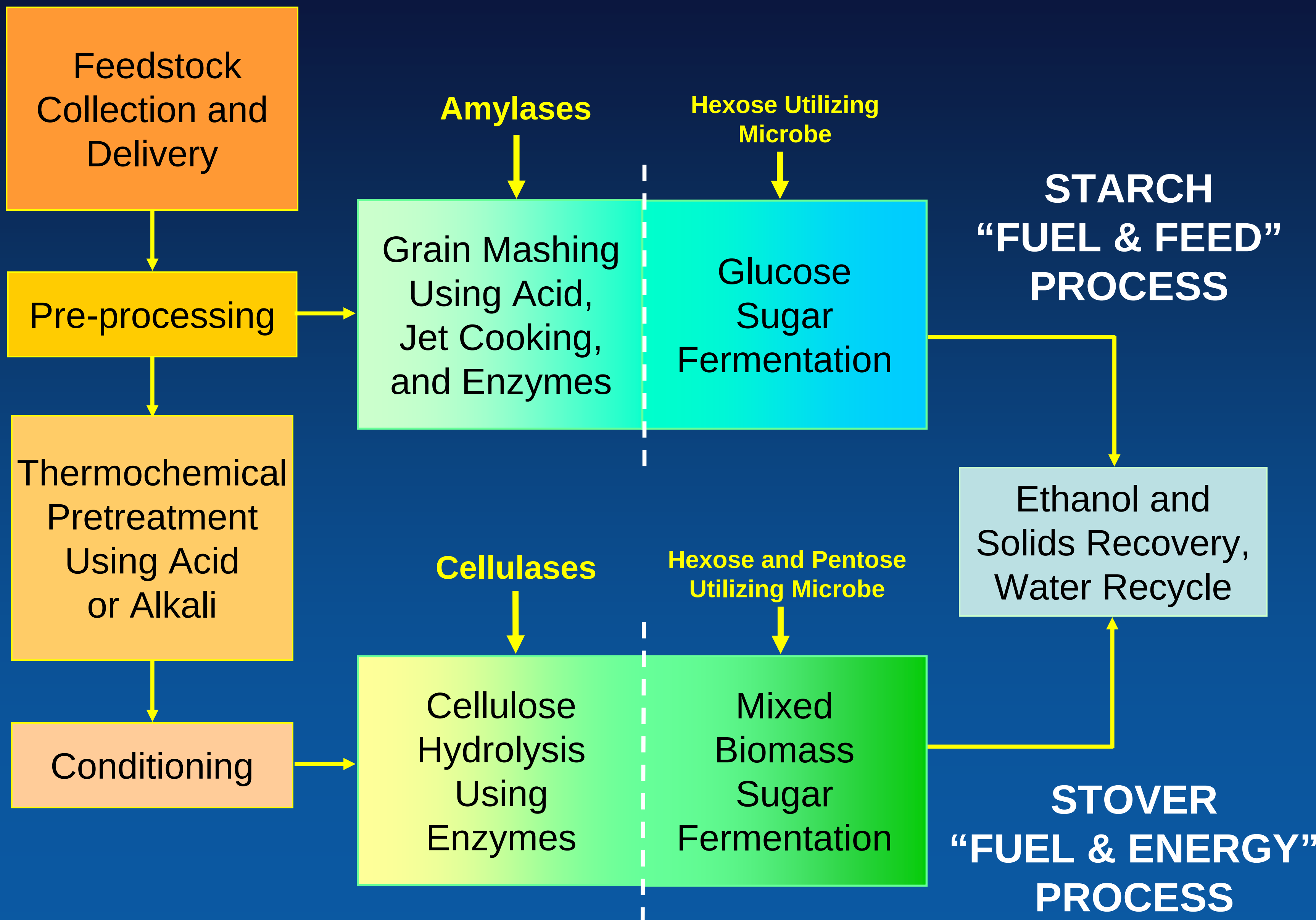
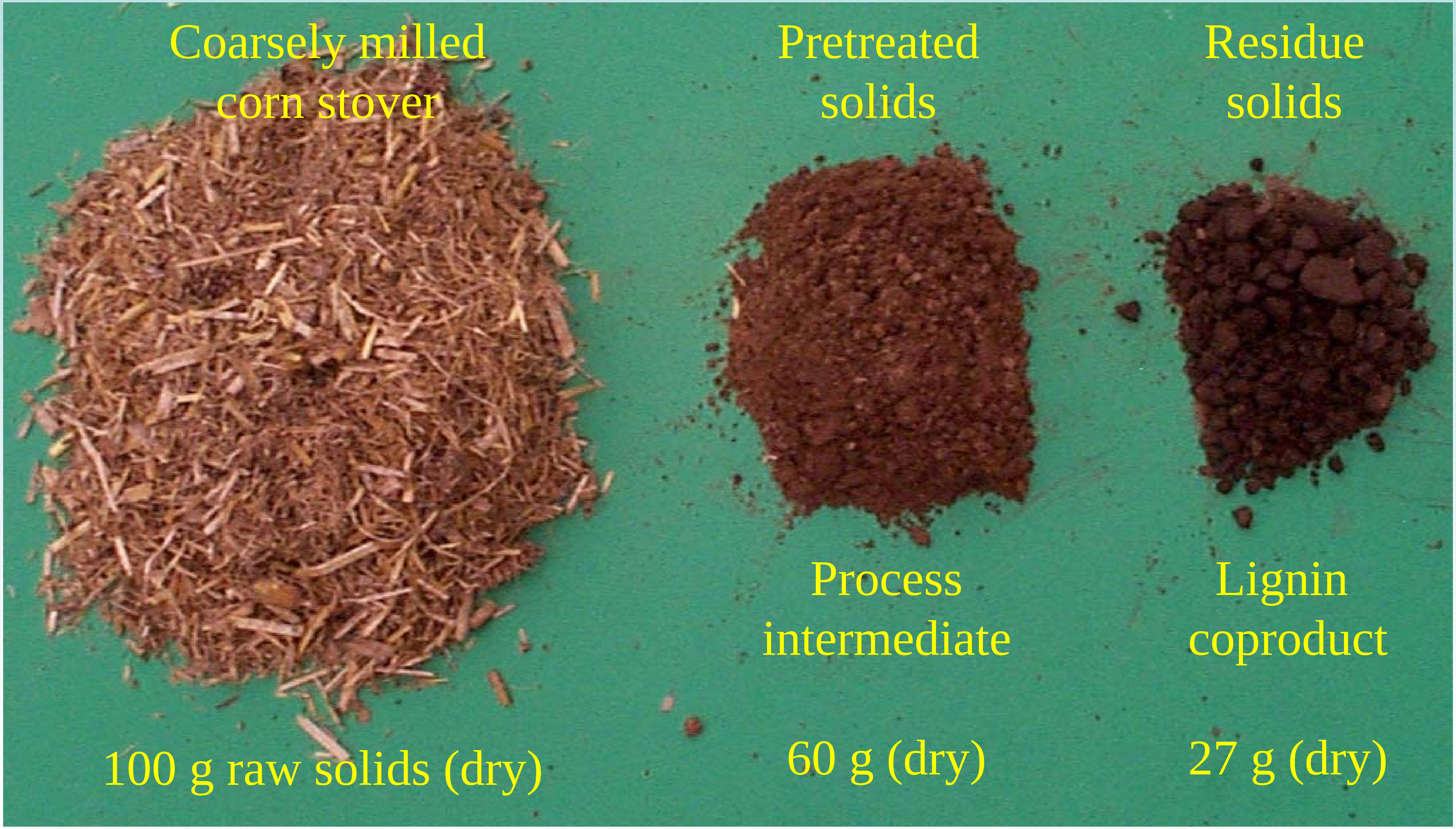
Carbohydrate Conversion Steps

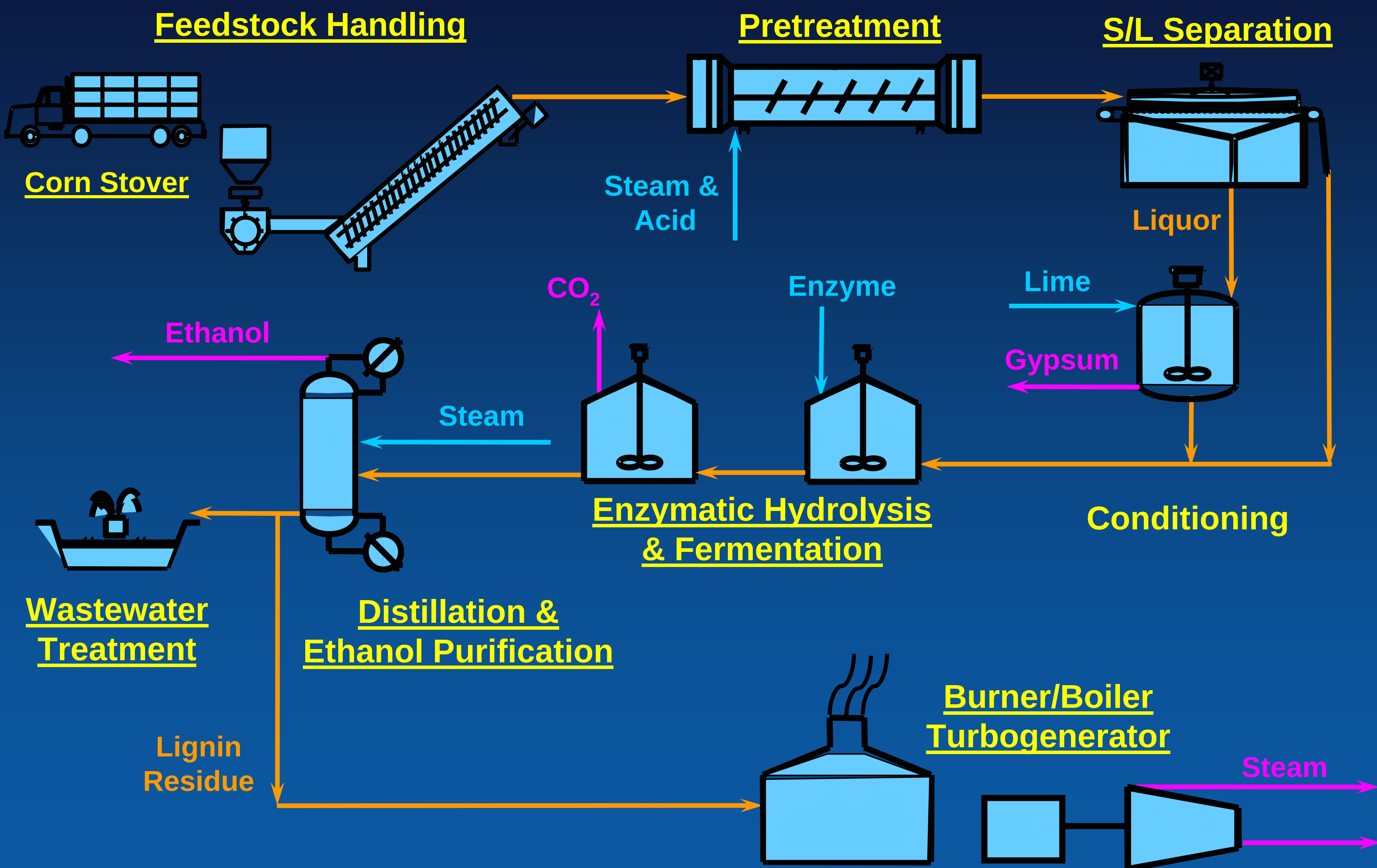


Conversion is Technically Feasible…



…the Challenge is Making it Economical!

Conceptual Stover-to-Ethanol Process

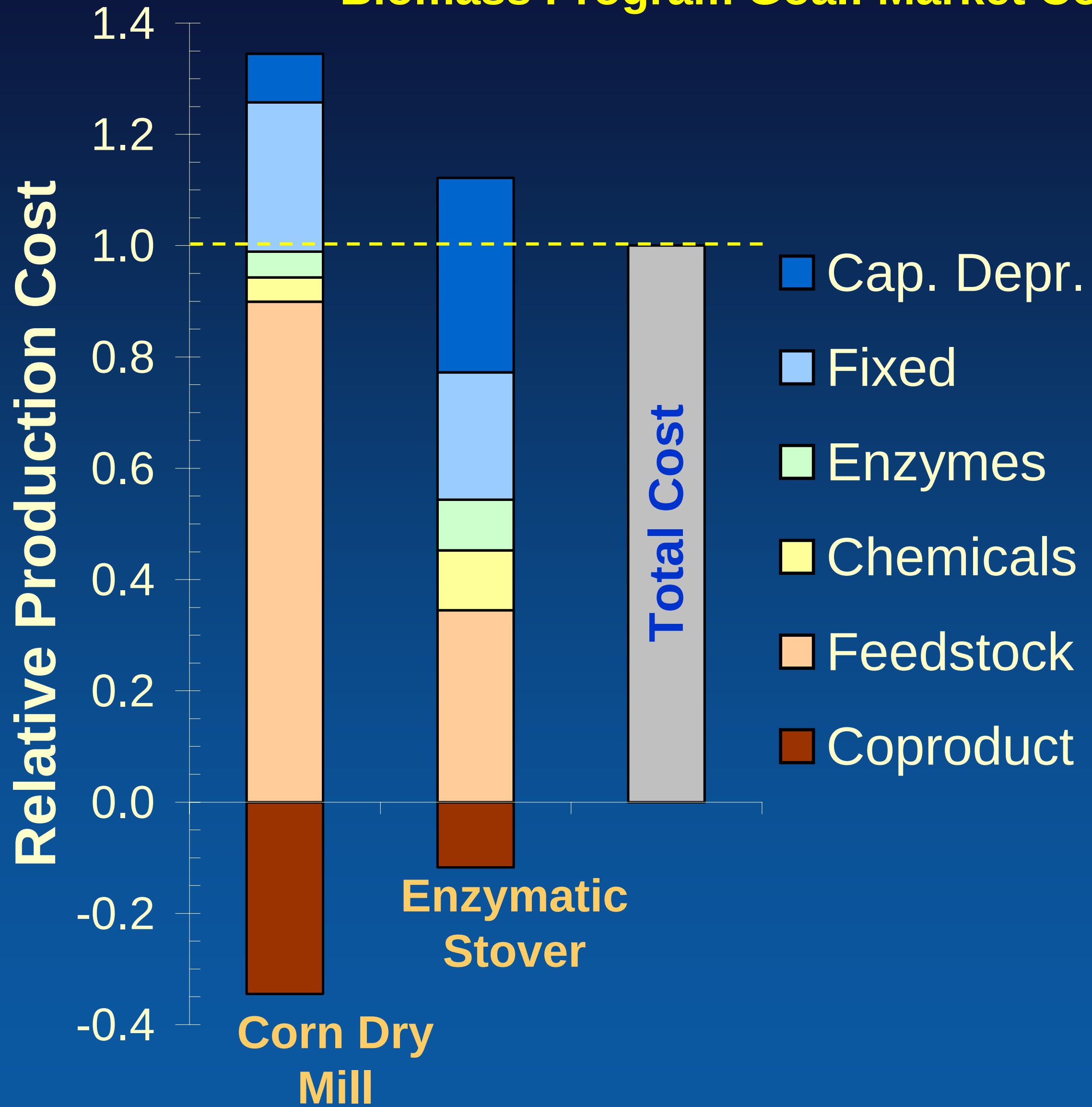


Cellulosics Must Compete with Starch

Corn Grain is King in America!

Comparative Economics

Biomass Program Goal: Market Competitiveness



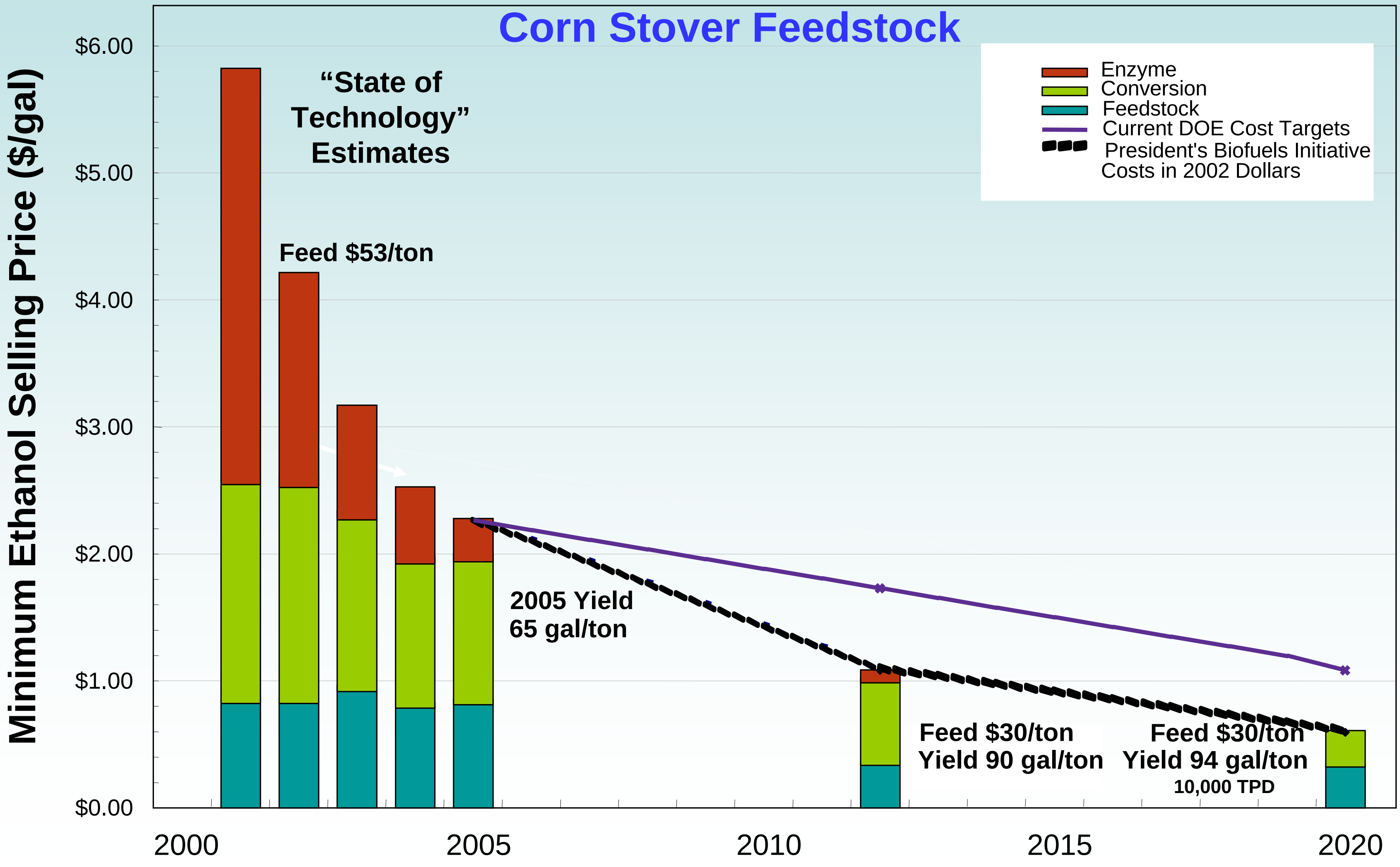
Costs driven by

- 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



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➢ ***Remaining Technical Barriers/R&D Foci***

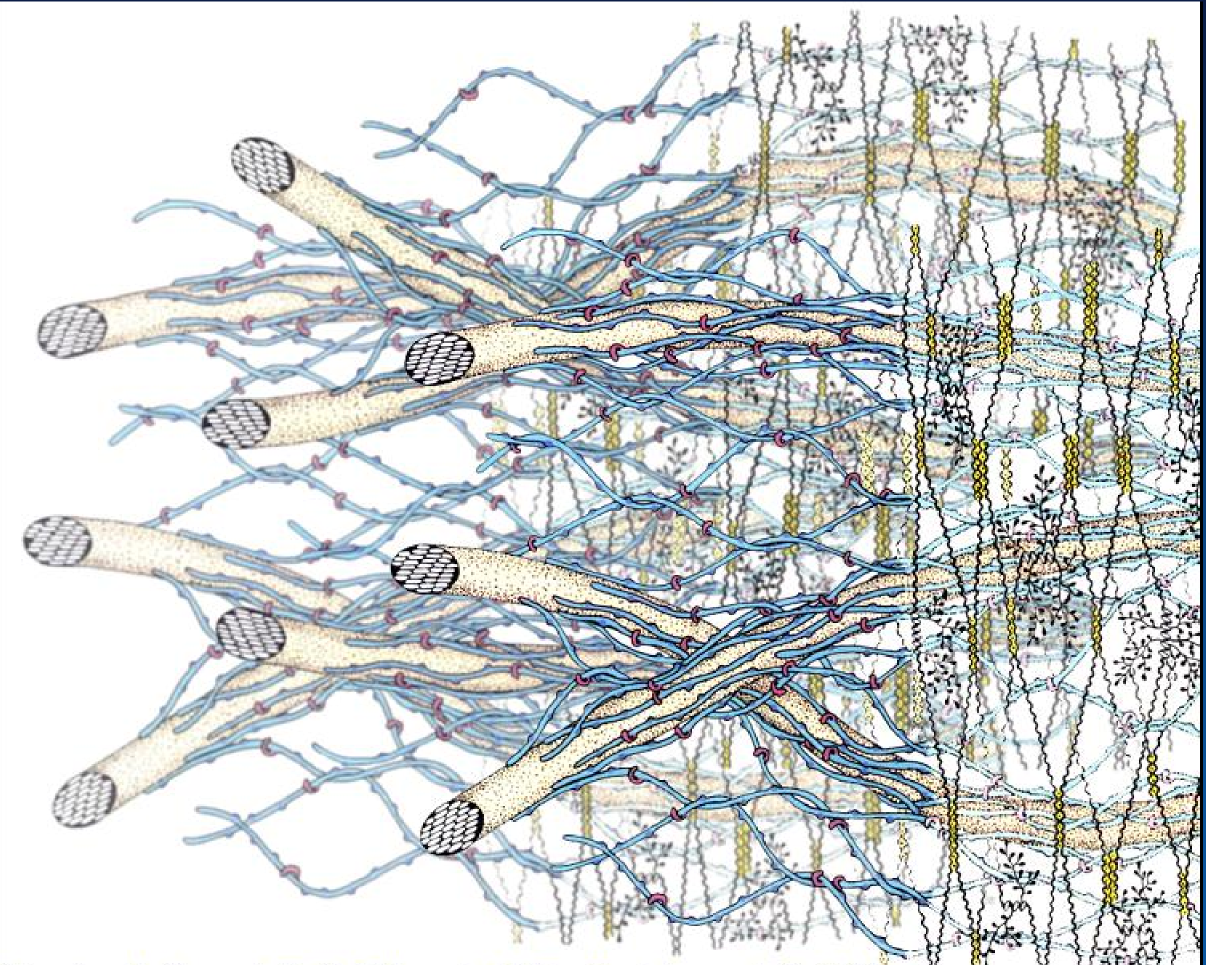
- **Outlook**

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

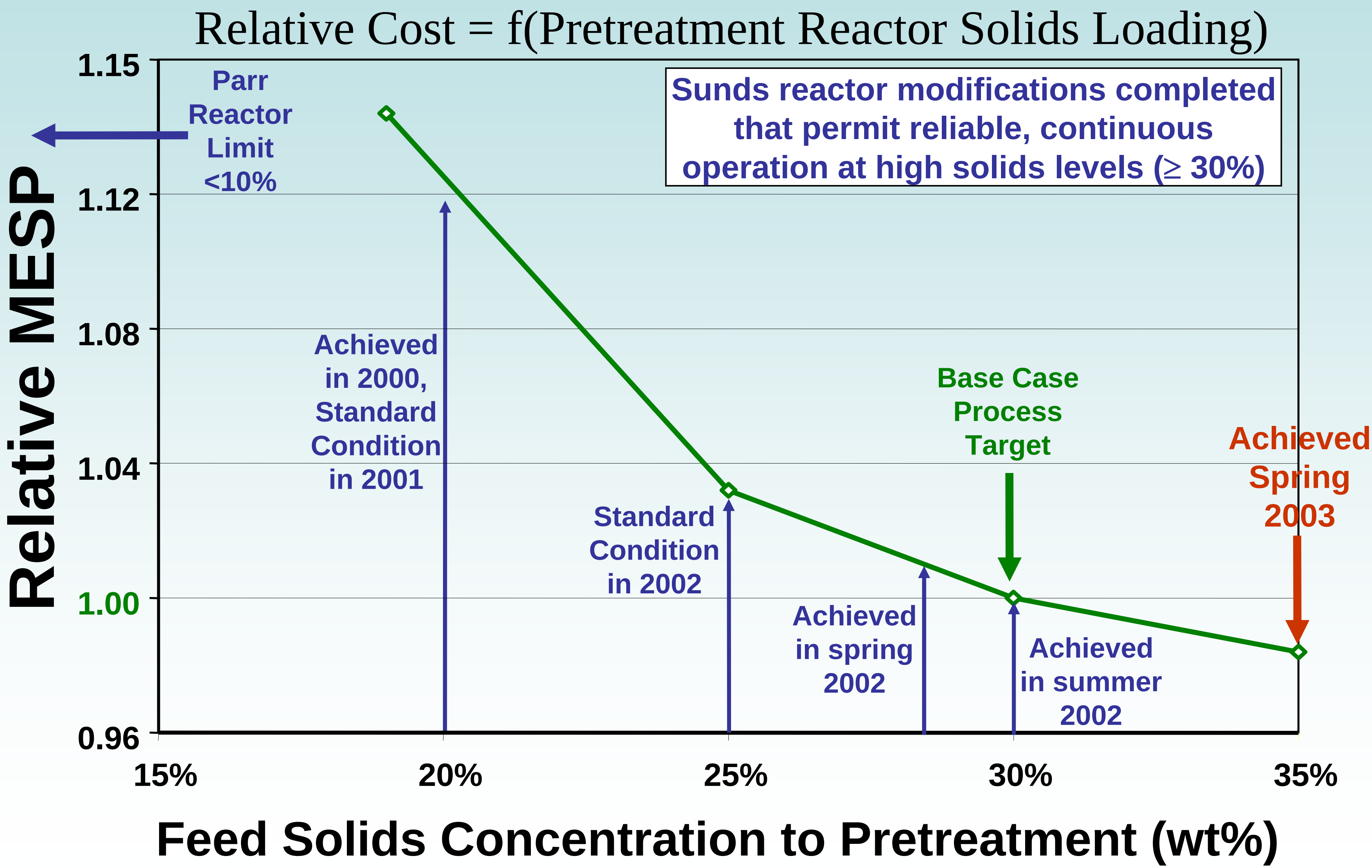
1st R&D Barrier: Cell Wall Recalcitrance

- 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.

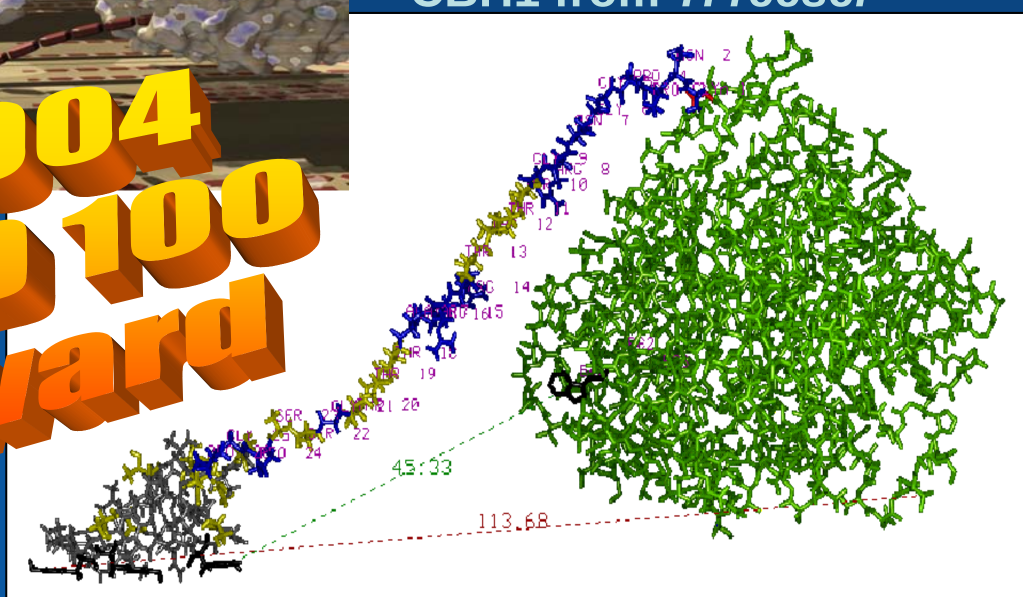
High Solids Pretreatment Demonstrated
Key to High Sugar Concentrations and Lower Cost



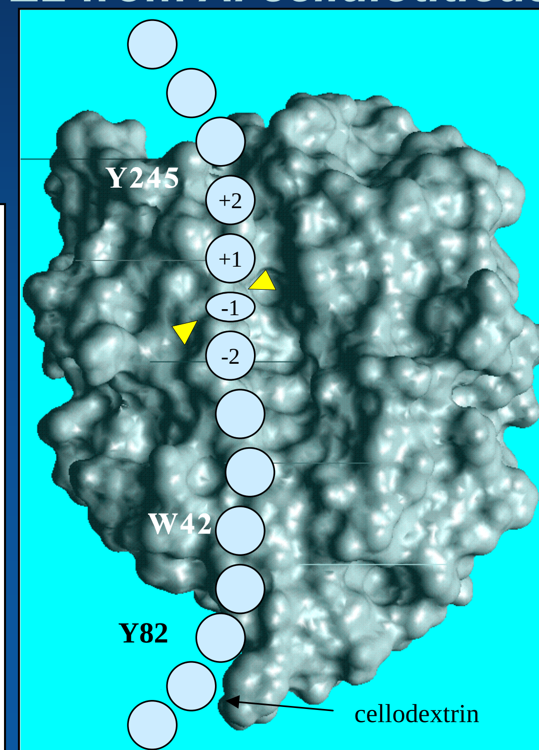
Enzyme Costs Have Fallen Sharply

- **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)

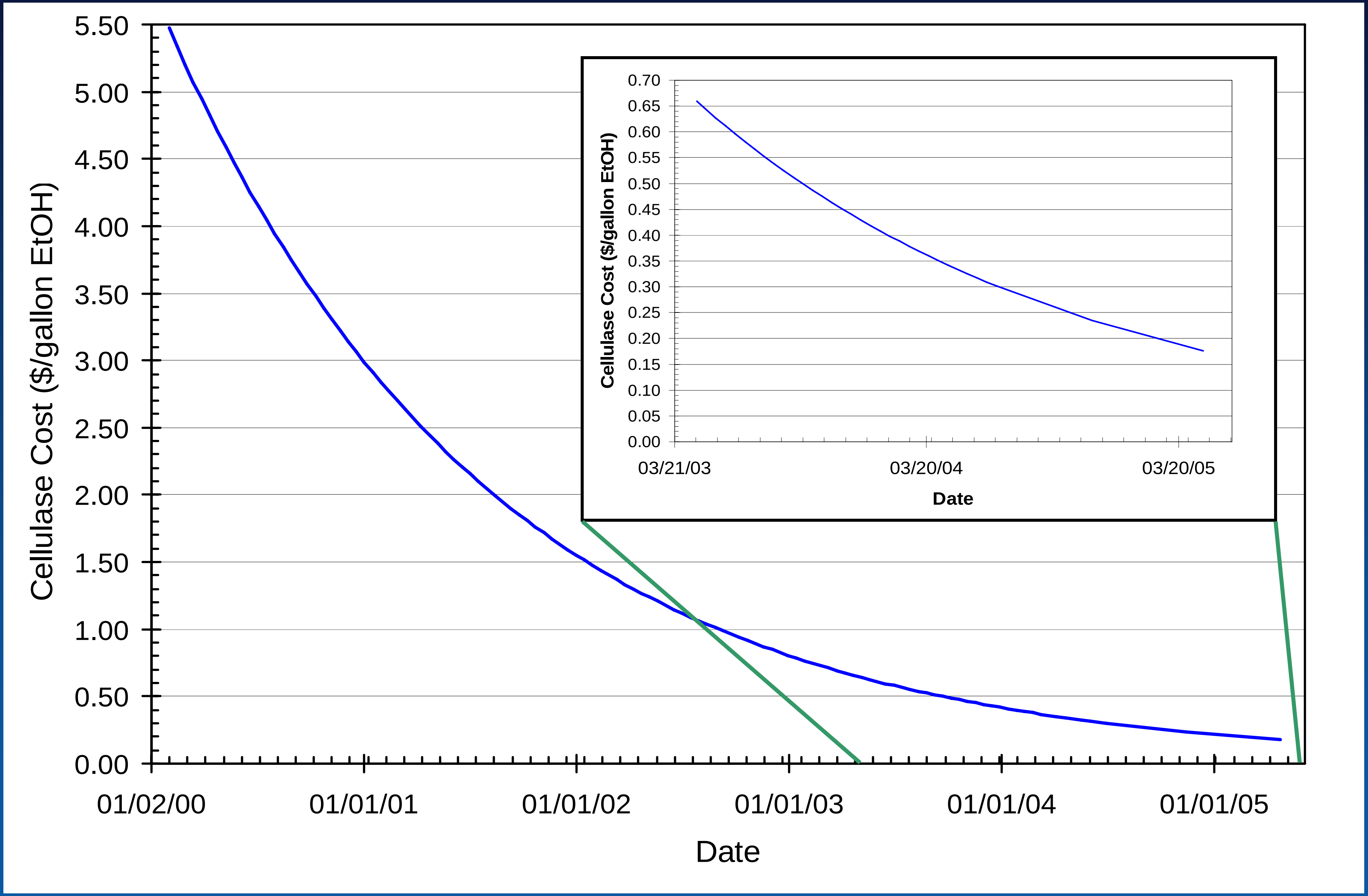
CBH1 from *T. reesei*



E1 from *A. cellulotiticus*

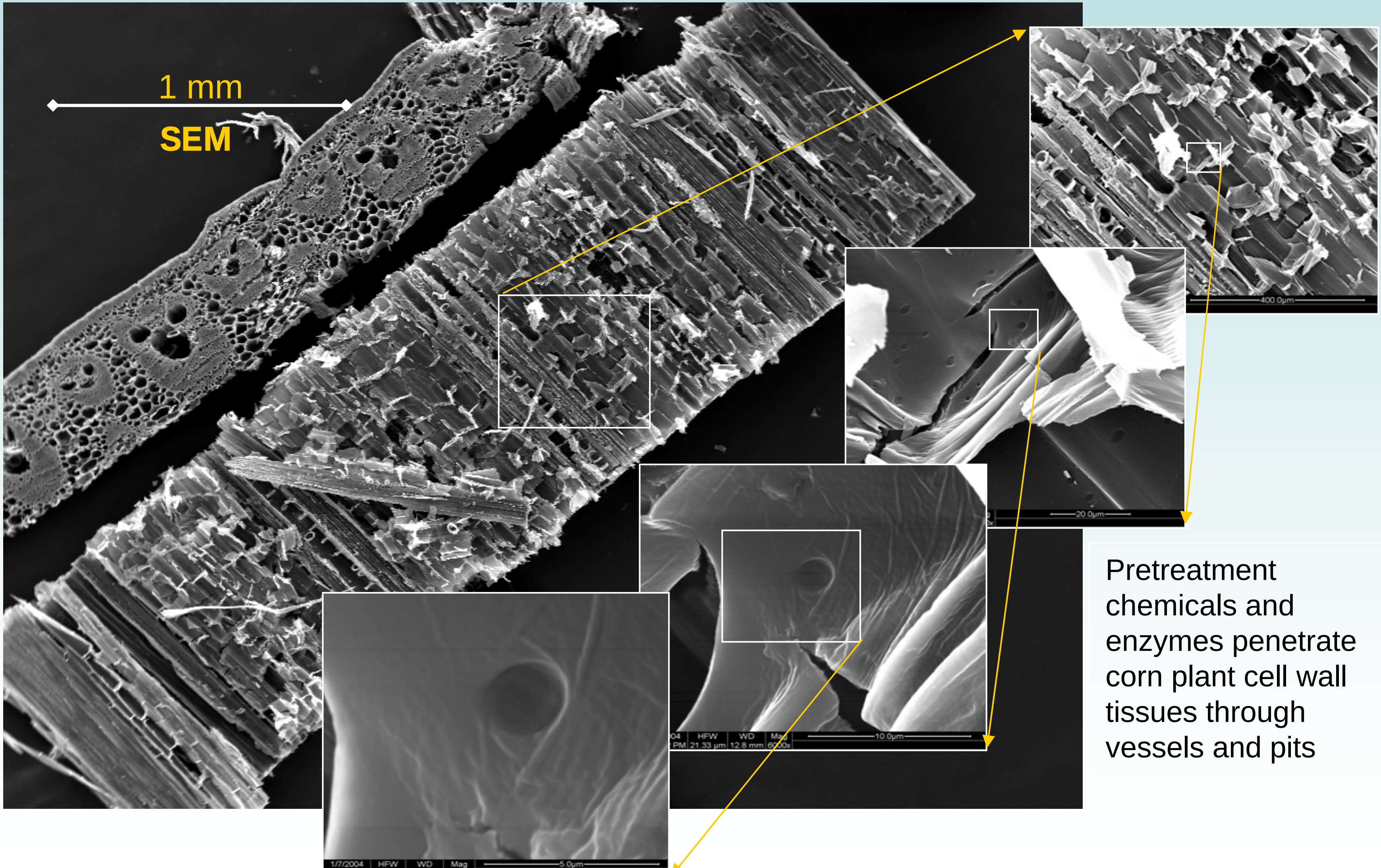


Enzyme Cost No Longer Showstopper



Learning How Molecules Move in Biomass

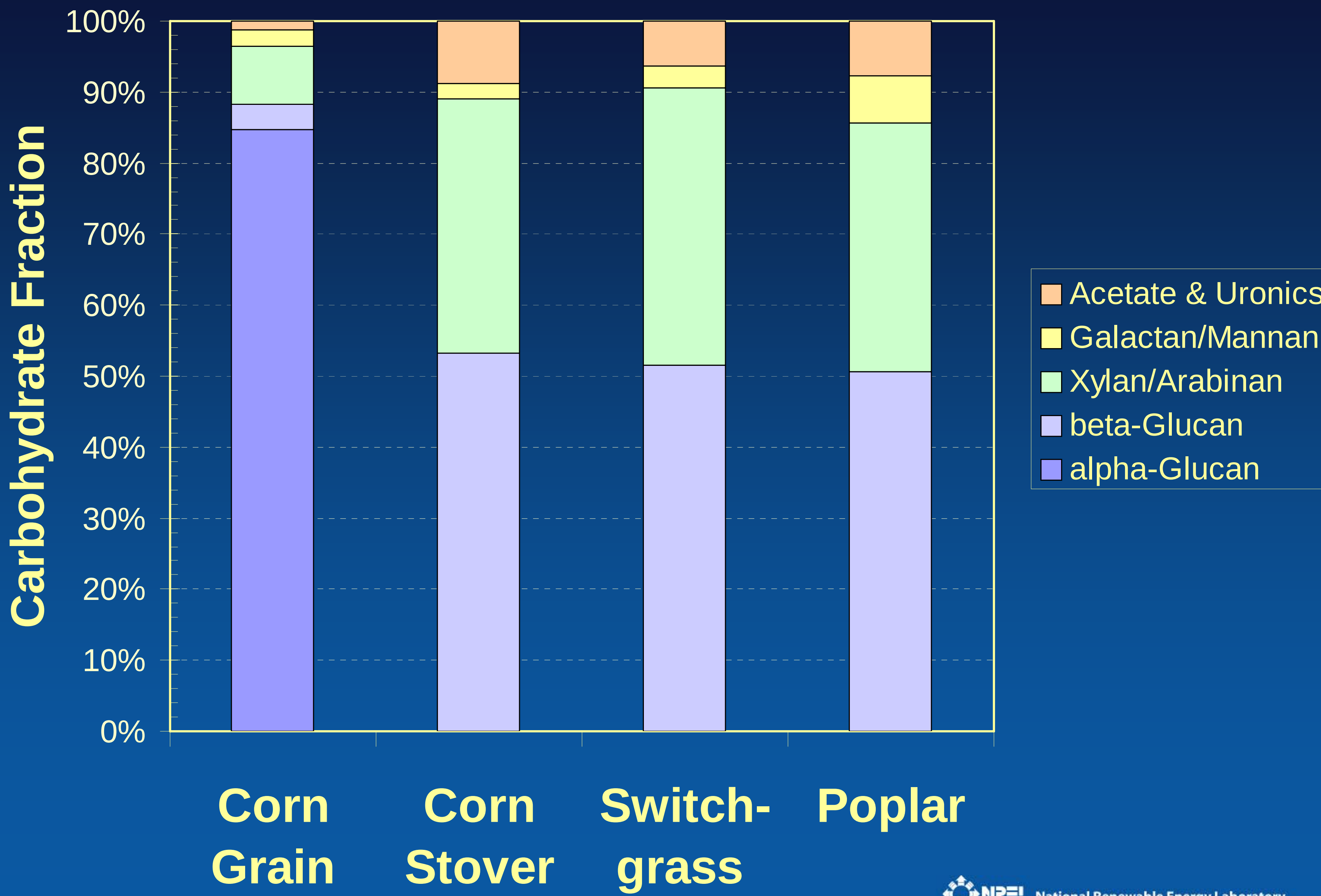
Through Imaging at Scale of Cell Wall Ultrastructure



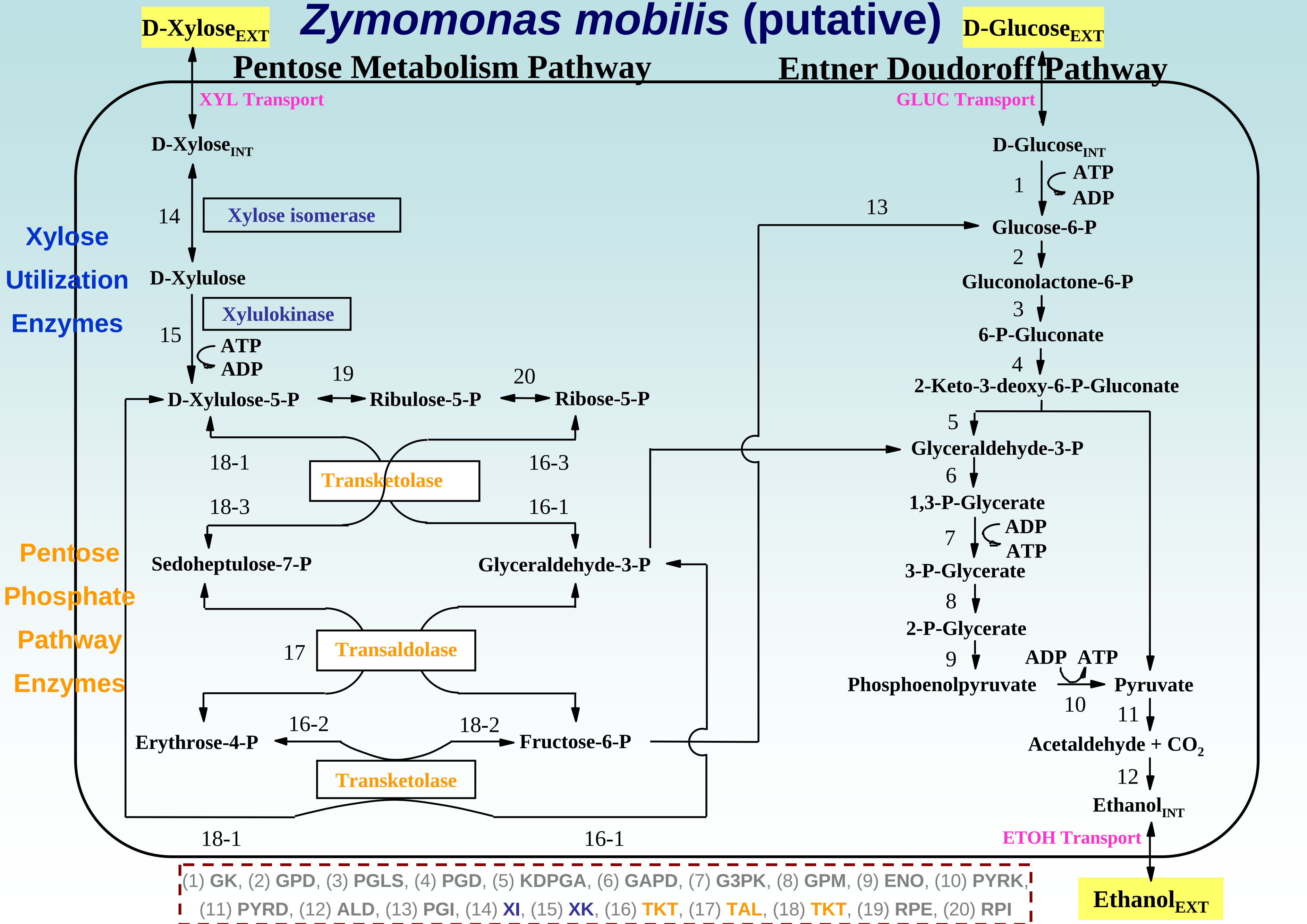
Pretreatment chemicals and enzymes penetrate corn plant cell wall tissues through vessels and pits

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

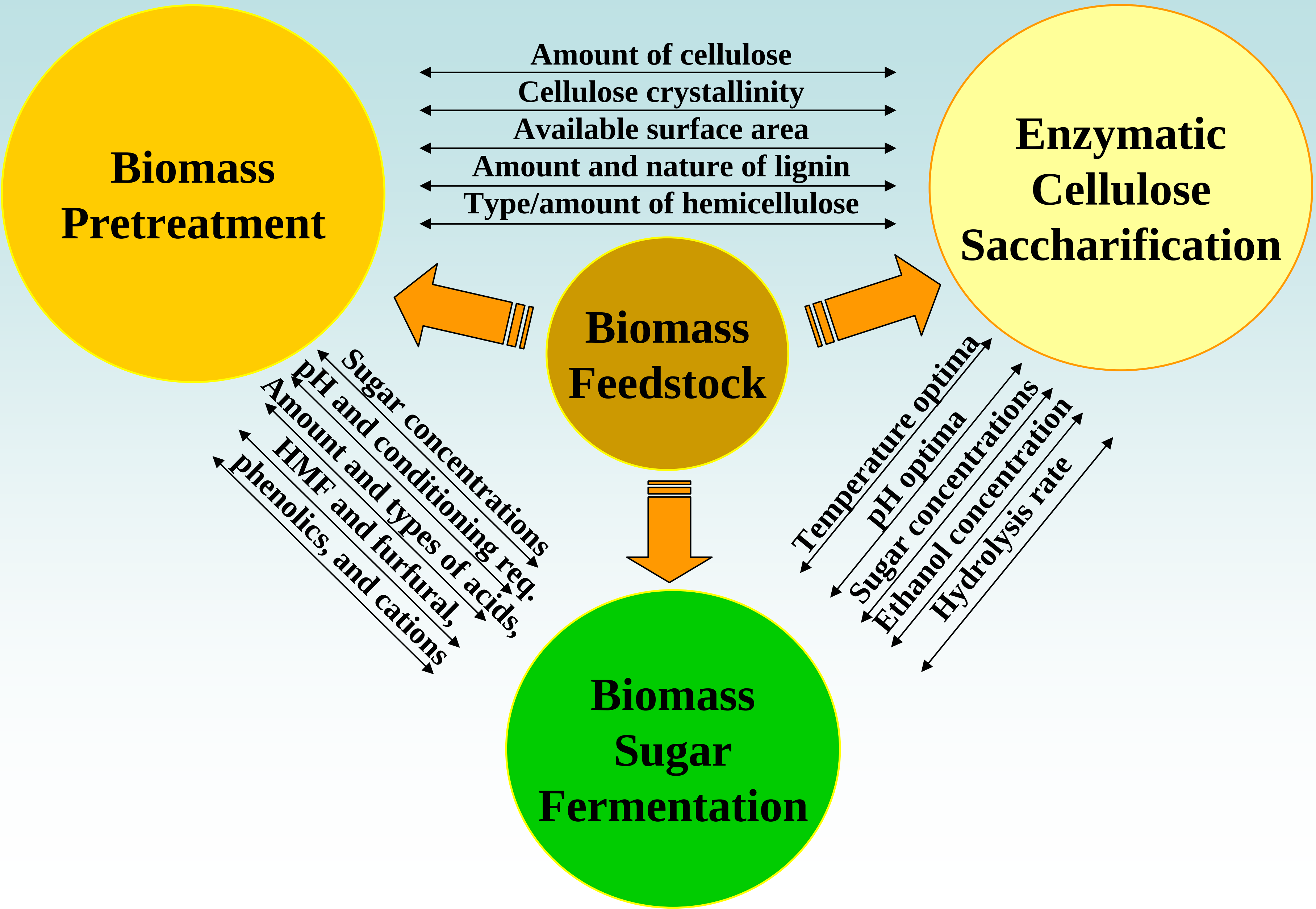
2nd R&D Barrier: Pentosan Utilization



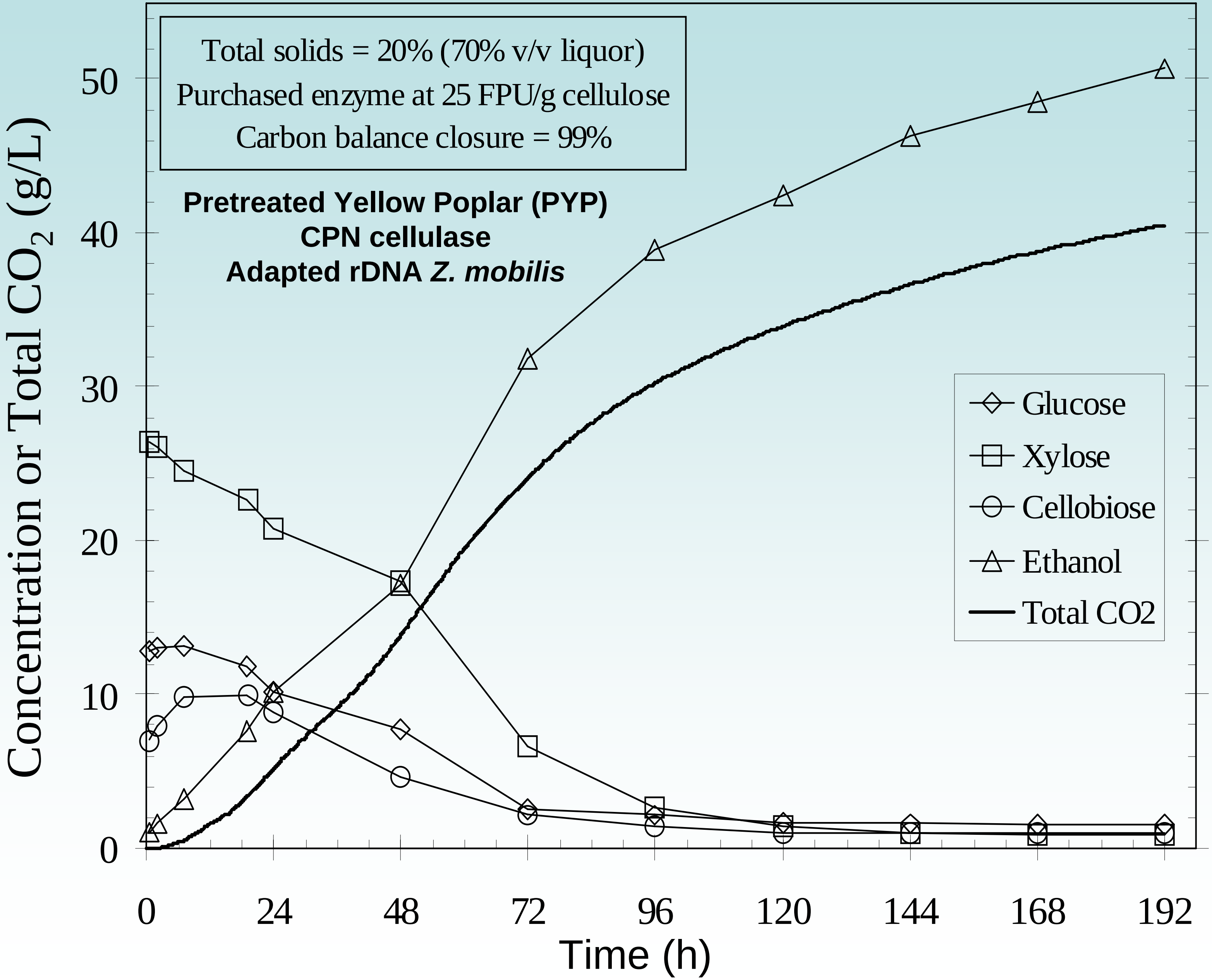
Cofermentation Pathway in Engineered *Zymomonas mobilis* (putative)



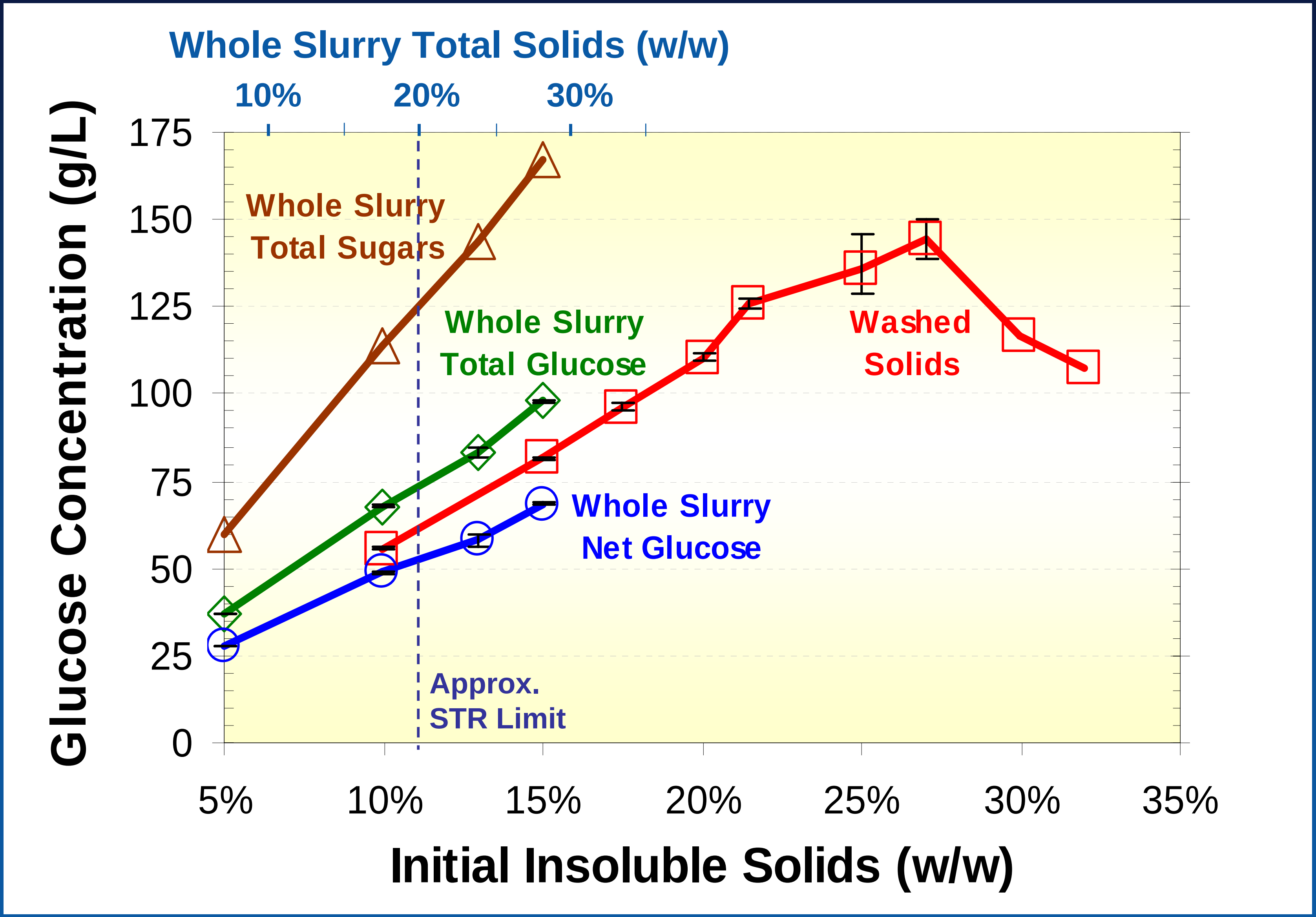
3rd R&D Barrier: Process Integration



Mini-pilot Scale Integrated SSCF



Intensified Processing Key to High Titers
Example: Glucose Production from Whole Slurry



High Solids Enzymatic Saccharification

Pretreated corn stover, 45ºC, 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