A Novel Slurry Based Biomass Reforming Process

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Project ID: PDP 1

Overview

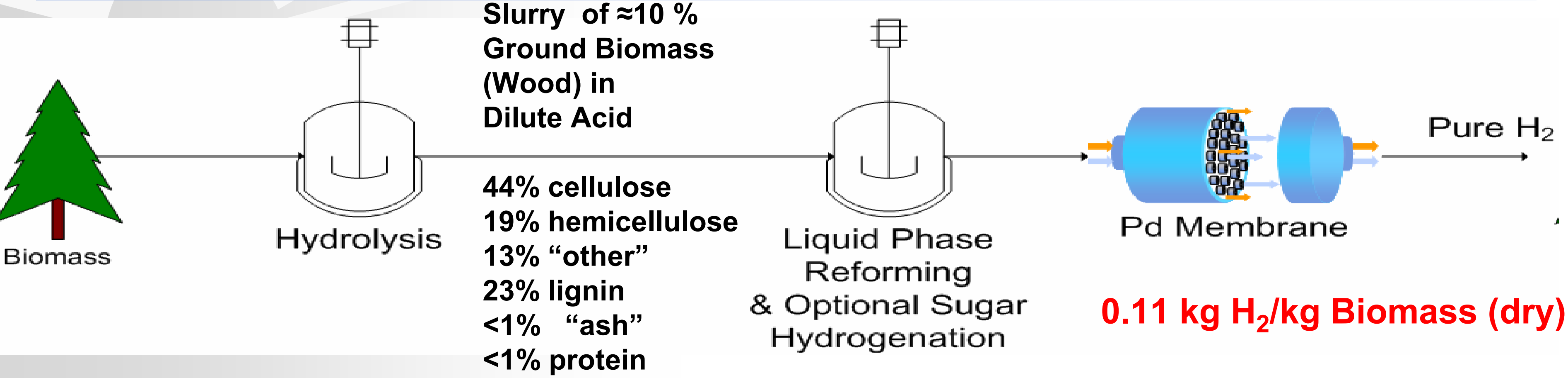
Timeline
- Start – May 2005
- End – Oct 2008
- ≈10% Complete

Budget
- Total Project Funding
  - DOE share - $2.9M
  - Contractor share - $737k
- Funding Received in FY06
  - $0k
- Funding for FY07
  - $700k (projected)

Barriers
- Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan
  - V. Feedstock Cost and Availability
  - W. Capital costs and efficiency of technology

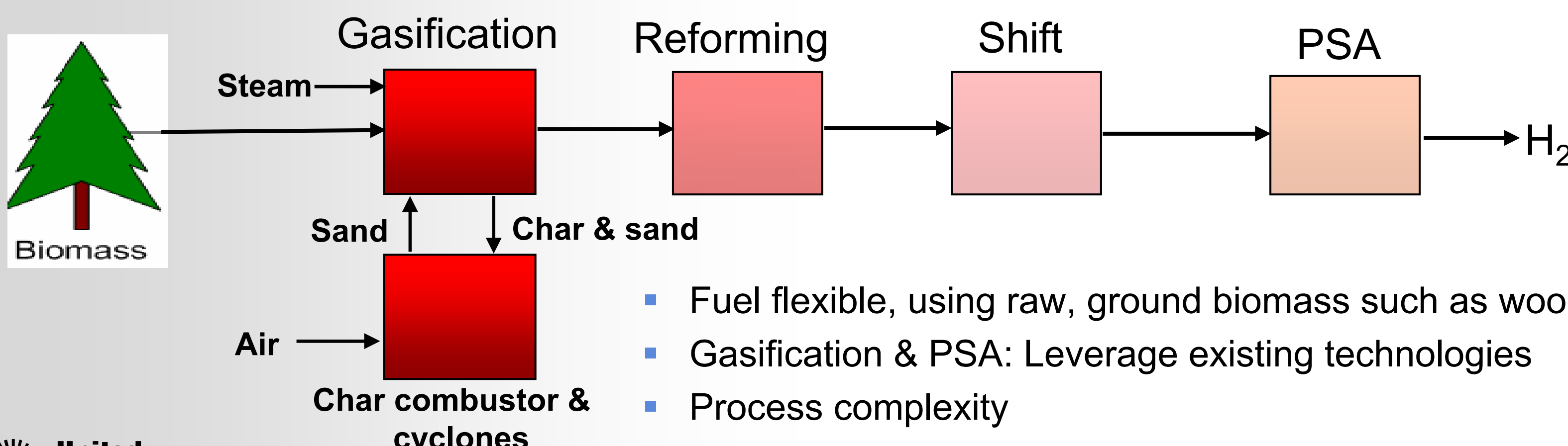
Partners
- University of North Dakota Environment Energy Research Center

Approach: Biomass Slurry to Hydrogen Concept



- Fuel flexible, using raw, ground biomass such as wood or switch grass
- Carbon neutral means to produce Hydrogen
- H_2 separation: Leverage experience with Advanced Pd membranes

Biomass Gasification to Hydrogen Concept



- Fuel flexible, using raw, ground biomass such as wood or switch grass
- Gasification & PSA: Leverage existing technologies
- Process complexity

Objectives

- (2Q2007) Illustrate, through an initial feasibility analysis on a **2000 ton/day** (dry) biomass plant design, that there is a viable technico-economical path towards the DOE's 2012 efficiency target (**43% LHV**) and assess the requirements for meeting the DOE's cost target **($1.60/kg H_2)**.

- (3Q2007) Demonstrate, through preliminary results, that an acid tolerant, model sugar or sugar alcohol solution reforming catalyst has been synthesized.

- Future Work (pending funding)
  - Hydrolysis Work
    - Optimum hydrolysis conditions: Energy and Capital Cost
    - Hydrolysis product chemical composition and physical properties
    - Sugar identification and concentrations
    - Identification and quantification of low molecular weight organics
    - Solubility, average MW and surfactant/foaming properties of lignin fraction
  - Catalysis discovery and testing
  - Micro-scale continuous operation of membrane reformer with batch hydrolysis
    - ~500 hr catalyst performance test
    - Collection of material and heat balance data important for plant design
  - Final Economic and Energy Analysis for Final Report

Biomass Hydrolysis and Reforming Processes Modeling Basis

- Dilute acid hydrolysis

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H_3O^+} nC_6H_{12}O_6$$

- Liquid phase reforming

$$C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2$$

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$$

- H_2 separation

Pd membrane is used for H_2 separation

- Lignin combustion

$$C_{7.4}H_{14}O_{1.4} + 10.2O_2 \rightarrow 7.4CO_2 + 7H_2O$$

- Sulfur recovery

$$SO_2 + 0.5O_2 \rightarrow SO_3$$

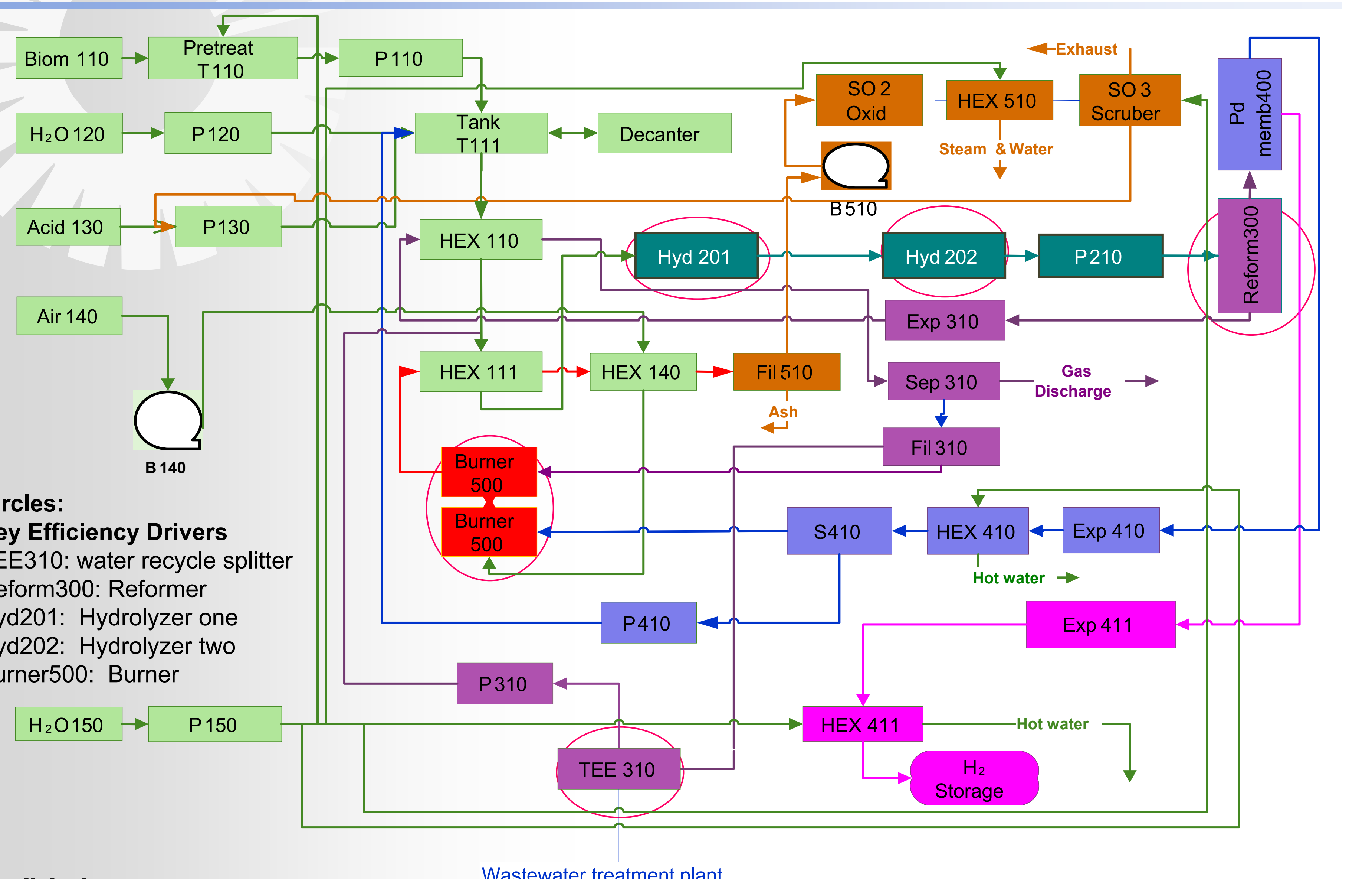
$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$\text{LHV Energy Efficiency} = \frac{\text{LHV of product } H_2 + \text{Energy recovered} - \text{Energy consumed}}{\text{LHV of biomass feed}}$$

Modeling and Simulation Assumptions

- An adiabatic efficiency: 75% for all rotating equipment.
- Heat losses: 4–5% of the heat load on heat exchangers.
- Energy consumption for biomass pretreatment: 1.8% of the biomass feed LHV.
- Pd alloy membrane selectivity of H_2: 100%
- The biomass feedstock: 75% cellulose, hemicellulose or other oligimers, that could be converted to soluble, reformable oxygenates by the hydrolysis process. The balance, 25%, is lignin, $C_{7.4}H_{14}O_{1.4}$.
- Two-stage dilute acid hydrolysis processes operated at temperatures between 190 °C and 215 °C.
- For modeling purposes only, all reformable oxygenates are “glucose”.
- For modeling purposes 95% “glucose” yield was considered to be only a function of temperature.
- In the baseline design, the yield of H_2 and CO_2 from glucose: 94% over the advanced high activity, high selectivity catalyst system.

Block Flowsheet Diagram for Proposed Biomass Reforming Plant



Circles:
Key Efficiency Drivers
TEE310: water recycle splitter
Reform300: Reformer
Hyd201: Hydrolyzer one
Hyd202: Hydrolyzer two
Burner500: Burner

Key Features of Proposed Biomass Reforming Plant

- Sulfur tolerant Pt-alloy rafts/nano-engineered mixed metal oxide catalysts will be developed for liquid phase oxygenates (sugar) reforming

- Lignin, byproduct fuel gas and unrecovered H_2 are burned to provide thermal energy thus increasing system efficiency.

- Recycling of the hot water used for hydrolysis increases system intensity.

- Sulfur recovery & recycle as H_2SO_4 lowers costs and minimizes emissions

- 54.2% LHV energy efficiency (46.6% plant H_2 efficiency) achieved through comprehensive thermal integration

$$\text{Process Energy Efficiency} = \frac{\text{LHV of product } H_2 + \text{Energy Recovered}}{\text{LHV of biomass feed} + \text{Energy consumed}}$$

$$\text{Plant } H_2 \text{ Efficiency} = \frac{\text{LHV of Product } H_2}{\text{LHV of Biomass Feed} + \text{Energy Consumed}}$$

← DOE H2A definitions

$$\text{LHV Energy Efficiency} = \frac{\text{LHV of product } H_2 + \text{Energy recovered} - \text{Energy consumed}}{\text{LHV of biomass feed}}$$

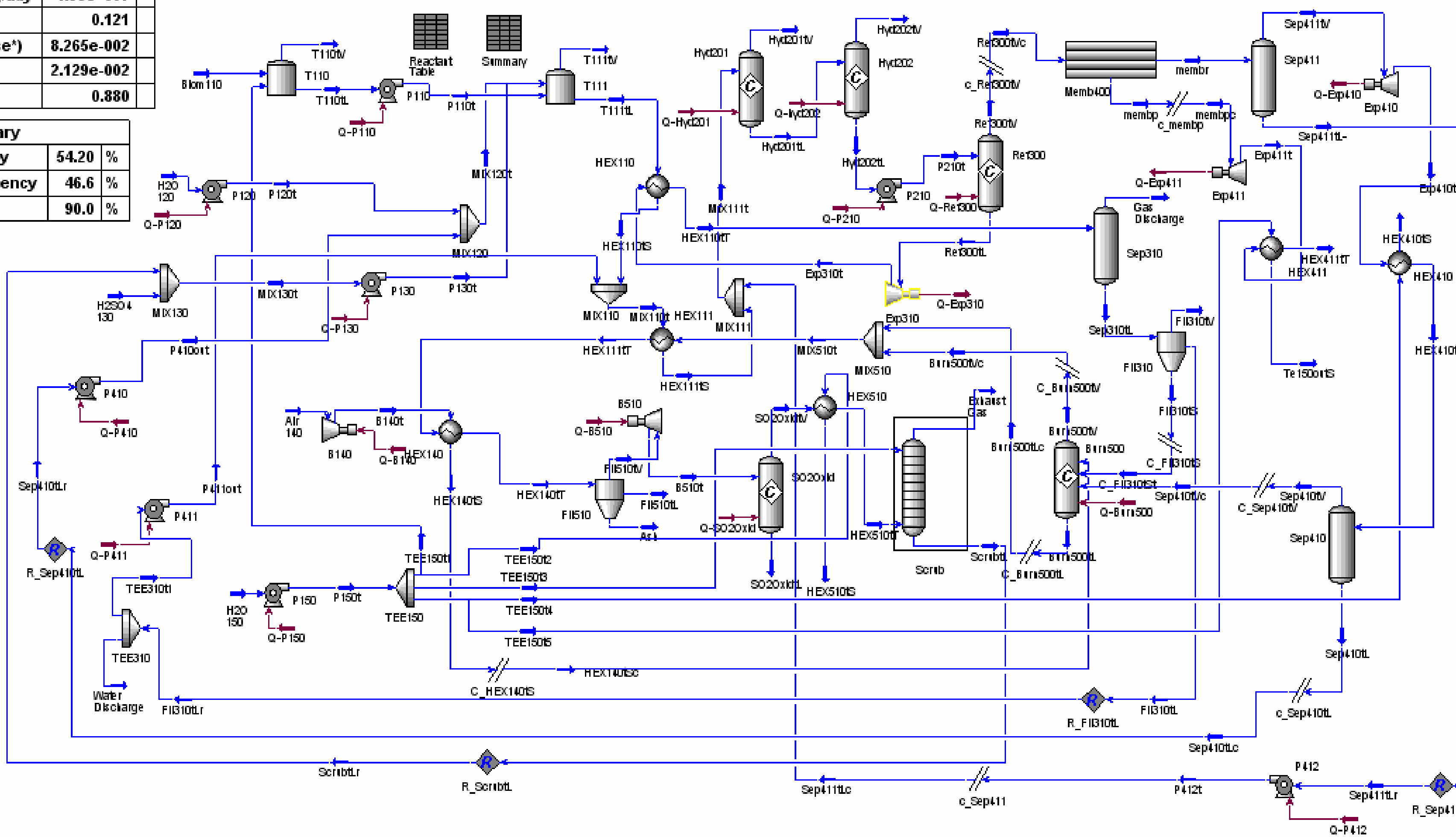
← UTRC definition

Biomass Reforming Plant HYSYS Flowsheet Used for Initial Optimization Through Parameter Sensitivity Studies

- 2000 ton(dry)/day biomass feed

Reactant Table	
Total mass flow, kg/day	1.95e+007
H2SO4 conc. mol/L	0.121
Mass Frac (Cellulose*)	8.265e-002
Mass Frac (Lignin*)	2.129e-002
Mass Frac (H2O)	0.880

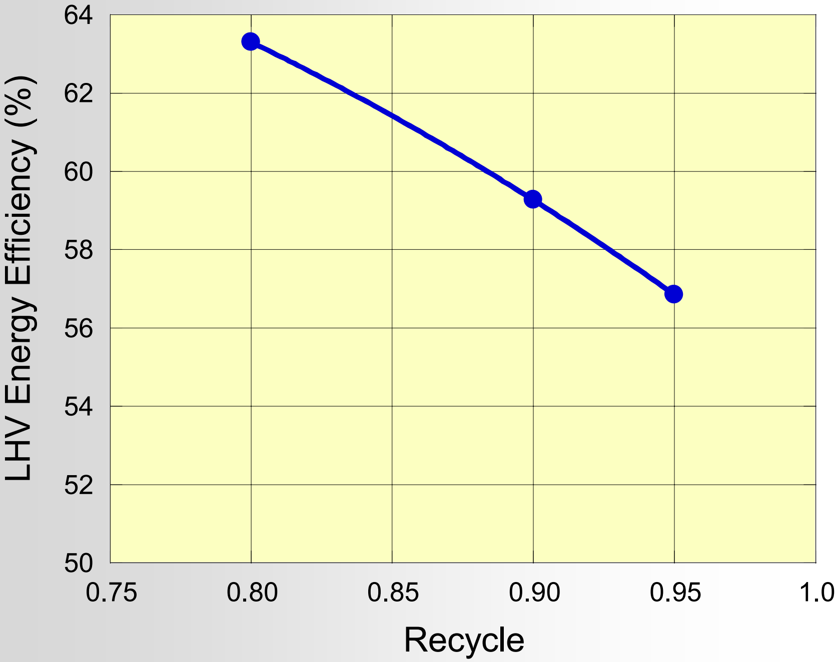
Summary		
LHV Energy Efficiency	54.20	%
Plant Hydrogen Efficiency	46.6	%
H2 Recovery	90.0	%



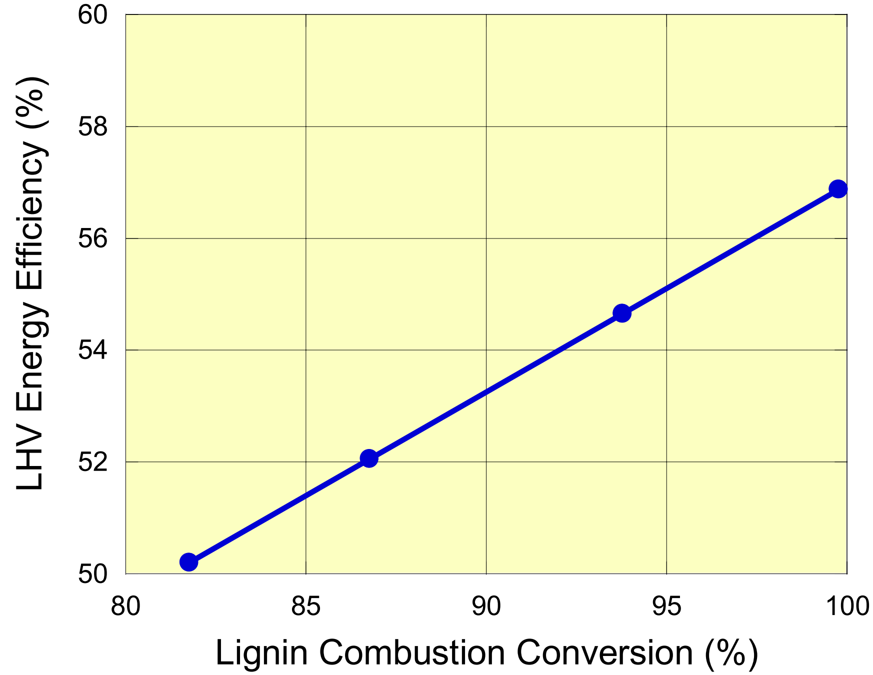
Parameter Sensitivity Studies, One Parameter Varied & Others Held Fixed: Out of 40, 2 Were Very Important & 7 Important

- Two of the most important:
  - TEE 310 process water splitter recycle affects strongly the efficiency:
    - Most of energy goes into heating water,
    - At given water input, increased recycling dilutes the system, requiring more energy
  - Increasing combustion of unconverted biomass increases plant energy recovery

TEE 310 Water Fraction To Recycle

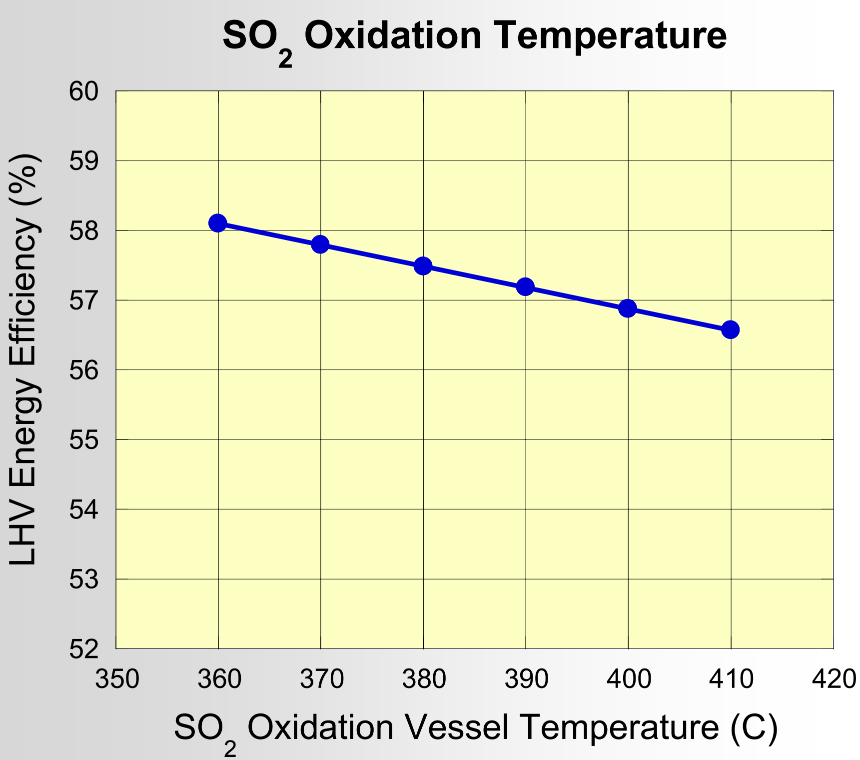


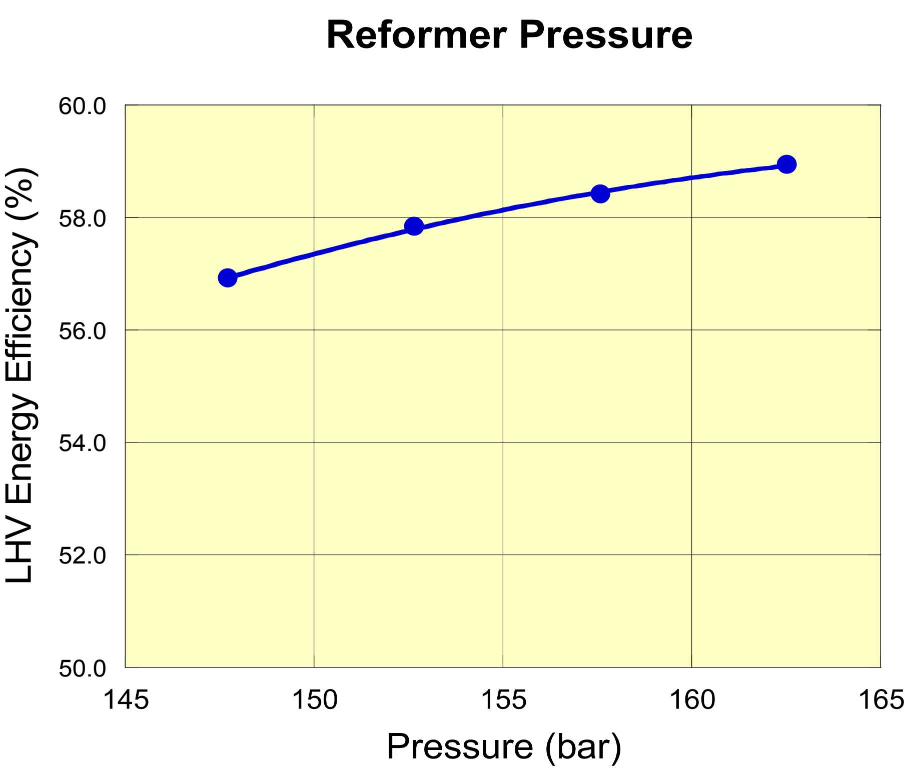
Lignin Combustion Conversion



Parameter Sensitivity Studies 2 : Efficiency Increases with Reformer Pressure & Lower SO_2 Oxidation Temp.

- Increase of reformer pressure is limited by Capital Cost & Chemistry
- SO_2 oxidation temperature has negative impact on the efficiency





Major Drivers for LHV Energy Efficiency

Several parameters have been identified to have strong impact on system efficiency. For example, Lignin combustion in the burner provides thermal energy to the system.

Tee310 splitter recycles hot process water. System efficiency increases with decreased hot water recycle.

Parameter	Impact on Efficiency
Hydrolysis Stage One Temperature	+ +
Hydrolysis Stage Two Temperature	+ +
Reformer Pressure	+ +
Reformer Glucose Conv. To H_2	+ +
Reformer Glucose Conv. To CH_4	+ +
SO_2 Oxid Vessel Temperature	- -
Burner Temperature	+
Burner Lignin Combustion	+ + +
Tee310 Flow Ratio (H_2O recycle)	+ + +

+ slightly positive impact
++ positive impact
+++ very positive impact
- Negative impact

Design of Experiments

- Statistical Design of Experiments.
  - 9 factors
  - 61 experiments
  - 5 replicates used to measure/check computational/round off errors
  - Modified central composite design for response surface study

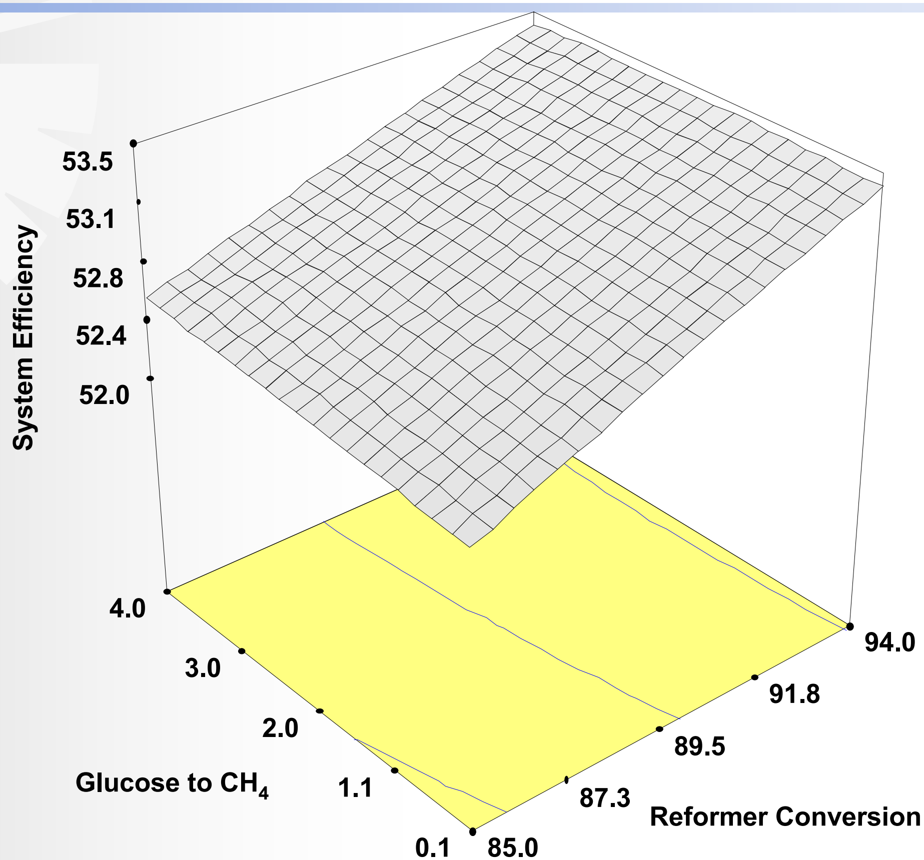
- 61 cases were generated and run by using HYSYS.

- Effects of multi parameters on the system efficiency were obtained.

- 2-D and 3-D response surface maps were created from the Design of Experiments results.

- Operating region for achieving greater than 50% efficiency was identified from 2-D and 3-D maps.

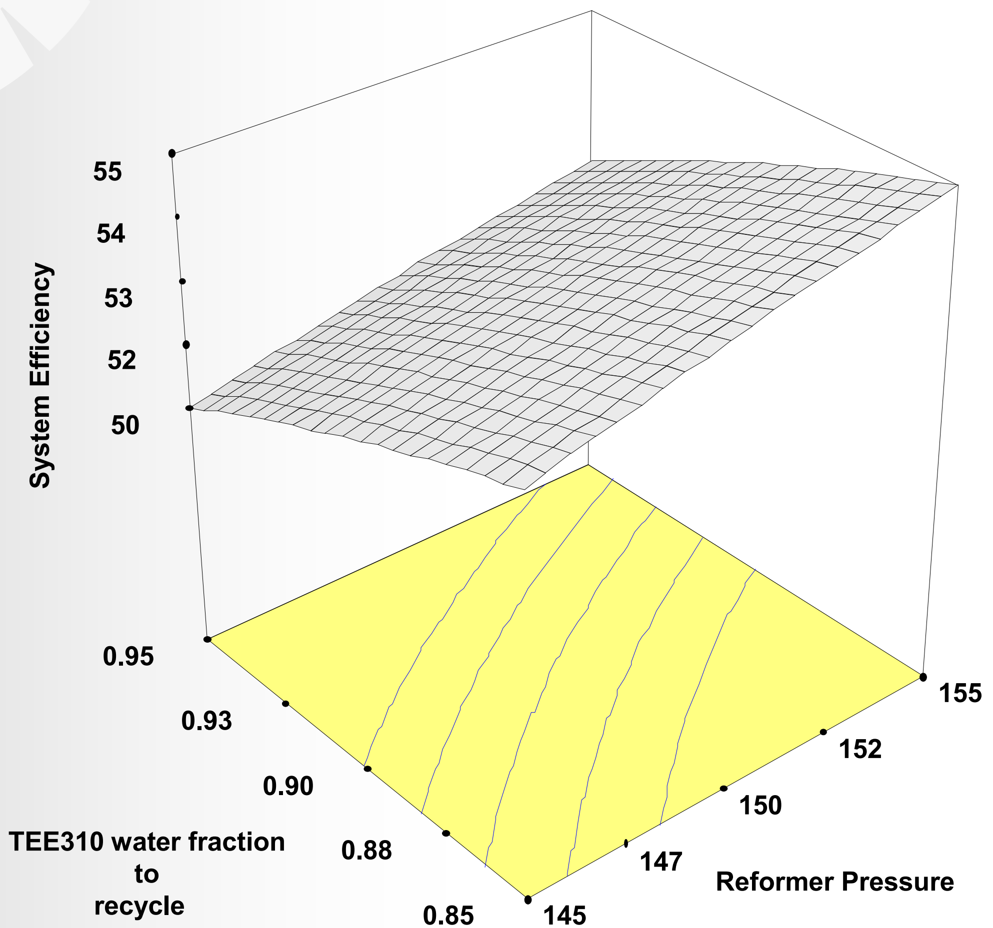
Reformer conversion drives system efficiency



- Conversion of sugars to methane has a positive effect on efficiency
- Methane combustion provides plant energy

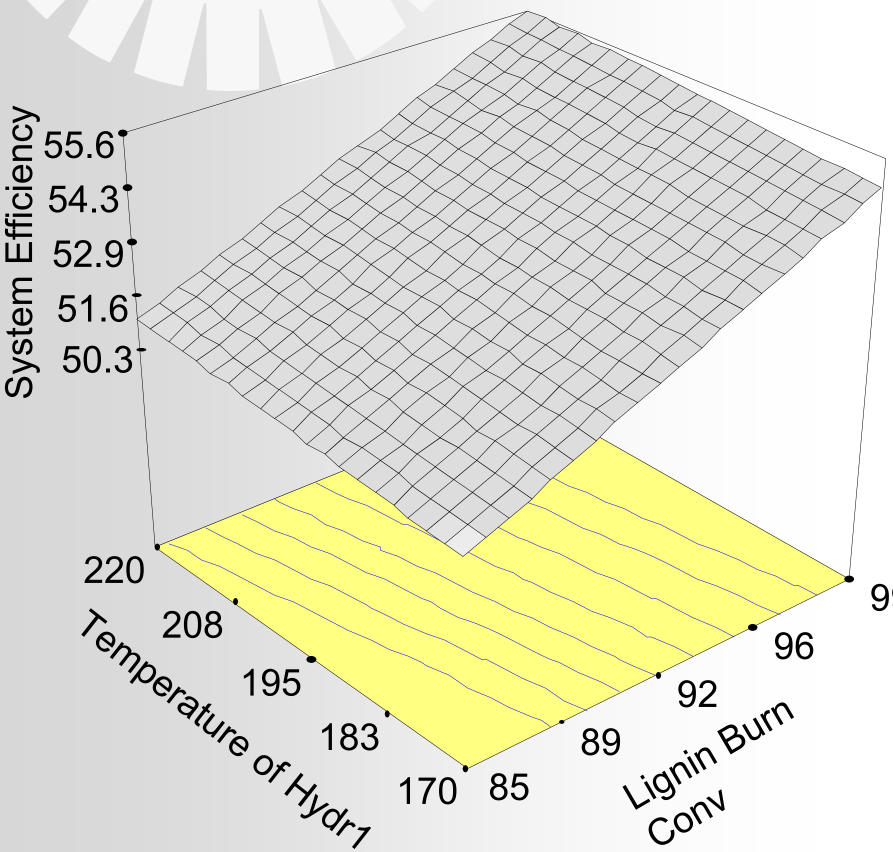
Higher pressure & optimal H_2O recycle boosts efficiency

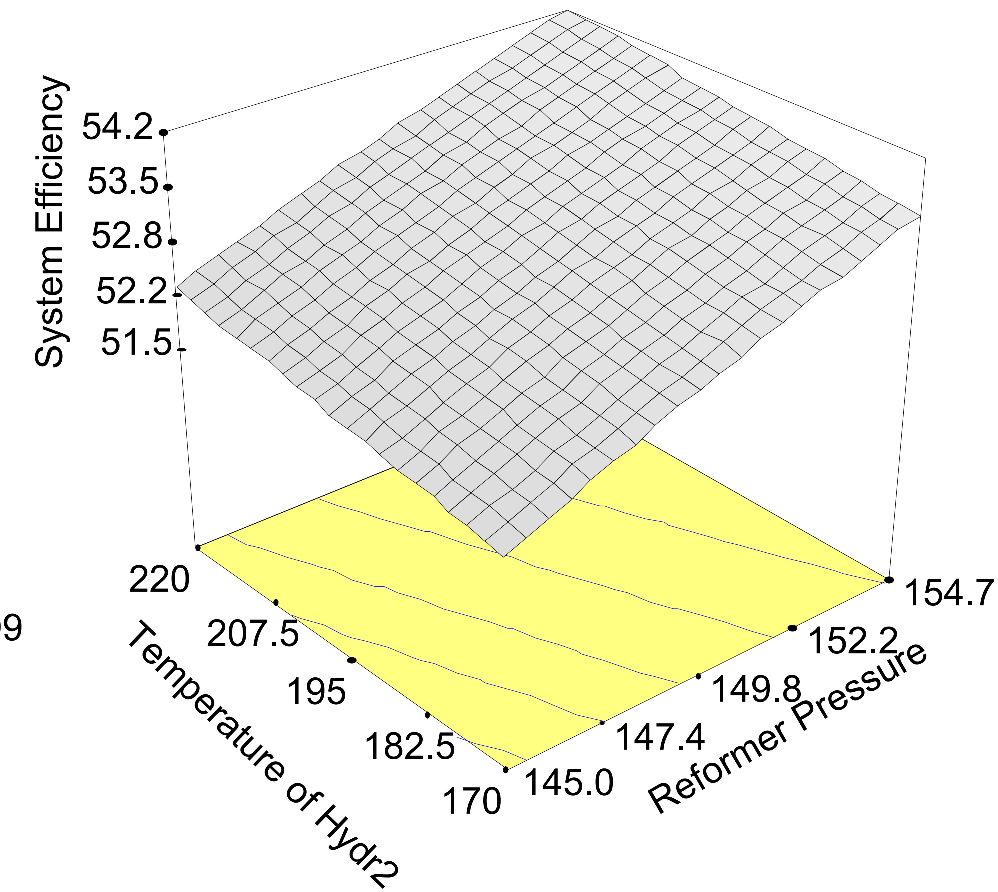
- LHV energy efficiency > 52% at reformer pressures >147 bar
- At given water input, increased recycling dilutes the system, requiring more energy



Lignin combustion, system pressure, & hydrolysis conditions have a strong effect on efficiency

• >50% LHV efficiency can be achieved when the lignin combustion/heat recovery exceeds 85% and the temperature of hydrolyzer 1 is greater than 170 °C





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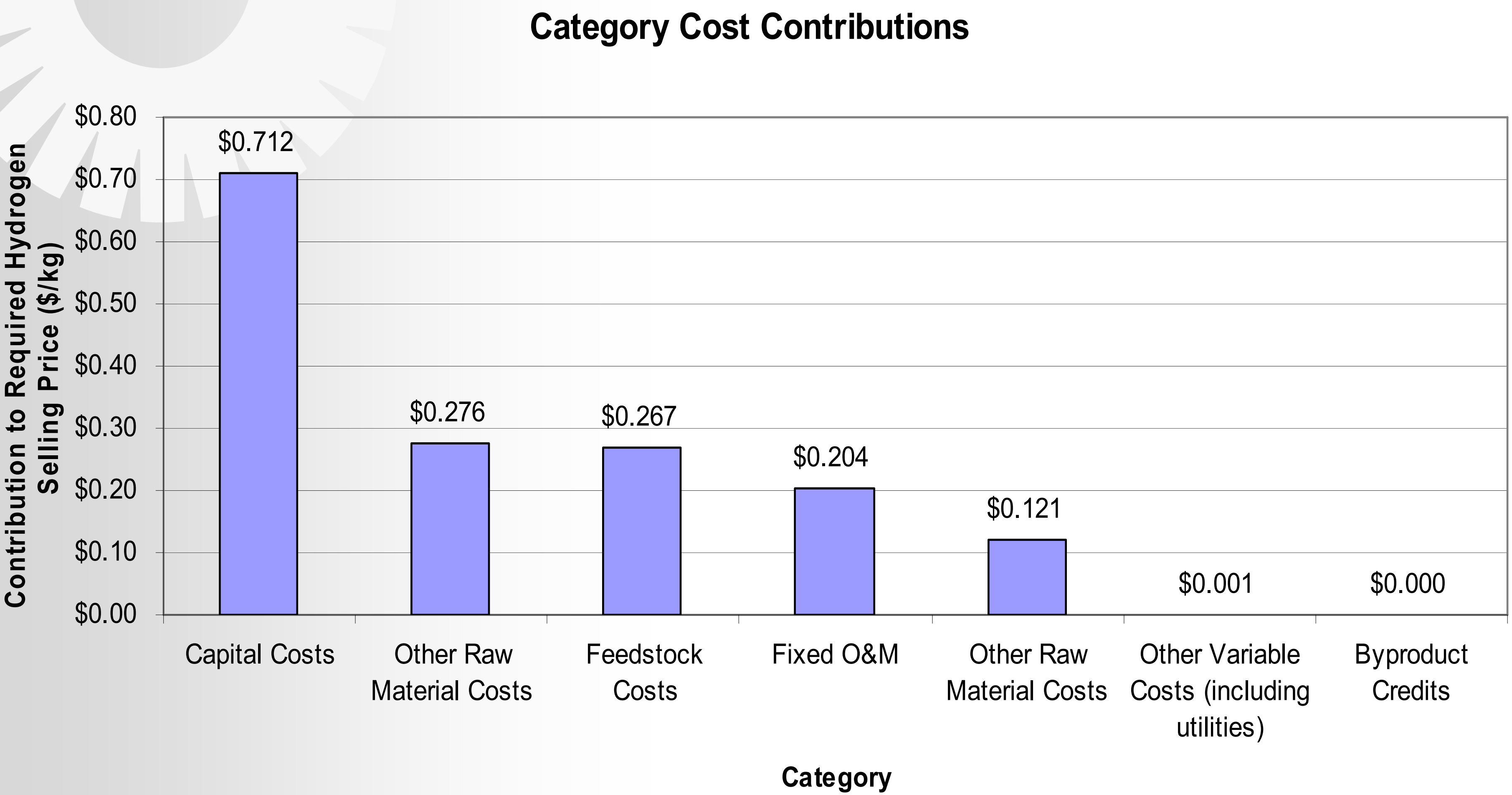
Preliminary economics on baseline plant design

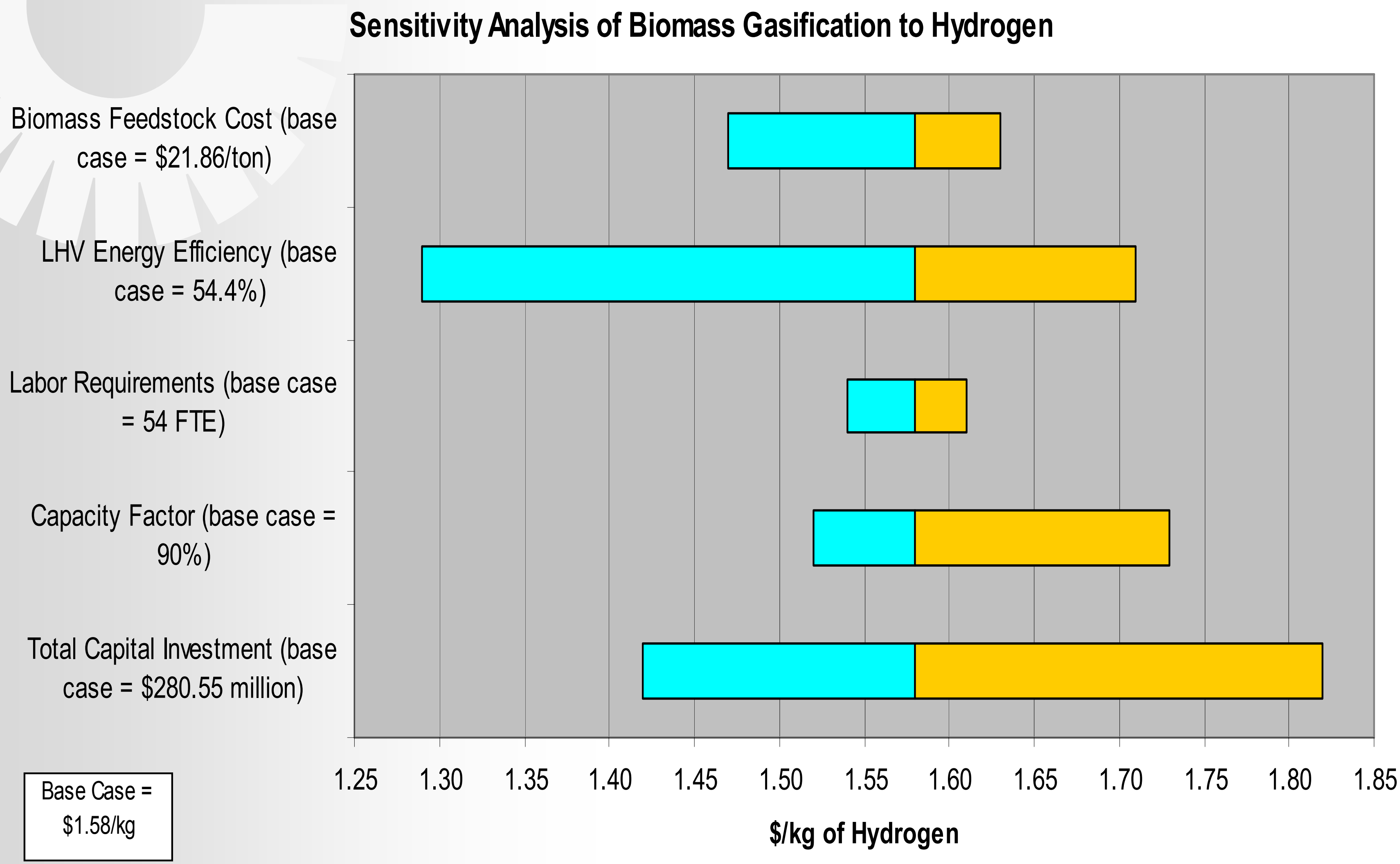
DCF CALCULATION OUTPUTS:	
Required Hydrogen Selling Price (Year 2005 Real Dollars/kg)	$1.581
Required Hydrogen Selling Price (Start-up Year (Nominal) Dollars/kg)	$1.581
After Tax Real IRR	10.0%
Pre Tax Real IRR	14.0%
After Tax Nominal IRR	12.1%
Pre Tax Nominal IRR	16.2%
After Tax Real Capital Recovery Factor	0.102
After Tax Nominal Capital Recovery Factor	0.122
Total Real Fixed Charge Rate	0.139
Total Nominal Fixed Charge Rate	0.170
NPV	$0

Major H_2 Selling Price Drivers Are Capital, Other Raw Material, and Feedstock Costs



Catalysts are included in additional raw material cost

Preliminary economics on baseline plant design(3)



Summary

- Biomass reforming plant design with a system HYSYS simulation LHV efficiency of 54% is proposed.
- The thermally integrated design yields high efficiency and minimizes sulfur emissions.
- Major drivers on the efficiency were identified in parameter sensitivity studies.
- > 50% LHV efficiency operating regime identified through DOE studies.
- Hydrolysis and reforming catalyst/reactor performance targets identified.
- Hydrogen production cost of \$1.60/kg H_2 is achievable with this process.

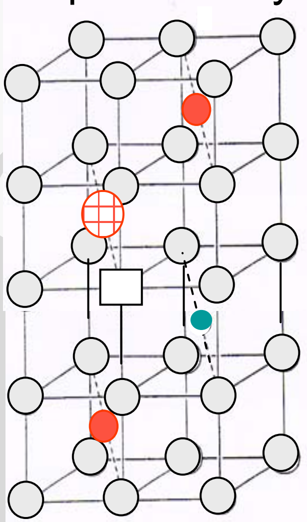
Future Work

- (2Q2007) Illustrate, through an initial feasibility analysis on a 2000 ton/day (dry) biomass plant design, that there is a viable technico-economical path towards the DOE's 2012 efficiency target (43% LHV) and assess the requirements for meeting the DOE's cost target ($1.60/kg H_2).
- (3Q2007) Demonstrate, through preliminary results, that an acid tolerant, model sugar or sugar alcohol solution reforming catalyst has been synthesized.
- Pending future funding, hydrolysis optimization; additional catalyst development, including atomistic modeling; and a 1-kW scale demonstration and final techno-economic analysis at the end of the project.

UTRC Catalyst Discovery Approach

Atomistic catalyst design, synthesis, characterization, reaction studies & kinetic analysis

Conceptual Catalyst Design



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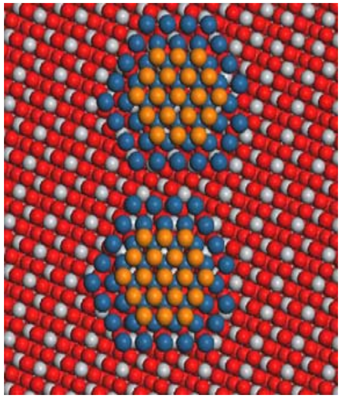
Catalyst Synthesis

High active surface area
Nanocrystalline structure
~100% NM dispersion

⇔

Quantum Mechanical Atomistic Modeling for advanced catalyst design



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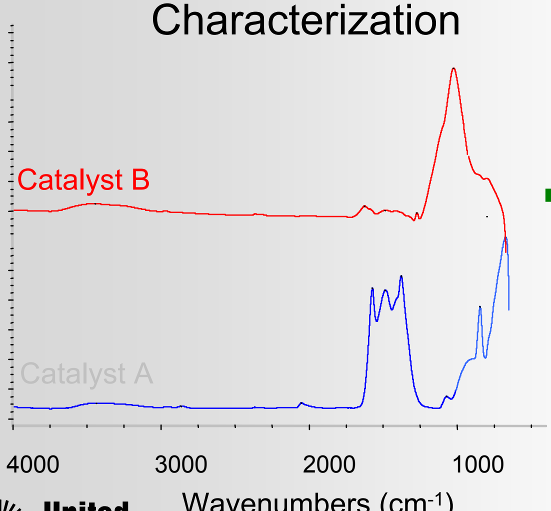
Characterization



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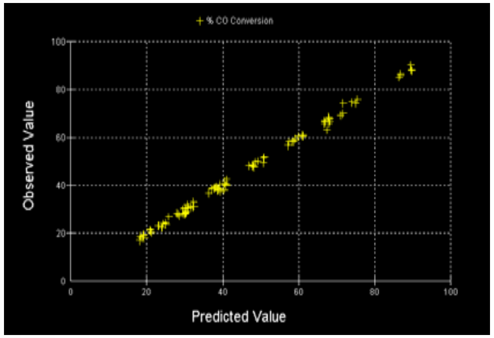
Kinetic Expressions Derived From Reaction Data



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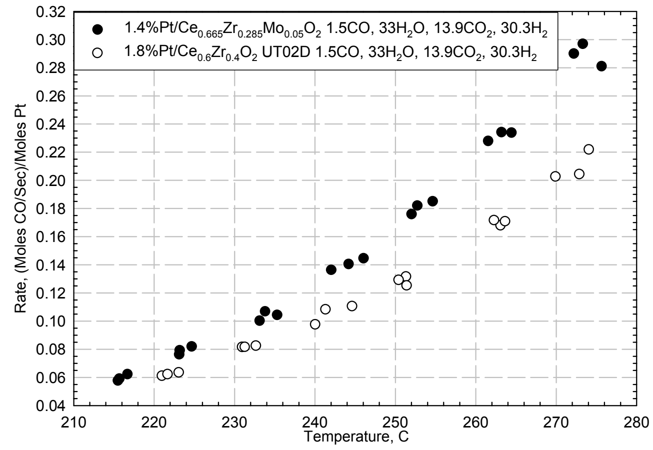
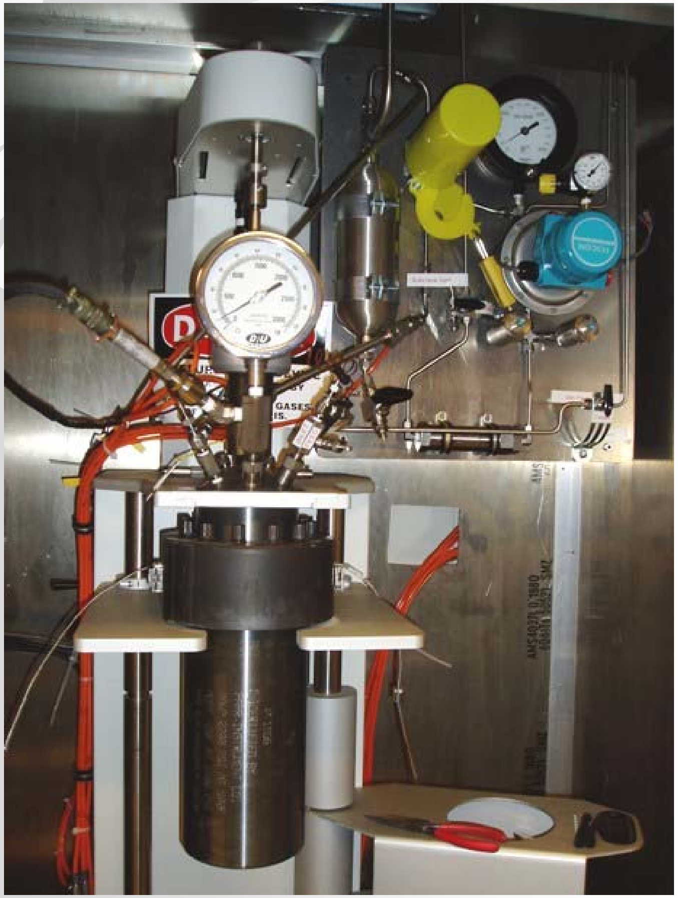
Superior Performance



Laboratory Capabilities for Catalyst Development



Autoclave for Hydrolysis / Reforming

Biomass Test Rig – reforming of cellulose and hemicellulose materials to form H_2 and CO_2