A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

NREL National Renewable Energy Laboratory

Innovation for Our Energy Future

R&D Needs for Integrated Biorefineries The 30 x 30 Vision

(30% of 2004 Motor Gasoline Supplied by Biofuels by 2030)

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4th Annual California Biomass Collaborative Forum
March 27, 2007

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Presented at the California Biomass Collaborative 4th Annual Forum held March 27-29, 2007 in Sacramento, California.

The President's Biofuels Initiative: The 30x30 Vision

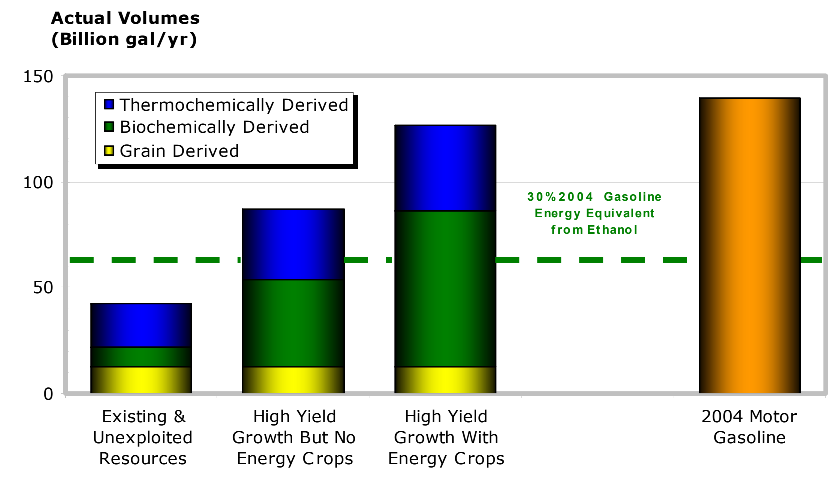
Transformation through Intermediates (sugars)

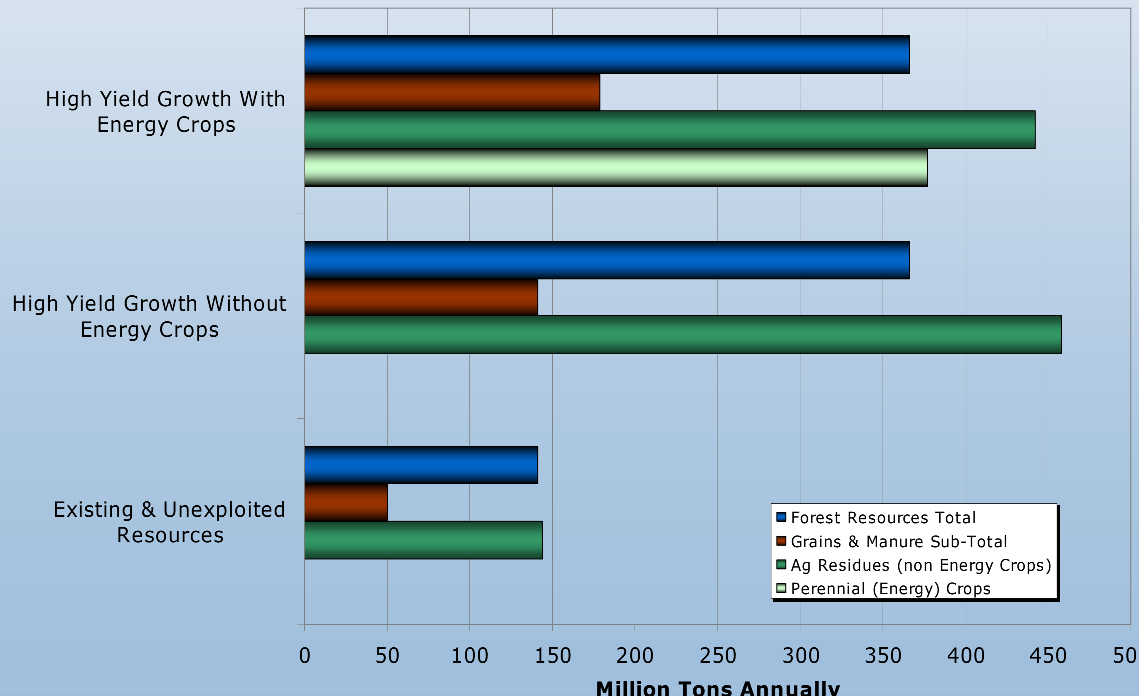
"Biochemical conversion"

main difference is in the primary catalysis system

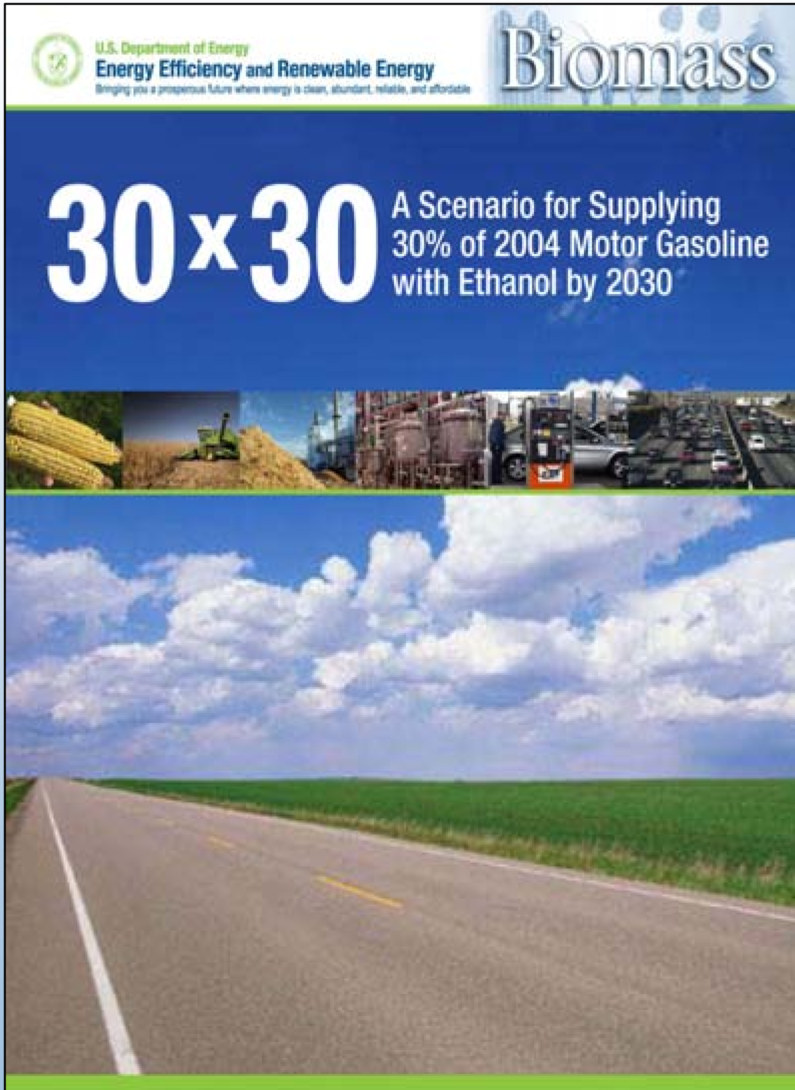
Reduction to building blocks (CO, H_2)

"Thermochemical conversion"





30 X 30 Plan Development in Support of OBP



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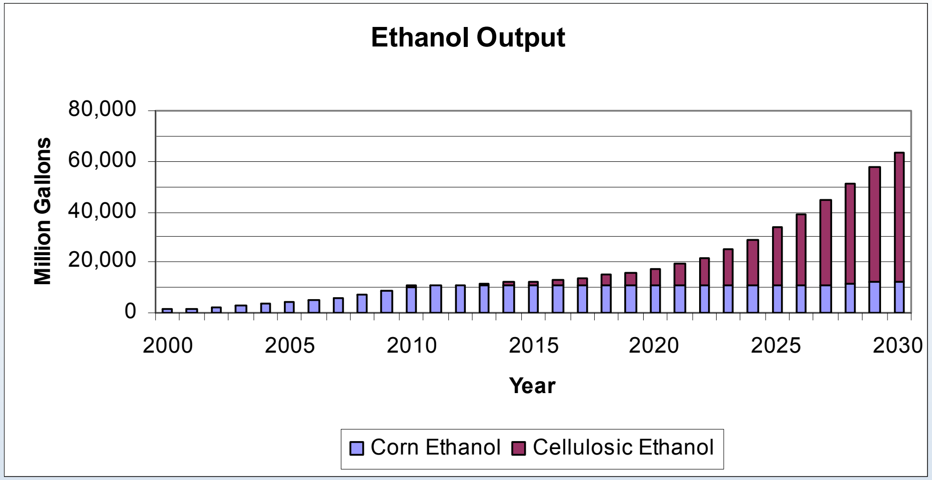
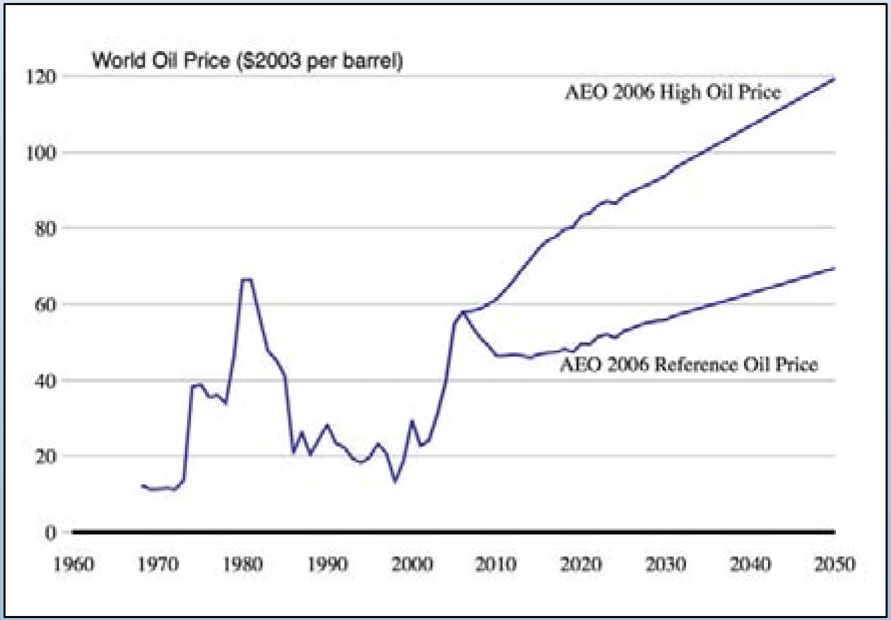
30 X 30 Scenario Model-Developed

- System dynamics model
- Dynamic implications of how the marketplace behaves in response to new technology
- Models behaviors of:
  - Investors
  - Farmers
  - Policymakers
- Can test different strategies to see whether or not they lead to successful achievement of the 30 x 30 goal
- Drivers can be either technology price targets or policy incentives





Five Critical Aspects to Achieving the 30 x 30 Scenario

1. Continue rapid deployment of starch based ethanol technology in the next decade

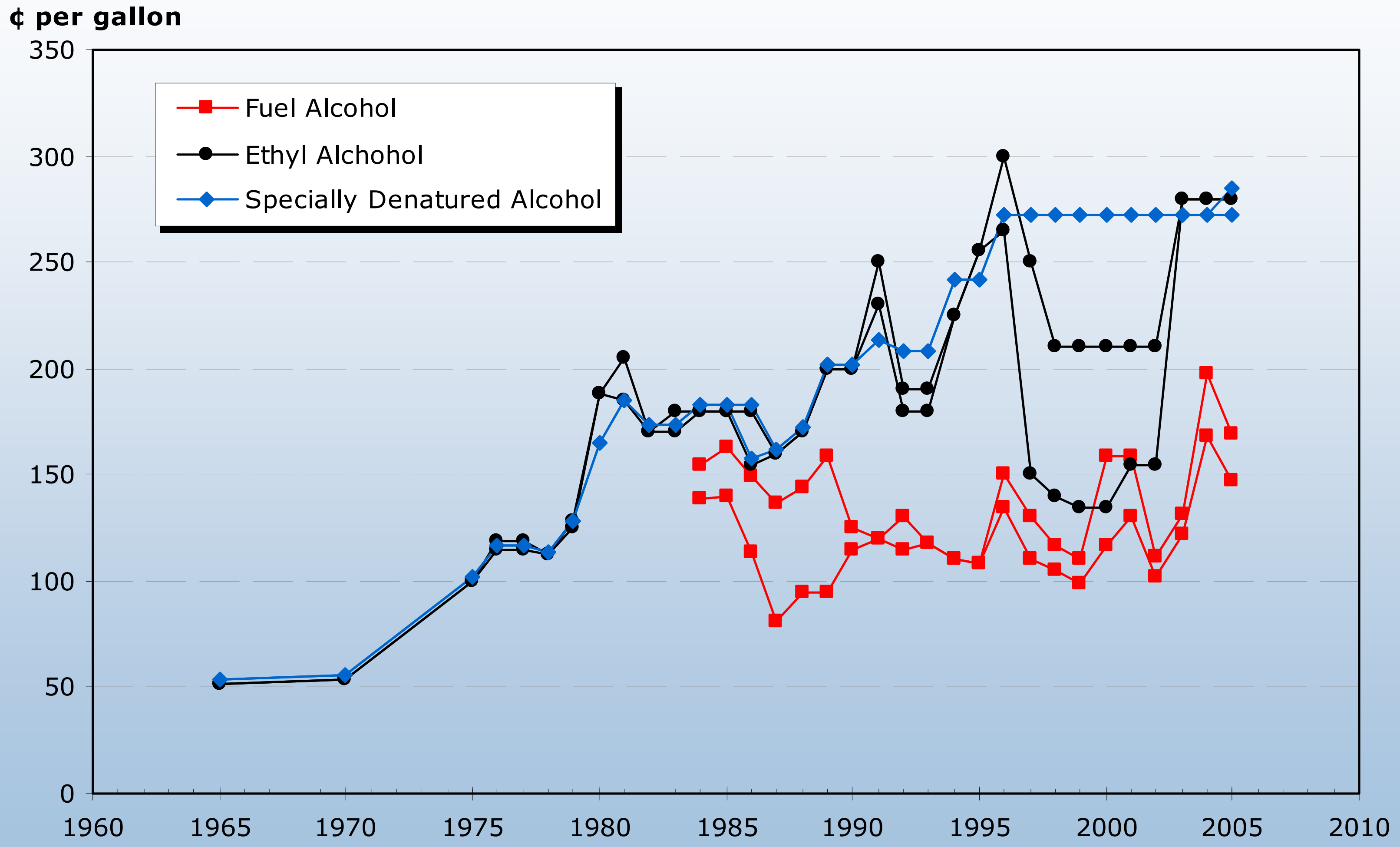
2. Achieve “$1.07/gallon” production cost target in 2012

3. Cost share deployment with industry to reduce risk hurdle

4. Achieve the advanced technology target to reduce the conversion cost component of the ethanol production cost by addressing identified barriers in 2025 – 2030

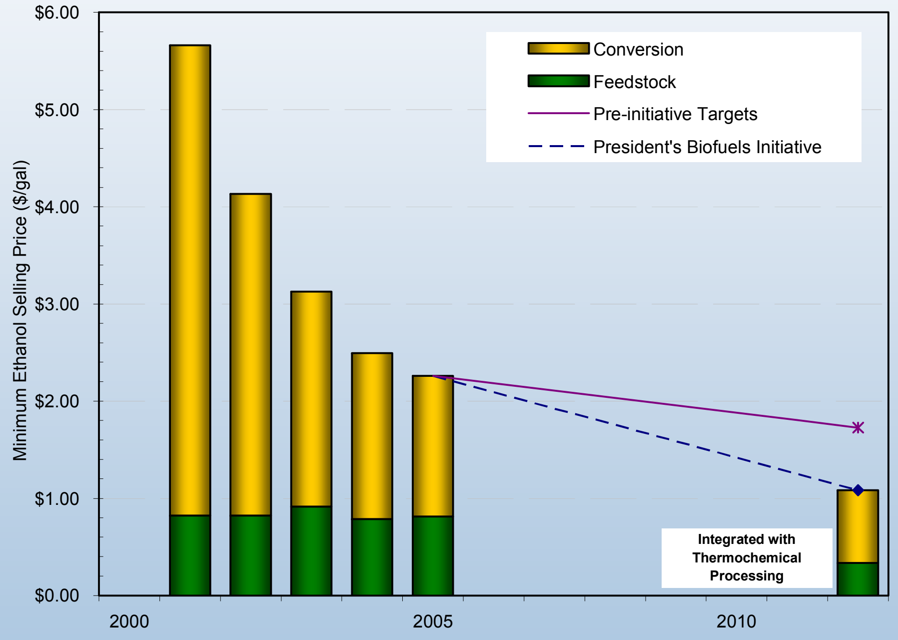
5. Continue tax incentive of $0.50/gallon and raise Renewable Fuels Standard ceiling to 20 billion gallons or develop more dynamic market driven incentive

Historic Fuel Ethanol Prices

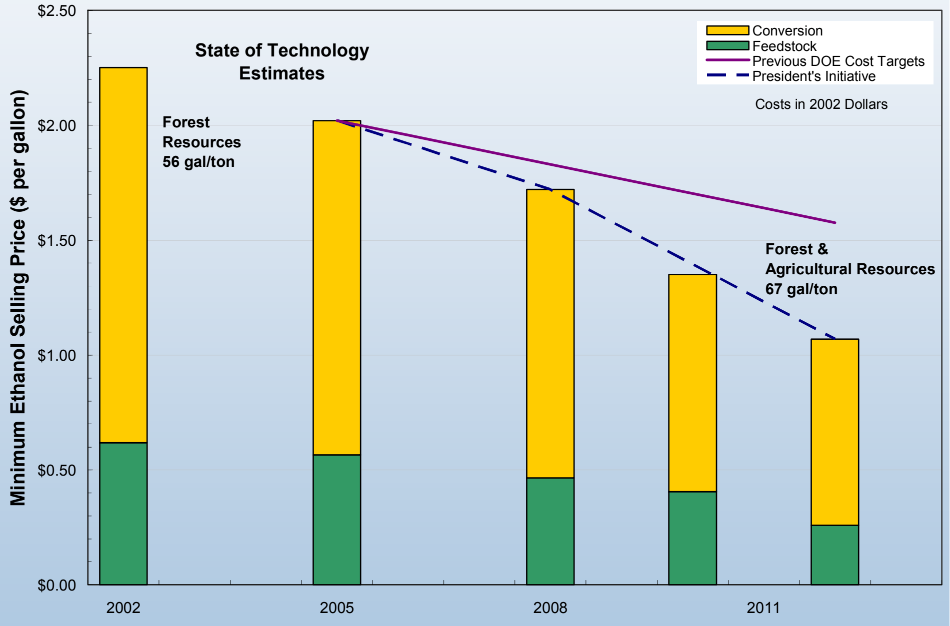


Achieving the $1.07 Production Cost Target by 2012

Biochemical



Thermochemical



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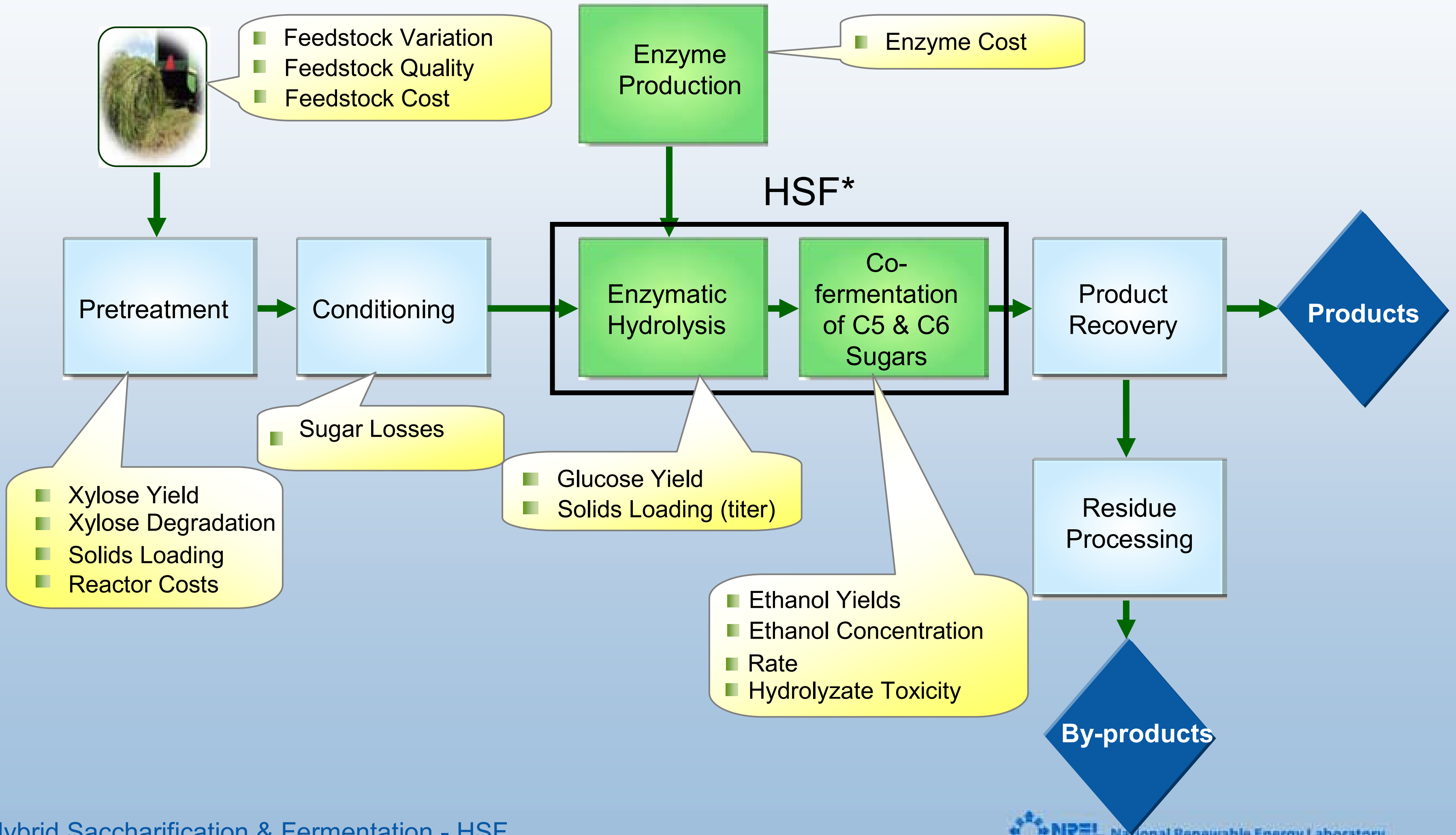
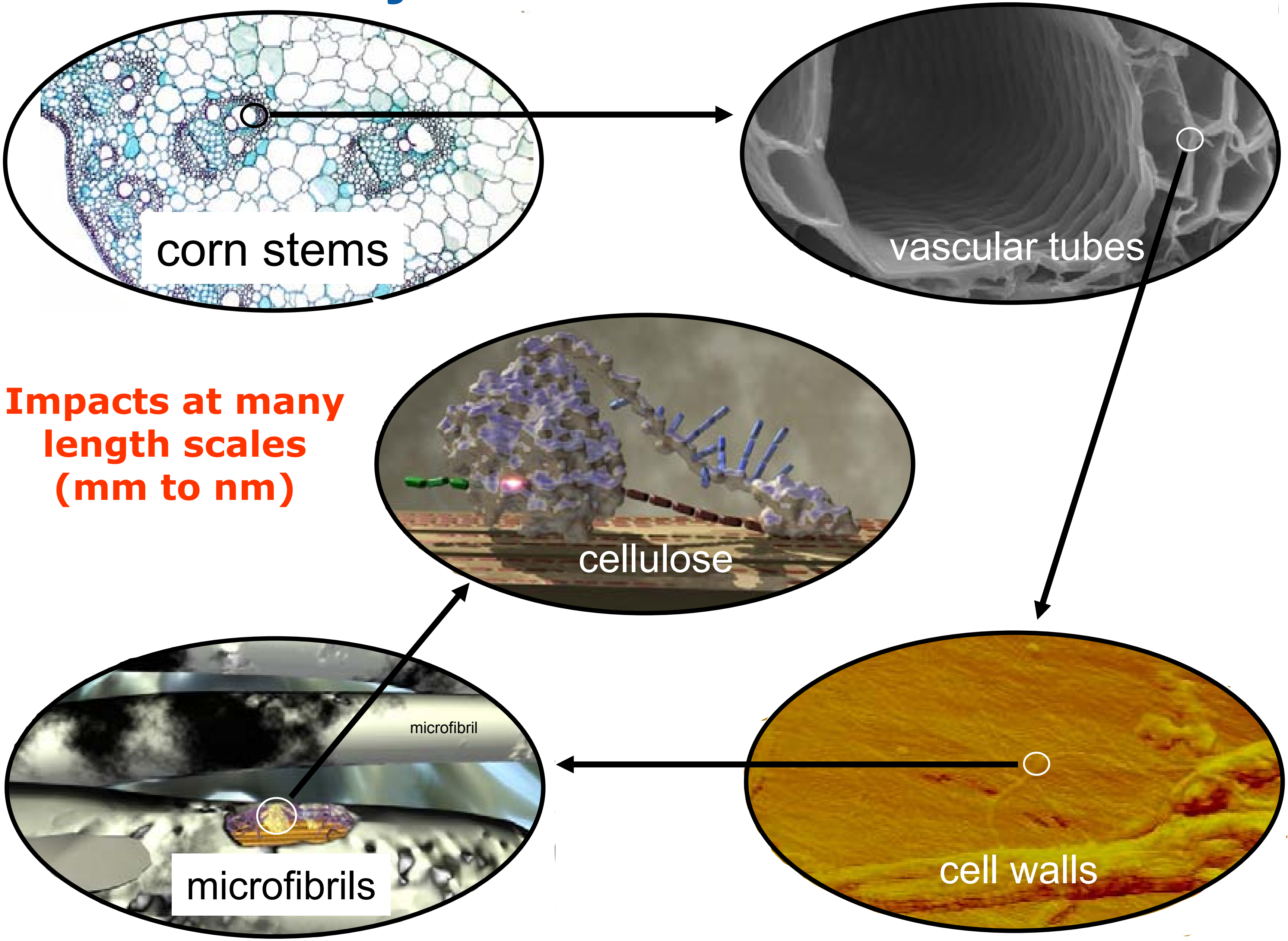
Technical Barrier Areas for $1.07 Biochemical Ethanol



*Hybrid Saccharification & Fermentation - HSF

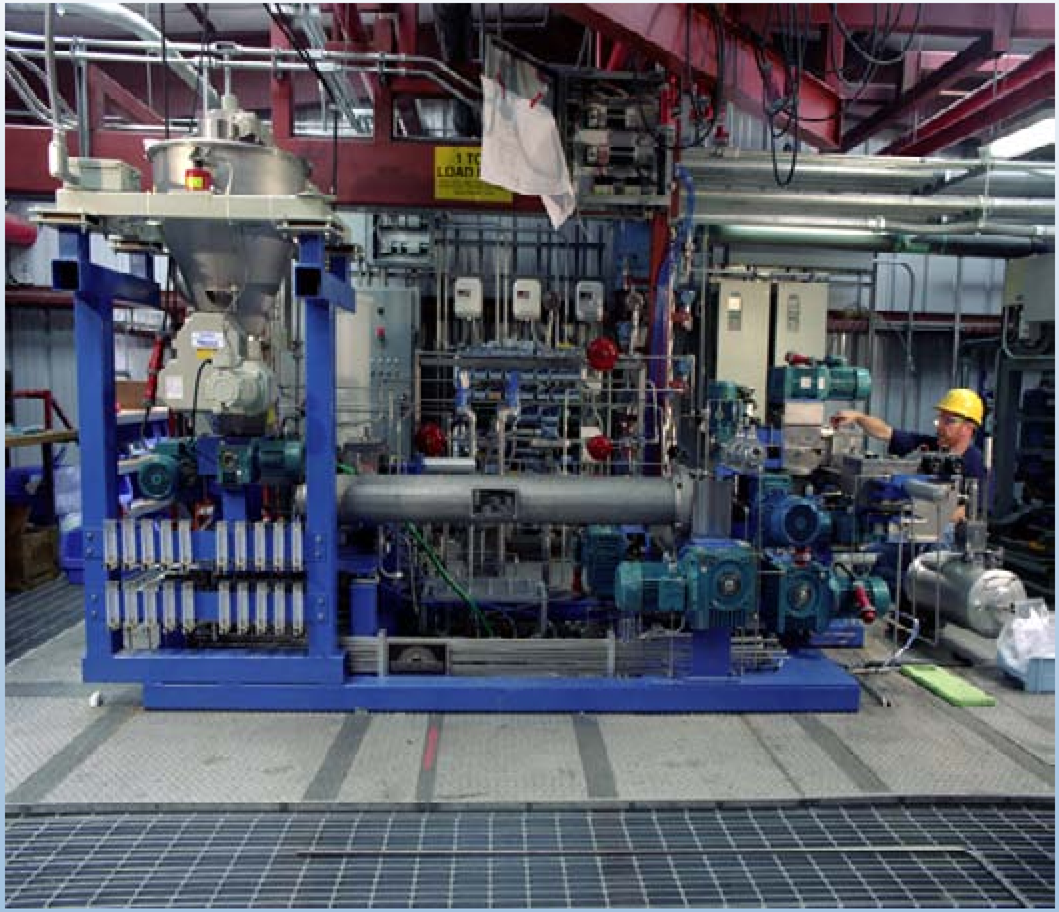
Summary: Biomass Recalcitrance

Impacts at many length scales (mm to nm)

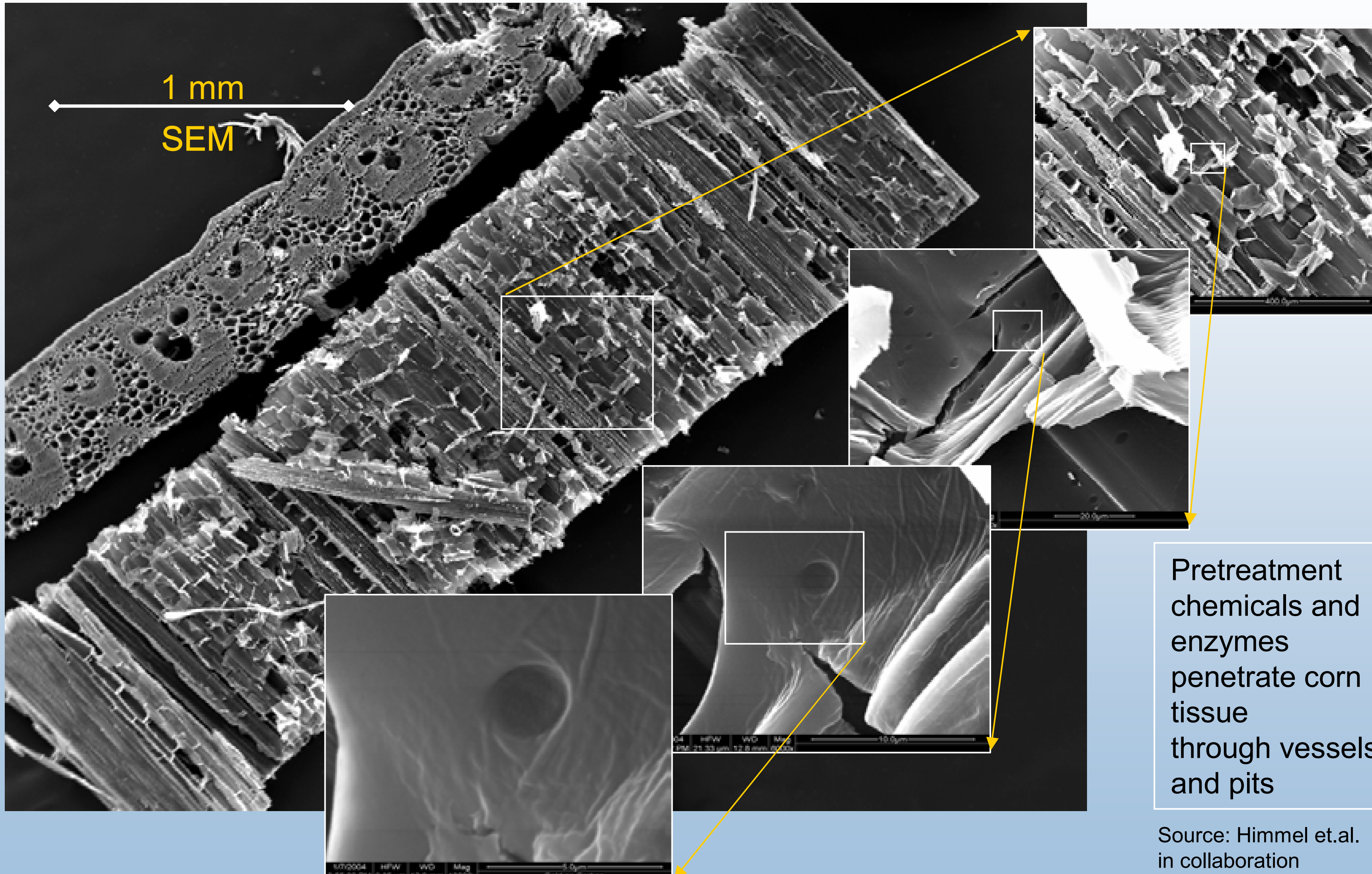


Pretreatment

- Converts hemicellulose to fermentable sugars
- Makes cellulose susceptible to enzymatic hydrolysis



How Do Chemicals Penetrate Biomass?



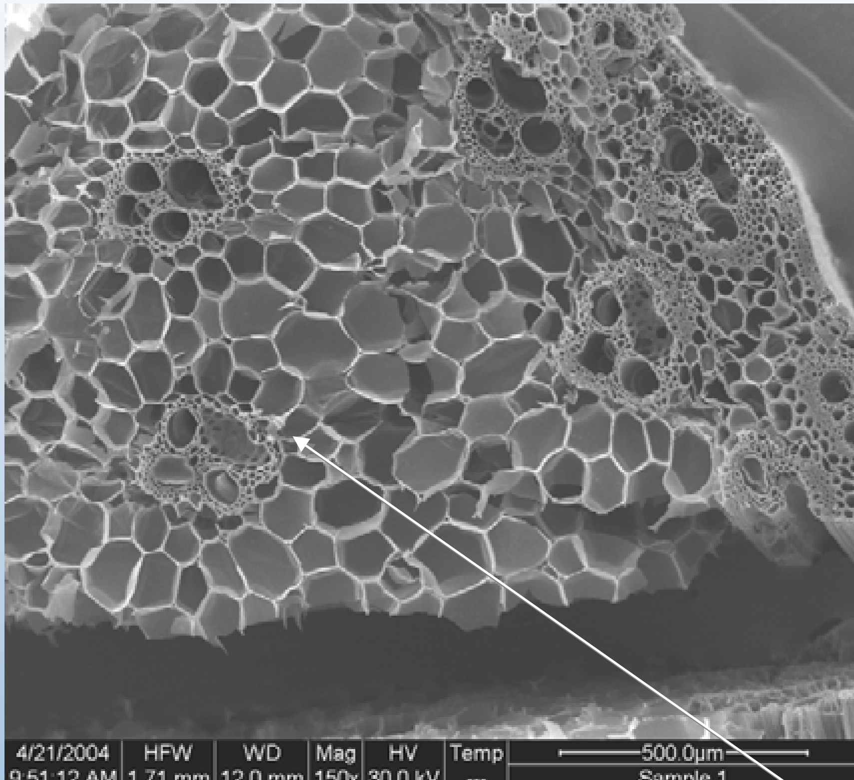
Pretreatment chemicals and enzymes penetrate corn tissue through vessels and pits

Source: Himmel et.al.
in collaboration
with the CSM EM Facility
(2004)

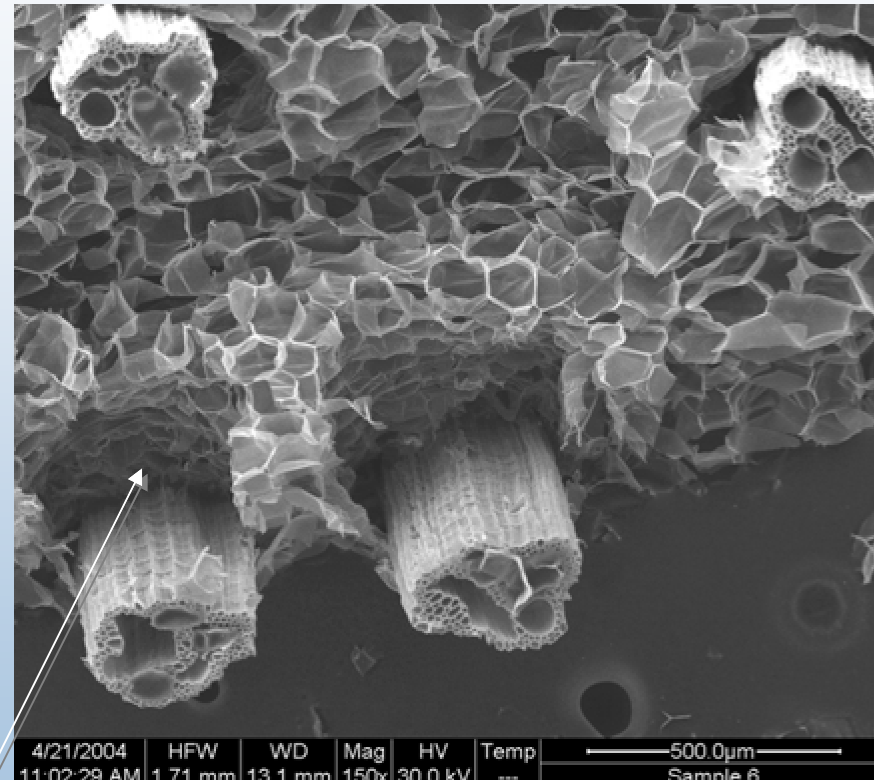
Saccharification

- Enzymatic hydrolysis of cellulose or starch to glucose

Buffer treated corn stover



Enzyme treated corn stover

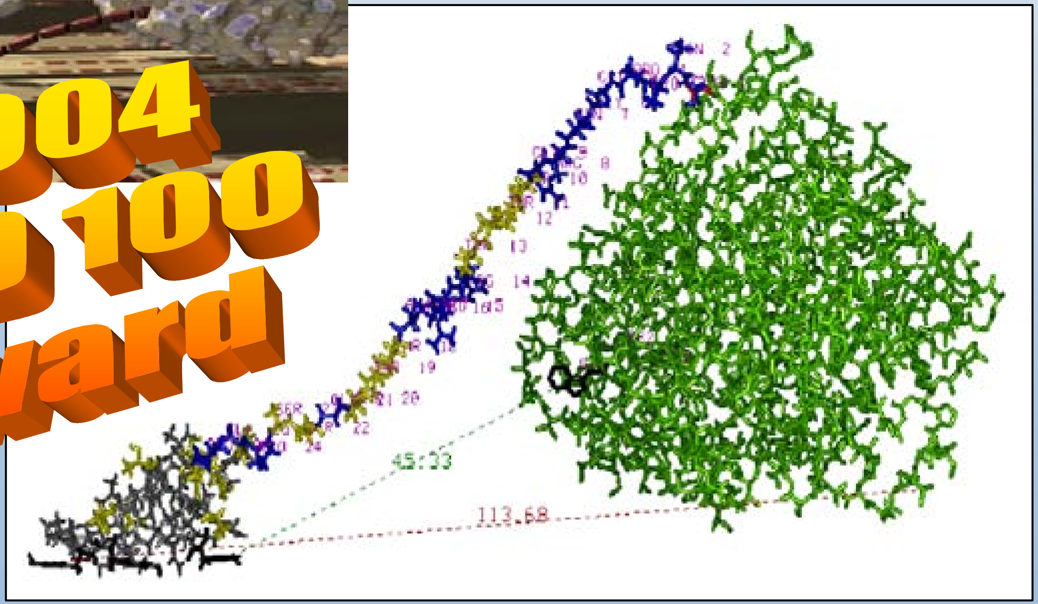


Note: zone around vascular bundle is eroded compared to native (suggests enzymes leak through pores in bundle)

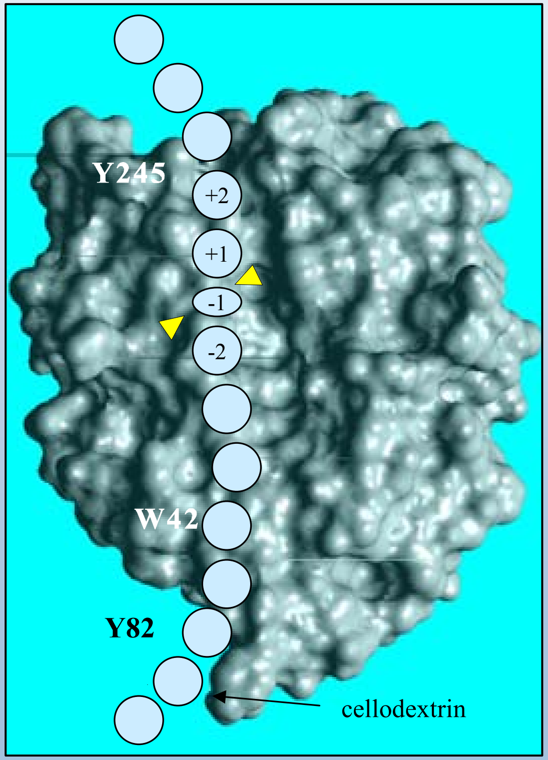
Enzyme Costs Have Fallen Sharply

- **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 20-30X reduction (by subcontract metric)

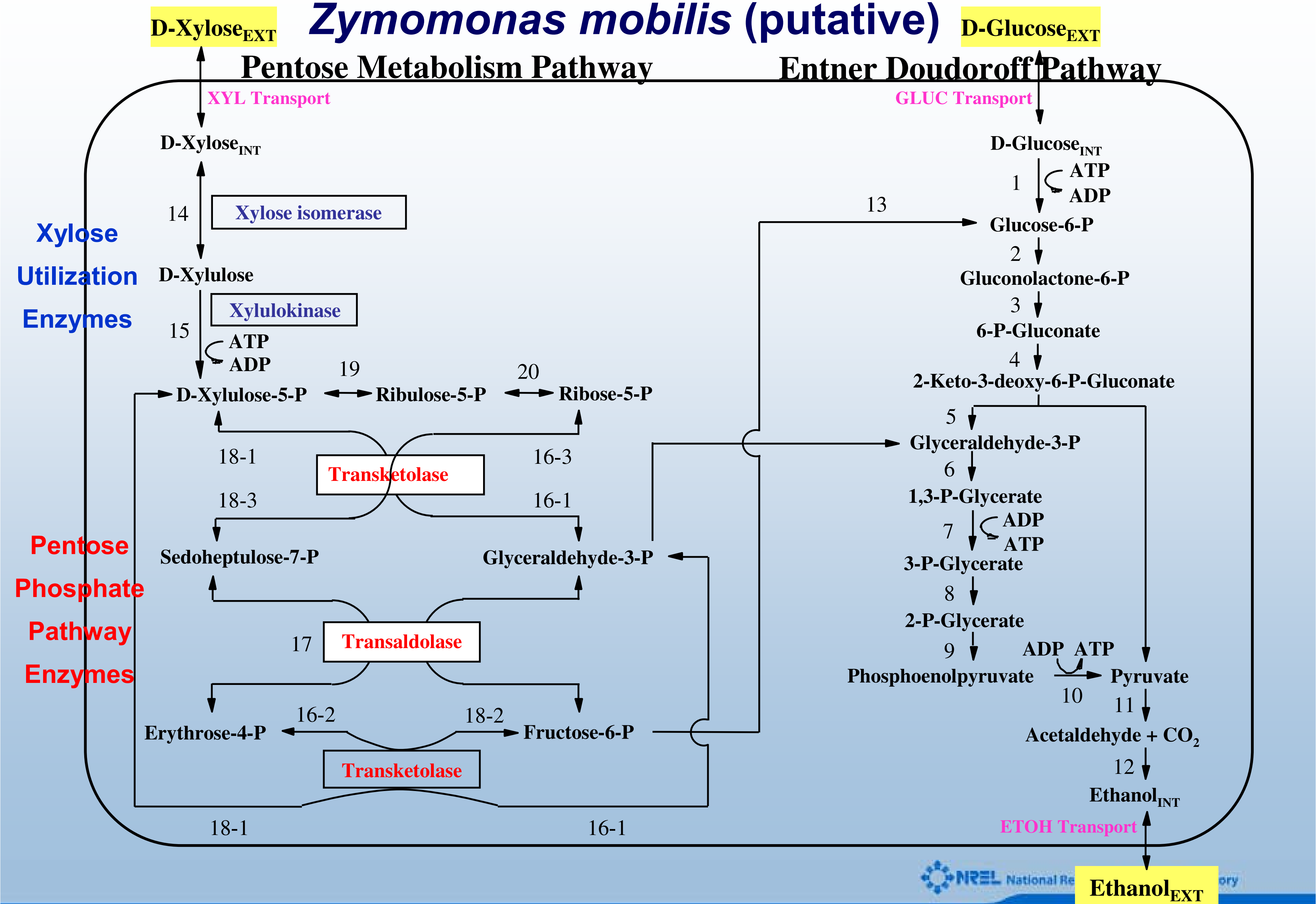
CBH1 from *T. reesei*



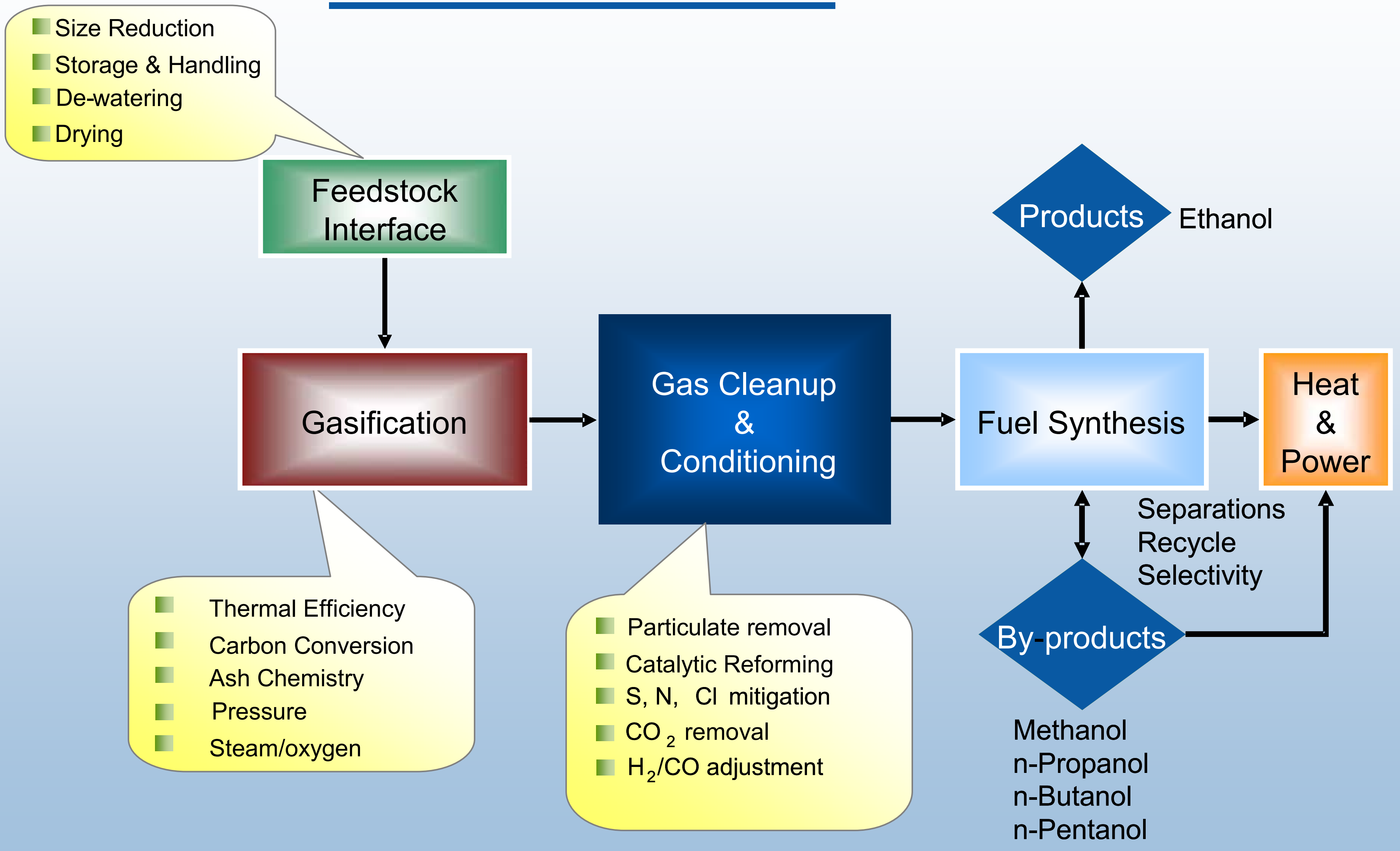
E1 from *A. cellulotiticus*



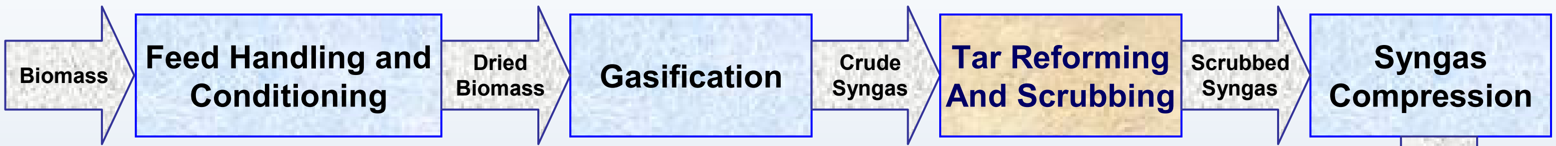
Cofermentation Pathway in Engineered *Zymomonas mobilis* (putative)



Technical Barrier Areas for $1.07 Thermochemical Ethanol



Thermochemical Route to Ethanol

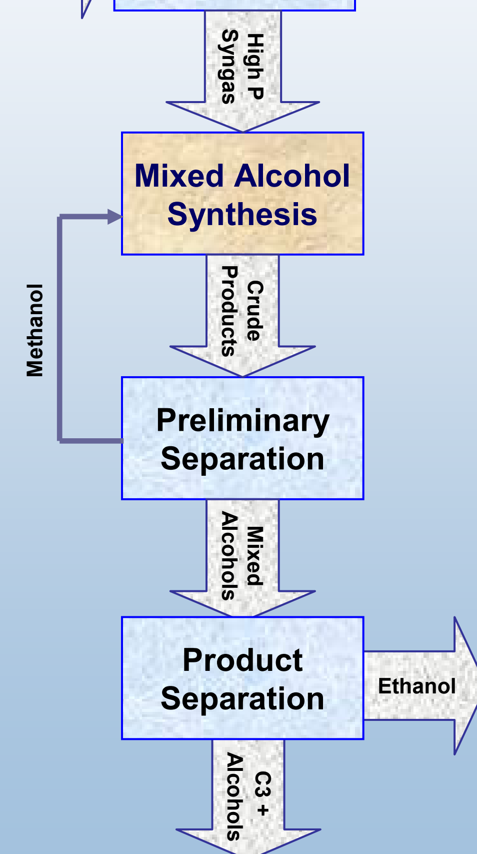


Overall Stoichiometry:

$$nCO + 2_nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$$

Optimal H2/CO ratio ~ 1 – 1.2 due to water-gas shift (WGS) activity of catalysts

Reactions largely kinetically controlled



Gasification R&D for "$1.07" Thermochemical Ethanol Target

- Gas Cleanup and Conditioning – Tar Reforming Catalyst Development
  - Consolidated tar and light hydrocarbon reforming to reduce capital and operating costs

Tar Reformer Performance - % Conversion

Compound	Current	Goal
Methane (CH_4)	20%	80%
Ethane (C_2H_6)	90%	99%
Ethene (C_2H_4)	50%	99%
Tars (C10+)	95%	99.9%
Benzene (C_6H_6)	70%	99%
Ammonia (NH_3)	70%	90%

- Advanced Catalysts and Process Improvements for Mixed Alcohol Synthesis
  - Increase single pass conversion efficiency (38.5% to 50%)
  - Improve selectivity (80% to 90%)
  - Improve yields at lower synthesis pressure
- Fundamental Gasification Studies
  - Technical validation of comparable syngas quality from biorefinery residues and wood residues

Pros & Cons of Mixed Alcohol Catalysts

Catalyst Class	Benefits	Negatives	LIkely C2+ alcohol STY g/L/hr possible
Std MeOH Cu-Zn-Al	Excellent performance & commercial record	Highly sensitive to reduction, sintering, Cl- & S	Very low
Modified Methanol (Cu/Zn/Al + X)	Easy to make & retrofit into existing units	Low overall yields, same sensitivity as parent Cu-Zn-Al, branched prods may dominate.	> 50, < 500
Molybdenum Sulfide	Good linear alcohol selectivity is claimed	S required in feed, & S is in product, highly sensitive to the activation process & O2 HC yield possibly high	500-1000
Molybdenum Oxide + XYZ	No S required, good linear product yield	Composition not optimized, HC yield higher than desired	800-1200
Rhodium based +XYZ	Good ethanol selectivity	Composition not optimized, high costs for Rh, HC yields are too high	500-1000
Fischer-Tropsch + modifiers	Good activity & many opportunities for improvement	Composition is not optimized alcohol selectivity may be too low HC yields may be high?	400-1000
Mixed Composite Catalysts (Inui claims)	Good reported C2+ yields reported, many possible improvements & refinements	Very complex system, optimization difficult,, yields of HC, acids & aldehydes are too high	600 - >1000

X, Y, Z = various modifiers or promoters

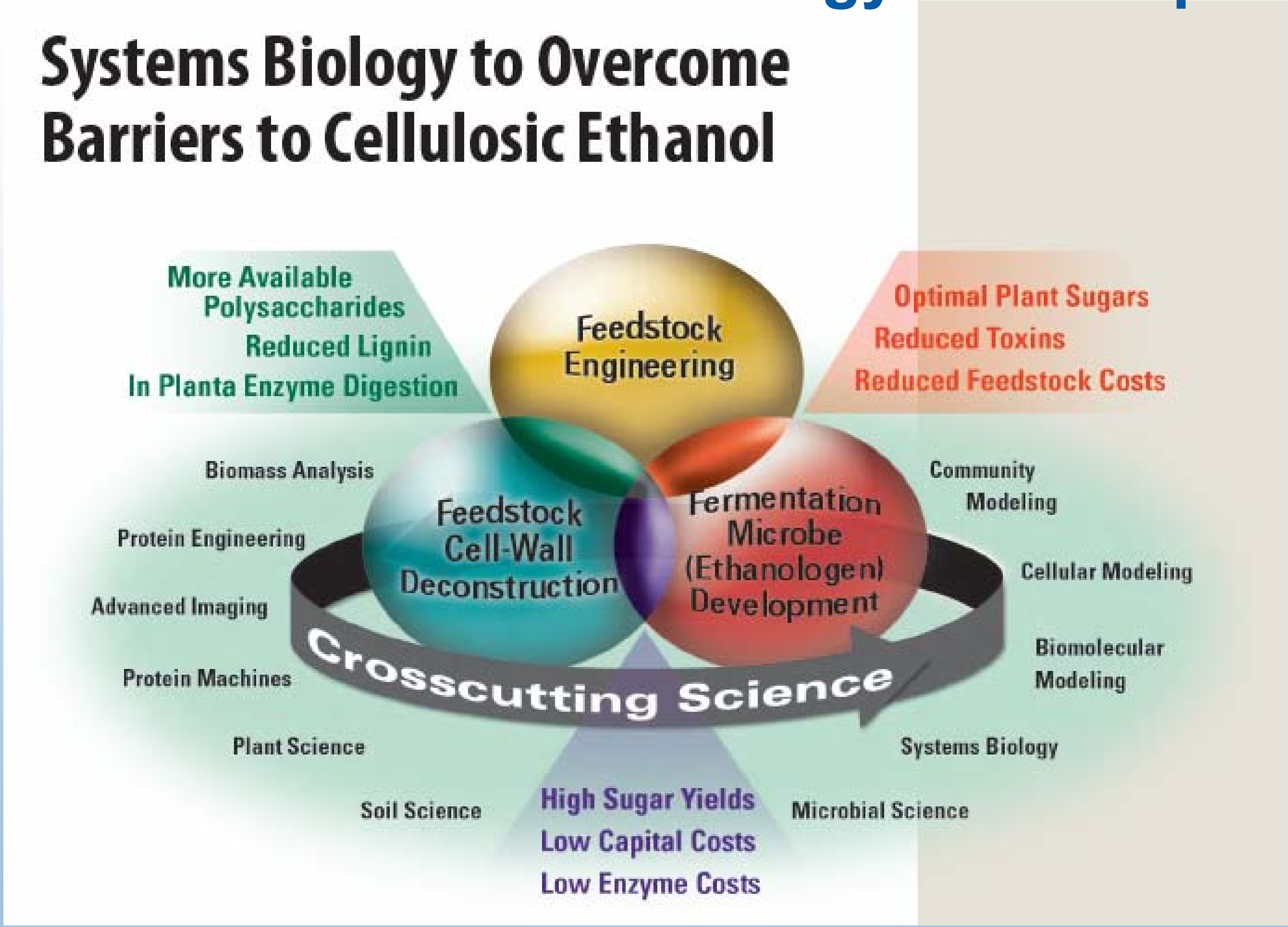
ALTERNATE SYNGAS ROUTES
Using "Already Developed" Technology

(Syngas fermentations not considered)

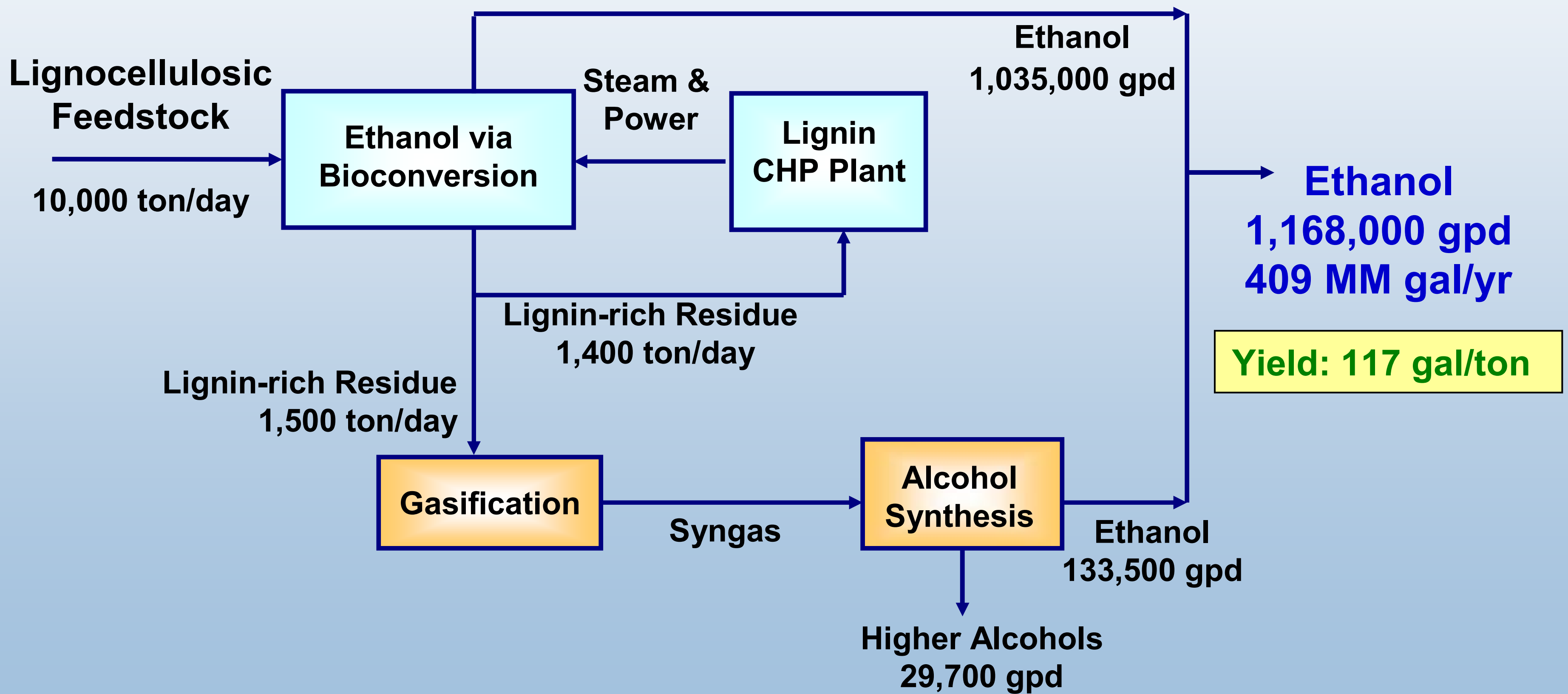
Catalytic Step 1	Catalytic Step 2	Catalytic Step 3	+	-
Syngas to DME + MEOH in one step over Cu-Zn-Al combined w/ dehydration cat	DME + MEOH to mixed C2-C4 Olefins over ZSM-5 MTO* catalyst	Olefins hydration to mixed C2-C4 alcohols over H2PO4 catalyst	DME defeats MeOH equilibrium limit, DME+MeOH is ideal feed for MTO	3 steps (but all are highly efficient)
Syngas to MeOH over std. Cu-Zn-Al	MeOH +CO to Acetic acid, w/homogeneous Rh, Ir & Ru	Acetic acid hydrogenation to ethanol	All steps highly efficient, only EtOH produced	3 steps (possibly can combine #2 & #3 with development)
Syngas to DME + MEOH in one step over Cu-Zn-Al combined w/ dehydration cat	DME + MEOH to gasoline hydrocarbons over a ZSM-5 MTG* catalyst	none	All steps Claimed highly efficient, gasoline produced	No Ethanol, possibly some olefin co-product, high aromaticity

*MTO = Methanol to Olefins MTG = Methanol to Gasoline,
Catalysts are variants of modified ZSM-5

From DOE GTL Bioenergy Roadmap



2030 Target for a Large Cellulosic Biorefinery to Integrate BC & TC Paths



S. Phillips and J. Jechura

Questions?