A Novel Slurry Based Biomass Reforming Process

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Project ID #PD006

Overview

- Timeline
  - Start: May 2005
  - End: March 2011
  - 75% Complete
- Budget
  - Total Project Funding
    - DOE share: $3M
    - Contractor share: $750k
  - Funding Received in FY09
    - $600k
  - Funding for FY10
    - $590k
- 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
    - Wood reforming studies

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 H_2 production
  - Efficiency & H_2 cost exceed gasification targets
  - Capital costs dependent on H_2 delivery pressure & H_2 separation membrane
  - **Current costs assume a precious metal based catalyst**
- Development of cost effective catalysts for liquid phase reforming of biomass hydrolysis-derived oxygenates
  - **Switch to base metal catalyst decreases hydrogen cost by ≈$0.20/kg H_2**
- Proof-of-concept demonstration of a micro-scale pilot system based on liquid phase reforming of biomass hydrolysis-derived oxygenates
  - **Phase II work now started**

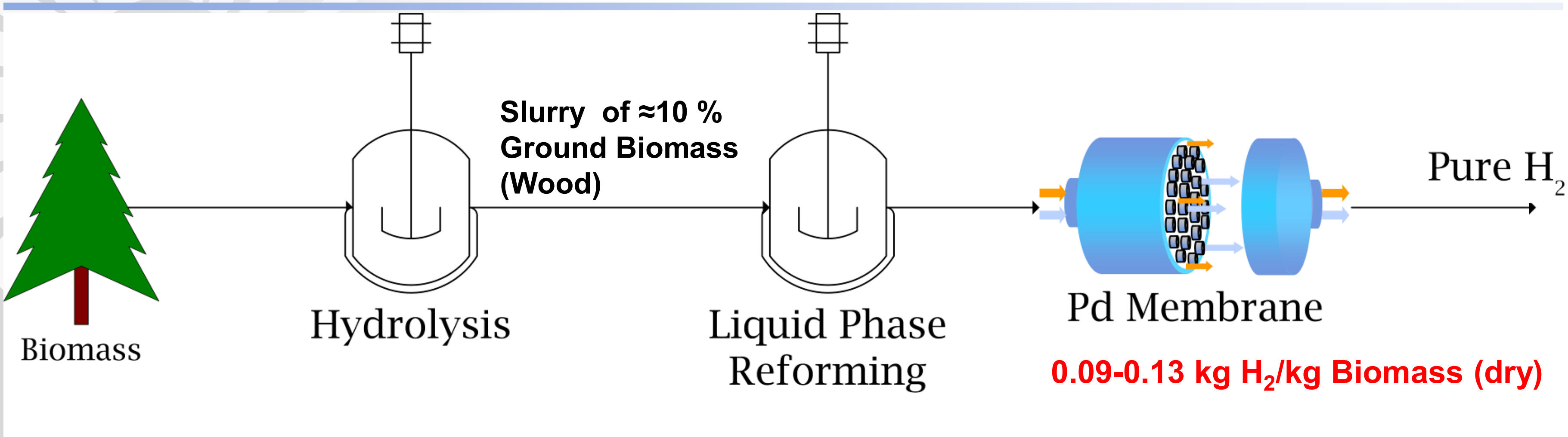
	Target	2009 Status
Hydrogen Cost (Plant Gate)[a]	1.60 $/gge	$1.27/kg H_2 ($0.95/kg – $2.13/kg)
Total Capital Investment	$150M	$177M ($71M – $365M)
Energy Efficiency[b]	43%	55% (55% – 58%)

a. Gallon of gasoline equivalent (gge) ≈ kg H_2

b. Plant H_2 Efficiency

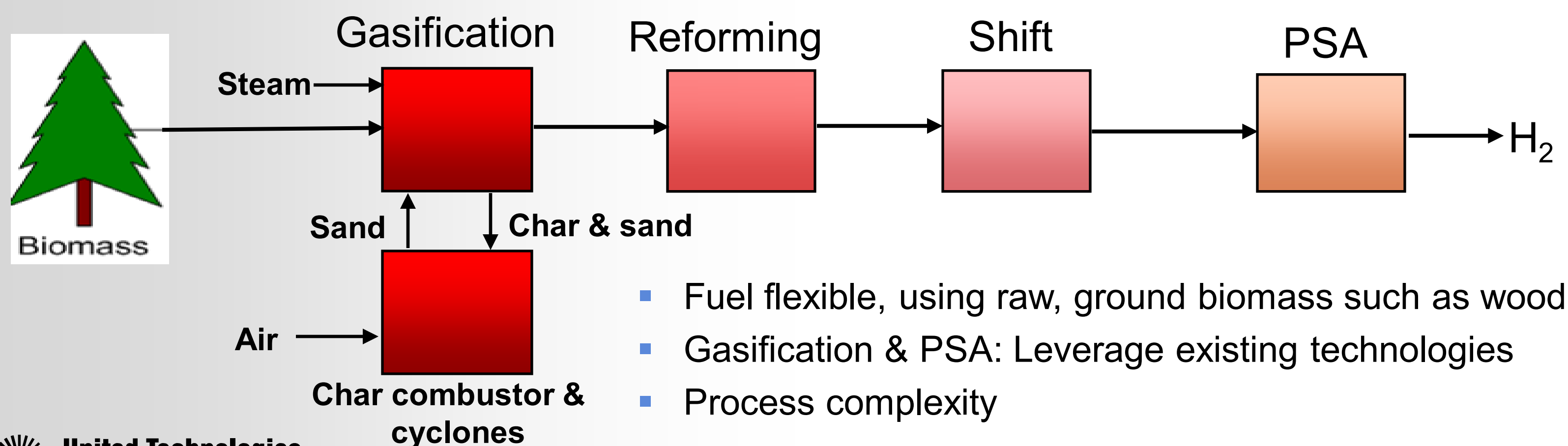
$$\text{Plant } H_2 \text{ Efficiency} = \frac{\text{LHV of Product } H_2}{\text{LHV of Biomass Feed} + \text{Energy Consumed}}$$

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

Alternative: Biomass Gasification to Hydrogen Concept

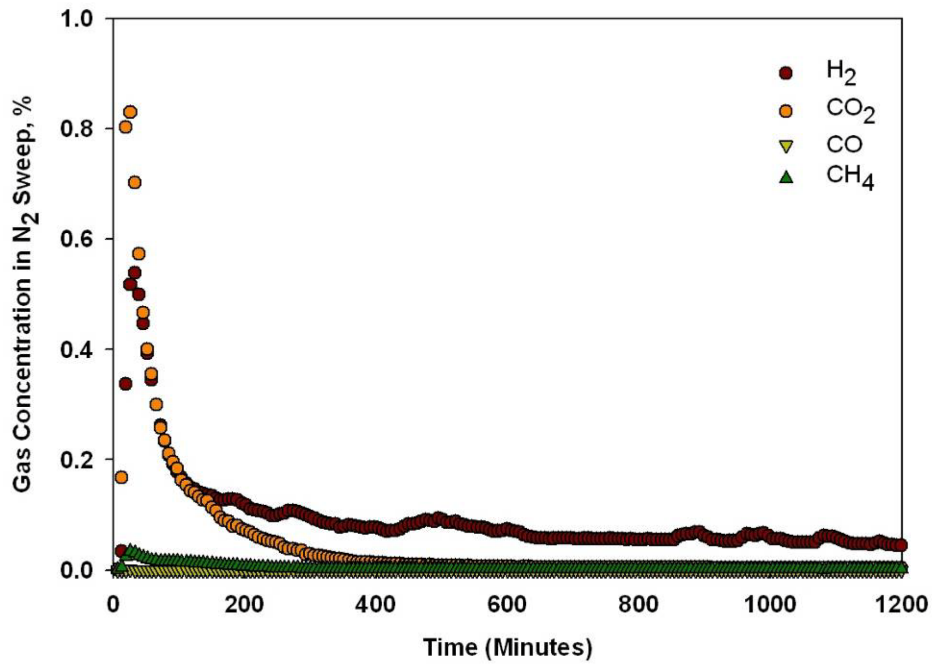


- Fuel flexible, using raw, ground biomass such as wood or switch grass
- Gasification & PSA: Leverage existing technologies
- Process complexity

2009 Accomplishment: Total Reforming of Yellow Poplar

Demonstrated ≈100% conversion of yellow poplar to H_2 (75% LHV efficiency)

Titanium Semi-Batch Reactor



Effluent product profiles from the hydrolysis and liquid phase reforming of 1 wt% yellow poplar at 310 °C in 0.1M K_2CO_3 with a 0.5 L/min N_2 sweep gas.

Reaction product liquor (The white solid is potassium titanate formed from the reactor walls.)

- Semi-batch conversion of yellow poplar to H_2, CH_4, C_2H_6, & C_3H_8
- H_2 selectivity of 74% (among H_2 containing gases)
- For LHV_{wood} = 18 kJ/g; 75% of wood LHV is in hydrogen
- Complete conversion of wood, including lignin; trace organic acids left
- Burned alkanes could provide enough energy to run endothermic reformer

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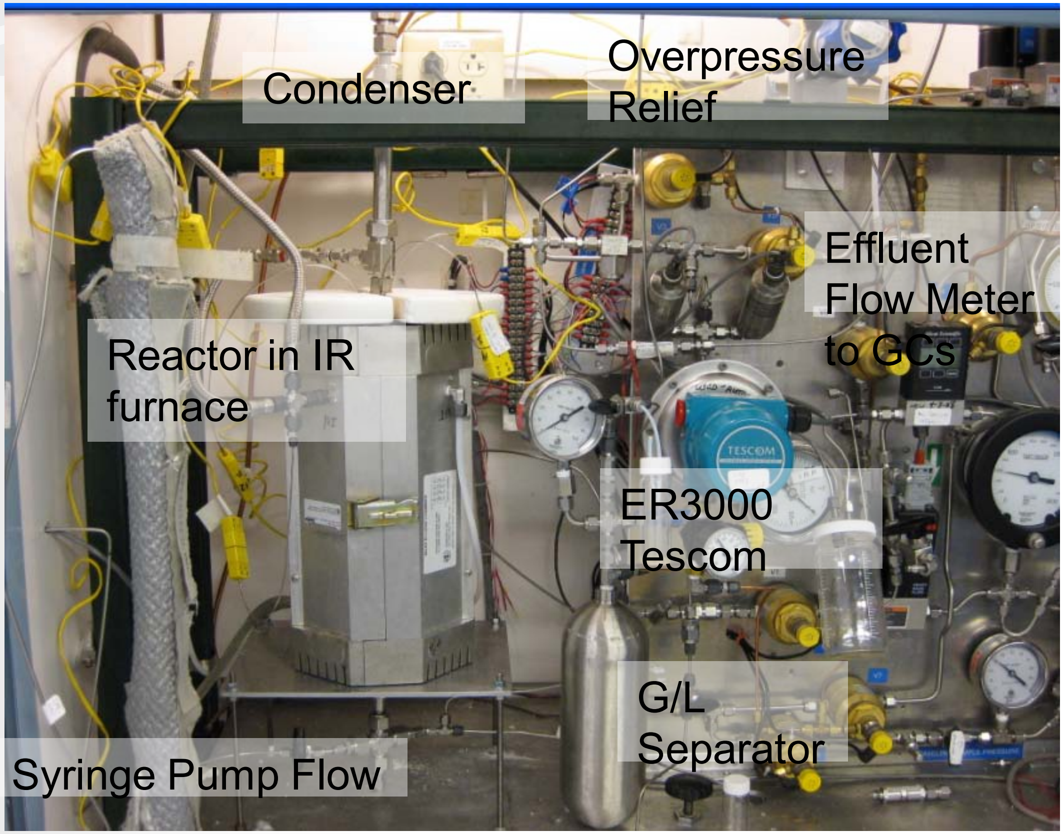
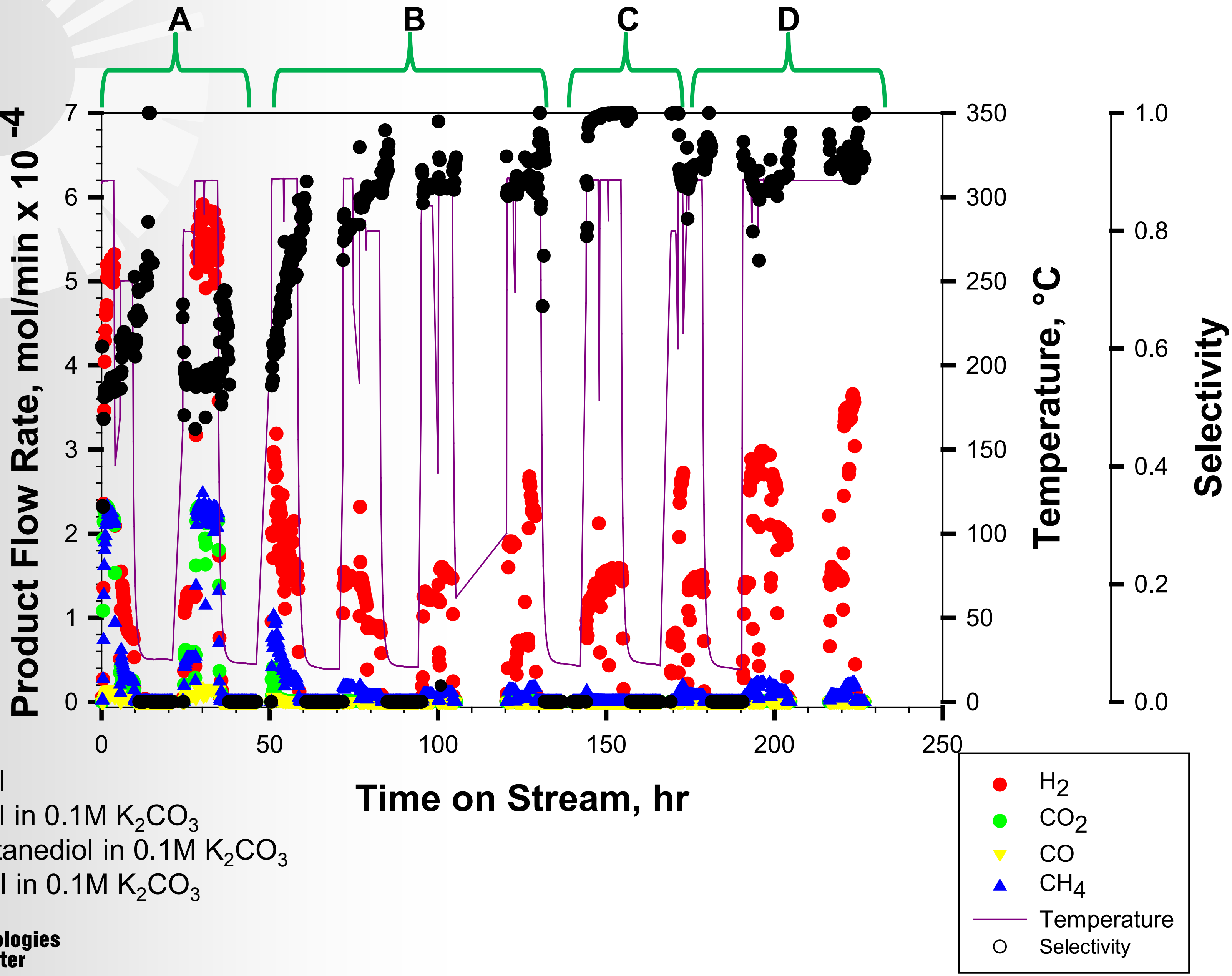
Technical: Plug Flow Reactor for Kinetics/Durability Studies



- ½-in OD Inconel 625 Reactor.
- High Pressure syringe pump for pulseless liquid feed.
- Dual GCs for Permanent Gas and Hydrocarbon analysis.

Technical: Durability Testing with 1% Ethanol



A- 1% Ethanol

B- 1% Ethanol in 0.1M K_2CO_3

C- 1% 1,4-Butanediol in 0.1M K_2CO_3

D- 1% Ethanol in 0.1M K_2CO_3

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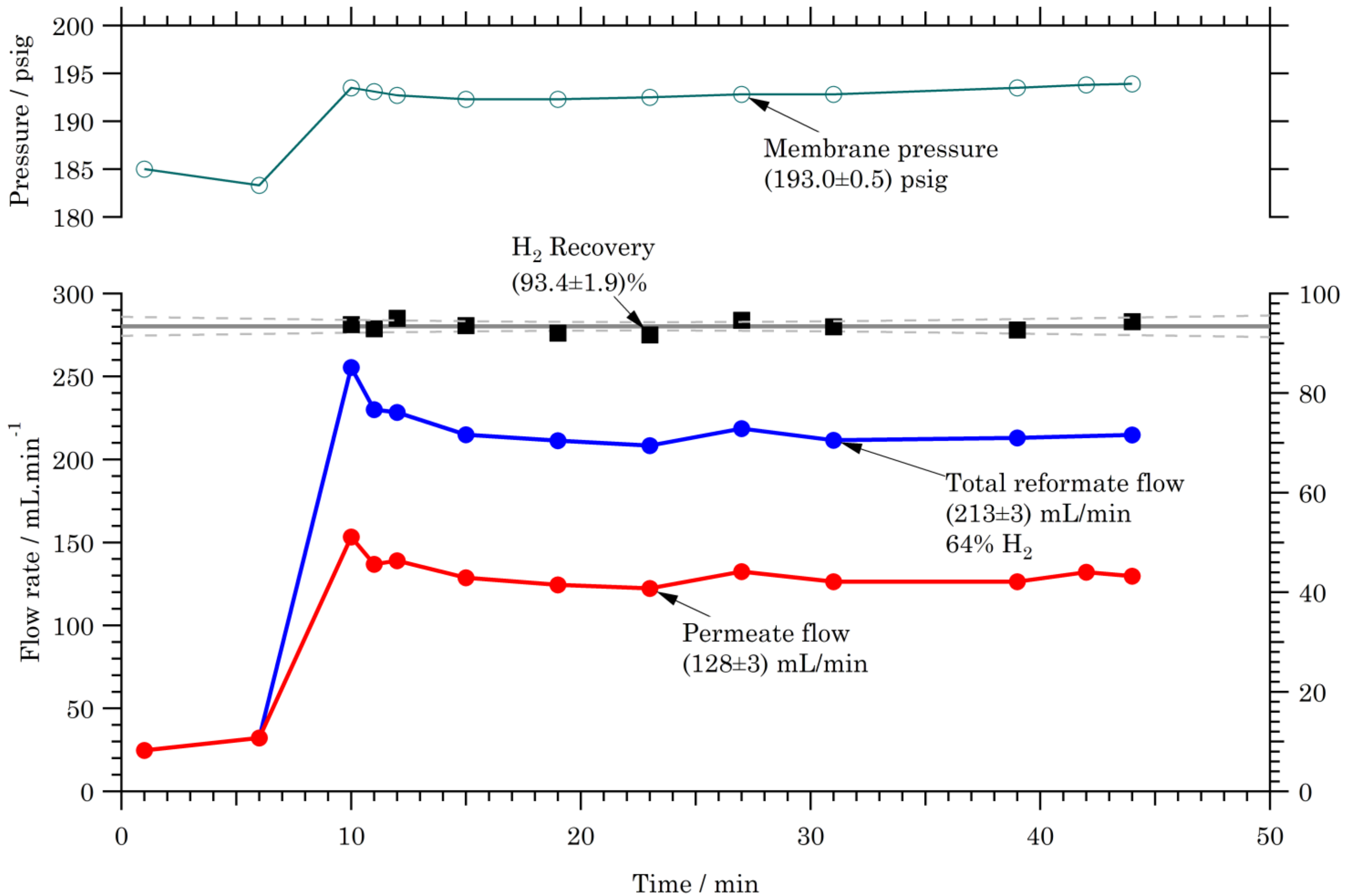
Technical: Demonstration with Pd Membrane



- Liquid phase reforming of 5% ethanol in flow reactor
- Reformer product gas containing 64% H_2 fed to membrane rig at 193 psig
- Separated hydrogen with a recovery of 93%

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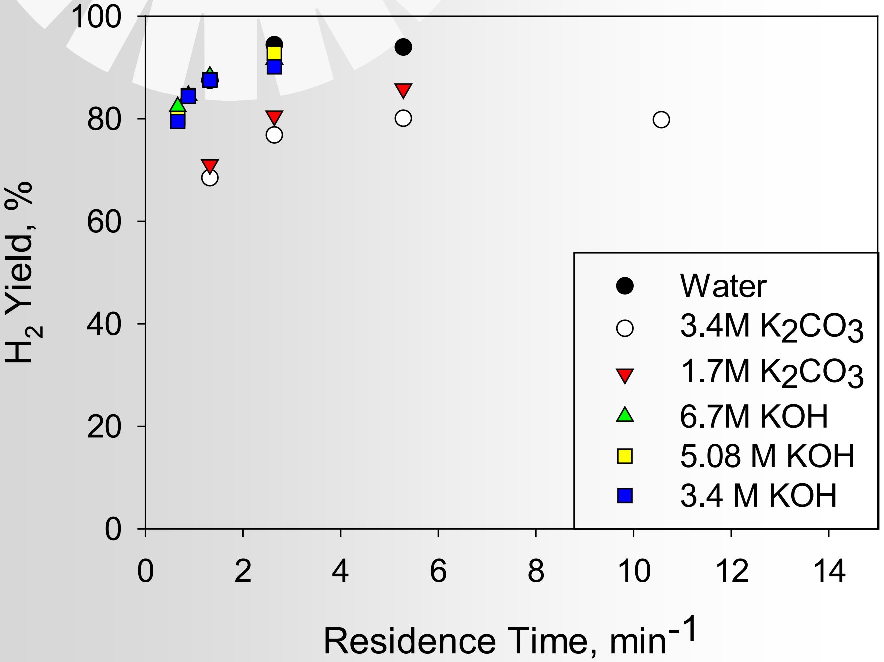
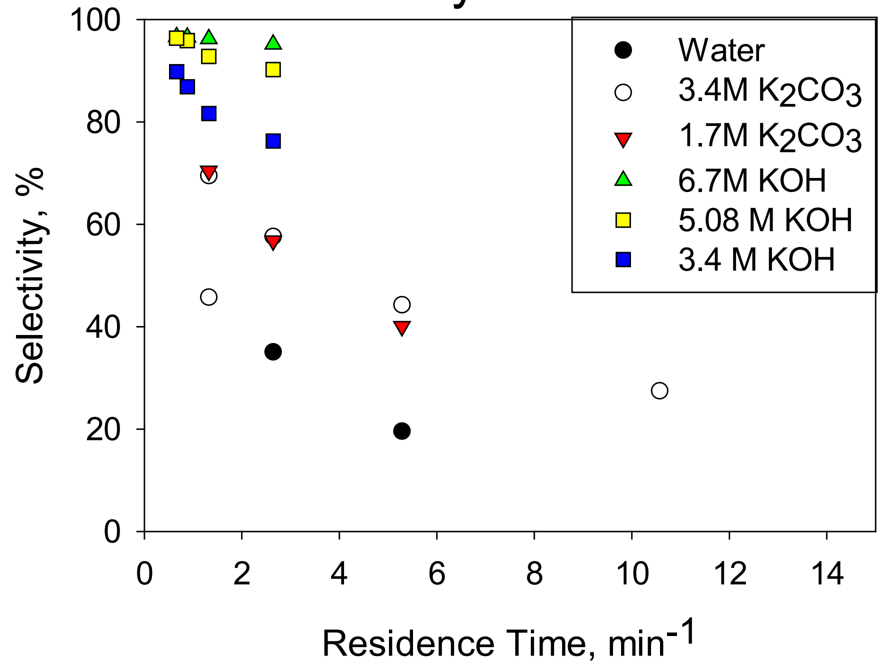
Technical: High pH Increases H_2 & Decreases CH_4

- *Moved to base metal catalyst to reduce cost (Raney Ni)*
- Methane generation with Raney nickel can be controlled by tailoring base concentrations.
- Increased base concentrations increased selectivity

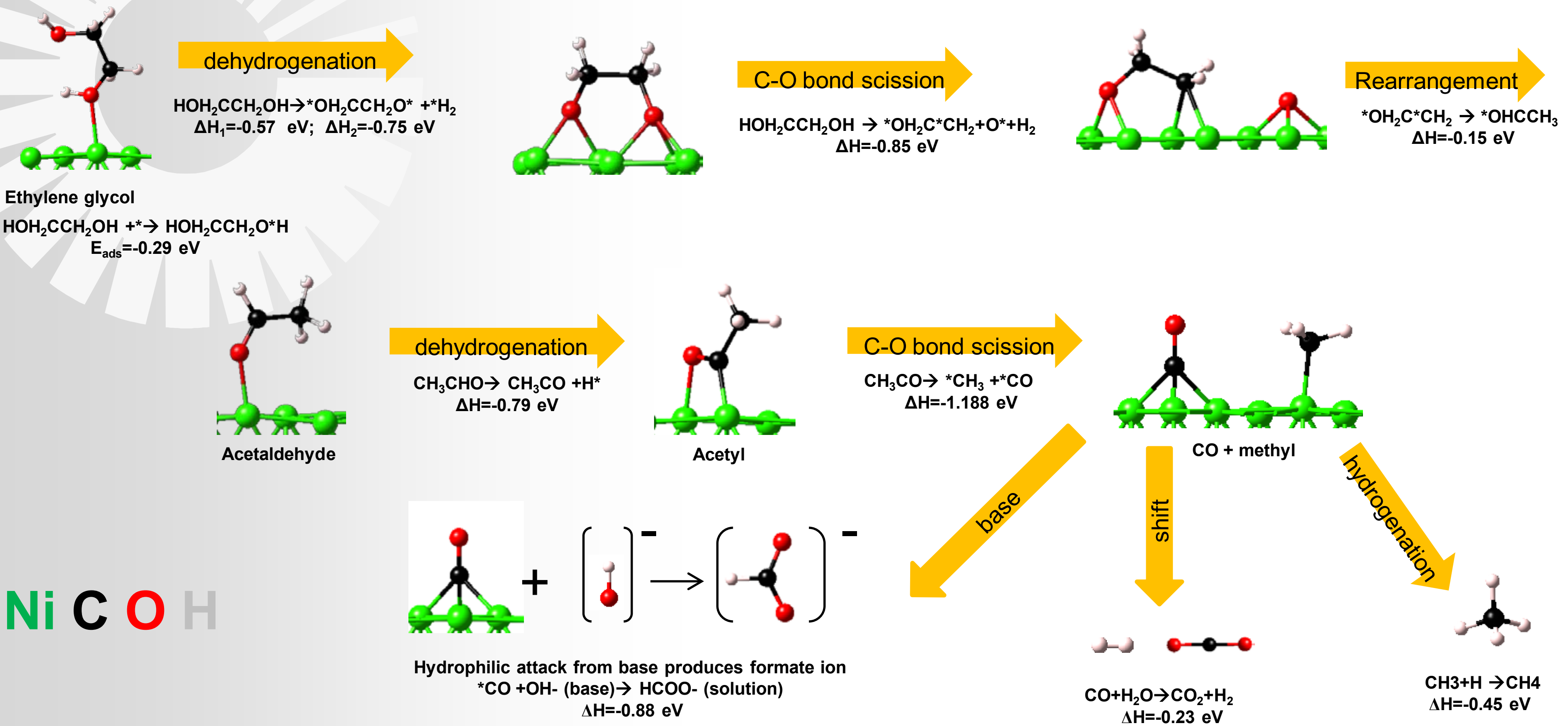




Unpromoted Raney Ni 5% EG, 310 °C, 120 atm

$$H_2\ \text{Selectivity} = \frac{2 \times H_2\ \text{in product gas stream}}{\text{Total H in product gas stream}} \times 100$$

Technical: Reforming of Ethylene Glycol over Ni



$$C_2H_6O_2 + 4KOH \longleftrightarrow 2K_2CO_3 + 5H_2 \quad \Delta G_{300^\circ C} = -423 \text{ kJ/mol}$$
$$C_2H_6O_2 + 2KOH \longleftrightarrow K_2CO_3 + H_2O + CH_4 + H_2 \quad \Delta G_{300^\circ C} = -315 \text{ kJ/mol}$$

With base

$$C_2H_6O_2 + H_2O \longleftrightarrow H_2CO_3 + CH_4 + H_2 \quad \Delta G_{300^\circ C} = -179 \text{ kJ/mol}$$
$$C_2H_6O_2 + 4H_2O \longleftrightarrow 2H_2CO_3 + 5H_2 \quad \Delta G_{300^\circ C} = -111 \text{ kJ/mol}$$

Without base

Technical: Liquid Phase Reforming of Raw Biomass

Complete conversion of 5 wt% wood feed to gaseous species

- Liquid phase reforming of raw biomass over Ni
- Commercially available wood flour
  - Hardwood mixture, 100 mesh
- 5 wt% wood at 310 °C, 120 atm in:
  - 0.2 M KOH
  - 2.0 M KOH
- Raney nickel, ~1:1 mass wood
- Low flow of N_2 Sweep gas

Technical: Liquid Phase Reforming of Raw Biomass

Complete conversion of 5 wt% wood feed to gaseous species

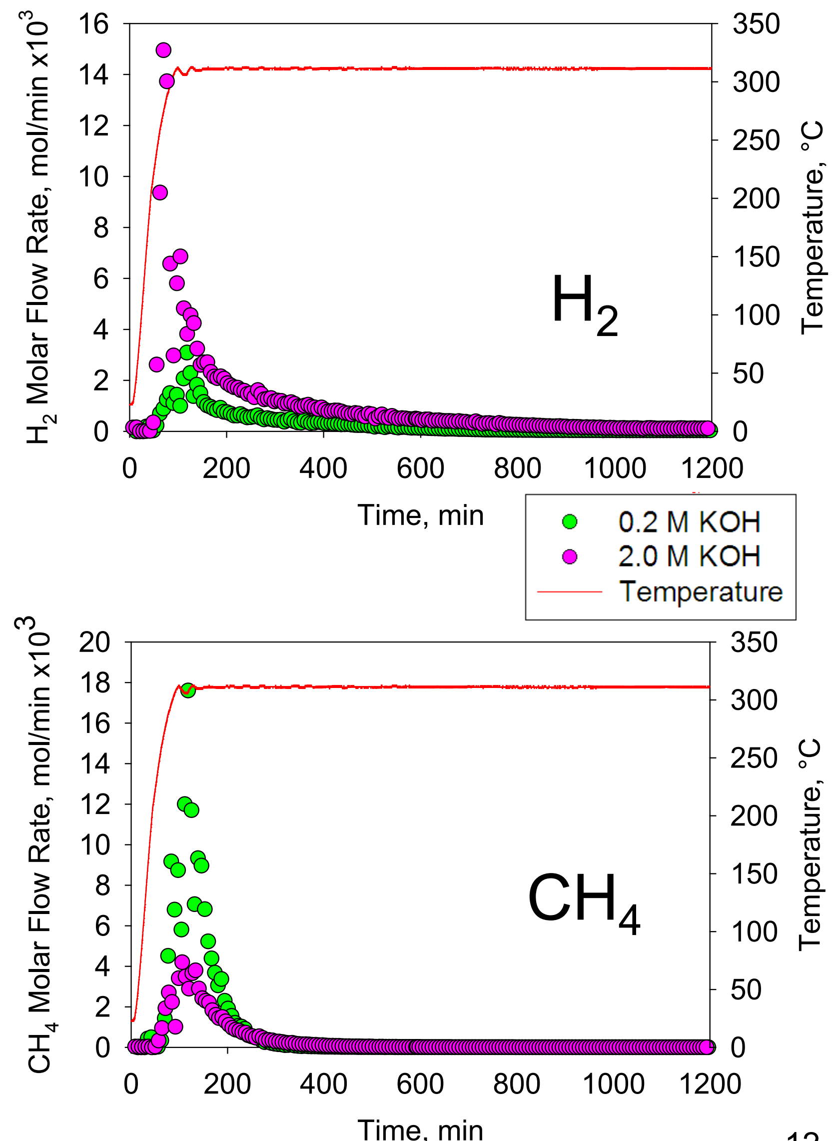
$$C_6H_{10}O_5 + 12KOH + H_2O \longleftrightarrow 6K_2CO_3 + 12H_2$$

0.2 M =0.05x Stoichiometric
2.0 M =0.5x Stoichiometric

- **Increased base increases selectivity**
  - 0.2 M KOH - 15% selectivity to H_2
  - Hydrogen Yield based on reforming ≈ 100%
  - C conversion into gas phase ≈ 100%

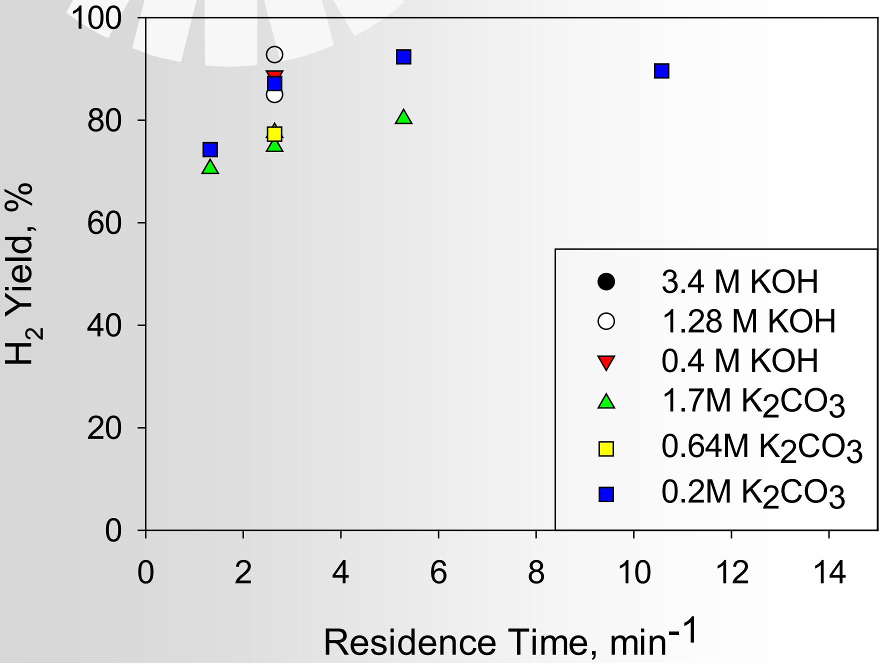
  - 2.0 M KOH - 60% selectivity to H_2
  - Hydrogen Yield based on reforming ≈ 75%

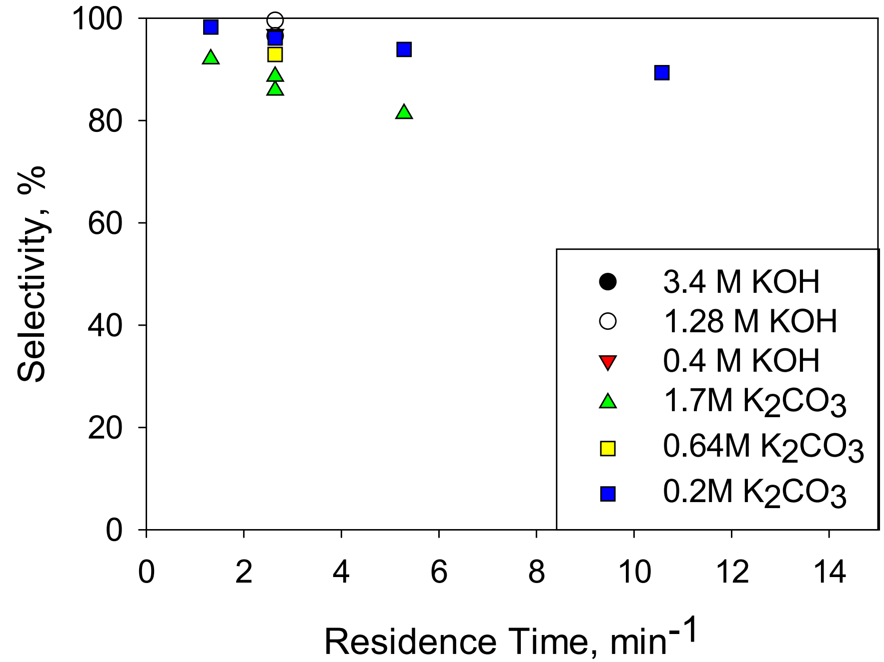
- Issues with increased base
  - **Increased base leads to high levels of intractable organic acids**
  - **Difficulty of recycling hydroxide base**



Technical: Promoted Ni Removes Need for High Base Levels

- *High H_2 selectivity and conversion*
  - *>90% conversion with >90% selectivity*
- *Enables use of dilute carbonate bases & low temperature CO_2 disengagement*





Promoted Raney Ni 2.5% EG, 310 °C, 120 atm

$$H_2\ \text{Selectivity} = \frac{2 \times H_2 \text{ in product gas stream}}{\text{Total H in product gas stream}} \times 100$$

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Technical: Construction of 12 L/min H_2 Demonstration System

Combine liquid phase reforming with advanced H_2 separation membrane

High Pressure
Inconel 625 Reactor
•310 °C, 120 atm

High Pressure
Wood Slurry Pump
•10% Slurry
•100-200 mL/min

Pd Membrane
Separator
•99.9999% H_2

Gas Liquid
Separator

Wood Slurry Mass
Flow Meter

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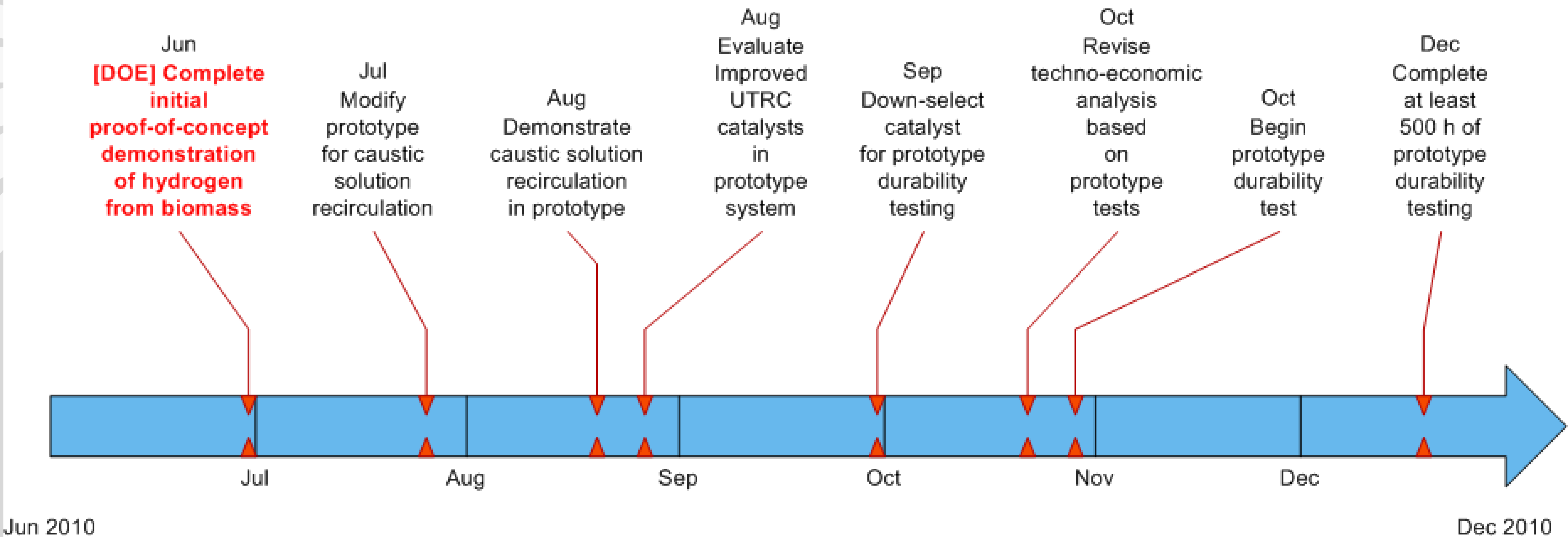
Collaborators

- University of North Dakota Energy and Environmental Research Center
  - 2010 objective to examine the effect of several variables (e.g., base concentration, temperature, and pressure) on batch LPR on base metal catalysts

- 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



2010

- Begin testing of prototype demonstration system
- Evaluate caustic solution recycle
- Evaluate and down-select final catalyst for durability study
- Revise techno-economic analysis based on demonstration system
- Perform 500-h durability study with demonstration system

Summary

- Demonstrated 100% conversion of wood with base metal catalyst


- Catalyst Development
  - Substituted base metal catalyst for precious metal
  - Promoted Ni catalyst maintaining high selectivity with dilute carbonate
  - Performed atomistic modeling to elucidate ethylene glycol LPR pathway
  - Catalyst durability >250 hours

- Reactor Design
  - Demonstrated Pd membrane integration with LPR flow reactor
  - Examined the effect of base concentration on H_2 selectivity

- Began construction of 12 L/min wood demonstration unit

Work performed under the DOE Grant DE-FG36-05GO15042 was authorized in part under a research license for the Aqueous Phase Reforming Process (Patent 6,699,457; 6,694,757; 6,694,758 [and all other licensed issued patents]) from Virent Energy Systems in Madison, Wisconsin.