

A Novel Slurry Based Biomass Reforming Process (DE-FG36-05GO15042)

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Overview

■ Timeline

- Start: May 2005
- End: August 2010
- 60% Complete

■ Budget

- Total Project Funding
 - DOE share: \$3M
 - Contractor share: \$750k
- Funding Received in FY08
 - \$800k
- Funding for FY09
 - \$0k

■ Barriers

- T. Capital Costs and Efficiency of Biomass Gasification/Pyrolysis Technology

■ Partners

- University of North Dakota Environment Energy Research Center (UND-EERC)
 - Hydrolysis experimental studies
 - Slurry characterization
 - Cost analysis
 - Proof-of-concept demonstration

Project Objectives & DOE Target Status

- Development of an initial reactor and system design, with cost projections, for a biomass slurry hydrolysis and reforming process for H₂ production
 - Efficiency & H₂ cost exceed gasification targets
 - Capital costs dependent on H₂ delivery pressure & H₂ separation membrane
- Development of cost effective catalysts for liquid phase reforming of biomass hydrolysis-derived oxygenates
 - Catalyst based on commercially scaled-up material
- Proof-of-concept demonstration of a micro-scale pilot system based on liquid phase reforming of biomass hydrolysis-derived oxygenates
 - Phase II work not yet started

	Target	Current Status	2008 Status
Hydrogen Cost (Plant Gate) ^a	1.60 \$/gge	\$1.27/kg H₂ (\$0.95/kg – \$1.85/kg)	\$1.58/kg H ₂ – \$2.16/kg H ₂
Total Capital Investment ^b	\$150M	\$177M (\$71M – \$365M)	\$203M – \$291M
Energy Efficiency ^c	43%	53.9% (53.9% – 58%)	46.6%

a. Gallon of gasoline equivalent (gge) ≈ kg H₂

b. Assuming 300 psig delivery pressure

c. Plant H₂ Efficiency

$$\text{Plant H}_2 \text{ Efficiency} = \frac{\text{LHV of Product H}_2}{\text{LHV of Biomass Feed} + \text{Energy Consumed}}$$

Technical Accomplishments: Economic Analysis

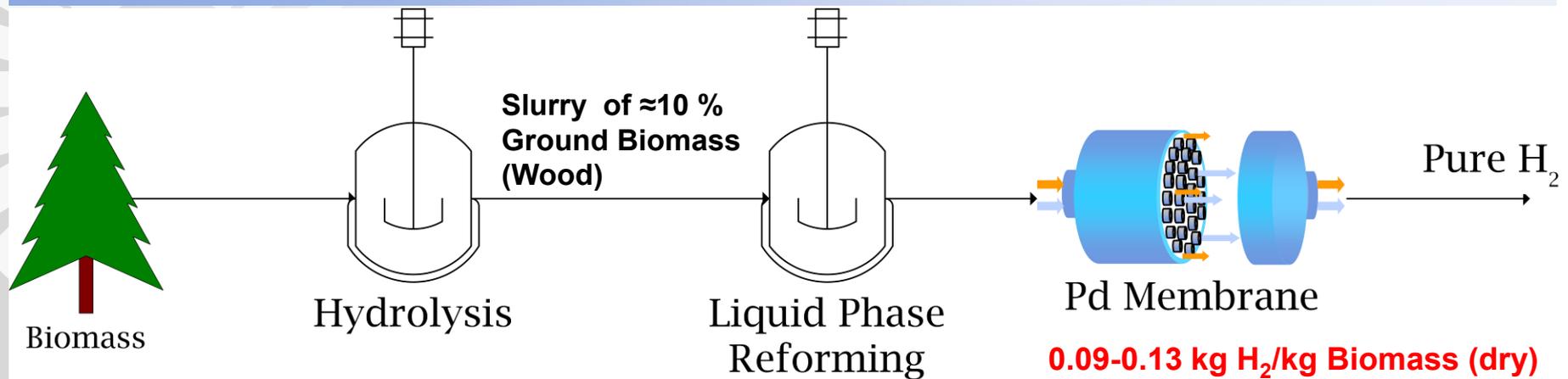
H₂ Compressor Is Best Choice for Delivery of H₂ at 300 psia atm

	H ₂ flux, SCFH/ft ²	Membrane cost, \$/ft ²	Capital cost, \$ million	Membrane cost in capital, %	Efficiency, %	H ₂ selling price, \$/kg	H ₂ production, kg/day
Compressor	60	1,500	365	73.8	53.9	1.85	2.65x10 ⁵
	200	1,500	177	45.7	53.9	1.27	2.65x10 ⁵
	200	100	101	5.3	53.9	1.04	2.65x10 ⁵

$$\text{Plant H}_2 \text{ Efficiency} = \frac{\text{LHV of Product H}_2}{\text{LHV of Biomass Feed} + \text{Energy Consumed}}$$

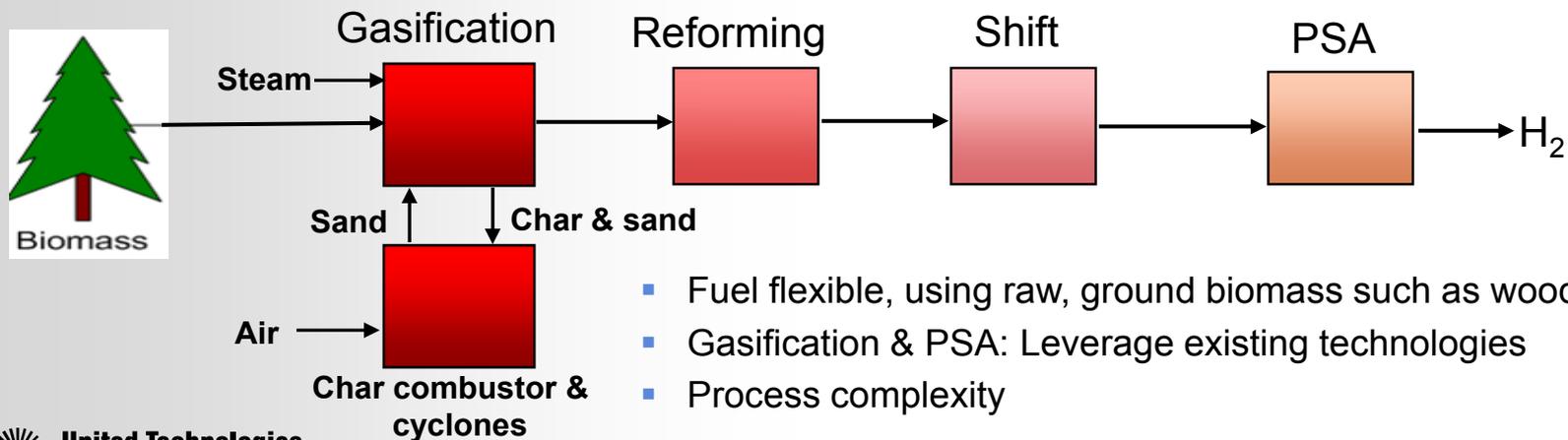
H₂ is delivered at 300 psia pressure

Approach: Biomass Slurry to Hydrogen Concept



- Fuel flexible, using raw, ground biomass such as wood or switch grass
- Carbon neutral means to produce Hydrogen
- H₂ separation: Leverage experience with Advanced Pd membranes

Alternative: Biomass Gasification to Hydrogen Concept

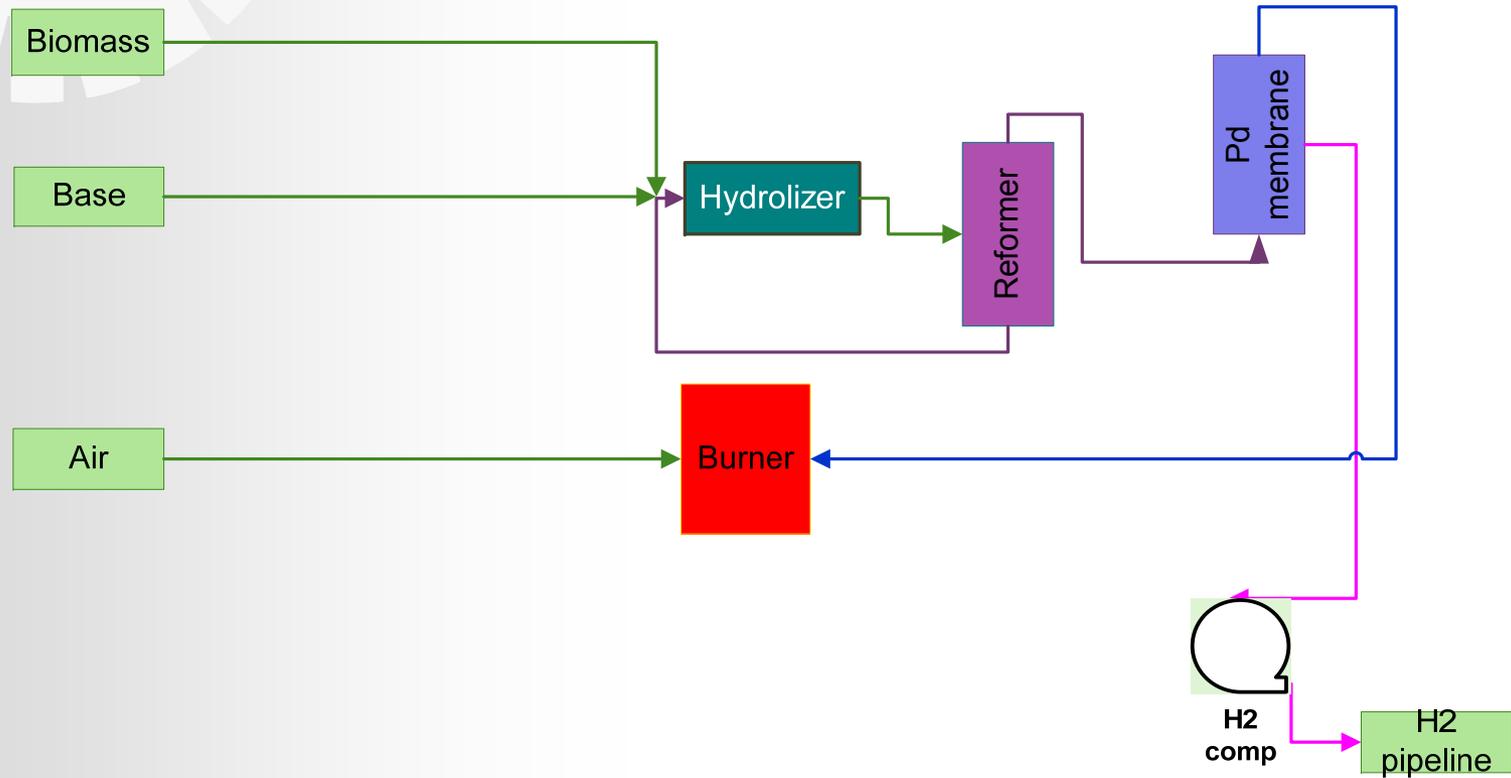


- Fuel flexible, using raw, ground biomass such as wood or switch grass
- Gasification & PSA: Leverage existing technologies
- Process complexity

Technical Accomplishments: 2008 Summary

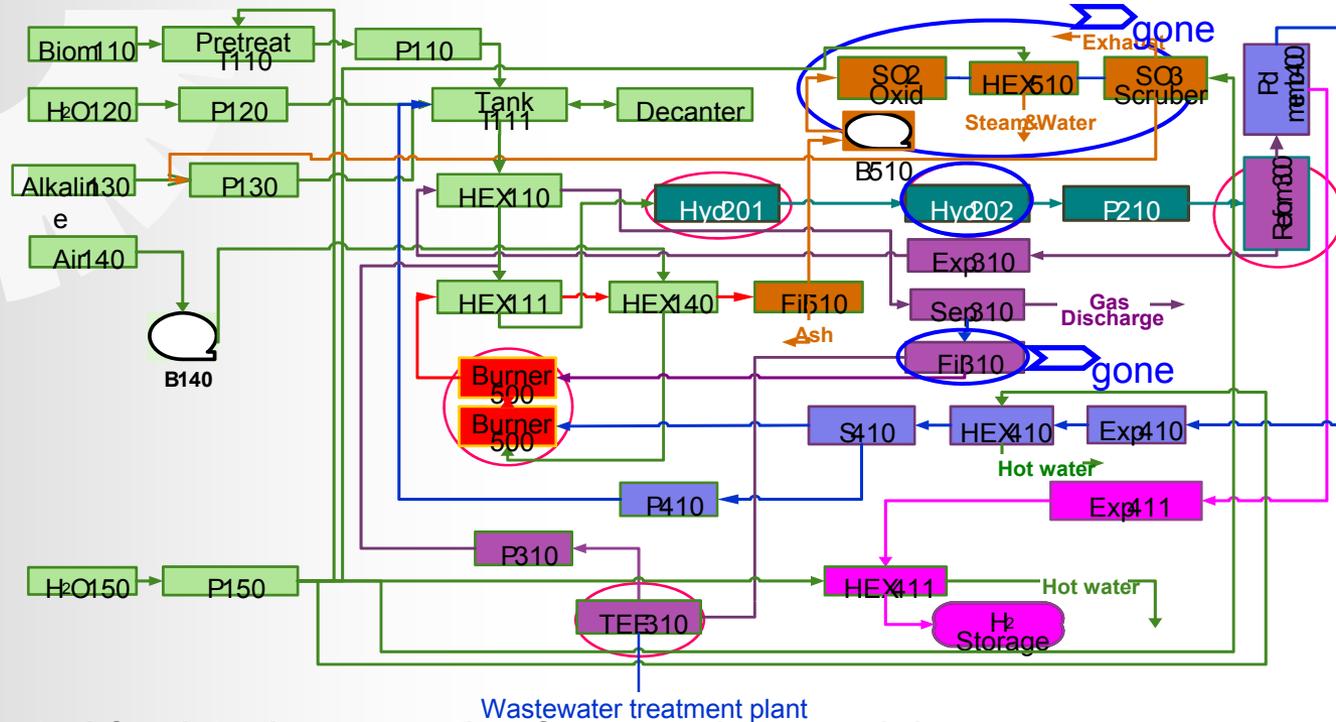
- Explored glycerol liquid phase reforming with atomistic modeling
- Modified experimental setup to ensure measurement of true hydrogen production rates
 - Semi-batch reactors used for screening
- Screened several catalyst candidates, including a commercially available Pt/Al₂O₃ as a baseline comparison
 - Downselected a ceria-zirconia based catalyst
- Examined reforming in the presence of acid (sulfur) and base
 - Performed material dissolution and char formation studies
 - Conducted biomass hydrolysis studies
 - Char formation prevented adequate catalyst evaluation
 - Concluded that alkali reforming avoided catalyst poisoning & side reactions that form char
- Proof-of-concept demonstrations of complete reforming of wood and wood components in alkali system

Simplified Diagram for Alkaline Reforming Plant



Technical Accomplishments: System Modeling

HYSYS Plant Design for Alkali Hydrolysis: Wood \rightarrow H_2 , CH_4 , C_2H_6 + C_3H_8



- Adjusted feedstock assumption from previous model
 - Now 72.6% cellulose; 27% lignin surrogate ($C_8H_8O_3$); 0.4% ash
- Reduced hydrolysis to one-step alkali process
 - Alkali is derived from potassium in wood
 - Complete hydrolysis of lignin
- Eliminated sulfur recovery
- Combust process gases instead of unconverted lignin
- Reduced reformer size based on ethanol kinetics

Technical Accomplishments: Economic Analysis

Revised Economic Projections for Alkali Hydrolysis

H ₂ delivery options	Membrane options	Membrane Flux / [SCFH/ft ²]	Membrane Cost / [\$/ft ²]	Membrane % of capital cost	Efficiency /%	H ₂ selling price / [\$/kg H ₂]
1 atm	DOE targets	200	1500	54.6	58.1	1.18
	DOE cost, reduced flux	60	1500	80.0	58.1	1.76
	UTRC advanced concept	200	100	7.4	58.1	0.95
150 psia (compressor)	DOE targets	200	1500	45.7	54.9	1.27
	DOE cost, reduced flux	60	1500	73.8	54.9	1.85
	UTRC advanced concept	200	100	5.3	54.9	1.04
300 psia (compressor)	DOE targets	200	1500	45.7	53.9	1.27
	DOE cost, reduced flux	60	1500	73.8	53.9	1.85
	UTRC advanced concept	200	100	5.3	53.9	1.04

- UTRC task of delivering H₂ at 300 psia requires either back pressure on membrane or compressor system, but compressor is more cost effective
- At DOE H₂ membrane targets, H₂ price is (\$1.18–\$1.27)/kg H₂
- Reduced flux membranes yield a H₂ price of (\$1.76 –\$1.85)/kg H₂
- **UTRC advanced concept membrane gives a H₂ price of (\$0.95 –\$1.04)/kg H₂**

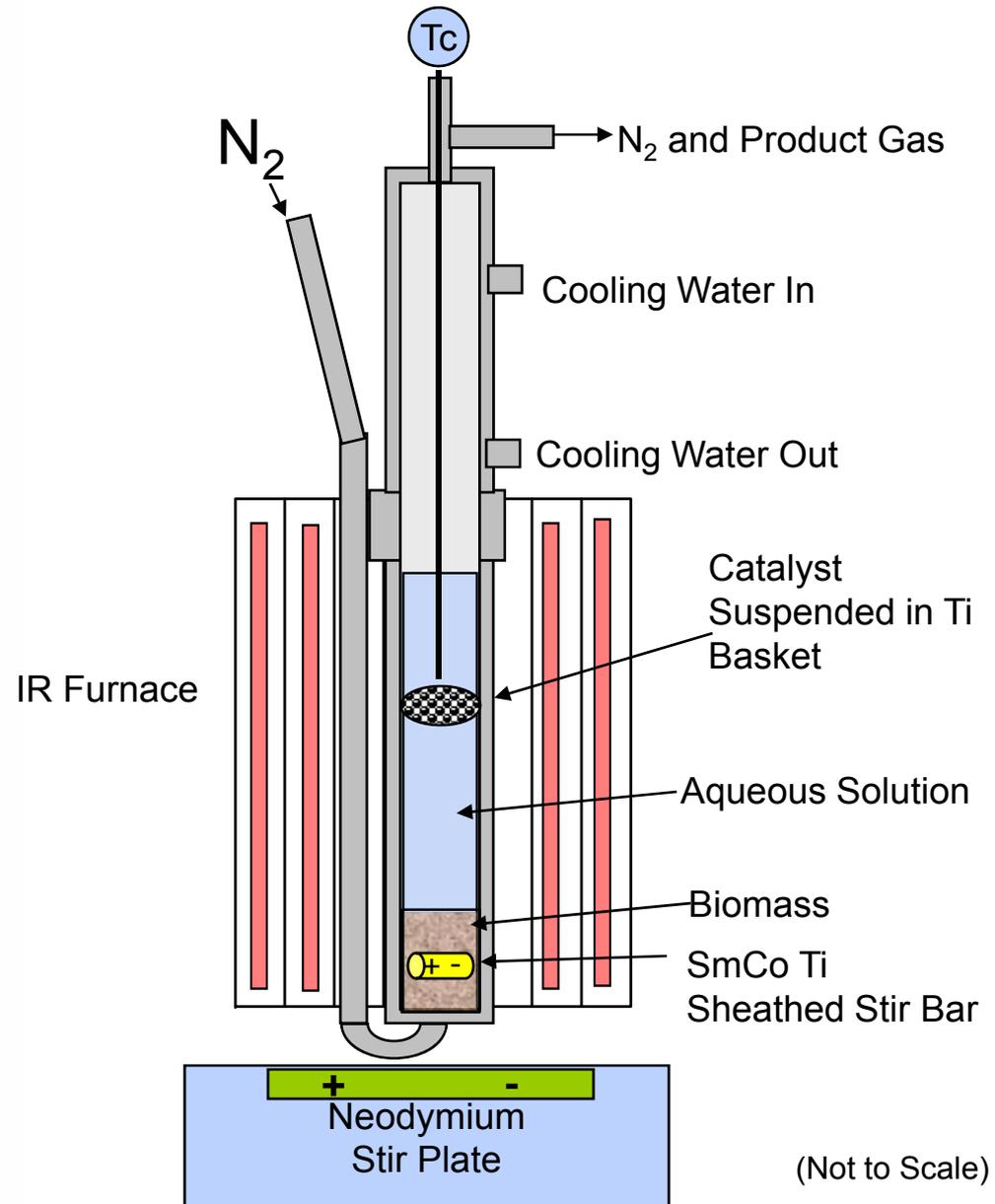
Semi-Batch Reactor

Titanium Reactor

Maximum Operating Conditions:

Pressure (2000 psig)

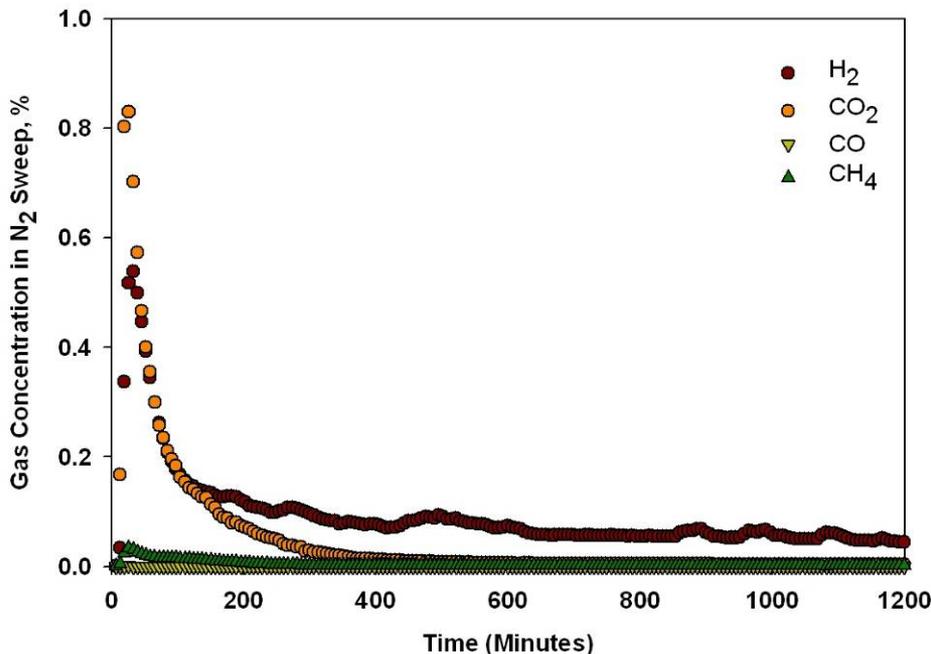
Temperature (310 °C)



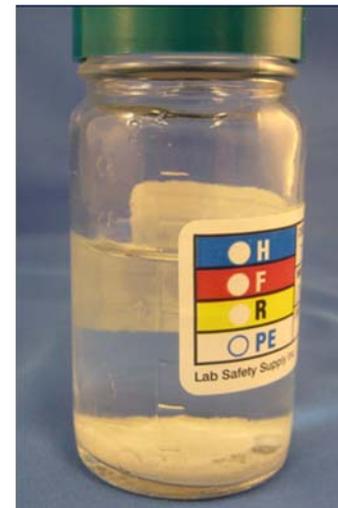
(Not to Scale)

Technical Accomplishments: Total Reforming of Yellow Poplar

≈100% conversion of yellow poplar to gas with continuous H₂ removal

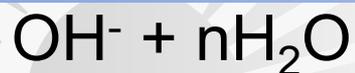


Effluent product profiles from the hydrolysis and liquid phase reforming of 1 wt% yellow poplar at 310 °C in 0.1M K₂CO₃ with a 0.5 L/min N₂ sweep gas.



- Semi-batch conversion of yellow poplar to H₂, CH₄, C₂H₆, & C₃H₈
- For LHV_{wood} = 18 kJ/g; If all H₂ is from reforming, H₂ LHV efficiency would be 75%
- Complete conversion of wood, including lignin: only trace organic carbon in liquid
- Alkane byproducts could provide enough energy to run endothermic reformer

Technical Accomplishments: Proposed Wood Reforming Pathway

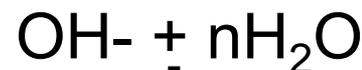


Hemicellulose
Cellulose
Lignin
Others

Heat
Peeling
Reaction

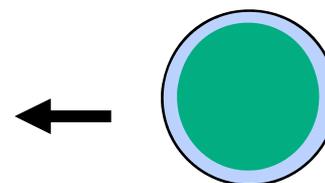
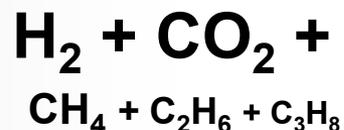
Reacted Glucose
Reacted C5 sugars
Uronic Acids

Lignin + Fragments



Alkyl & methoxy phenols etc.

Tar and Solids



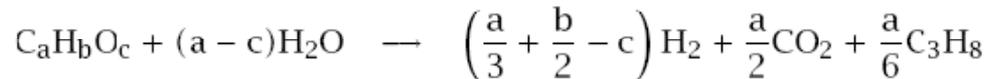
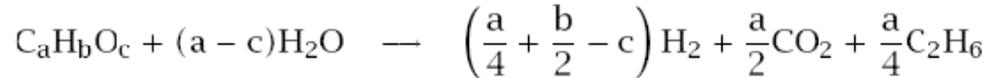
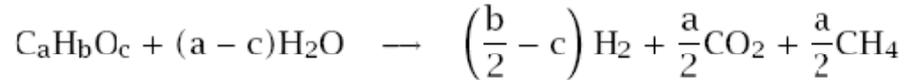
Nano-engineered
Catalyst

Unreformed hydrolysis products form intractable tars over time.

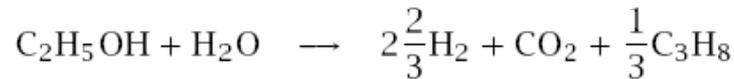
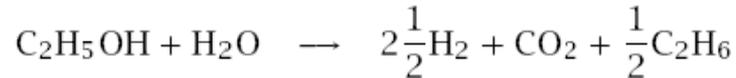
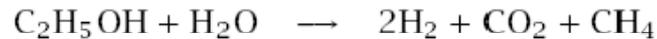
Technical Accomplishments: Ethanol Reforming

Reforming Reaction Network Determined from Ethanol Experiments

Generic Reaction Network



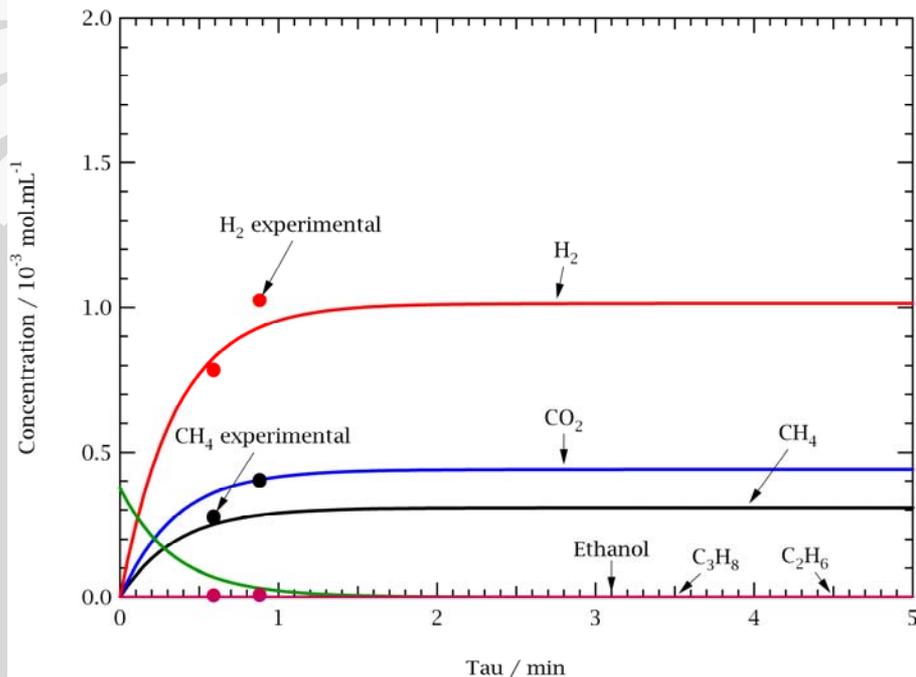
Ethanol Reaction Network



- Develop mathematical model based on simple feeds
- Extend model to more complicated feeds like wood via a surrogate compound based on compositional analysis
 - For example, yellow poplar might be represented by $C_6H_8O_4$
- Use models to understand H_2 selectivity, reactor sizing, and performance

Technical Accomplishments: Ethanol Reforming

Developed Kinetic Model for Reactor Sizing and Economics



$r_1 = k_1 C_{\text{feed}}$	$E_1 = 225 \text{ kJ.mol}^{-1}$
$r_2 = k_2 C_{\text{feed}}$	$E_2 = 155 \text{ kJ.mol}^{-1}$
$r_3 = k_3 C_{\text{feed}}$	$E_3 = 70 \text{ kJ.mol}^{-1}$
$r_4 = k_4 C_{\text{feed}}$	$E_4 = 126 \text{ kJ.mol}^{-1}$
$\tau = \frac{V}{q}$	

$$\frac{dC_{\text{feed}}}{d\tau} = \rho_{\text{cat}} (-r_1 - r_2 - r_3 - r_4)$$

$$\frac{dC_{\text{H}_2\text{O}}}{d\tau} = \rho_{\text{cat}} (-(2a - c)r_1 - (a - c)r_2 - (a - c)r_3 - (a - c)r_4)$$

$$\frac{dC_{\text{H}_2}}{d\tau} = \rho_{\text{cat}} ((2a + b/2 - c)r_1 + (b/2 - c)r_2 + (a/4 + b/2 - c)r_3 + (a/3 + b/2 - c)r_4)$$

$$\frac{dC_{\text{CO}_2}}{d\tau} = \rho_{\text{cat}} (ar_1 + (a/2)r_2 + (a/2)r_3 + (a/2)r_4)$$

$$\frac{dC_{\text{CH}_4}}{d\tau} = \rho_{\text{cat}} ((a/2)r_2)$$

$$\frac{dC_{\text{C}_2\text{H}_6}}{d\tau} = \rho_{\text{cat}} ((a/4)r_3)$$

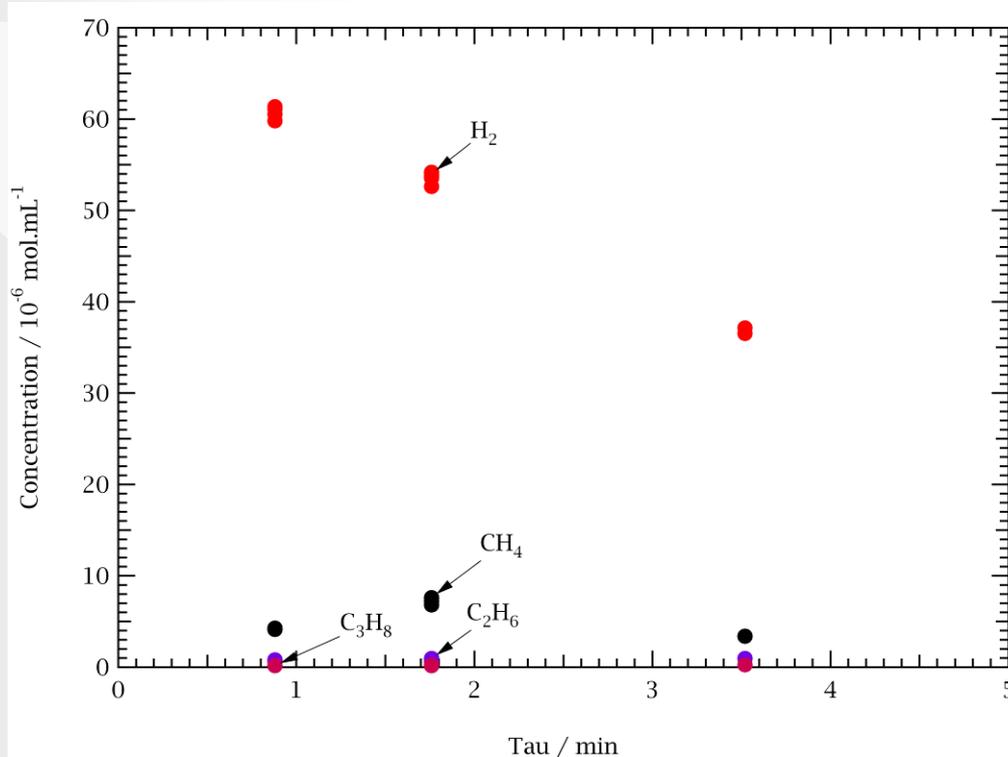
$$\frac{dC_{\text{C}_3\text{H}_8}}{d\tau} = \rho_{\text{cat}} ((a/6)r_4)$$

Ethanol reforming at 310 °C compared to model

- Preliminary flow reactor tests confirmed model for ethanol system
- Ethanol system performance understood
- Reforming to H₂ LHV efficiency ≈ 52.7% for a 1.7 wt% ethanol feed
- Goal is to extend the model to wood feedstocks

Technical Accomplishments: Yellow Poplar Flow Reactor

Beginning to Understand the Flow Operation & Kinetics of Wood Reforming

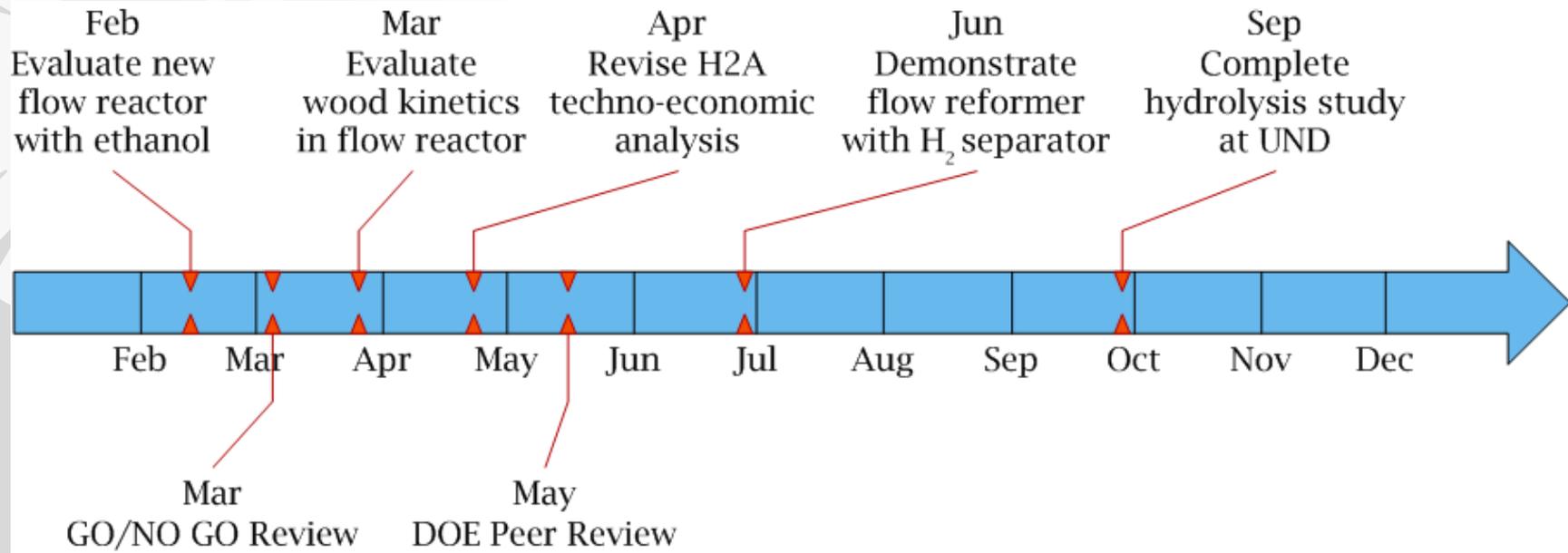


- First flow reactor tests with hydrolyzed wood
- Much higher H_2/CH_4 yields than with ethanol
- Reactor packing material deteriorated, causing apparent activity loss:
New Packing Identified
- Hydrolyzed wood liquor is unstable, darkens rapidly and develops solids, may require process design change.

Collaborators

- University of North Dakota Energy and Environmental Research Center
 - Subcontractor for hydrolysis studies & demonstration
 - Contract signed in December 2008
 - Secured of hybrid poplar for UTRC & UND studies
 - Effort currently focused on characterizing components of alkali hydrolyzed biomass
 - 2009 objective to examine the effect of several variables (e.g., base concentration, temperature, and pressure) on hydrolysis products and conversion
- Catalyst oxide support technology was transferred to a vendor
- Membrane Technology Development on DE-FC26-07NT43055
 - Power+Energy (Industry)
 - Manufacture of hydrogen separators
 - UTRC alloy fabrication
 - Metal Hydride Technologies (Ted Flanagan from Univ. of Vermont)
 - Fundamental experiments on hydrogen solubility
 - Experimental measurements of alloy systems for thermodynamic phase modeling

Proposed Future Work



2009

- Evaluate kinetic model on wood reforming
- Complete techno-economic analysis
- Demonstrate reformer operation with a H₂ separator
- Complete UND hydrolysis study

Future: Phase 2

- Develop 1-kWe demonstration system

Summary

- Provide overview of project progress
 - Demonstrated >97% conversion of wood to hydrogen with high efficiency
 - Developing kinetic understanding through model compounds (e.g., ethanol)
 - Commenced Flow reactor experiments to extend kinetic model to wood
 - System efficiency and economics favorable compared to gasification
- GO/NO GO decision: Received a GO decision in March 2009
- Future work: Reactor Design, Base Treatment Protocol, catalyst morphology and catalyst atomic/electronic structure, reformer+membrane demonstration

Supplemental Slides

- Supplemental slides follow

Modeling and Simulation Assumptions

- 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 H₂: 100%
- The biomass feedstock: 72.6% cellulose, 27% lignin surrogate (C₈H₈O₃) and 0.4% ash.
- Biomass feedstock price is: \$0.05/kg (dry basis; twice the value in the H2A tool)
- One-stage hydrolysis processes operated at temperature of 310 °C.
- 95% conversion of cellulose was assumed based on our preliminary experimental results.
- In the baseline design, the yield of H₂ and CO₂ from glucose: 90% from sugar hydrolyzed from cellulose and 95% from lignin surrogate over the advanced high activity, high selectivity catalyst system.
- Ultra-pure H₂ from membrane compressed to 300 psia for pipeline

Approach: UTRC Catalyst Discovery Paradigm

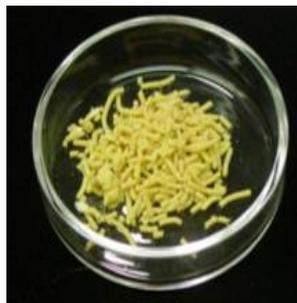
Successfully Employed to Develop High Activity, Long Lived (>5X) Catalysts

Conceptual Catalyst Design

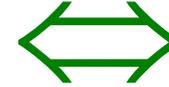
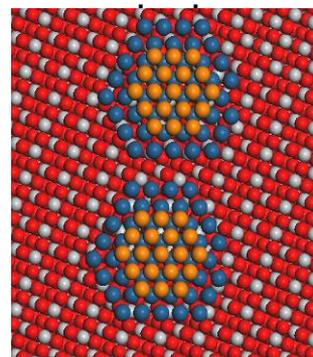
- Literature Search: Catalyst Chemistry
- Nano-Engineering Specifications:
 - Pore Sizes,
 - Porous Particle Sizes



Catalyst Synthesis

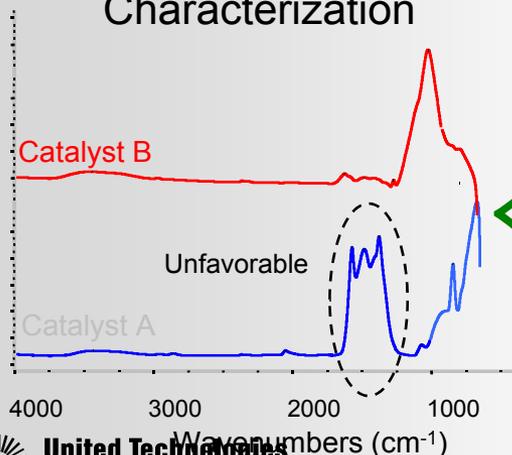


Quantum Mechanical Atomistic Modeling for advanced catalysts

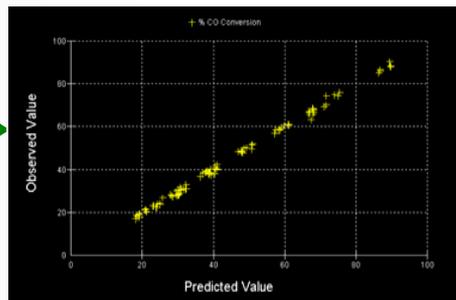


High active surface area
Large pore Nanocrystalline structure
~100% NM dispersion

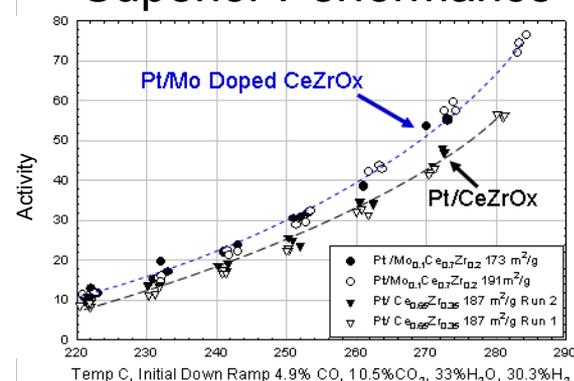
Characterization



Kinetic Expressions Derived From Reaction Data



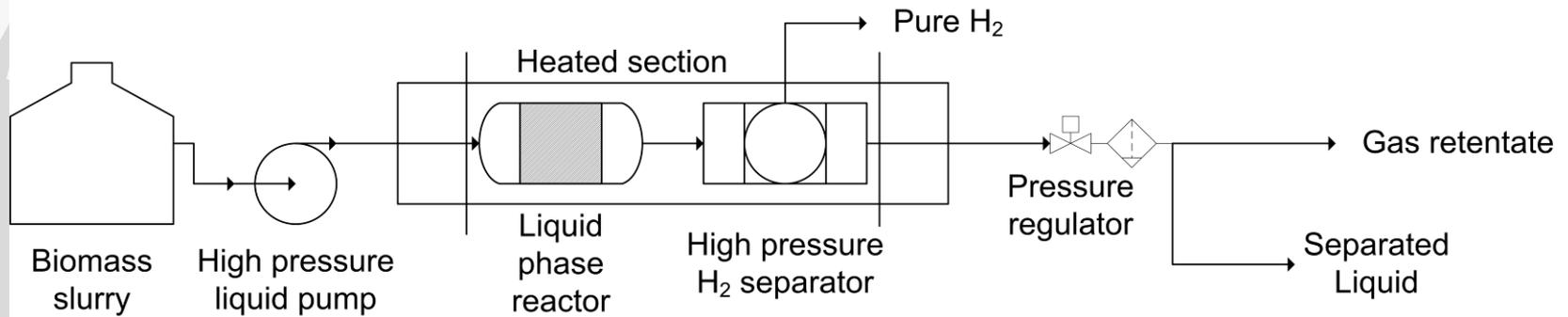
Superior Performance



Higher Activity Catalyst with Similar Pt & Surface Area

Targeted 1-kWe Demonstration System

Combine liquid phase reforming with advanced H₂ separation membrane



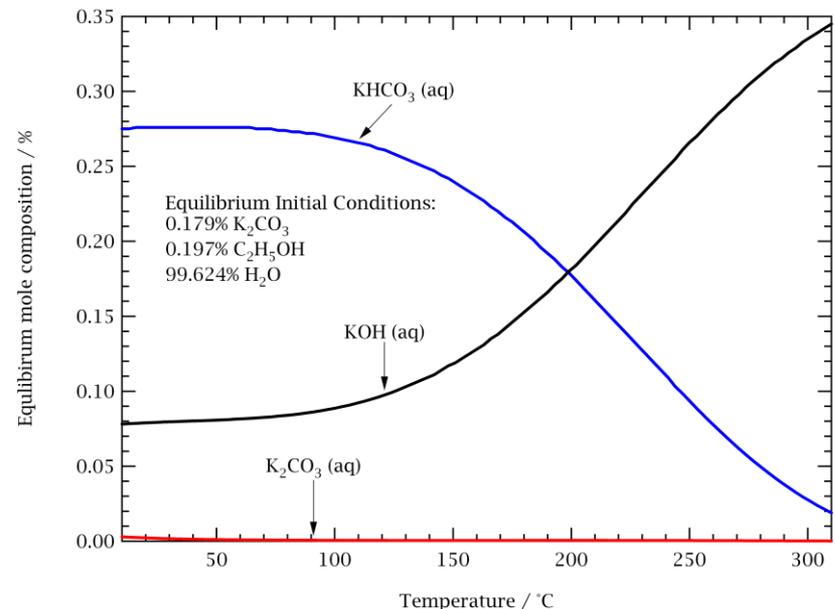
- Combine technology advances from Biomass to H₂ program with advanced high pressure H₂ membrane concept
 - Operation at $T \approx 310 \text{ }^\circ\text{C}$, $P > 1417 \text{ psig}$
- 1 kWe H₂ requires 12.1 L/min H₂ (2 kW H₂)
 - 5.4 L/h (90 mL/min) of biomass slurry ($\approx 10 \text{ wt}\%$ biomass)
 - Reactor volume $< 0.5 \text{ L}$
- Energy required only for liquid pumping and heating of membrane reactor

History- Overall Scheme

- Initial plan was aqueous phase reforming of biomass in acid
 - Use acid to hydrolyze biomass
 - Develop novel sulfur tolerant catalyst to reform hydrolyzed species
- Numerous technical hurdles, including:
 - Sulfur poisoning, catalyst dissolution, support dissolution, hydrolysis optimization.
 - Attempts to create sulfur tolerant catalyst unsuccessful
 - Activities in catalyst development further deterred by discovery of charring issues in acid hydrolysis of real biomass
 - Glycerol testing indicated acid catalyzed polymerization
- Course changed to use of base:
 - Similar technical challenges, catalyst competition, corrosive environment, little literature
 - However, there exists a path for hydrolysis
- Have proven feasibility of system
 - Complete conversion of raw biomass to gas at 310°C with >70% selectivity to H₂.

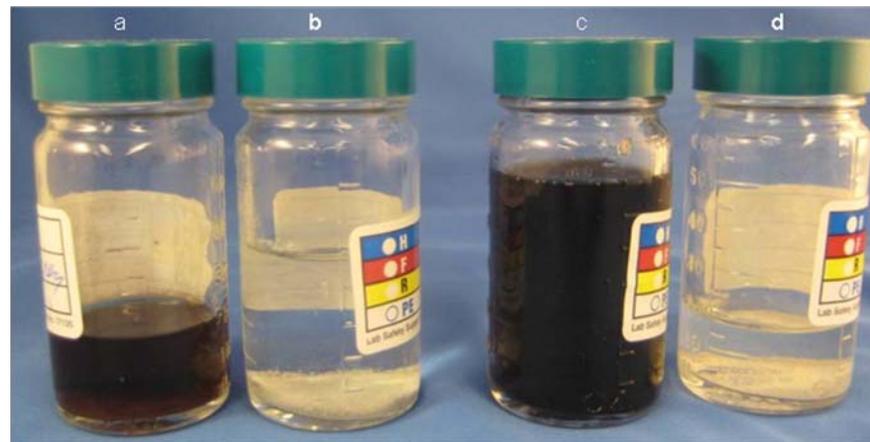
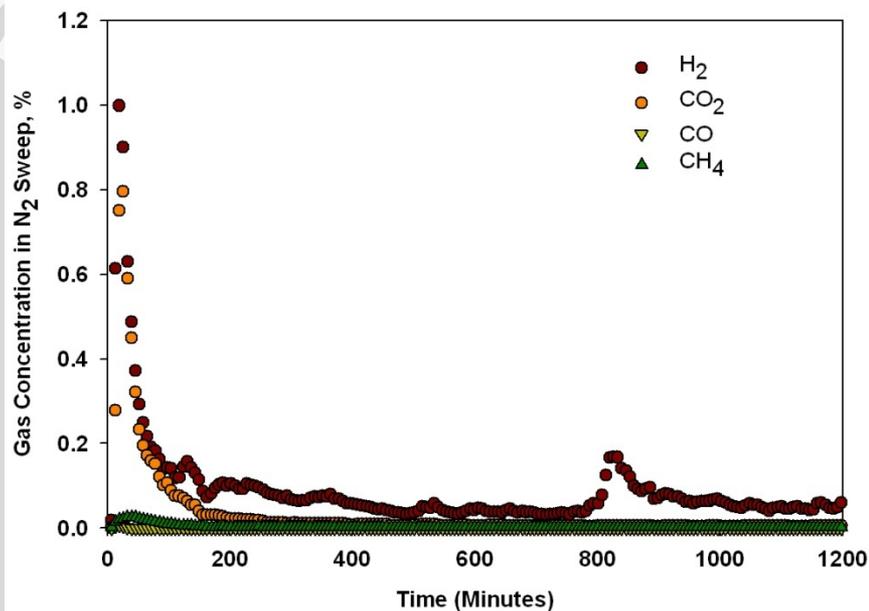
Potassium Species

- Questions regarding which base to use
 - KOH pH 14
 - K_2CO_3 pH 10.5
 - $KHCO_3$ pH 8.5
- K_2CO_3 chosen for study
 - Behaves like KOH at high temperatures
 - Recyclable
- Issues closing carbon balance
 - CO_2 Scrubbing



Reforming with Wood Components

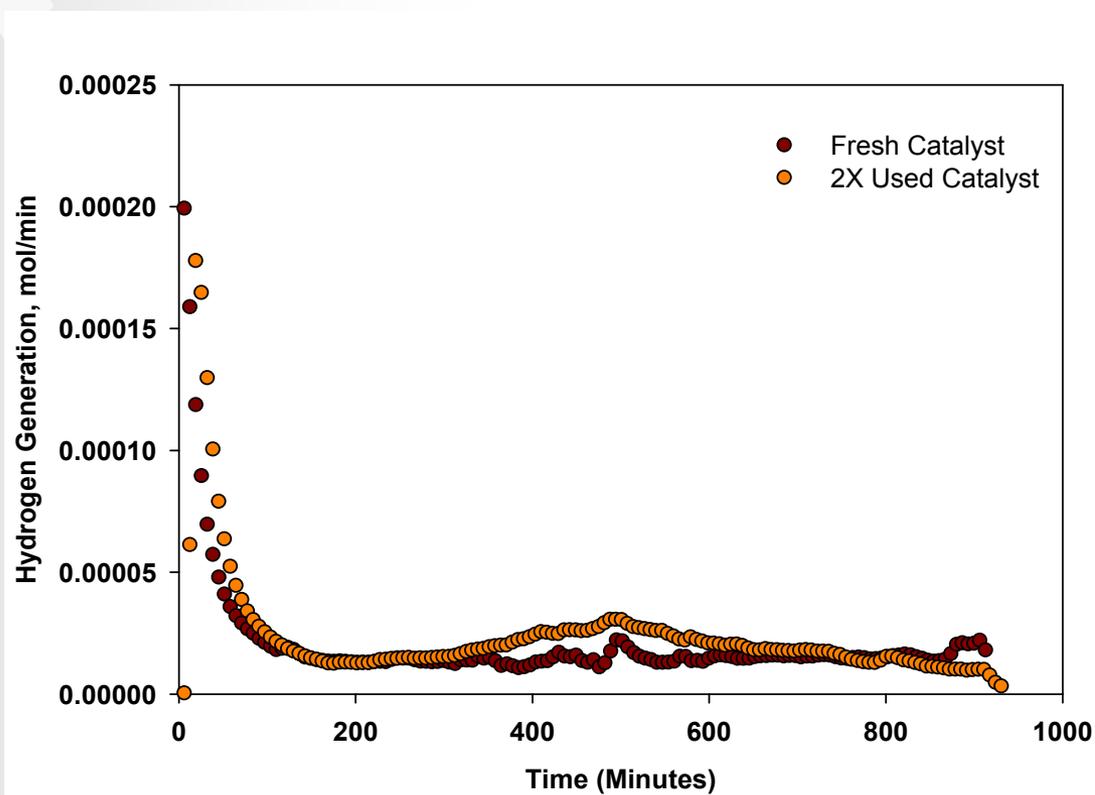
- Cellulose, Hemicellulose, Lignin comprise ~43.9, 15.7, 26.0 wt% wood
- 1% Feed in 0.2M KOH at 310°C, 110atm, 2% Pt-3% Re/Ce_{0.55}Zr_{0.45}O₂



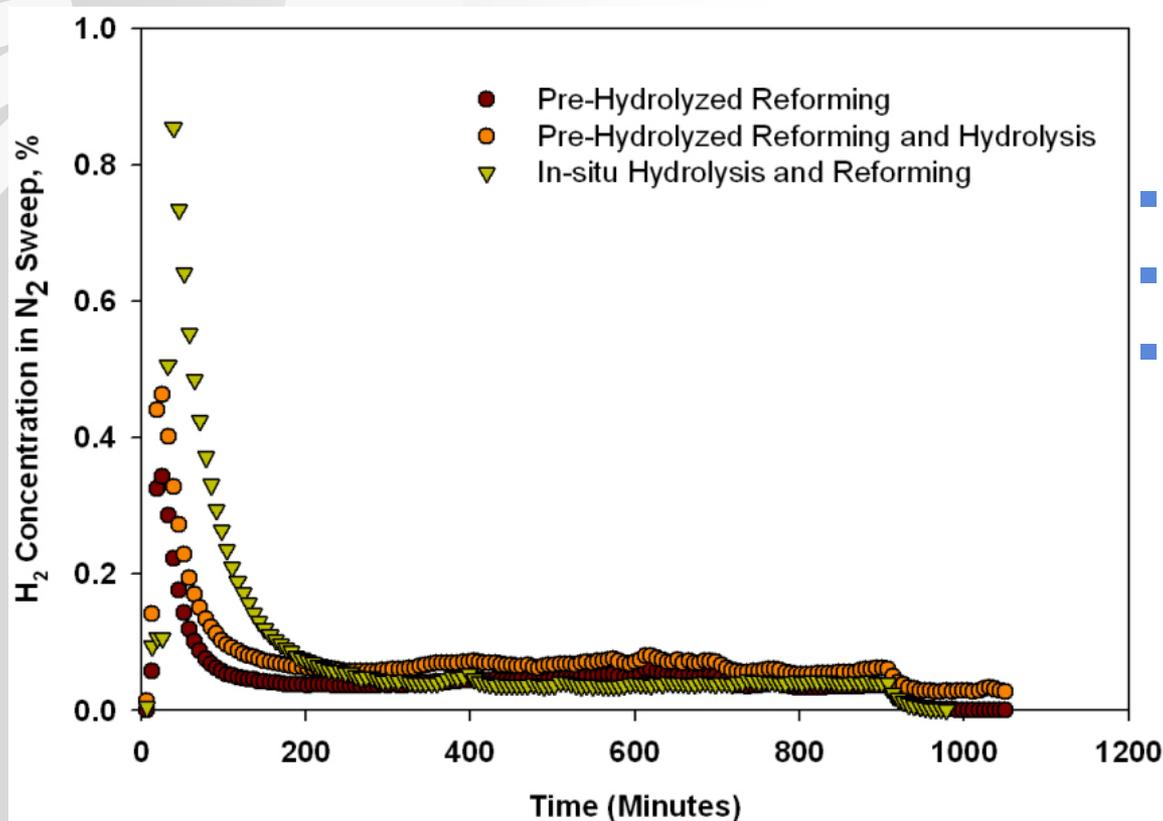
- Complete LPR of Cellulose and Xylan in 0.2M KOH
- H₂ Selectivity >80%
- Increased temperature led to increased conversion

LPR with Wood Components- Catalyst Stability

- 1% Cellulose in 0.2M KOH at 310°C, 110atm, 2% Pt-3% Re/Ce_{0.55}Zr_{0.45}O₂
- Repeated 3X, no apparent loss in activity



Pre-Hydrolysis vs. In-Situ Hydrolysis



- 1% Yellow Poplar at 310°C
- Matched conversion
- Matched selectivity

