# 2009 DOE Hydrogen Program

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## Hydrogen Generation from Biomass-Derived Carbohydrates via the Aqueous-Phase Reforming Process

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Project ID # PD_03_Rozmiarek

# Overview

## Timeline

- Start – September 2005
- Finish – September 2009
- Percent complete ~ 85%

## Barriers

| Barriers Addressed | | |
|---|---|---|
| A) Reformer Capital Cost | C) O&M | |
| D) Feedstock Issues | E) Greenhouse Gas Emissions | |
| **Targets** | **2012** | **2017** |
| Production Unit Capital Cost | $1 million | $600 k |
| Feedstock Cost Reduction | $2.10 / gge | $1.55 / gge |
| Total $H_2$ Cost | $3.80 / gge | < $3.00 / gge |

## Budget

- Total project funding
  - DOE share – 1,954 K
  - Contractor share – 676 K
- Funding received in FY2008 – 1,125k
- Funding for 2009 – 415 k

## Partners

- Interactions/ collaborations
  - ADM
  - University of Wisconsin

# Renewable Hydrogen Production Using Sugars and Sugar Alcohols

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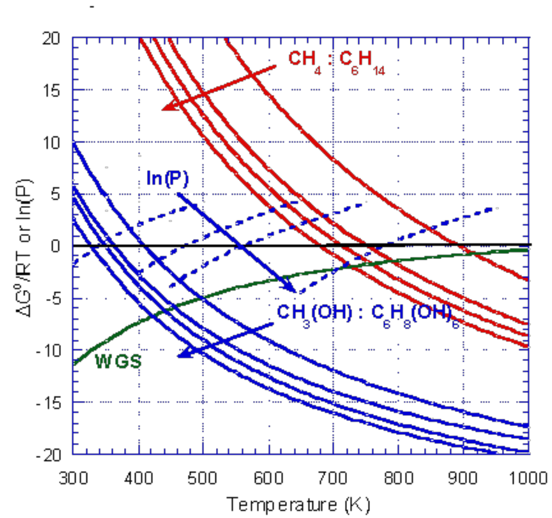
- **Problem:** Need to develop renewable hydrogen production technologies that utilize diverse feedstocks.

- **Relevance:** The BioForming® process is a platform that enables the use of renewable sugar and sugar alcohol feedstocks for hydrogen production, reducing greenhouse gas emissions compared to traditional $H_2$ production technologies.

- **Description:** The process uses aqueous phase reforming (APR) to cost effectively produce hydrogen from a range of feedstocks. The key breakthrough is a proprietary catalyst that operates in the aqueous phase and has high hydrogen selectivity at low temperature.

- **Impact:** Sugars and sugar alcohols are capable of producing hydrogen for $2 to $4/gge.

- **IP Position:** Exclusive worldwide licenses have been granted, multiple new patent applications placed, and solid trade secret position established.




10 kg/day Hydrogen Pilot Plant

# Objectives

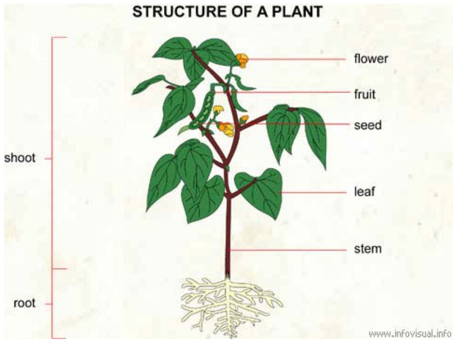
| | |
|---|---|
| Overall | Design a $H_2$ generating system that uses low cost sugars or sugar alcohols that can meet the DOE $H_2$ cost target of <$3 / gge for 2017.<br><br>Complete an initial reactor design and process definition for a 10 kg/day demonstration system |
| 2008/2009 | Continue fundamental catalyst development and analysis to increase the thermal efficiency of the APR system<br><br>Continue development of the APR catalyst and reactor system that converts glucose to hydrogen<br><br>Complete hydrogenation fundamental study(UW)<br><br>Interact with PNNL on data exchange and fundamental surface science study<br><br>Operate reactor development pilot plant (scale-up testing)<br><br>Develop initial PFD and catalytic reactor design for 10 kg/day demonstration system<br><br>Review techno-economic performance of the APR system |

# 2008/2009 Milestones

- ✓ Fundamental Catalysis Review
- ✓ Hydrogen Production Tech Team (HPPT) Visit & Program Review
- ✓ Completion of UW-Madison Catalyst Studies
- ✓ Reactor Development Unit Testing
- Catalyst Evaluation
- Initial Reactor Design and PFD for 10 kg/day Demonstration
- Re-evaluation of Technology Progress versus DOE $H_2$ Program Goals

# Technical Approach
# Biomass Derived Liquids

$$6\ CO_2 + 12\ H_2O \rightarrow 6\ O_2 + C_6\,(H_2O)_6$$




Harvest → Pretreatment

Carbohydrates

**Glucose**
Mannose
Fructose
Sucrose

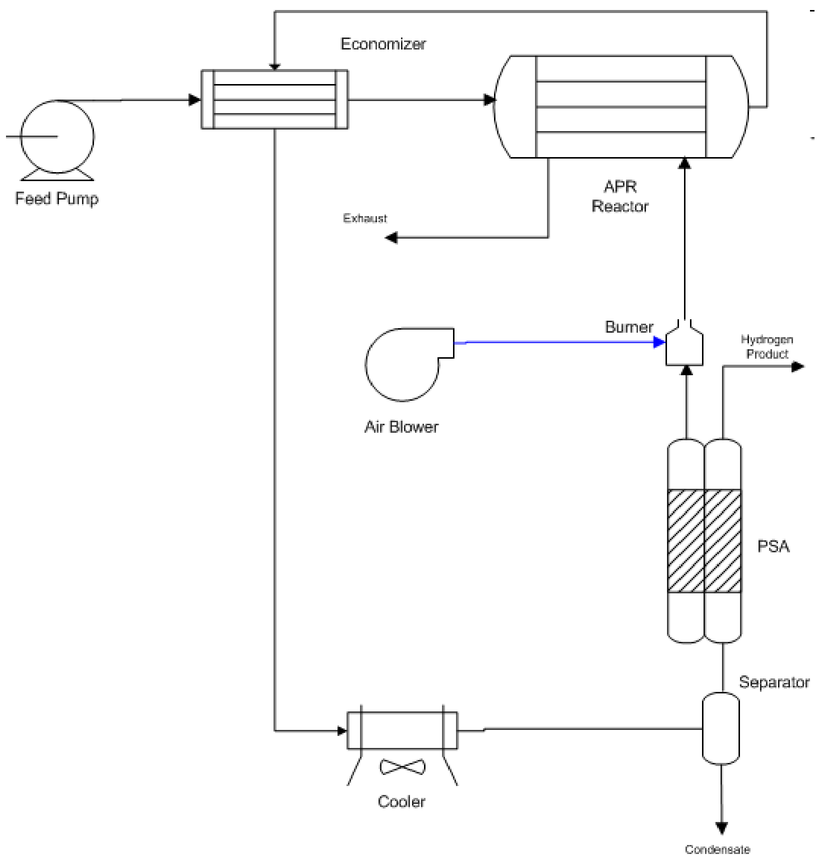
$H_2$ → Sugar Alcohols

Sorbitol
Mannitol
Glycerol
Ethylene Glycol

Enzyme → Alcohols

Methanol
Ethanol
Butanol

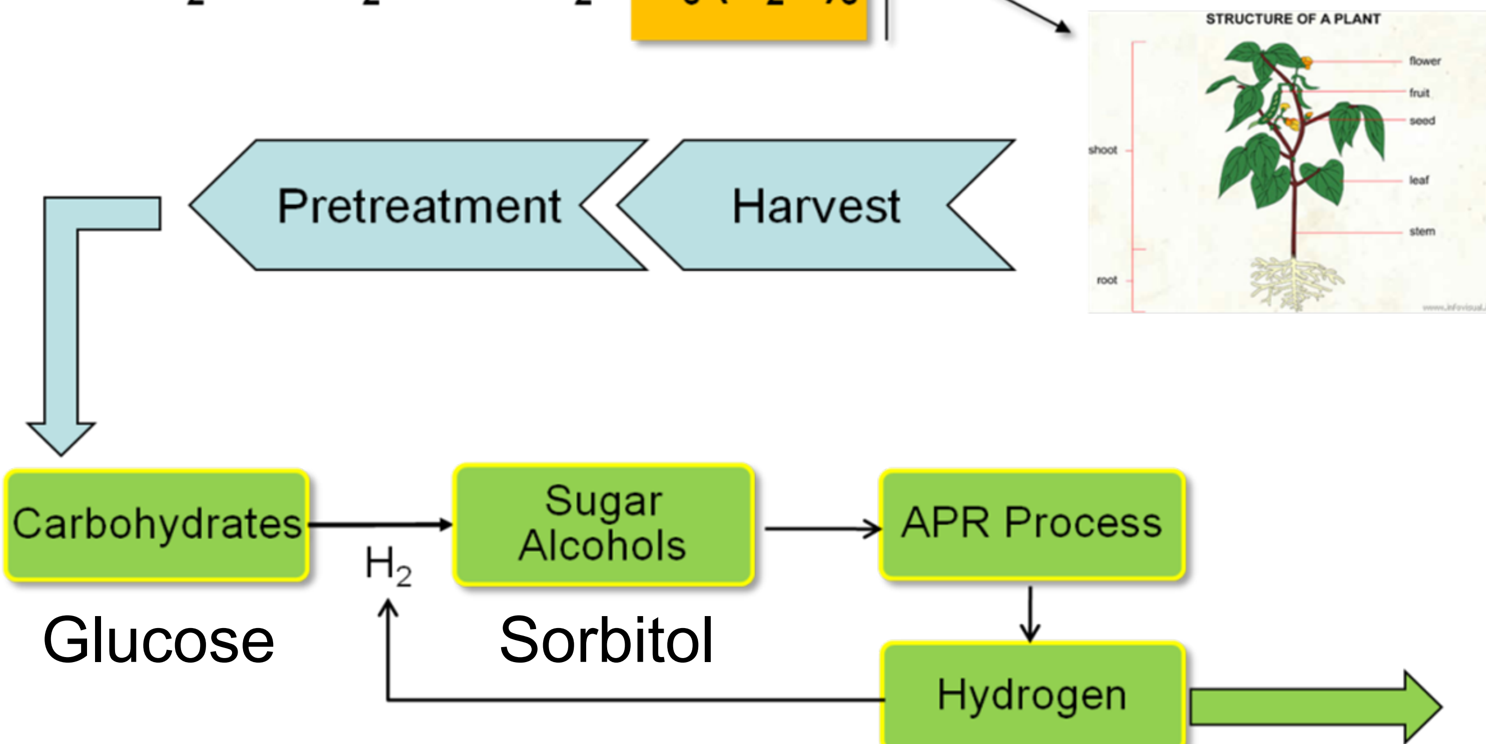
# Hydrogen Production using the BioForming Process



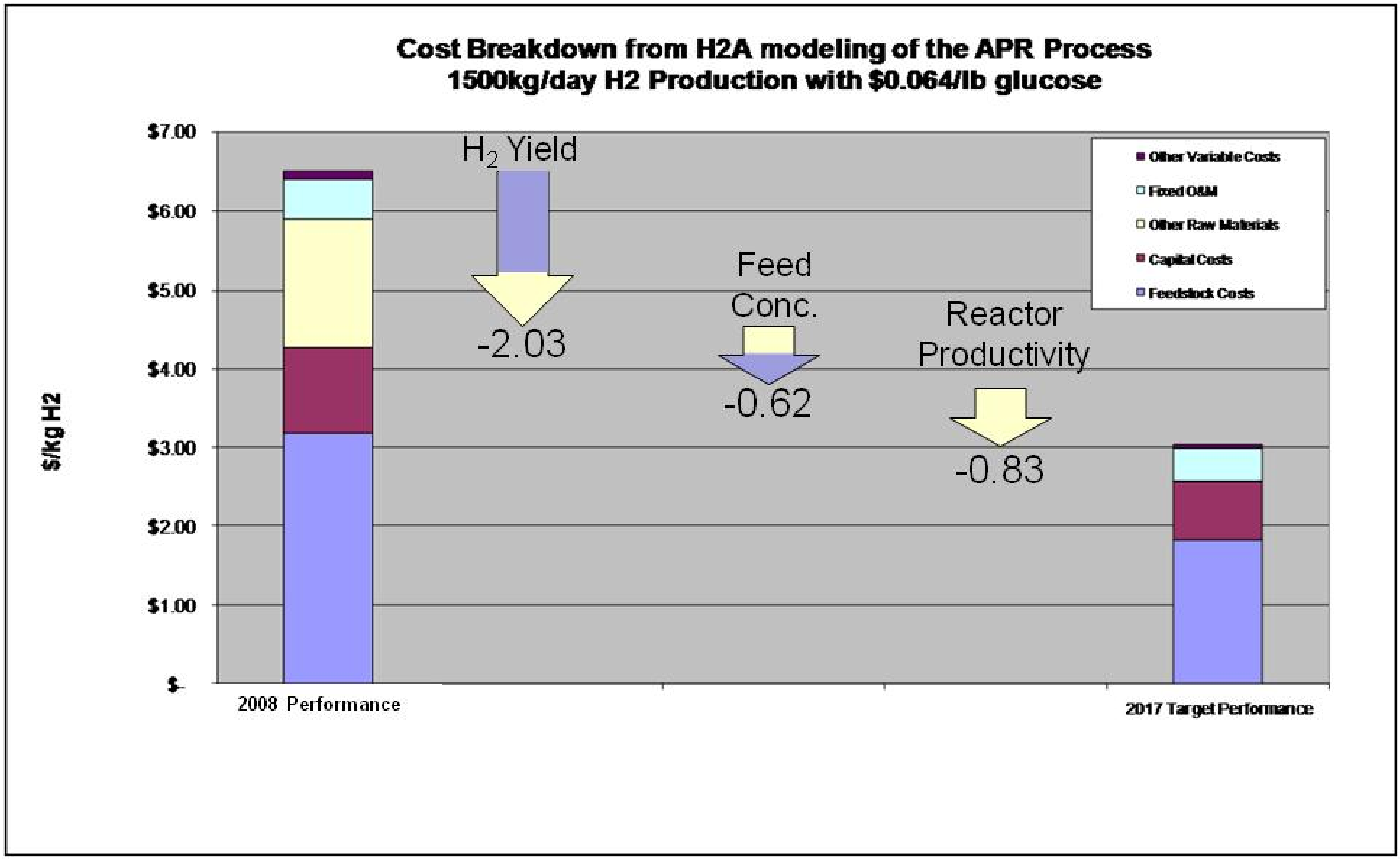

- Simple Catalytic Process
  - No Water Gas Shift
  - No Steam System
  - No Gas Compressor
  - No Desulphurizer
- Energy Efficient
- Scalable
- Feedstock Flexible

# Technical Approach – Glucose

$$6\ CO_2 + 12\ H_2O \rightarrow 6\ O_2 + C_6\ (H_2O)_6$$

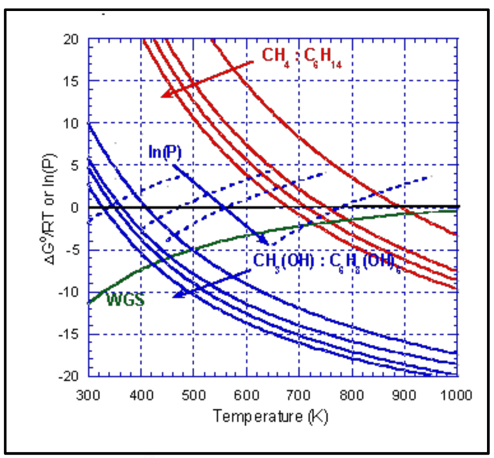


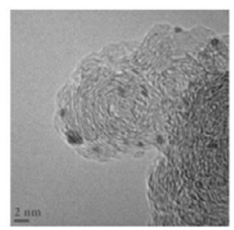
# 2008 Cost Breakdown – H2A

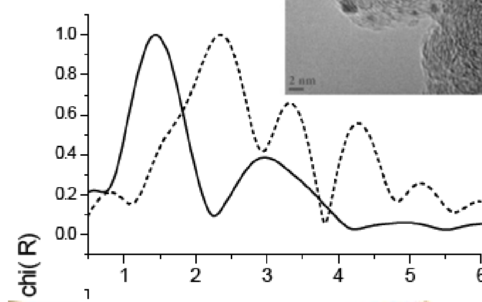


# Fundamental Experimental Fronts

- APR Fundamentals
  - Detailed Chemistry Pathway Development (Virent)
  - Detailed Metal and Support Chemistry Development (Virent)
  - Thermodynamic Relationships – Preferred Chemical Routes (Virent)
  - Detailed Catalytic Surface Science (PNNL)
- Glucose Hydrogenation Fundamentals (UW-Madison)




$$glucose_{,aq} + \theta_v = \theta_{glucose}$$

$$H_{2,aq} + \theta_v = \theta_{H2}$$

$$\theta_{glucose} + \theta_{H2} \rightarrow sorbitol_{,aq} + 2\theta_v$$

$$rate = \frac{kK_{H_2}K_{gluc}C_{H_2}C_{gluc}}{\left(1+K_{gluc}C_{gluc}+K_{H_2}C_{H_2}\right)^2}$$

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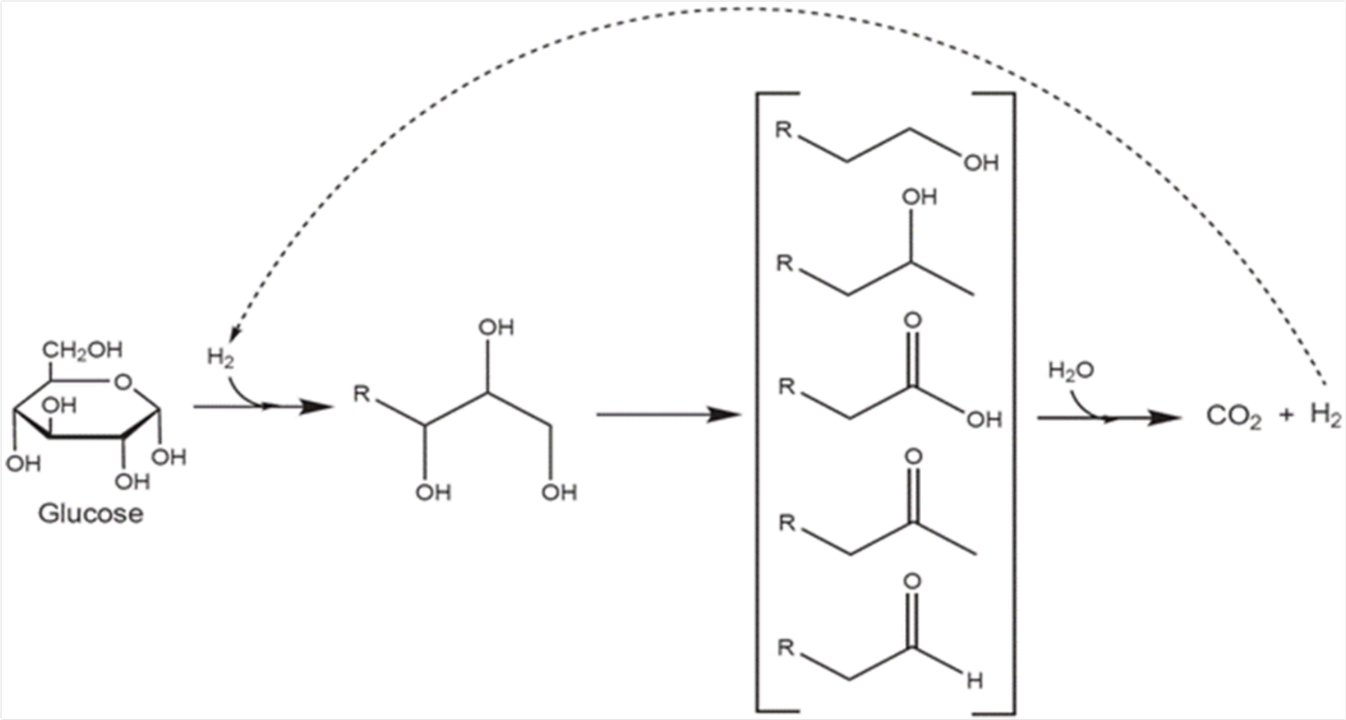
THE UNIVERSITY of WISCONSIN MADISON

# Hydrogenation Fundamentals

- Study focused on detailed catalytic activity and kinetic modeling for the hydrogenation of glucose to sorbitol
- Catalyst Characterization
  - 2.5 wt% Ru/C
  - 44% dispersion
- Apparent Reaction Orders
  - Glucose = 1
  - Hydrogen = 0.7
- Apparent Activation Energy (55 kJ/mol)
- Effect of Gluconic Acid Exposure
- Kinetic Modeling
  - Surface reaction activation energy
  - Enthalpy and entropy of adsorption for glucose and hydrogen
  - Best fit kinetic model established

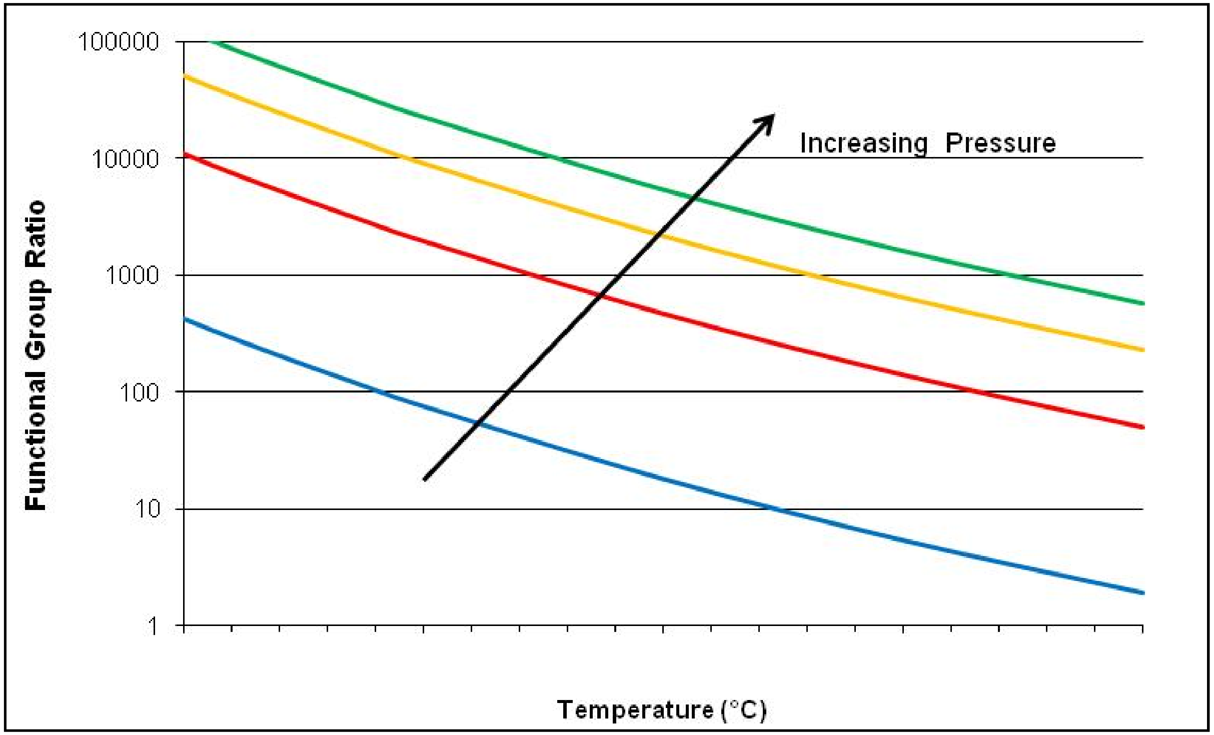
# APR Chemistry Fundamentals

- Detailed chemical reaction pathways have been developed through in-depth investigation of the APR process
- Identified intermediate species detrimental to optimum $H_2$ production
- Identified preferred chemical routes for high efficiency production of $H_2$ from glucose

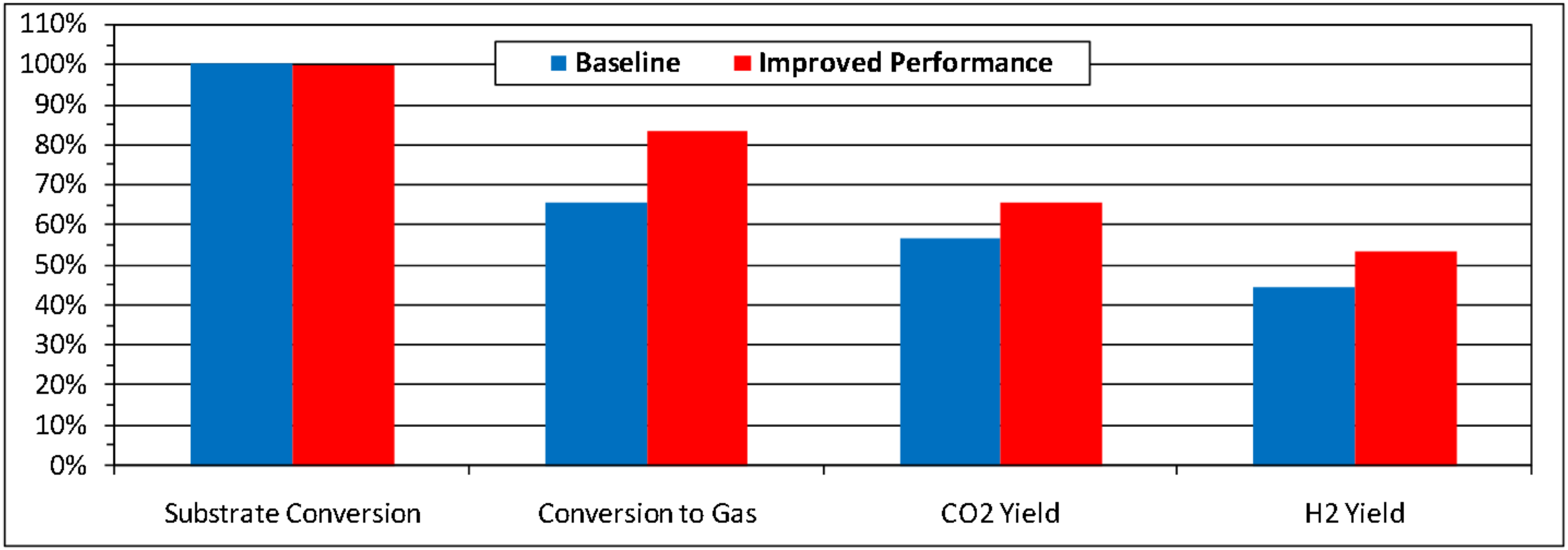


# Thermodynamics Fundamentals

- Identified preferred and detrimental chemical routes for the high efficiency production of $H_2$ from glucose
- Reviewed thermodynamic equilibrium of various compound functionalities
- Thermodynamics led to the investigation of a potential optimized reaction regime

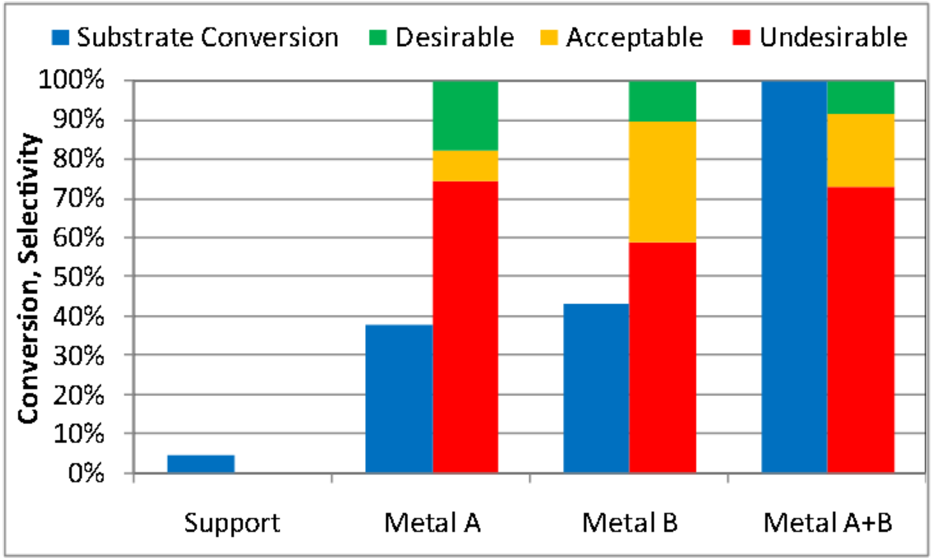


# Benchmark Performance

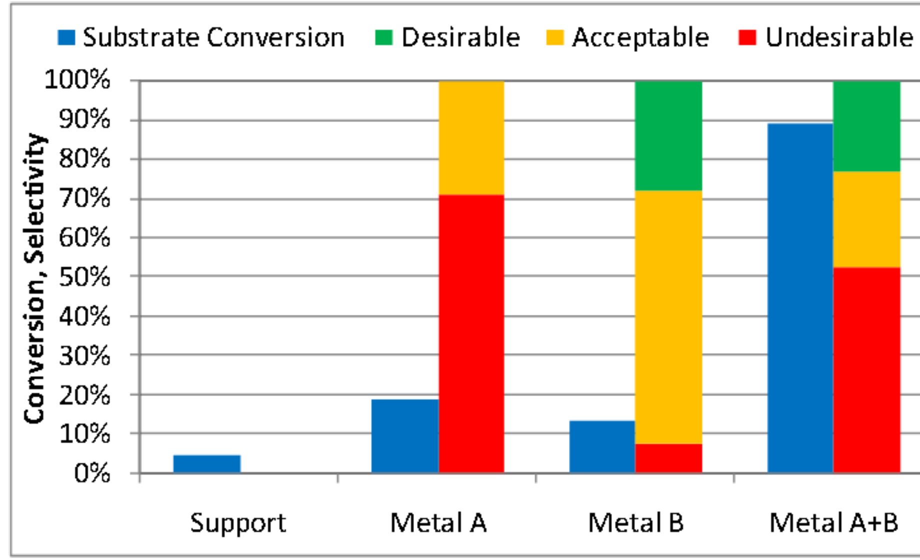



- Fundamental review of chemical pathways led to greater understanding of desired pathways and associated thermodynamics
- Optimization of operating conditions
- Improved $H_2$ yield and conversion to gas
- >10% reduction in $H_2$ cost

# Catalyst Fundamentals – Model Components




Model Compound 1



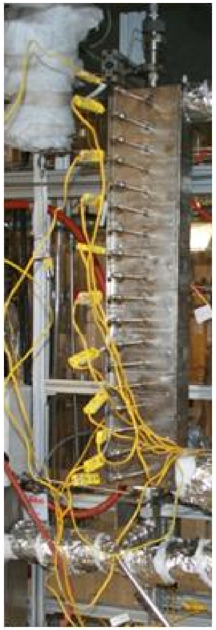

Model Compound 2

- Model compounds utilized to provide very detailed understanding of reaction
- Functionalities investigated using specific model compounds
- Conversion vs. Selectivity
  - Catalyst and Substrate functionality affect reaction
  - Compound 1 more active but towards undesirable products
  - Metal A+B most active but minimal selectivity towards acceptable and desirable
- PNNL fundamental surface science

# Hydrogen Pilot Plant Development

Catalyst Development Unit

Develop



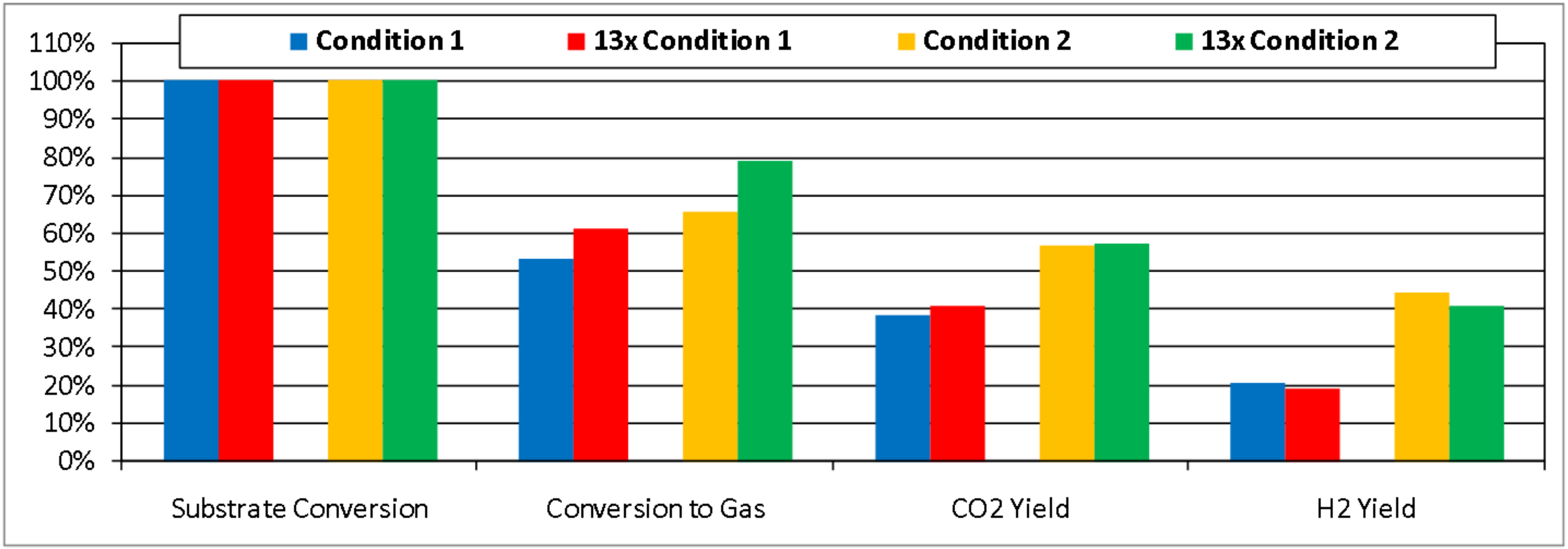
Reactor Development Unit

Scale-Up

Process Development Unit (PDU)

Number-Up

# Reactor Scale Up




- Heating Media – Heat provided by heating fluid versus electric
- Reactor Dimensions – Increased tube diameter and length
- Instrumentation – Increased level in conjunction with heating media allows for the determination of heat transfer coefficients
- Demonstrated ability to scale up reactor 13x while maintaining similar $H_2$ performance and enhanced conversion to gas

# 2008/2009 Accomplishments

- Glucose to $H_2$ Fundamentals
  - Developed detailed catalytic and kinetic information for hydrogenation
  - Developed detailed information for the APR system
    - Preferred Chemistry Pathways
    - Thermodynamics
    - Metal and Support Functionality
- APR Process Development
  - Identified optimized operational regime for the APR reaction
    - Increased $H_2$ Yield
    - Increased Conversion to Gas
  - Completed reactor scale-up operation
    - Maintained $H_2$ Yield and Increased Conversion to Gas
    - Obtained information required for demonstration scale reactor design
  - Reduced cost of $H_2$ production > 10% (H2A Basis)

# Future Work Plan

- Continue evaluation of APR catalysts and reactor system that converts glucose to hydrogen with focus on increasing system efficiency.
- Complete initial reactor design and associated PFD for 10 kg/day demonstration system
- Review techno-economic performance of the APR system utilizing the updated H2A platform
- Re-evaluate the technology progress versus DOE $H_2$ program goals
- Continue interaction with PNNL on fundamental surface science
- Final Project Reporting and Close-out

# Overall Project Summary

- APR
  - A promising and cost competitive technology for the production of renewable $H_2$
  - Technology development still required to reach DOE cost targets
- Techno-Economic Analysis
  - Development pathways identified to reach 2012 and 2017 goals
  - Identified most cost sensitive aspects and continuing to improve
    - $H_2$ Yield
    - Feed stock concentration
    - Reactor productivity
- Catalyst Development
  - Technology Progress to Date
    - >10 X reduction in hydrogen cost
    - 700 X scale-up reactor demonstrated