Cellulosic Ethanol Cost Target

BETO Platform Peer Review

Plenary Talk

May 21, 2013

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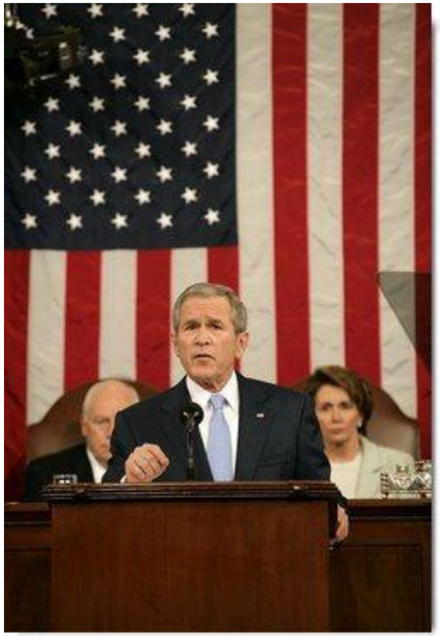
State of Technology Background

Mission Clearly Dictated



2006 State of the Union

"America is addicted to oil…the best way to break this addiction is through technology."

"Our goal is to make cellulosic ethanol practical and cost competitive within 6 years."

2007 State of the Union

"Reduce U.S. gasoline usage by 20% in 10 years – 75% from new fuels and 25% from vehicle efficiency"

"Mandatory fuel standard to require 35B gallons of renewable and alternative fuels by 2022."

State of Technology Background

Cost Targets Developed

- **Original 2012 cost target ($2002) was based on competitiveness with corn ethanol (2006 timeframe)**
  - *Historic corn prices were ~$2-3/bushel giving an initial target of $1.07 that eventually inflated ($2007) to $1.33/gal ethanol*
  - *Roughly equivalent to gasoline production at $65/BBL crude*

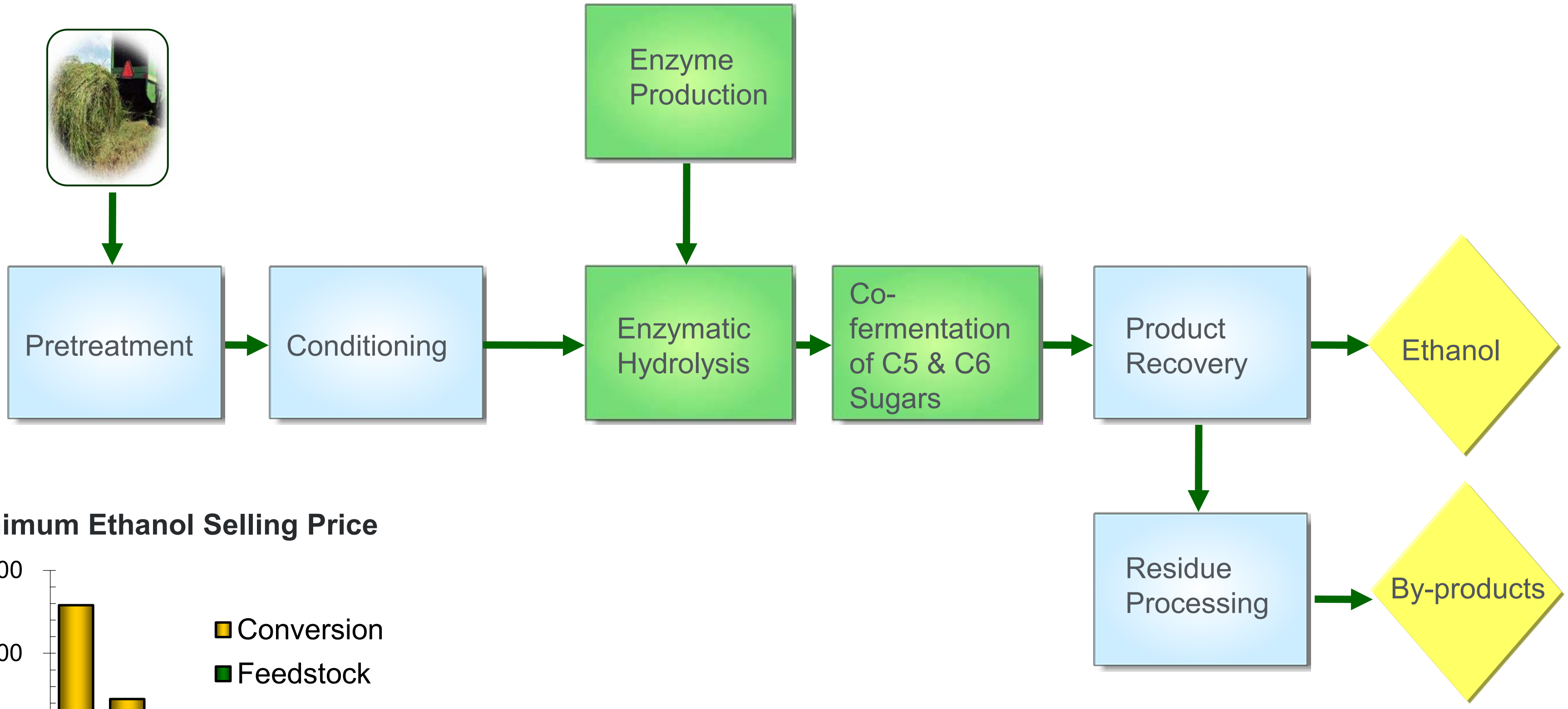
- **Updated 2012 cost target ($2007) was based on competitiveness with gasoline (2009 timeframe)**
  - *$1.76/gallon ethanol (year $2007) equivalent to $2.62/gallon (GGE), wholesale gasoline price projected for 2012 using AEO 2009 reference oil case*
  - *Roughly equivalent to gasoline production at $95/BBL crude*

Organization	Oil Price Forecast in 2012 (2007$/barrel)	Ethanol Production Cost (2007$/gallon ethanol)
EIA, AEO2009, High Oil Price Case	116	2.06
EIA, AEO2009, Reference Case	95	1.76
EIA, AEO2009, Low Oil Price Case	51	1.04

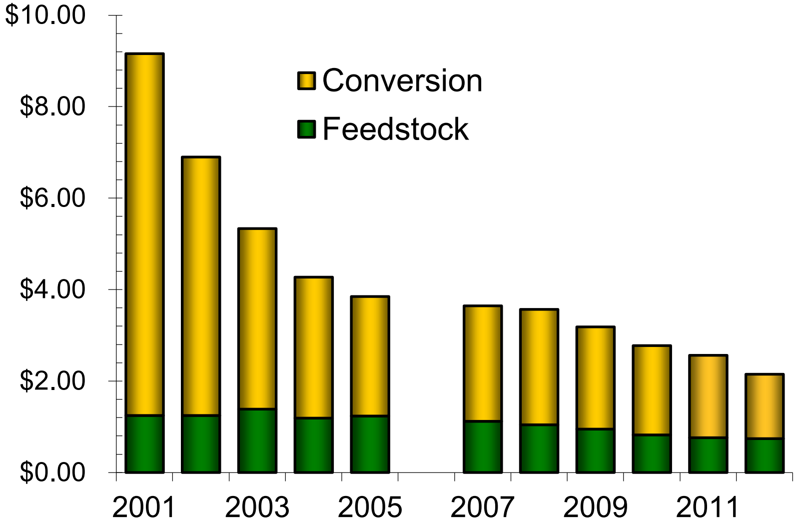
- **Original Design Reports updated to ~$2.00/gal target (2011 timeframe)**
  - *Total bottoms up approach with no end cost target in mind*
  - *Incorporation of state of the art knowledge on capital costs, financing assumptions, process design*
  - *Roughly equivalent to gasoline production at $110/BBL crude*

State of Technology Background

Biochemical Design Report



Minimum Ethanol Selling Price



- **Conceptual design of a 2,000 tonnes/day commercial plant**
- **Basis for NREL pilot plant design and for connecting R&D targets to cost targets**
- **Extensively peer reviewed**
- **Yields demonstrated in NREL pilot plant**

BC Conversion to Cellulosic Ethanol

Pretreatment and Conditioning

Major Needs

- Good Cellulose Digestibility out of Pretreatment
  - *enzymes will need to convert ~90% glucan to glucose*
- Conversion of Hemicellulose to Sugars
  - *enzymes weren't capable of converting unreacted xylan / xylo-oligomers*
- Efficient Conditioning Strategy
  - *optimum pH ~5-6 (enzymes) and ~6-8 (fermentation organisms)*
- Fully Integrated, Process Relevant Demonstration Capability
  - *integrated pilot scale experimental data w/Aspen model to estimate commercial scale*
  - *better understanding of impacts downstream needed*

Approach

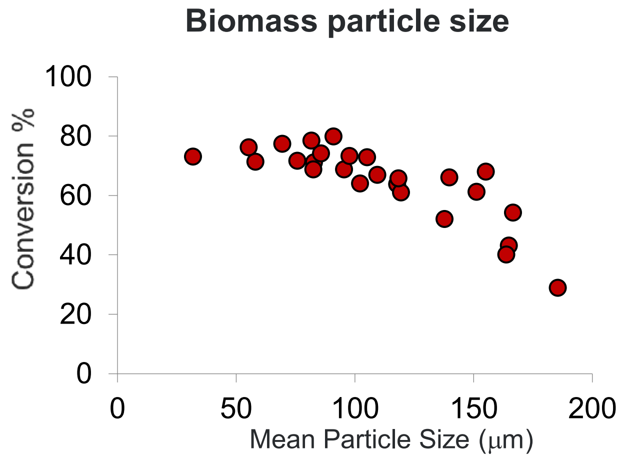
- National Lab, Academic and Industry R&D
  - *national lab/academic R&D, pretreatment development between NREL/DuPont, CAFI, expansion of IBRF, BRCs, targeted pilot scale solicitations*

BC Conversion to Cellulosic Ethanol

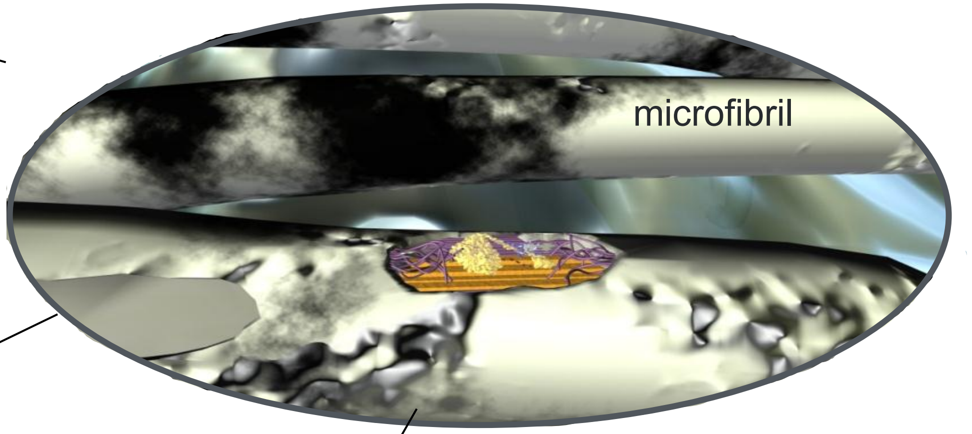
Cellulose to Sugars (C_6)

Objectives

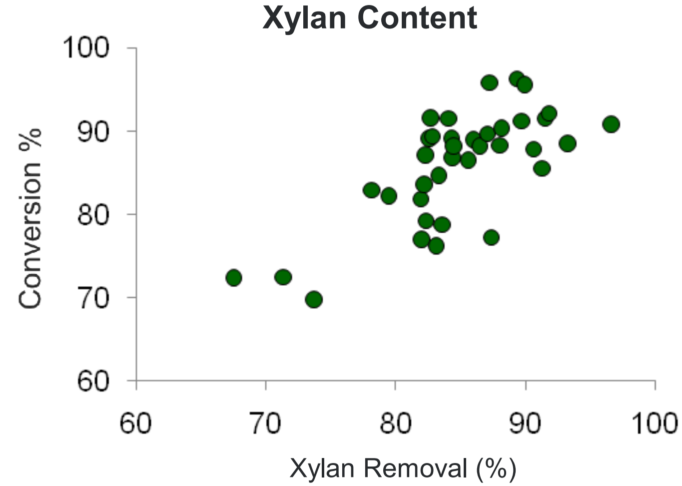
- Define cellulase interactions at the plant cell wall that are important for efficient hydrolysis
- Determine how pretreatment affects major plant cell wall features and subsequently impacts cellulase activity



Biomass particle size



Other Factors



Xylan Content

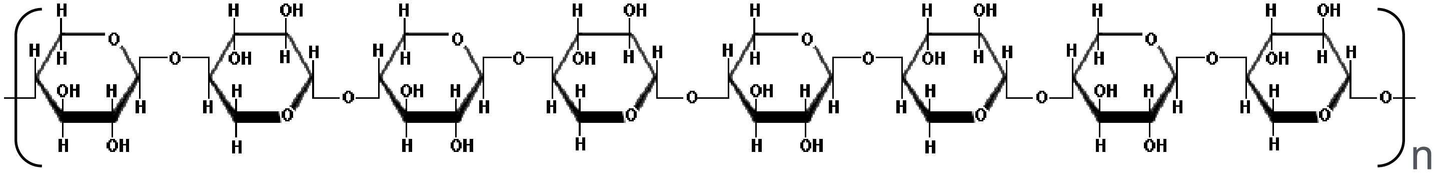
Quantification of Impact

Cellulose crystallinity, Xylan content, Particle Size > Lignin Distribution, Biomass Porosity > Cellulose Morphology/Dp

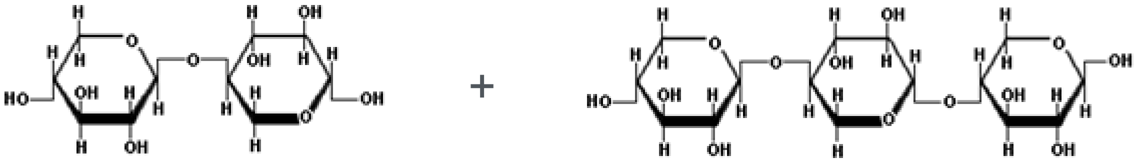
BC Conversion to Cellulosic Ethanol

Hemicellulose to Sugars (C_5)

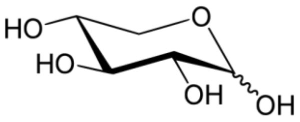
Xylan



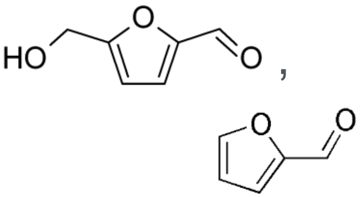
Oligomeric Xylose

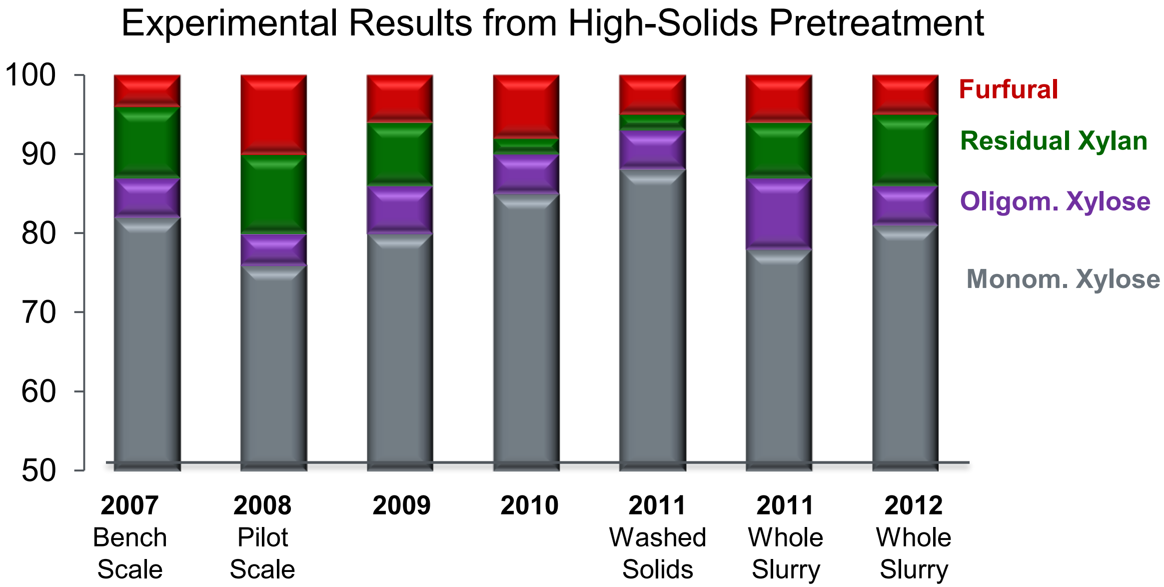


Monomeric Xylose



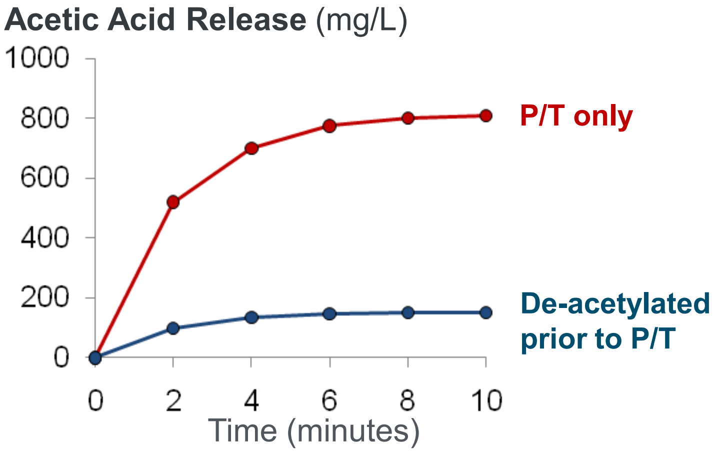
Degradation Products



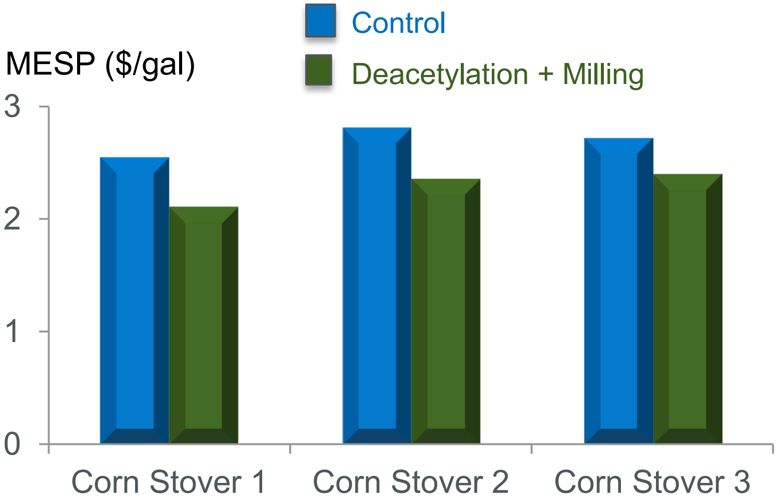


BC Conversion to Cellulosic Ethanol

Pretreatment Changes for 2012



Economic Analysis of Deacetylation/Milling



Economic Incentives

Decreased Pretreatment Severity

- Lower pressure/temp and acid concentration
- Less sugar degradation, neutralization

Lower Acetic Acid / Furfural Concentrations

- Less enzyme/strain inhibition

Better Cellulose Digestibility

- Higher yields / lower enzyme dosages

Waste Water Treatment Cost Reductions

BC Conversion to Cellulosic Ethanol
Enzymatic Saccharification

Major Needs

- Cost of Enzymes
  - *Production costs, loading requirements lead to enzyme costs being 10-20x too high*
- Conversion of Cellulose and Hemicellulose to Sugars (C_6 and C_5 respectively)
  - *enzymes will need to convert ~90% glucan to glucose from pretreated biomass*
  - *capability of converting unreacted xylan / xylo-oligomers (xylanase activity incorporation)*
  - *operation in whole slurry mode (inhibition tolerance)*
  - *better understanding of enzyme surface interaction*
- Fully Integrated, Process Relevant Demonstration Capability
  - *integrated pilot scale experimental data w/Aspen model to estimate commercial scale*

Approach

- National Lab, Academic and Industry R&D
  - *targeted R&D, investment in BSCL to explore enzyme/surface interactions to catalyze enzyme specific activity improvements, expansion of the IBRF*
- Two Enzyme Cost Reduction Solicitations Aimed at Industry

BC Conversion to Cellulosic Ethanol

Enzyme Cost Reduction Solicitation

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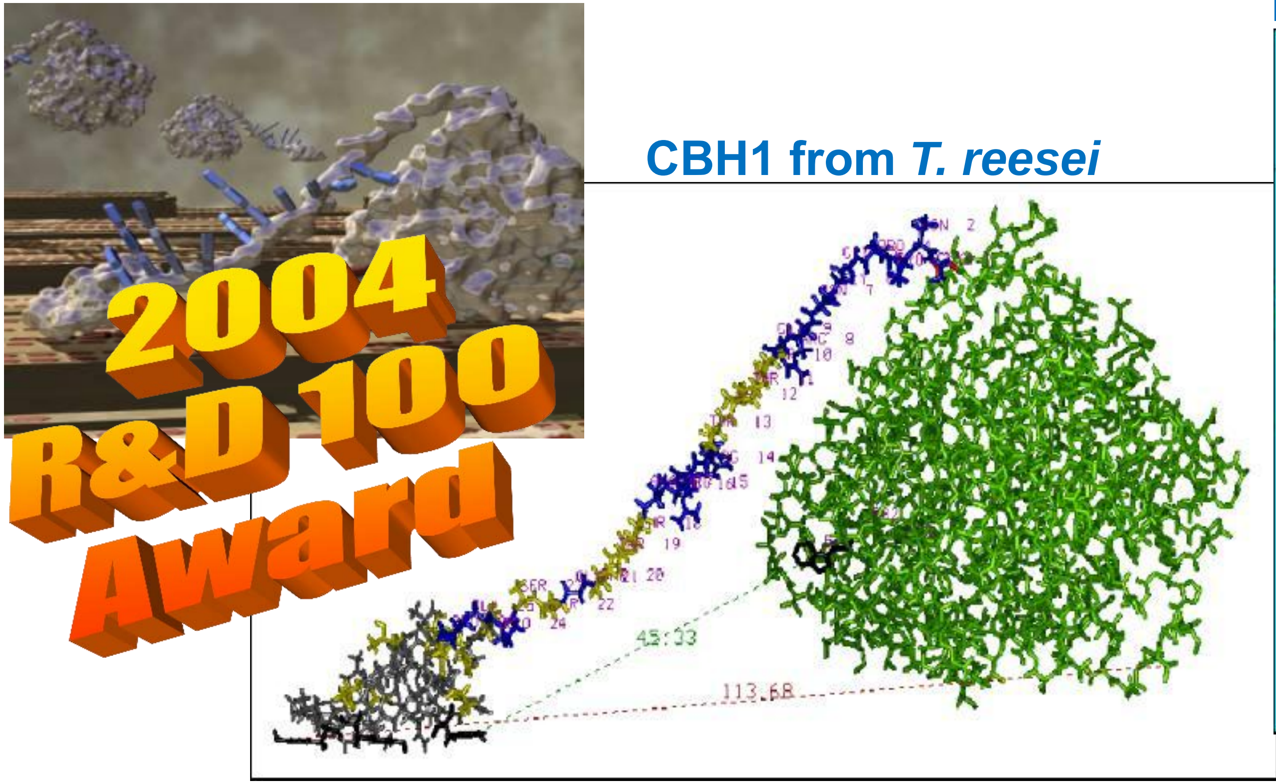
Genencor and Novozymes Cost-shared Subcontracts (2000-2005)

- Focus: lower production cost, increase enzyme system efficacy

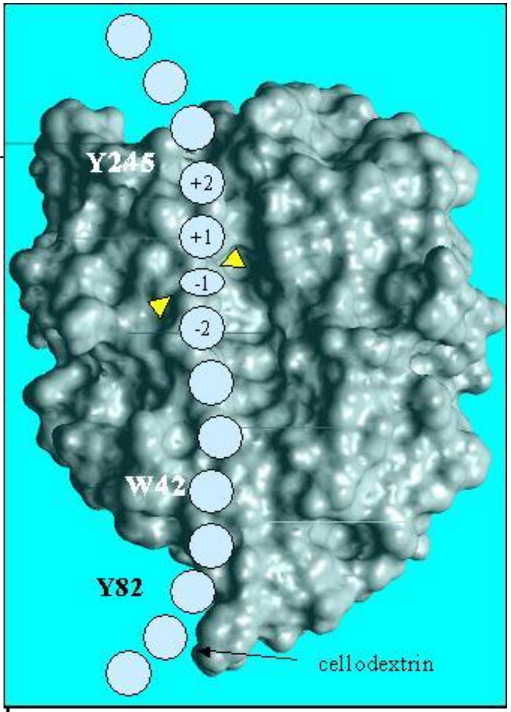
  Enzyme cost (\$/gallon EtOH) = Prod. Cost (\$/kg) x Usage Req. (kg/gallon EtOH)
- Cellulase cost reduced 20 fold

2nd round of DOE grants started in 2008 (DSM, Genencor, Novozymes, Verenium)



CBH1 from *T. reesei*

E1 from *A. cellulotiticus*



BC Conversion to Cellulosic Ethanol

Enzymatic Saccharification

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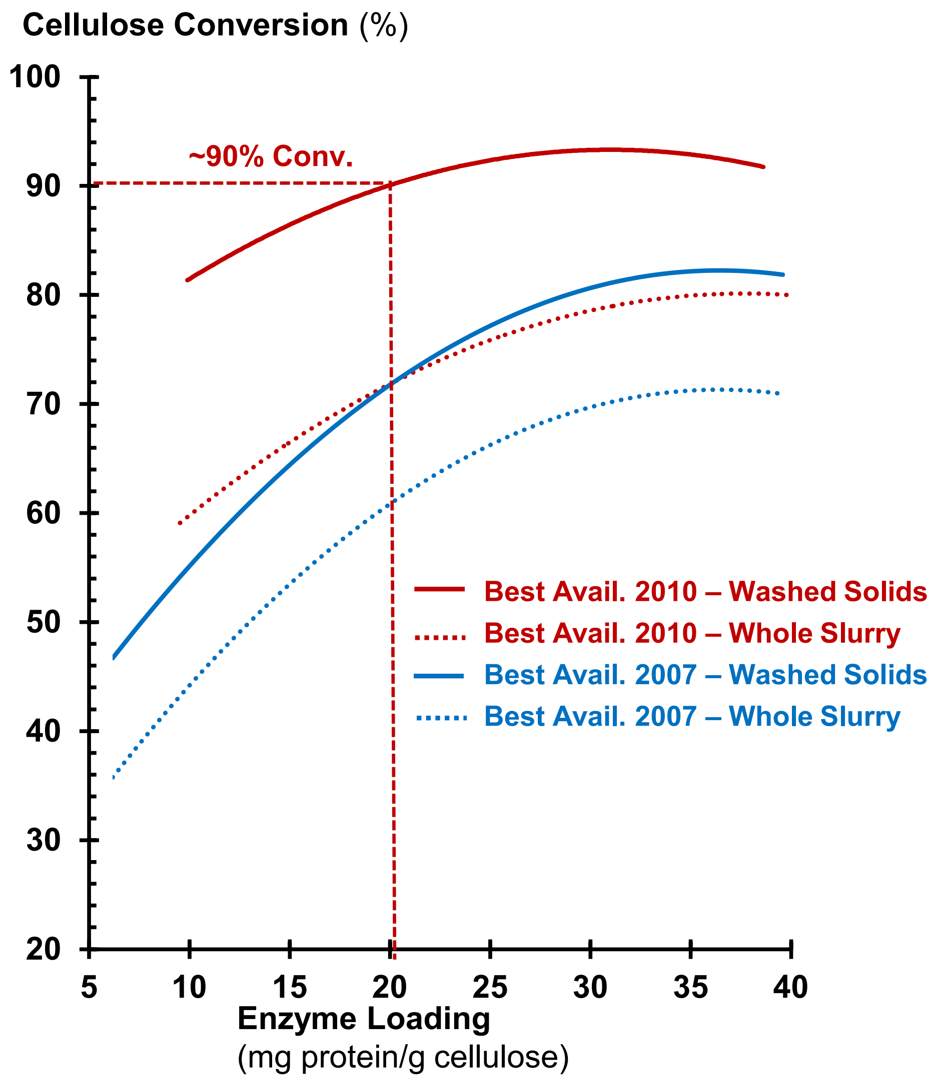

2010:

CTec 1 (Novozymes) @ 40 mg/g

- ~90% Cellulose to Glucose (Washed Solids)
- ~70% Cellulose to Glucose (Whole Slurry)

2011:

CTec 2 (Novozymes) @ 40 mg/g

- >90% Cellulose to Glucose (Washed Solids)
- >80% Cellulose to Glucose (Whole Slurry)

CTec 2 @ 20 mg/g

- ~70-75% Cellulose to Glucose (Whole Slurry)

2012:

De-acetylation + CTec 2 @ 20 mg/g

- ~78% Cellulose to Glucose (Whole Slurry)

BC Conversion to Cellulosic Ethanol

Fermentation

Major Needs

- C_5 Sugar Utilization
  - *Incorporation of Xylose and Arabinose utilization*
- Inhibitor Identification and Mitigation
  - *strains will need to convert sugars at ~85-90% rate from biomass deconstruction*
  - *inhibitor (acids, salts, end product, etc) tolerances needed understanding / mitigating*
  - *combination of P/T design and strain development*
- Fully Integrated, Process Relevant Demonstration Capability
  - *need to be developing strategies on relevant intermediate cellulosic sugar streams*

Approach

- National Lab, Academic and Industry R&D
  - *targeted R&D, NREL/DuPont collaboration on strain development, inhibitor mitigation*
- Strain Development Solicitation Aimed at Industry

BC Conversion to Cellulosic Ethanol
Strain Development

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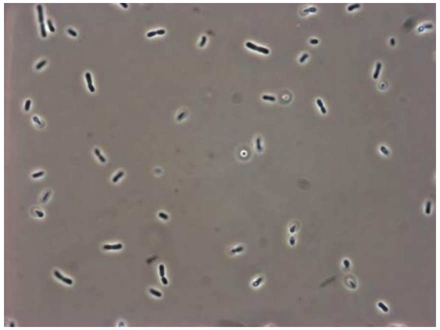
Microbial conversion of sugars to products



Development of *Zymomonas*

Introduced Xylose Utilization - 1994

Introduced Arabinose Utilization - 1995

Combined pentose utilization - 1997

Stabilization by integration - 1999

Further Development in CRADA with DuPont
2002-2007

DOE Grants to Further Strain Development (2007-2011)

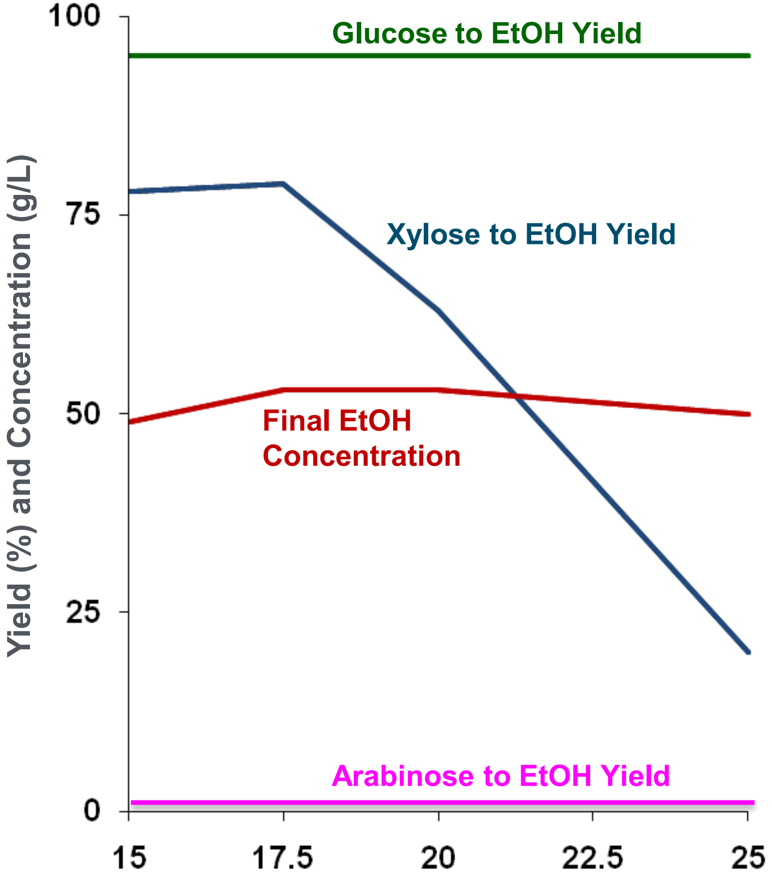
- Cargill
- Mascoma
- Purdue / ADM
- DuPont
- Verenium

BC Conversion to Cellulosic Ethanol

Fermentation - End Product Inhibition

Fermentation vs. Solids Loading

Zymomonas mobilis 8b



(~100 g/L starting sugar concentration ~150 g/L)

2010:

Zymomonas mobilis 8b (NREL)

- ~95% Glucose to Ethanol
- ~79% Xylose to Ethanol
- No arabinose conversion demonstrated at NREL
- Ethanol titer ~50 g/L

2011:

Zymomonas mobilis A7 (DuPont)

- 95% Glucose to Ethanol
- 85% Xylose to Ethanol
- 47% Arabinose to Ethanol
- Ethanol titer ~ 55 g/L

2012:

De-Acetylation / *Zymomonas mobilis A7* (DuPont)

- Decrease acetic acid and furfural dramatically
- 96-97% Glucose to Ethanol
- 93% Xylose to Ethanol
- 54% Arabinose to Ethanol
- Ethanol titer ~72 g/L

Cellulosic Ethanol
Biochemical Conversion of Corn Stover

Biomass Supply → Feedstock Logistics → Pretreatment /Conditioning → Enzymatic Hydrolysis → Fermentation → Ethanol

Production Cost Improvements: (2001 = $9.16; 2012 = $2.15)

Biomass Supply	Feedstock Logistics	Pretreatment /Conditioning	Enzymatic Hydrolysis	Fermentation	Ethanol
2001 = $1.25/gal		2001 = $1.37/gal	2001 = $4.05/gal	2001 = $0.60/gal	2001 = $1.90/gal
2012 = $0.34/gal	2012 = $0.49/gal	2012 = $0.27/gal	2012 = $0.39/gal	2012 = $0.15/gal	2012 = $0.51/gal
					(Balance of Plant)

Technology Improvements:

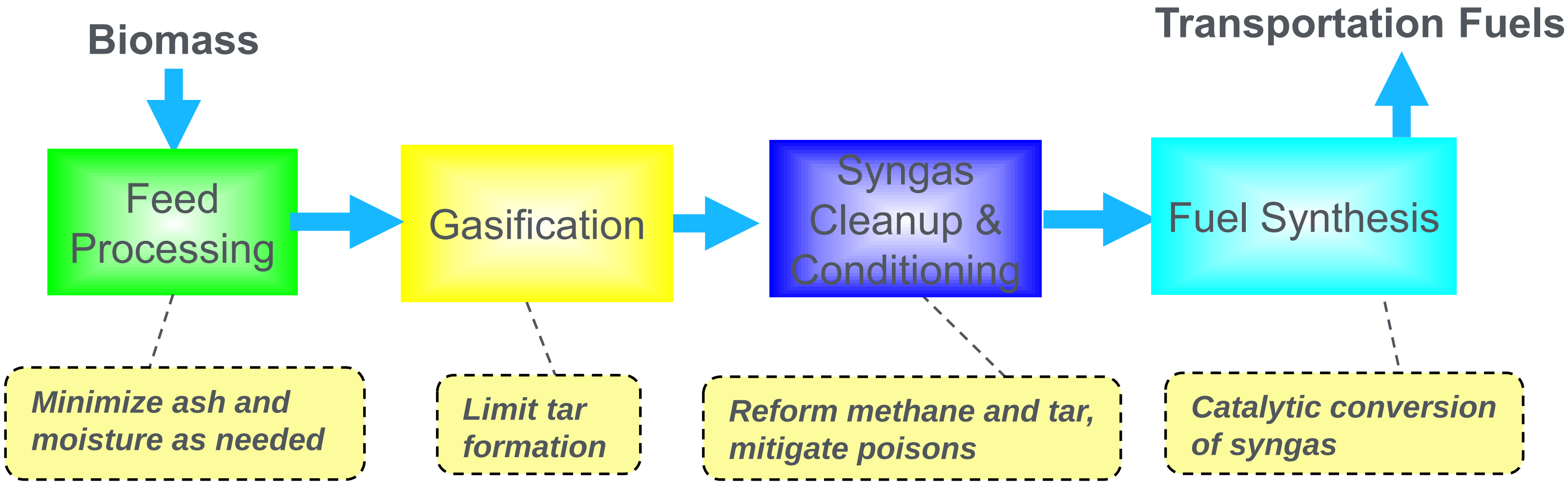
Biomass Supply	Feedstock Logistics	Pretreatment /Conditioning	Enzymatic Hydrolysis	Fermentation
Improved Biomass Supply Analysis • economic availability of feedstocks • feedstock prices specified by quantity and year • Incorporation of sustainability metrics • Development of four yield scenarios • Spatial distribution	**Better Collection Efficiency** • *43% to 75%* **Higher Bale Density** • *9.2% to 12.3%* **Lower Storage Losses** • *7.9% to 6%* **Higher Grinder Capacity** • *17.6 to 31.2 ton/hr*	**Better Xylan to Xylose Yields** • *63% to 81%* **Lower Degradation Product Formation** • *13% to 5%* **Lower Acid Usage** • *3% to 0.3%* **Reduced Sugar Losses** • *13 to <1%* **Reduced Ammonia Loading** • *decreased by >70%*	**Enzyme Cost Reductions** • *$3.45 to $0.36/gal* **Enzyme loading Reductions** • *60 to 19 mg/g* **Higher Cellulose to Glucose Yields** • *64% to 78%* **Process Efficiency Improvements** • *washed solids to whole slurry mode of hydrolysis*	**Improved Overall Ethanol Yield** • *52% to 96%* **Better Xylose to Ethanol Yields** • *0% to 93%* **Better Arabinose to Ethanol Yields** • *0% to 54%* **Improved Ethanol Tolerance** • *36 to 72 g/L titers*

Scale Improvements:

Biomass Supply	Feedstock Logistics	Pretreatment /Conditioning	Enzymatic Hydrolysis	Fermentation
National to county-level detail	Model Estimates to Field/Pilot Demonstration	Bench (1L batch) to Pilot (1 ton/day, continuous)	Bench (1 L batch) to Pilot (1 ton/day, continuous)	Bench (1L) to Pilot (8000L)

State of Technology Background

Gasification Design Report



Biomass

Feed Processing

Gasification

Syngas Cleanup & Conditioning

Fuel Synthesis

Transportation Fuels

Minimize ash and moisture as needed

Limit tar formation

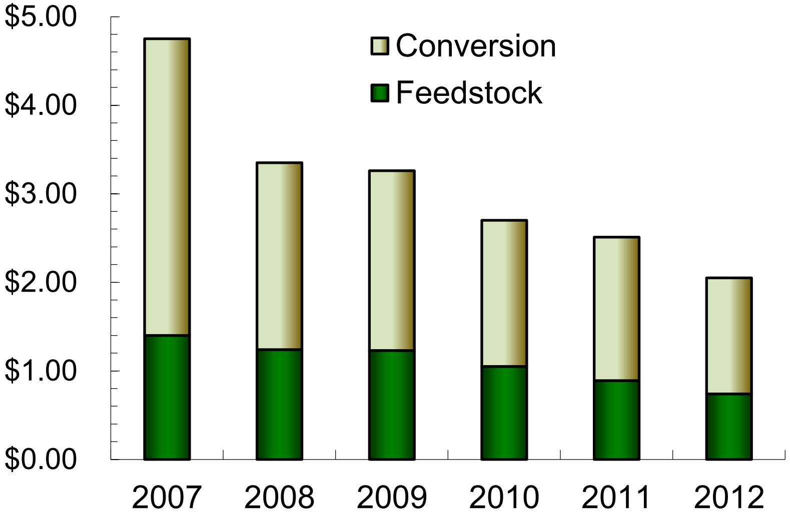
Reform methane and tar, mitigate poisons

Catalytic conversion of syngas

Biomass via synthesis gas to fuels

- Deconstruct biomass to light gases (CO & H_2)
- Convert syngas to mixed alcohols

Minimum Ethanol Selling Price



TC Conversion to Cellulosic Ethanol
Syngas Cleanup and Conditioning

Major Needs

- Identification/Development of appropriate tar/methane reforming catalyst
  - *reforming, regeneration and recycle properties important*
- Develop contaminant mitigation strategy
  - *improve catalyst robustness and/or contaminant removal/prevention*
- Fully Integrated, Process Relevant Demonstration Capability
  - *syngas specifications must be consistent with fuel synthesis needs*
  - *ability to test catalyst under process relevant conditions for long periods of time*

Approach

- National Lab and Industry R&D
  - *screening industrial reforming catalysts, development of novel catalysts, development of contaminant mitigation strategies, development of catalyst regeneration protocols*
  - *design/build of pilot scale catalyst regeneration capabilities at NREL*

TC Conversion to Cellulosic Ethanol
Syngas Cleanup Challenges and Approach

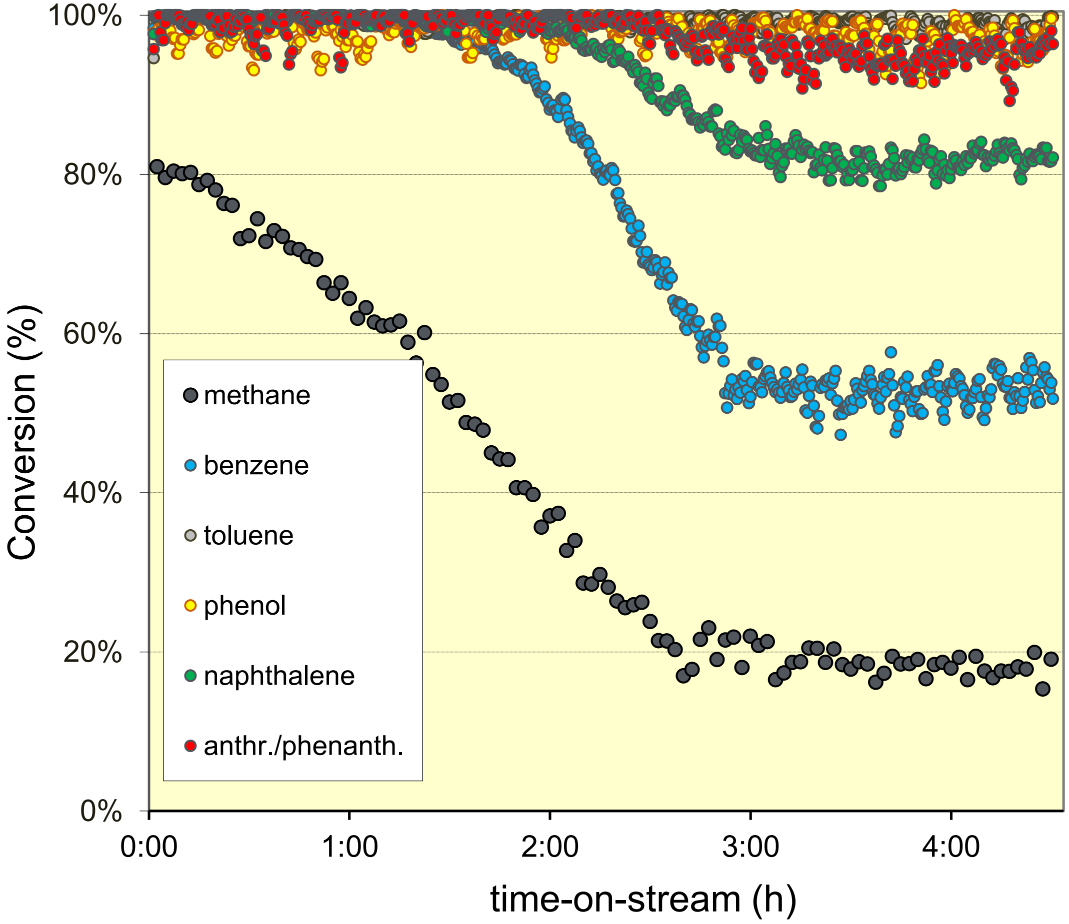
Fundamental Challenge:

Untreated syngas from biomass contains contaminants that poison tar cracking/methane reforming catalysts.

General Approaches:

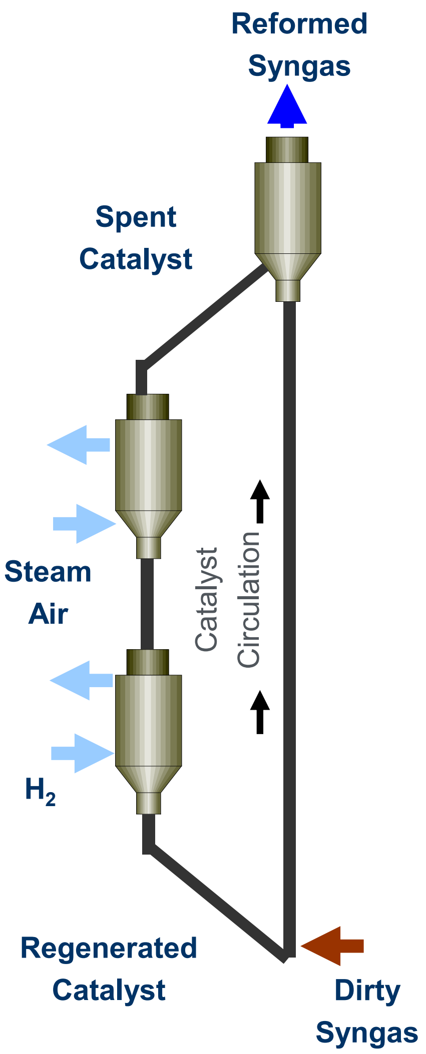
- Reduce contaminants before catalytic reforming
  - *Frequent/continuous regeneration of existing hot gas sorbents*
  - *Development of contaminant resistant hot gas sorbents*
- Crack tars/reform methane with contaminants present
  - *Frequent/continuous regeneration of existing catalysts*
  - *Development of contaminant resistant catalysts*
- Develop a process utilizing some combination of the approaches

TCPDU Reforming Catalyst Performance



TC Conversion to Cellulosic Ethanol
Reforming Catalyst Regeneration Strategy

Catalyst Regeneration Strategy



Reformed Syngas

Spent Catalyst

Steam

Air

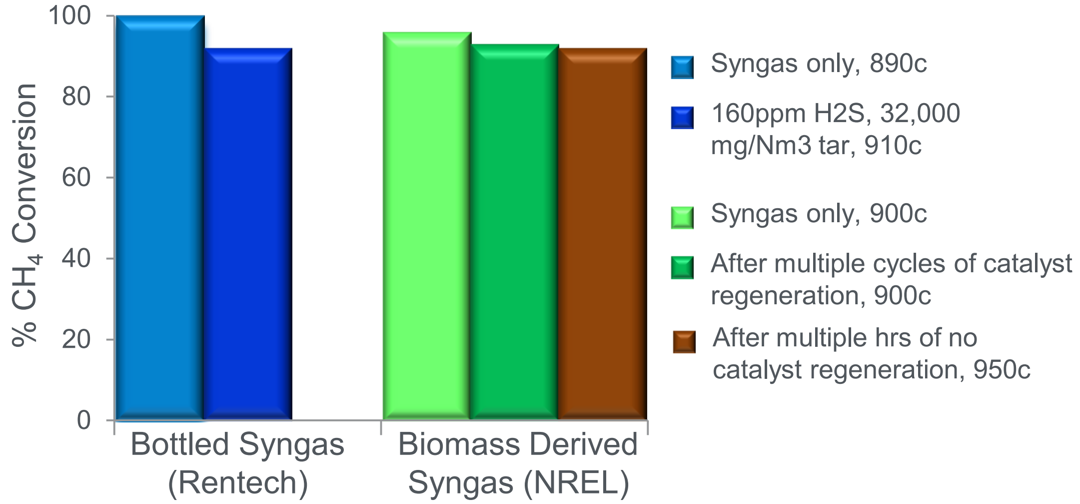
H$_2$

Catalyst Circulation

Regenerated Catalyst

Dirty Syngas

Methane Conversion During Continuous Regeneration



Hypothesis: Ni-alumina reforming catalyst is regenerable after reaction with H_2S in raw syngas

- Regenerability extent determined by contact time and process conditions (gas compositions, temperature)
- Industrial collaborator demonstrated > 92% CH_4 conversion under regenerating conditions after 100 hrs (spiked bottled syngas) - 2009
- NREL demonstrated > 90% CH_4 conversion after multiple regeneration cycles at typical temperatures and >90% CH_4 conversion with no regeneration at higher temperatures – 2010/11
- Applying optimum regeneration strategy at scale -2011/12

TC Conversion to Cellulosic Ethanol

Mixed Alcohol Synthesis

Major Needs

- Development of Alcohol Synthesis Catalyst
  - *major improvements in both selectivity and productivity needed*
  - *minimize methanol and hydrocarbon production*
  - *nothing commercially available; even literature data sparse*
  - *needs to be compatible with syngas stream from biomass*
- Integrated Testing Capabilities Needed
  - *catalyst development capabilities (bench and/or pilot scale) and syngas generation from biomass capabilities not co-located anywhere*
- Model Development to Incorporate Recycle Streams

Approach

- National Lab and Industry R&D
  - *strategy to pursue 2 classes of alcohol synthesis catalysts (Rh based and MoS_2 based)*
  - *utilization of high throughput catalyst screening (small scale) capabilities at PNNL*
  - *development of bench (and eventually pilot) scale long run testing capabilities at NREL*
  - *strong collaboration with Dow to incorporate kinetic models for material recycle into state of technology cost models*

TC Conversion to Cellulosic Ethanol

Rh vs MoS_2 based catalysts

General Characteristics:

Rhodium Based	Molybdenum Sulfide Based
C2+ alcohol productivity (200-400 g/kg/hr)	C2+ alcohol productivity (300 g/kg/hr)
High C2+ oxygenates productivity (500-900 g/kg/hr)	Low C2+ oxygenates productivity (<50 g/kg/hr)
lower pressure (<1100 psig)	higher pressure (2000 psig)
low MeOH (single pass) (< 3% MeOH)	higher MeOH (single pass) (>25% MeOH)
lower selectivity to EtOH (Makes mixed oxygenates)	higher selectivity to EtOH
more contaminant sensitive (No sulfur)	less contaminant sensitive (Requires S)
higher initial catalyst cost	Lower initial catalyst cost
significant CH_4 byproduct (20-30%)	lower CH_4 byproduct (10-15%)

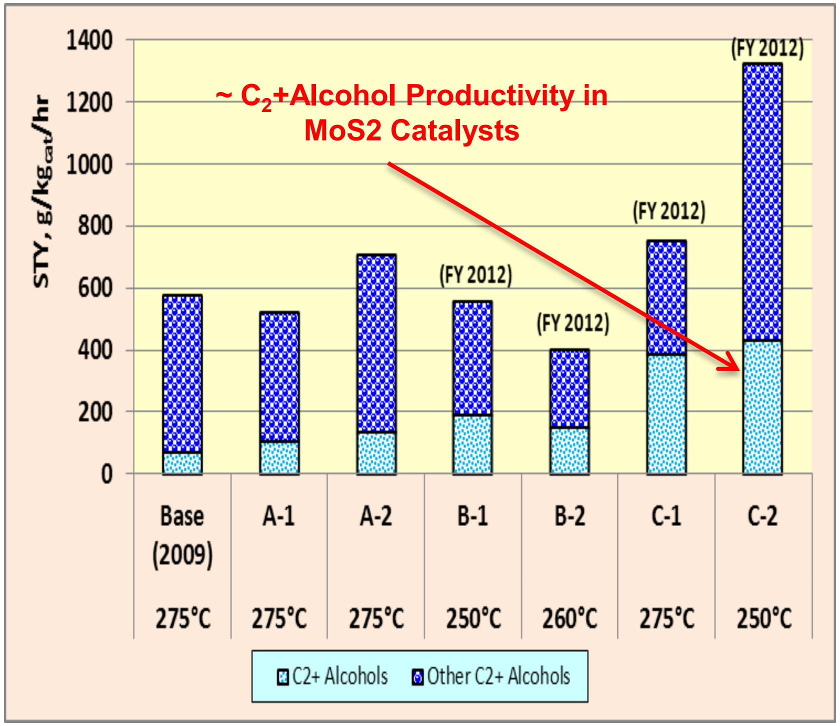
Strategy:

- PNNL pursue development of Rh catalyst and NREL/Industrial partner pursue MoS_2 catalyst

TC Conversion to Cellulosic Ethanol

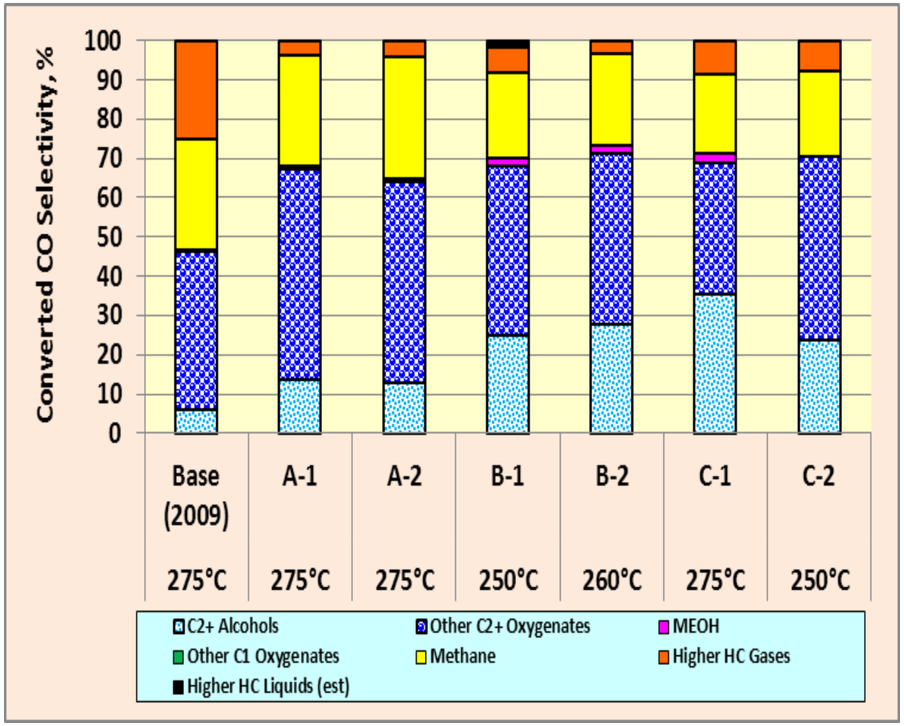
Rh Catalyst Development

Productivity



~ C_2+Alcohol Productivity in MoS2 Catalysts

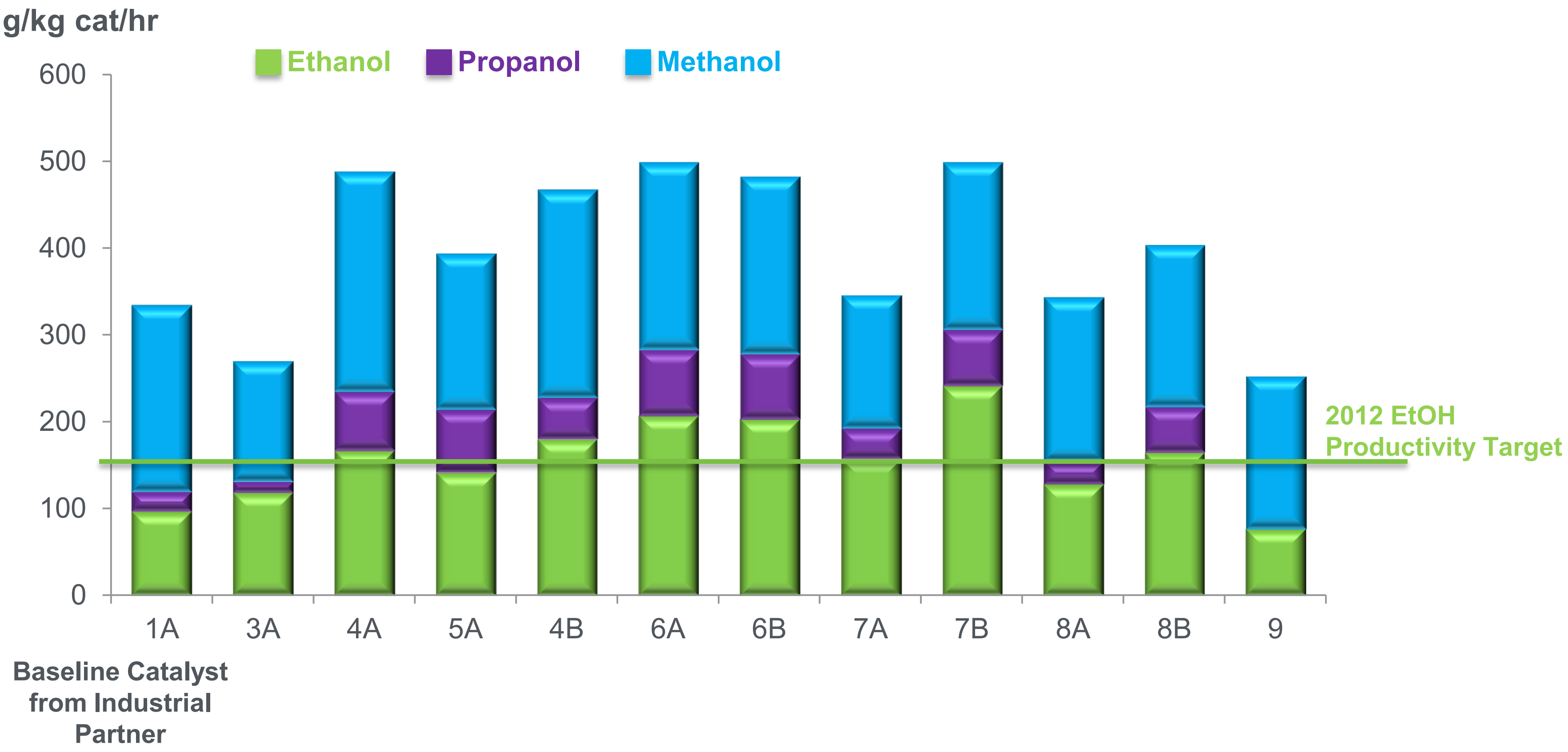
Selectivity



- Significant improvements made in productivity and selectivity to oxygenates
- High productivity to oxygenates in general
- Would need a way to capture value/yield for non-alcohol oxygenates and methane recycle
- Would need scale up validation (heat transfer, contaminant robustness, production, etc)

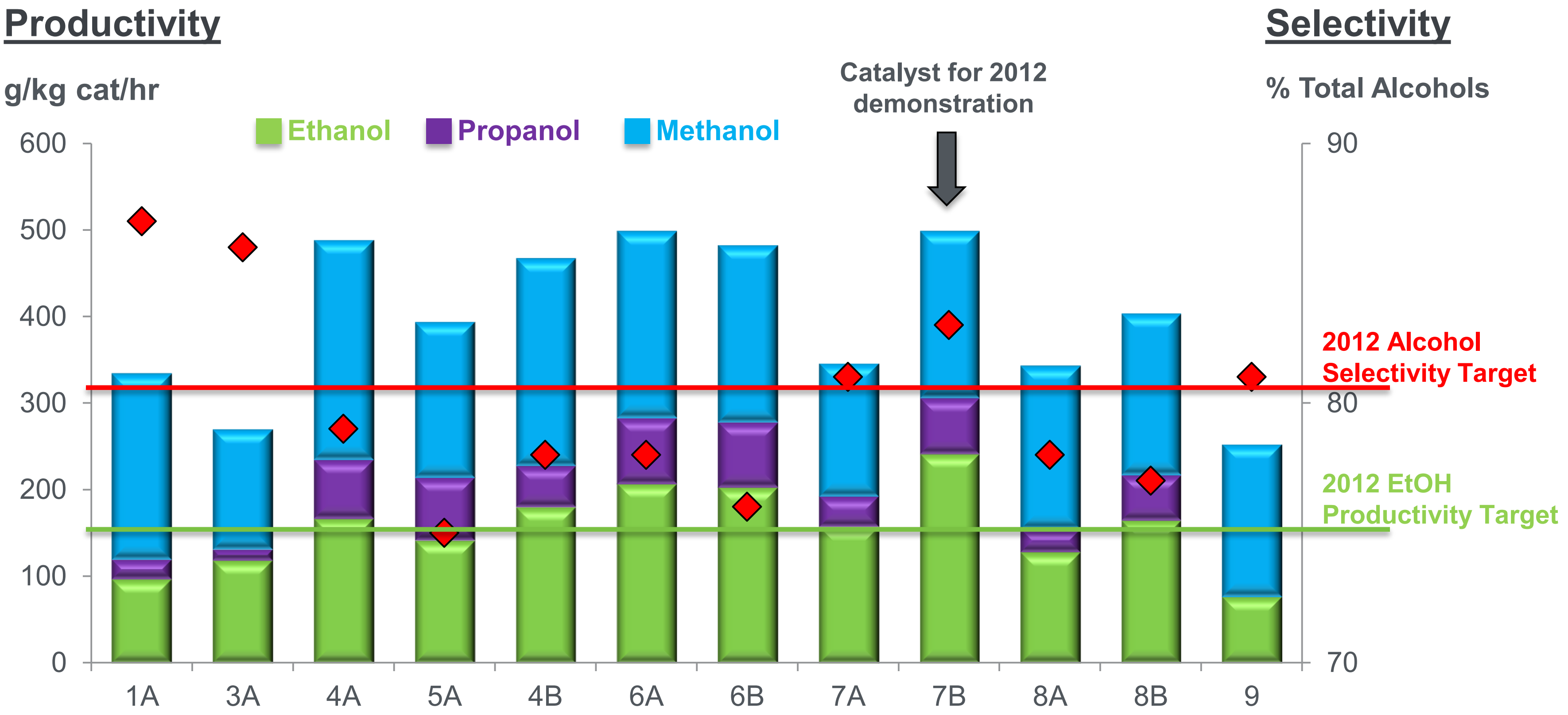
TC Conversion to Cellulosic Ethanol
MoS$_2$ Catalyst Development

Productivity



TC Conversion to Cellulosic Ethanol

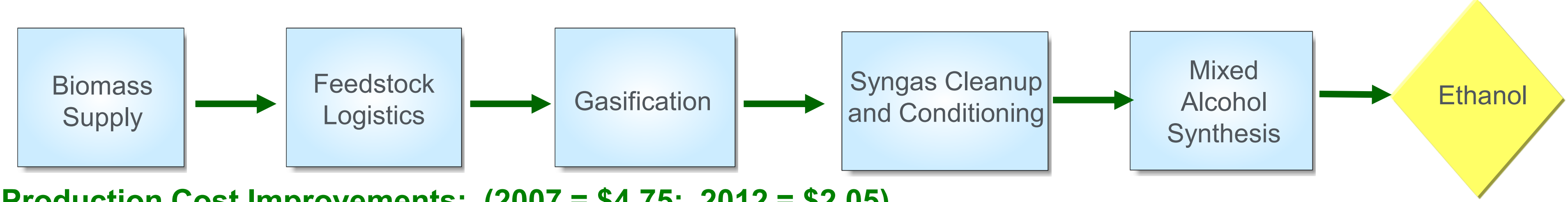
MoS_2 Catalyst Development



- Industrially relevant catalyst and corresponding kinetic model to quantify recycle
- Improved productivity and selectivity to meet 2012 targets at lower pressure
- Compatible with upstream syngas purity (e.g. more sulfur tolerant)
- Pilot scale testing equipment available at NREL

Cellulosic Ethanol

Thermochemical Conversion of Woody Biomass



Production Cost Improvements: (2007 = $4.75; 2012 = $2.05)

Biomass Supply / Feedstock Logistics: 2007 = $1.40/gal

2012 = $0.17/gal

2012 = $0.56/gal

2007 = $0.37/gal
2012 = $0.28/gal

2007 = $1.49/gal
2012 = $0.35/gal

2007 = $1.52/gal
2012 = $0.69/gal

2007 = ($0.03)/gal
2012 = $0.00/gal
(Balance of Plant)

Technology Improvements:

Improved Biomass Supply Analysis

- Economic availability of feedstocks
- Feedstock prices specified by quantity and year
- Sustainability metrics
- Development of four yield scenarios
- Spatial distribution

Increased Harvest Efficiency
- *65% to 80%*

Improved Collection Efficiency
- *65% to 75%*

Decreased Moisture During Transport
- *50% to 30%*

Increased Grinder Efficiency
- *65% to 75%*

Economic Analysis of Available Gasifiers
- *Impact of gasifier type, scale and produced syngas composition*

Better Understanding of Biomass Gasification Fundamentals
- *chemistry mechanisms, flow characteristics and feedstock variability*

Development of Analytical Methodology
- *Comprehensive tar and heteroatom quantification*

Improved Methane Conversion
- *20% to 80%*

Improved Tar Conversion
- *80% to 99%*

Lower Catalyst Replacement Rate
- *1 to 0.15% per day*

Optimized Catalyst Reforming and Regeneration
- *enables continuous operation*

Higher Ethanol Productivity
- *101 to >160 g/kg/hr*

Improved Overall Ethanol Yield
- *62 to >84 gal/ton*

Improved Repeatability

Decreased Cost of Catalyst Production

Scale Improvements:

National to county-level detail

Model Estimates to Field/Lab Tests

Pilot (1 ton/day)

Bench (g) to Pilot (1000 kg)

Bench (g) to Pilot (kg)

Conversion to Cellulosic Ethanol

Summary

2012 Cellulosic Ethanol Successful Demonstrations

- Developed pretreatment/conditioning strategy (bench and pilot scale) capable of releasing >80% of the hemicellulosic sugars in whole slurry mode
- Reduced Enzyme Costs >20x and developed strategy for further reductions
- Developed Industrially Relevant Strains Capable of Converting C_5 and C_6 Cellulosic Sugars at total conversion yields >95% and tolerant of ethanol titers of ~72 g/L
- Developed Syngas Cleanup Conditioning Catalyst/Strategy suitable for biomass
- Developed Mixed Alcohol Synthesis Catalyst suitable for biomass derived syngas
- Built/adapted fully integrated pilot scale capabilities for 2012 demonstration
- Demonstrated Cost Reductions that make cellulosic ethanol production cost competitive with gasoline production at ~$110/bbl crude oil
- Commercial demonstrations of similar design coming online

Leveragability to Hydrocarbons

- Biomass to sugar and syngas intermediate technologies still applicable
- Compositional analysis techniques fully applicable
- Pilot/bench scale equipment easily re-purposed
- Downstream technology development and integration needed

Cellulosic Ethanol Cost Target

Questions?