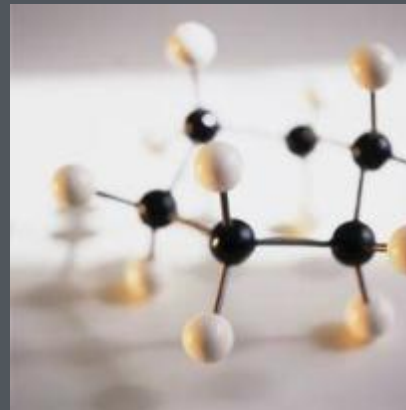


# Review of Recent Pilot Scale Cellulosic Ethanol Demonstration

U.S. DEPARTMENT OF  
**ENERGY**

Energy Efficiency &  
Renewable Energy

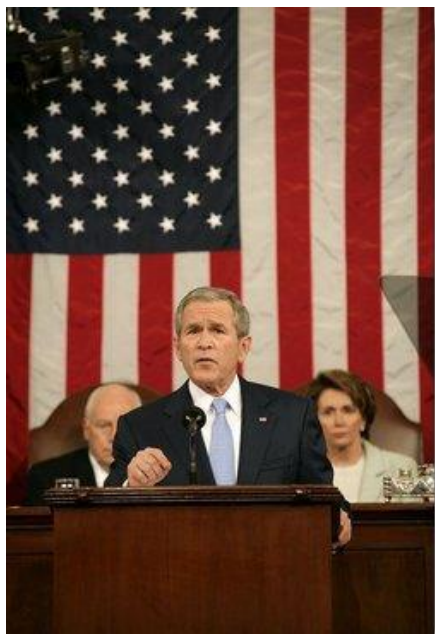


**Biomass 2013**

Cellulosic Technology Advances

July 31, 2013

Thomas Foust, Adam Bratis  
Director, Biomass Programs  
National Renewable Energy  
Laboratory (NREL)



### **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

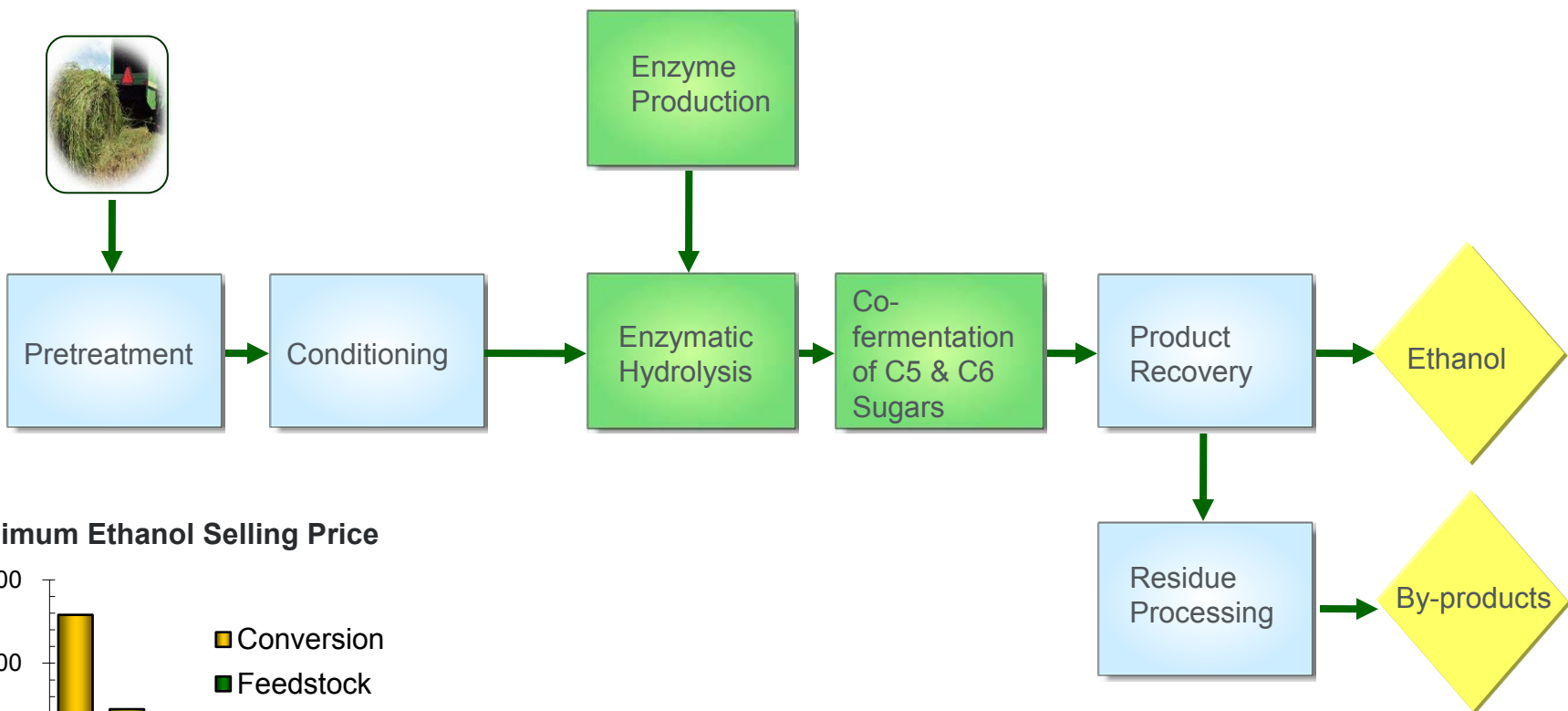
- **Original 2012 cost target (\$2002) was based on competitiveness with corn ethanol (2006 timeframe)**
  - *Historic corn prices were ~\$2-3/bushel giving an initial target of \$1.07 that eventually inflated (\$2007) to \$1.33/gal ethanol*
  - *Roughly equivalent to gasoline production at \$65/BBL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

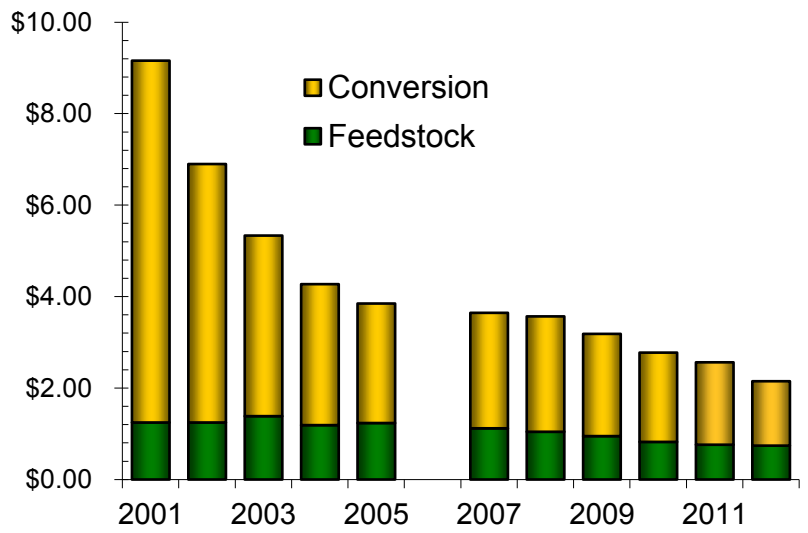
- **Original Design Reports updated to ~\$2.00/gal target (2011 timeframe)**
  - *Total bottoms up approach with no end cost target in mind*
  - *Incorporation of state of the art knowledge on capital costs, financing assumptions, process design*
  - *Roughly equivalent to gasoline production at \$110/BBL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

## 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*



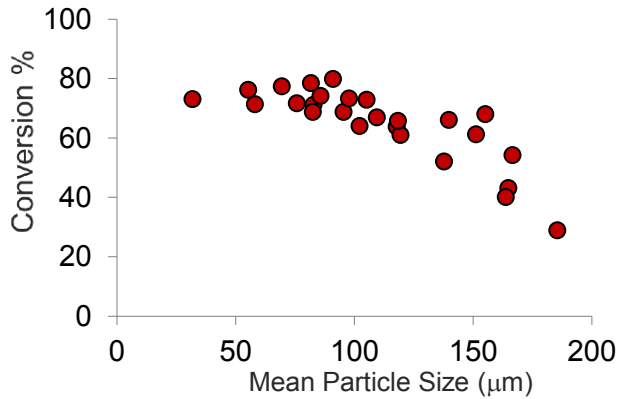
# BC Conversion to Cellulosic Ethanol

## Cellulose to Sugars ( $C_6$ )

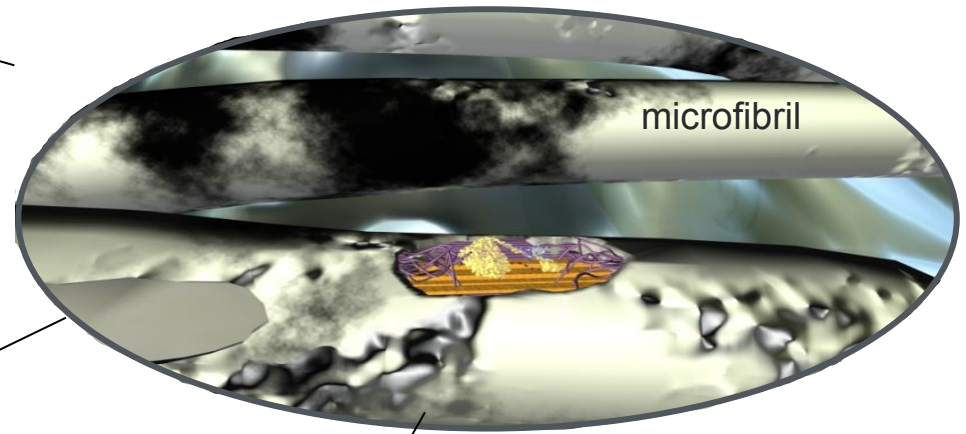
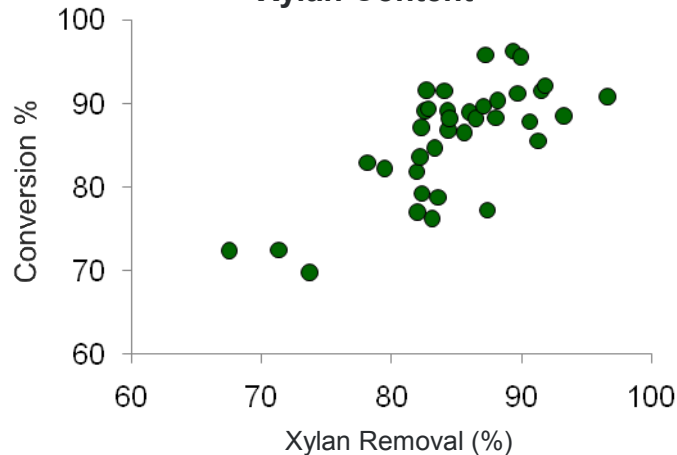
### Objectives

- 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**



**Xylan Content**



**Other Factors**

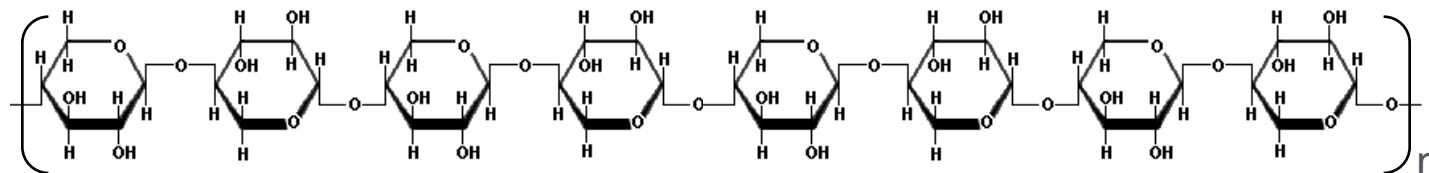
### **Quantification of Impact**

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

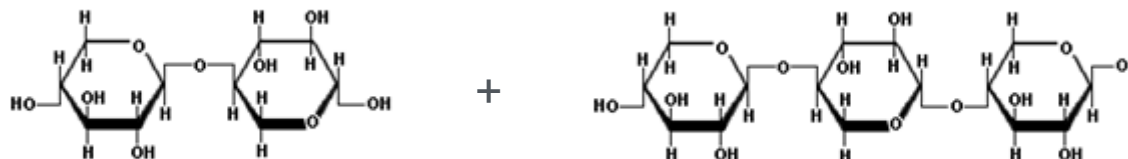
# BC Conversion to Cellulosic Ethanol

## Hemicellulose to Sugars (C<sub>5</sub>)

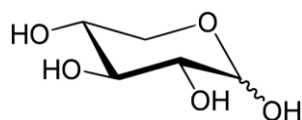
Xylan



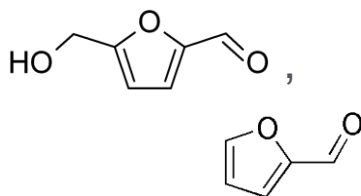
Oligomeric Xylose



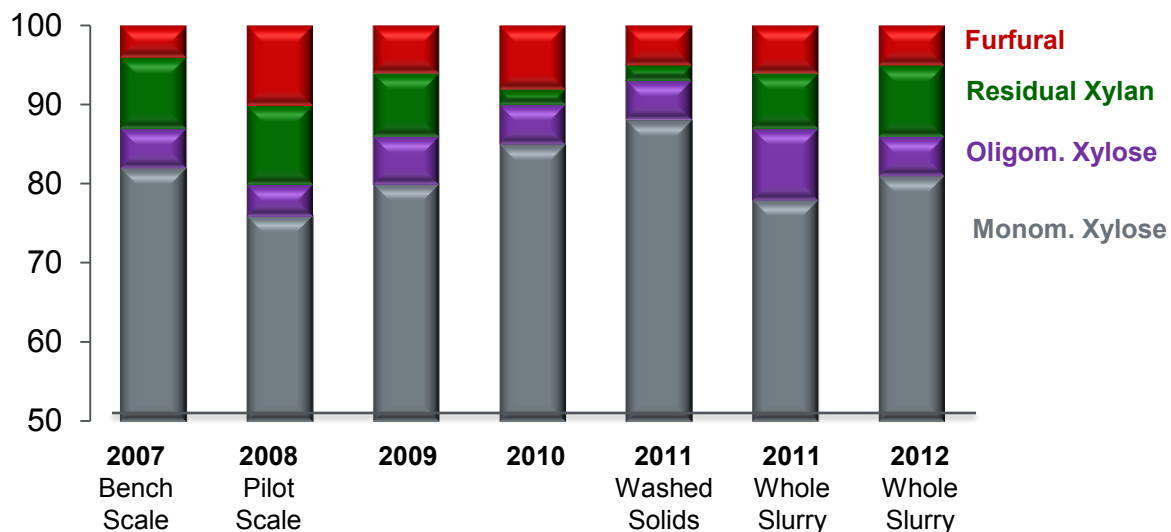
Monomeric Xylose



Degradation Products



Experimental Results from High-Solids Pretreatment



## 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<sub>6</sub> and C<sub>5</sub> 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

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

– Focus: lower production cost, increase enzyme system efficacy

$$\text{Enzyme cost (\$/gallon EtOH)} = \text{Prod. Cost (\$/kg)} \times \text{Usage Req. (kg/gallon EtOH)}$$

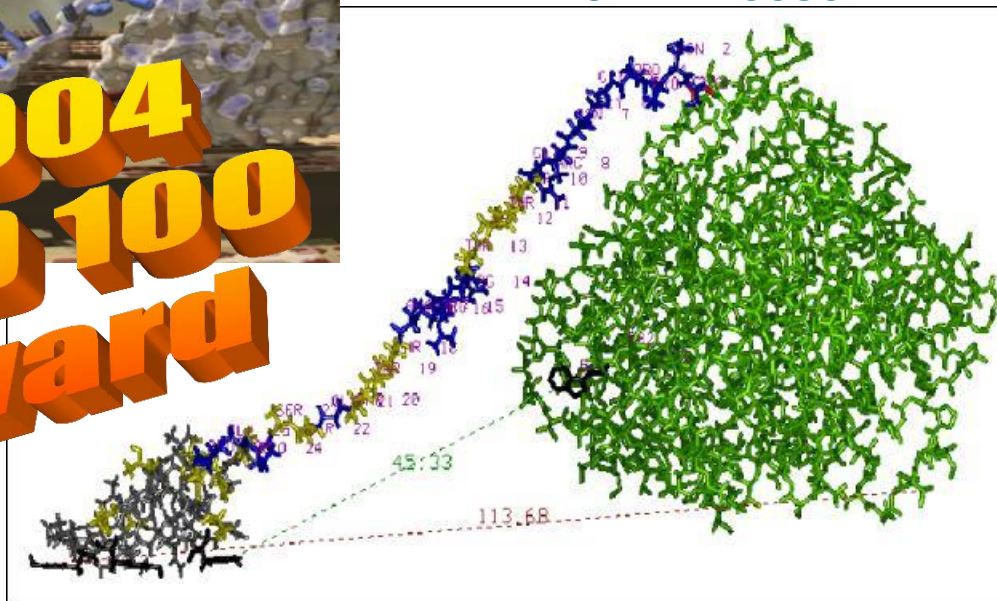
– Cellulase cost reduced 20 fold

**2<sup>nd</sup> round of DOE grants started in 2008 (DSM, Genencor, Novozymes, Verenum)**

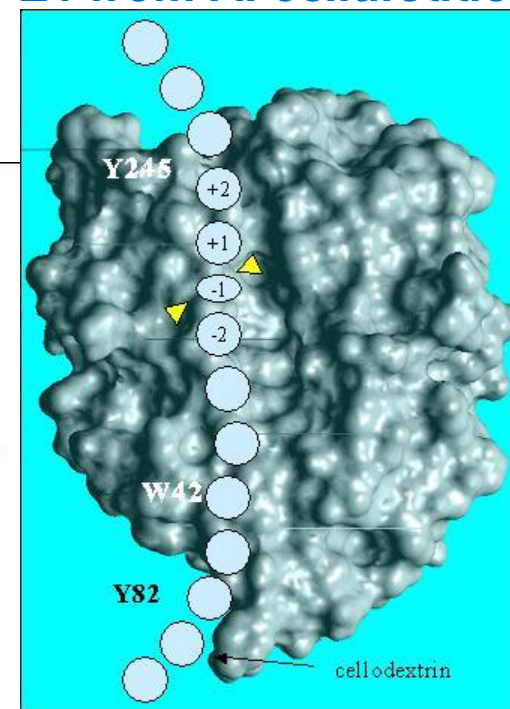


**2004  
R&D 100  
Award**

**CBH1 from *T. reesei***

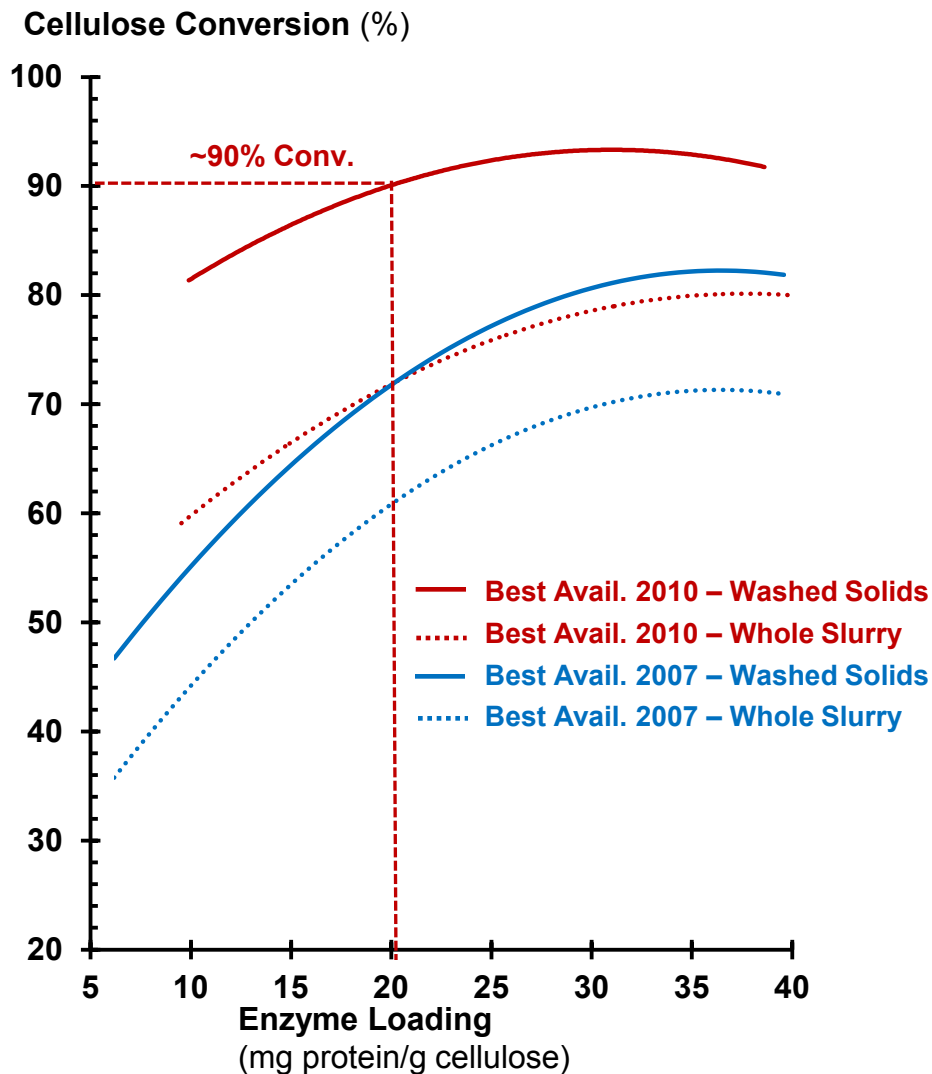


**E1 from *A. cellulotiticus***



# BC Conversion to Cellulosic Ethanol

## Enzymatic Saccharification



### 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)

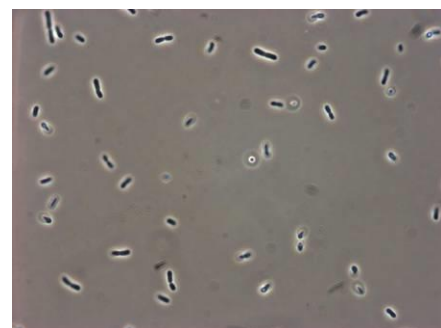
## Major Needs

- C<sub>5</sub> 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

## 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

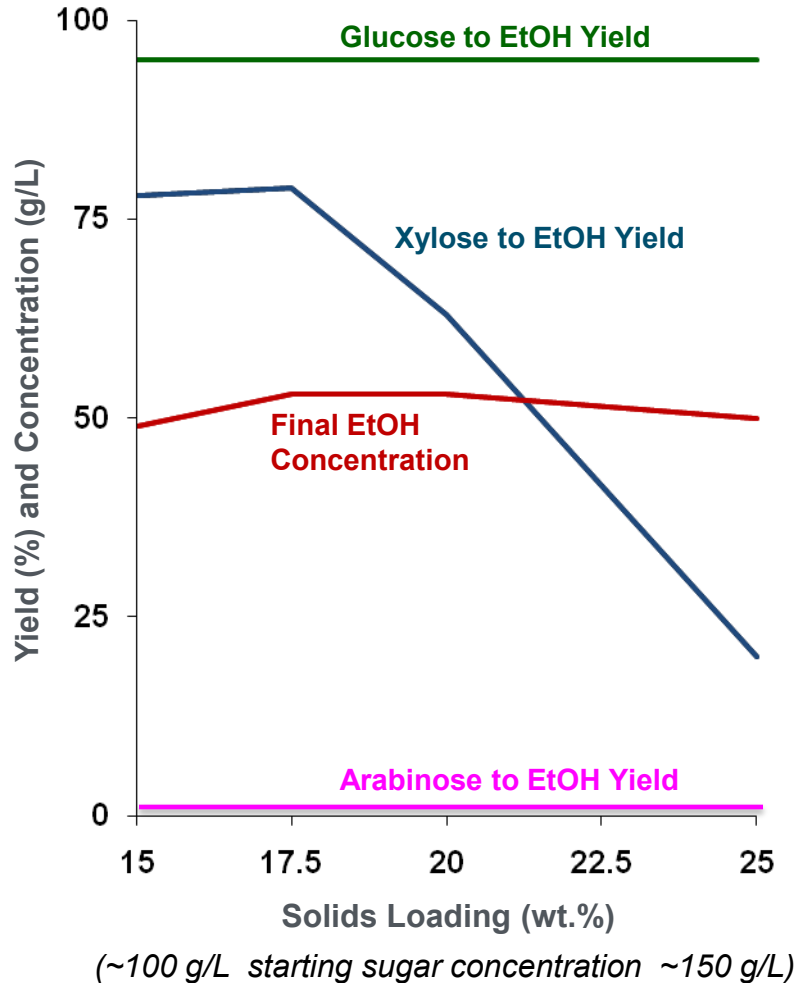


*The miracles of science™*



# BC Conversion to Cellulosic Ethanol Fermentation - End Product Inhibition

## Fermentation vs. Solids Loading *Zymomonas mobilis 8b*



### 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

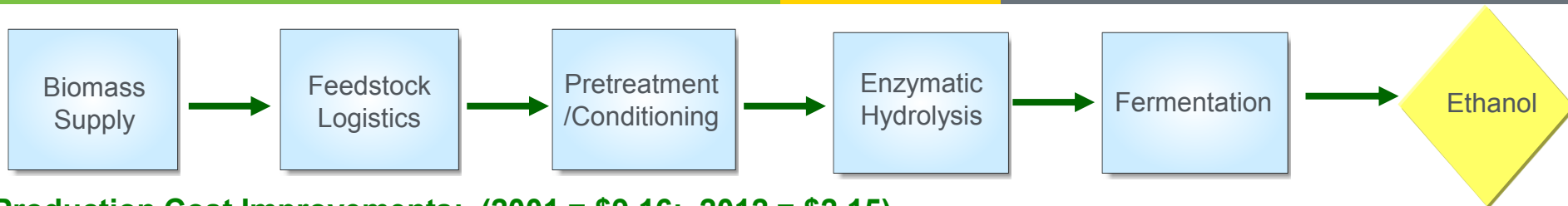
### 2012:

#### 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



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

2001 = \$1.25/gal  
2012 = \$0.34/gal

2012 = \$0.49/gal

2001 = \$1.37/gal  
2012 = \$0.27/gal

2001 = \$4.05/gal  
2012 = \$0.39/gal

2001 = \$0.60/gal  
2012 = \$0.15/gal

2001 = \$1.90/gal  
2012 = \$0.51/gal  
(Balance of Plant)

### Technology Improvements:

#### 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:

National to county-level detail

Model Estimates to Field/Pilot Demonstration

Bench (1L batch) to Pilot (1 ton/day, continuous)

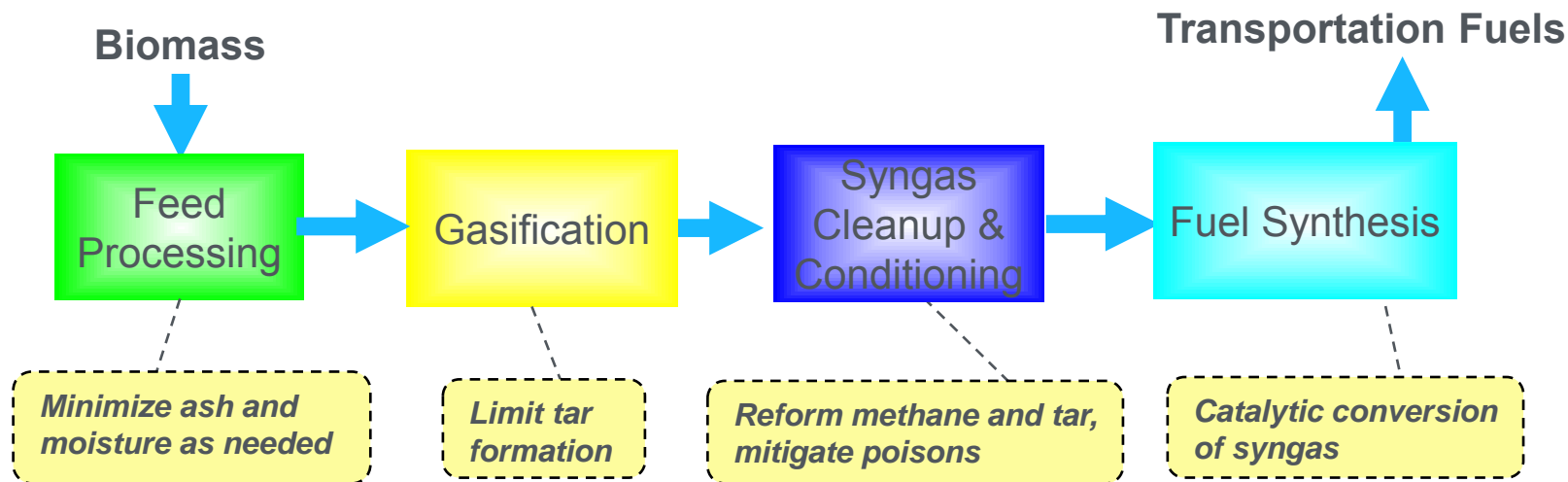
Bench (1 L batch) to Pilot (1 ton/day, continuous)

Bench (1L) to Pilot (8000L)



# State of Technology Background

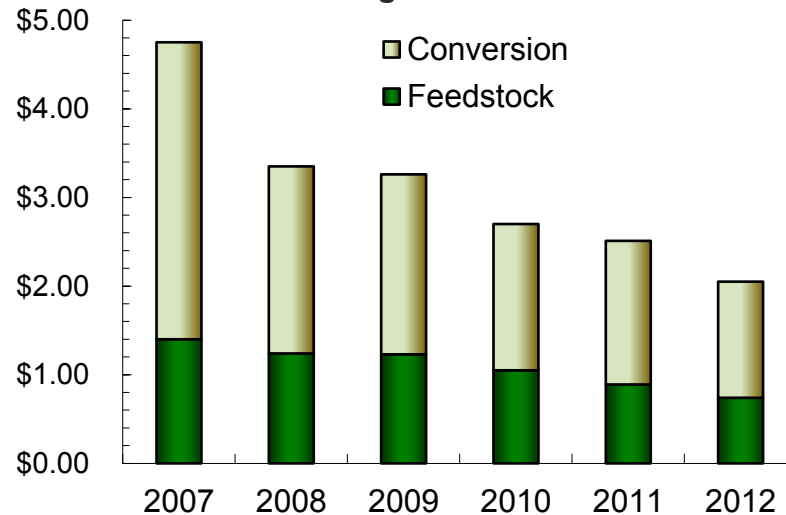
## Gasification Design Report



## Biomass via synthesis gas to fuels

- Deconstruct biomass to light gases (CO & H<sub>2</sub>)
- Convert syngas to mixed alcohols

Minimum Ethanol Selling Price



## 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

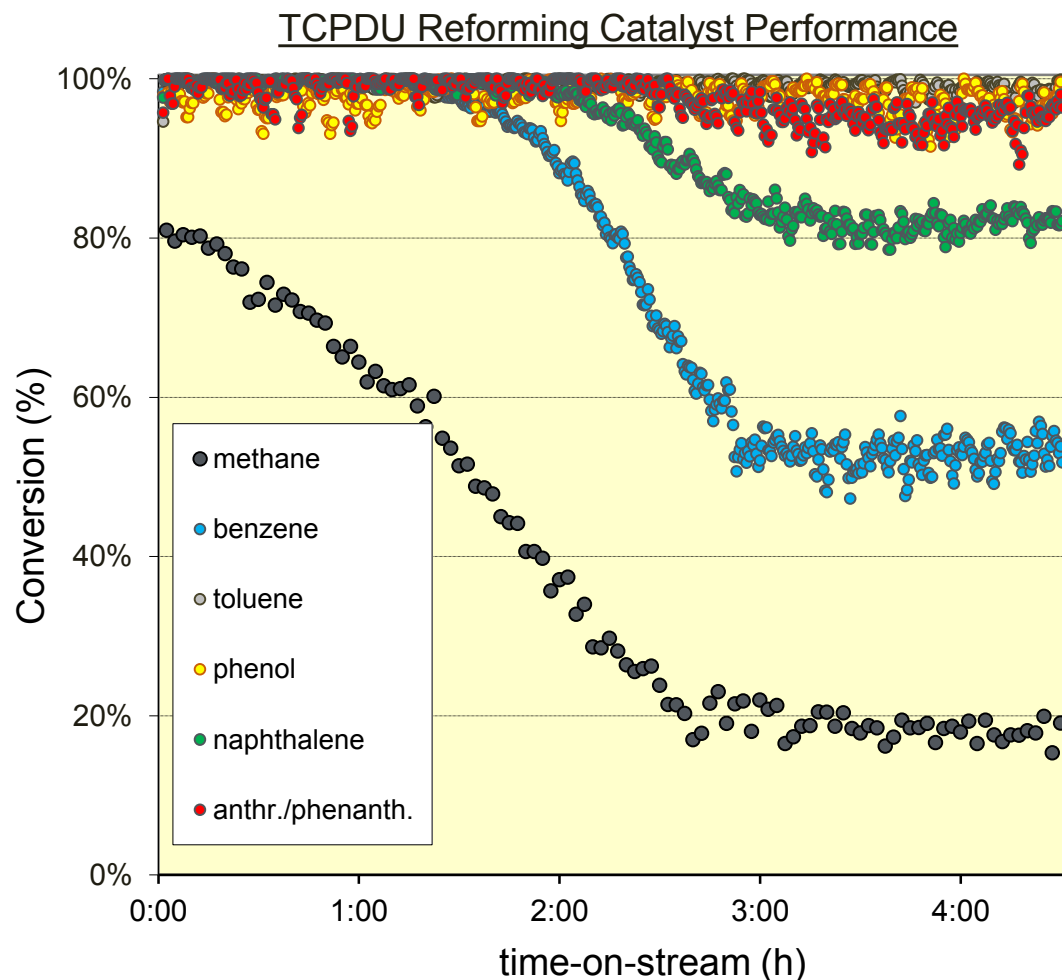
## Syngas Cleanup Challenges and Approach

### Fundamental Challenge:

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

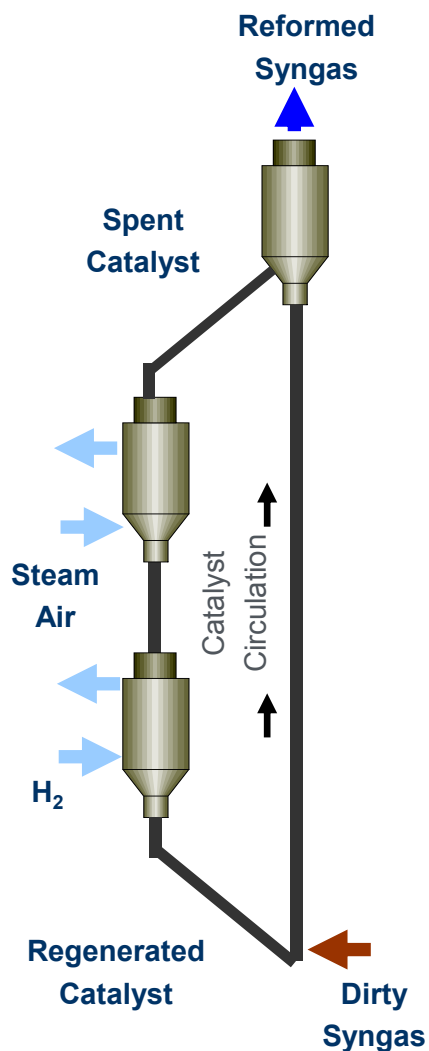
### General Approaches:

- 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

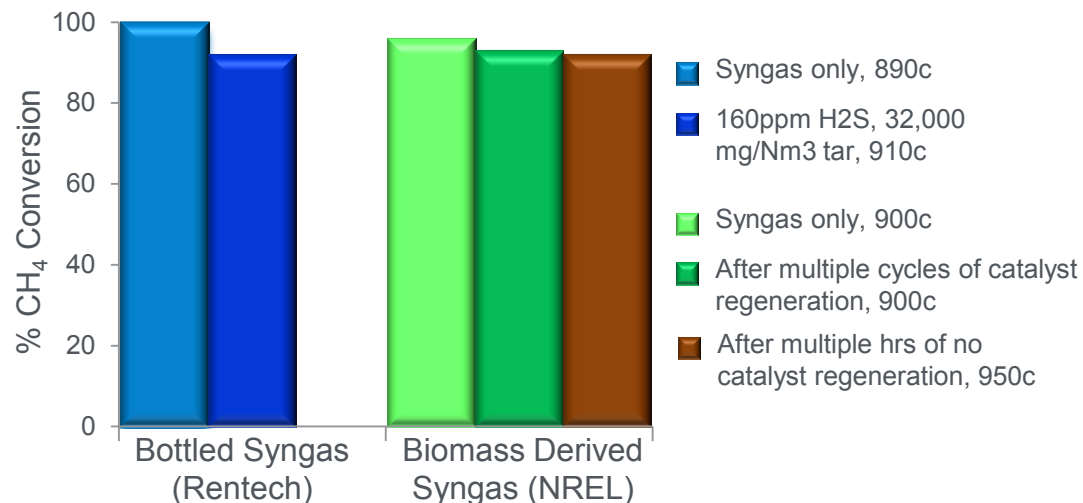


# TC Conversion to Cellulosic Ethanol Reforming Catalyst Regeneration Strategy

## Catalyst Regeneration Strategy



## Methane Conversion During Continuous Regeneration



Hypothesis: Ni-alumina reforming catalyst is regenerable after reaction with H<sub>2</sub>S in raw syngas

- Regenerability extent determined by contact time and process conditions (gas compositions, temperature)
- Industrial collaborator demonstrated > 92% CH<sub>4</sub> conversion under regenerating conditions after 100 hrs (spiked bottled syngas) - 2009
- NREL demonstrated > 90% CH<sub>4</sub> conversion after multiple regeneration cycles at typical temperatures and >90% CH<sub>4</sub> conversion with no regeneration at higher temperatures – 2010/11
- Applying optimum regeneration strategy at scale -2011/12

## 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<sub>2</sub> 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<sub>2</sub> 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 <sub>4</sub> byproduct (20-30%)	lower CH <sub>4</sub> byproduct (10-15%)

### Strategy:

- PNNL pursue development of Rh catalyst and NREL/Industrial partner pursue MoS<sub>2</sub> catalyst



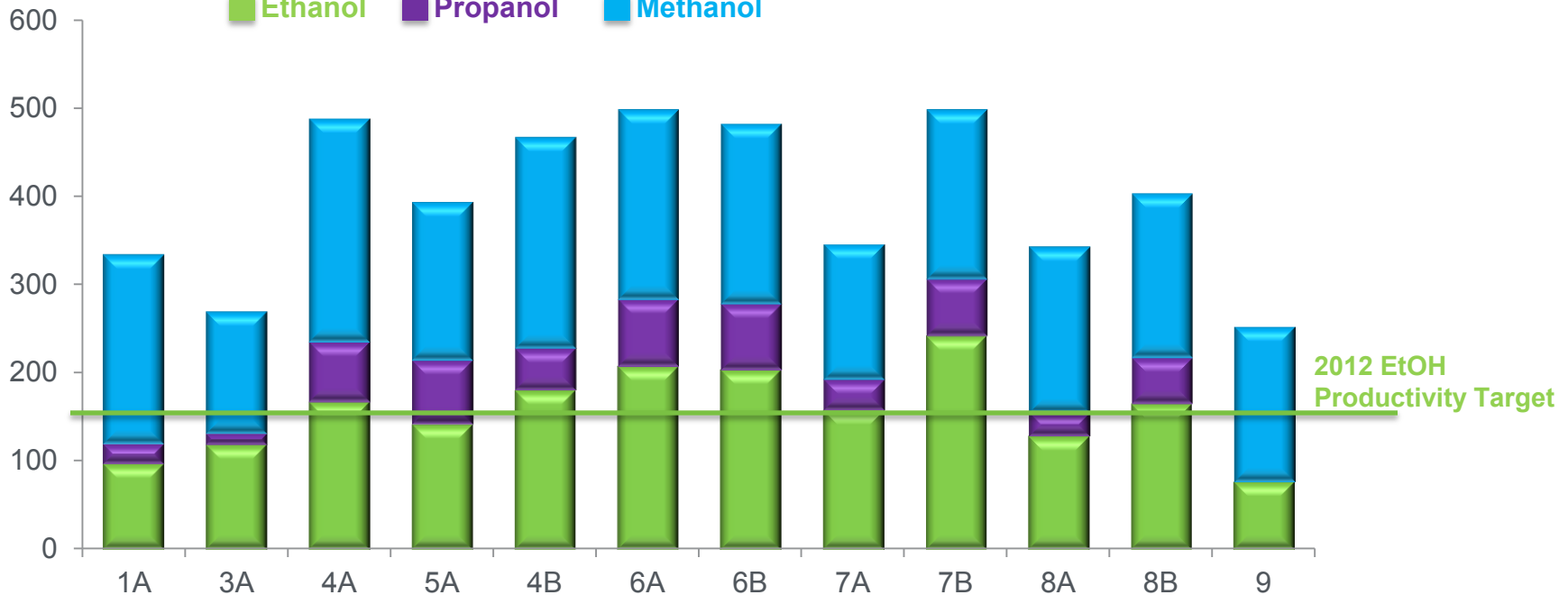
# TC Conversion to Cellulosic Ethanol

## *MoS<sub>2</sub> Catalyst Development*

### Productivity

g/kg cat/hr

■ Ethanol ■ Propanol ■ Methanol



Baseline Catalyst from Industrial Partner

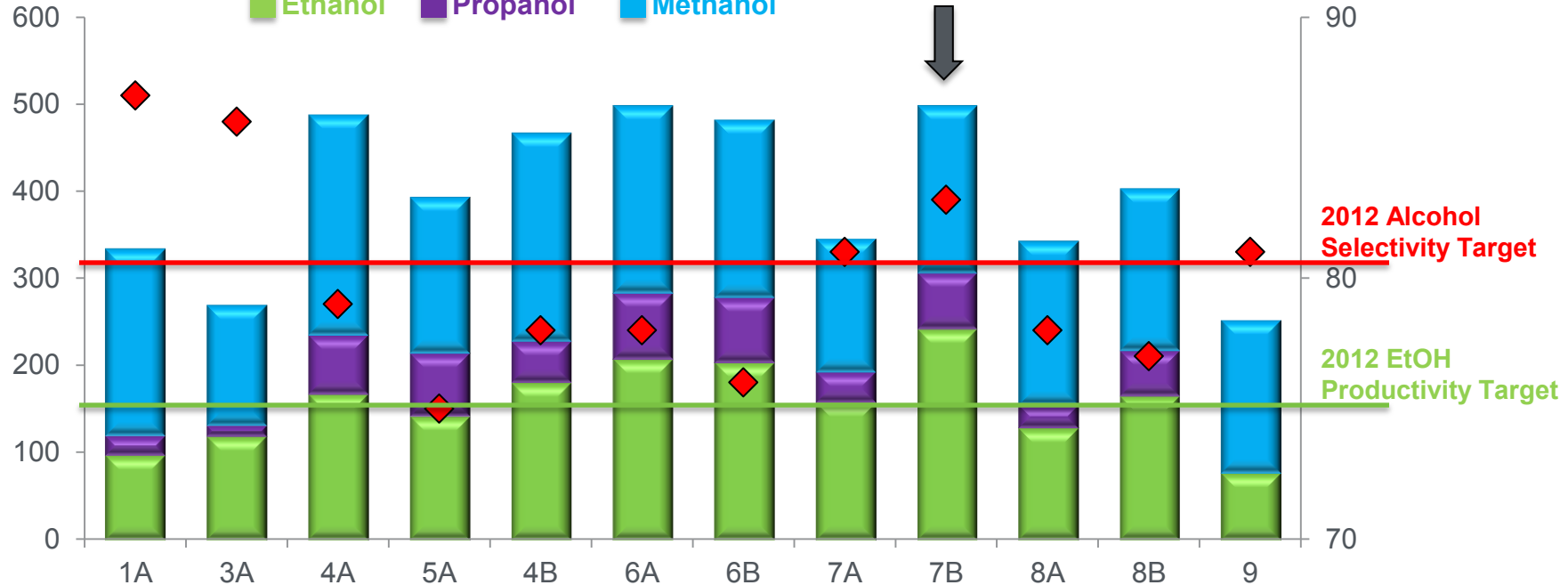
# TC Conversion to Cellulosic Ethanol

## MoS<sub>2</sub> Catalyst Development

### Productivity

g/kg cat/hr

Ethanol Propanol Methanol



### Selectivity

% Total Alcohols

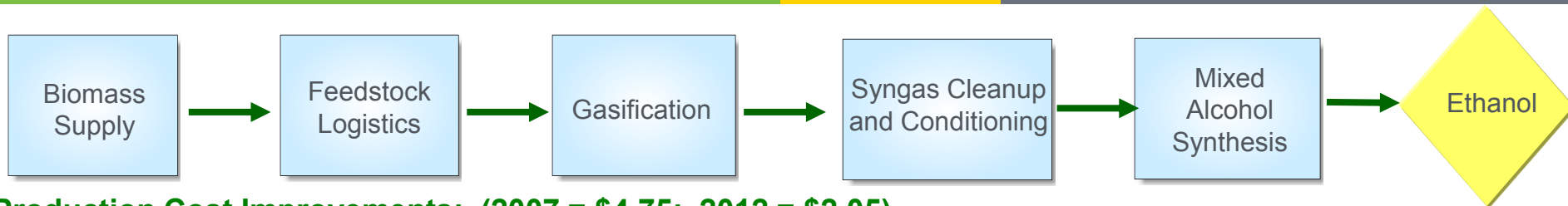
2012 Alcohol  
Selectivity Target

2012 EtOH  
Productivity Target

- 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)

2007 = \$1.40/gal 2012 = \$0.17/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)
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### 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)

## 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<sub>5</sub> and C<sub>6</sub> 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





# Questions?