A Novel Slurry Based Biomass Reforming Process

(DE-FG36-05GO15042)

S.C. Emerson, T. Davis, R. Hebert, A. Peles, S. Saitta, Y. She, J. Sheffel, R.R. Willigan, T.H. Vanderspurt, & T. Zhu

United Technologies Research Center

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Project ID #PD006

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DOE Hydrogen Program

Overview (Relevance)

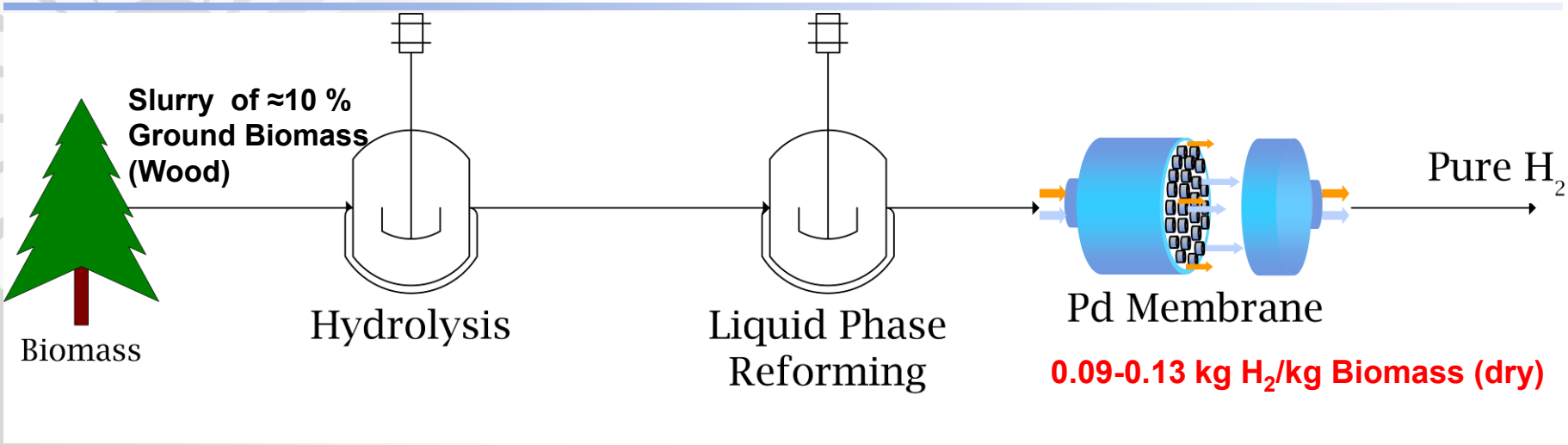
- Timeline
  - Project start: May 2005
  - Project end: June 2011
  - Percent complete: 100%
- Budget
  - Total project funding
    - DOE share: $3M
    - Contractor share: $750k
  - Funding received in FY10: $590k
  - Funding for FY11: $0k
- Barriers
  - T. Capital Costs and Efficiency of Biomass Gasification/Pyrolysis Technology
- Partners
  - Energy & Environmental Research Center at the University of North Dakota
    - Hydrolysis experimental studies
    - Slurry characterization
    - Wood reforming studies

Project Objectives (Relevance & Progress)

Developed batch and continuous process for liquid phase H_2 generation from woody biomass

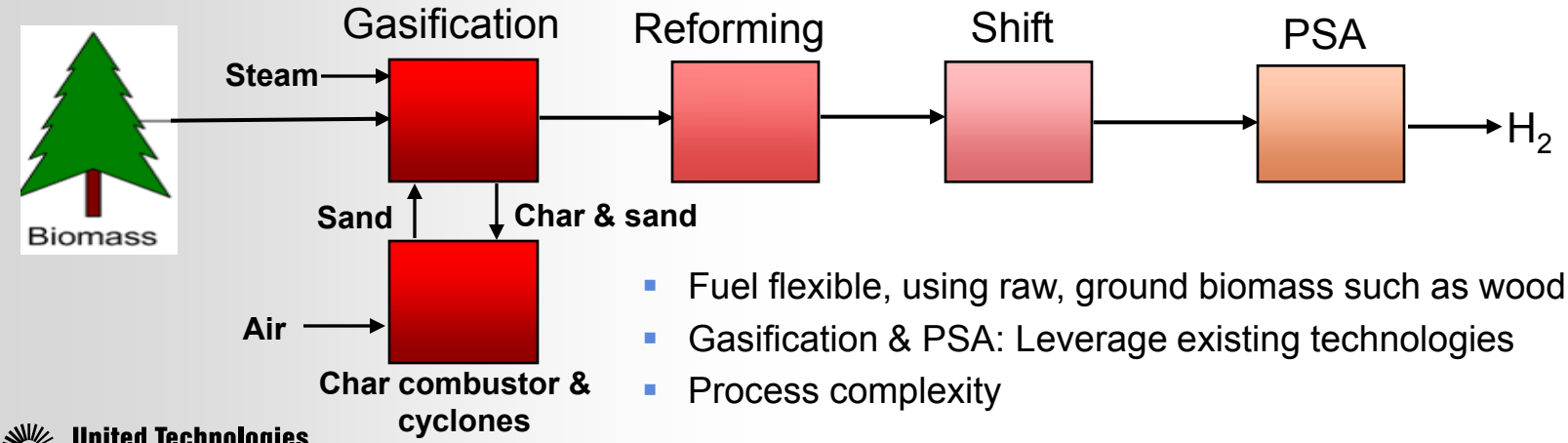
- Development of an initial reactor and system design, with cost projections, for a biomass slurry hydrolysis and reforming process for H_2 production
  - Efficiency & H_2 cost exceed 2012 gasification targets
  - Capital costs dependent on H_2 delivery pressure & H_2 separation membrane
- Development of cost effective catalysts for liquid phase reforming of biomass
  - Switching to base metal catalyst decreases hydrogen cost by ≈$0.20/kg H_2
  - Modifying Raney Ni increases selectivity toward H_2 from CH_4
- Proof-of-concept demonstration of a micro-scale pilot system based on liquid phase reforming of biomass
  - Demonstrated continuous operation at 50 g/min (1% wood)

Biomass Slurry to Hydrogen Concept (Approach)



- 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

Updated Economics for Base Metal Catalyst (Technical)

Lowest H_2 cost obtained using natural gas & electric grid; Carbon neutral & grid independent operation reduce efficiency and increase cost

- Wood cost = $41/ton
  - DOE cost target basis
- K_2CO_3 = $900/ton
  - 95% recycled
- Raney Ni catalyst = $20/lb
  - replaced every 3 years
- Reformer residence time = 8 min
- Catalyst/wood = 20 kg/kg
- Plant operation options
  - Natural gas combustion for heat
  - Electrical grid for pumps, etc.
  - Use product gas for heat
  - Use expanders for electricity generation
- Pd membrane contribution to H_2 Cost is $0.24/kg H_2

Natural gas mode with electrical grid (300 psia H_2)

Characteristics	Units	2012 Target	2000 tpd Plant Design
Hydrogen Cost (Plant Gate)	$/gge	1.60	**1.27** (1.05–1.84)
Total Capital Investment	$M	150	188 (116–370)
Energy Efficiency	%	43	**56.3**

Carbon neutral mode with electrical grid (300 psia H_2)

Characteristics	Units	2012 Target	2000 tpd Plant Design
Hydrogen Cost (Plant Gate)	$/gge	1.60	**1.54** (1.31–2.11)
Total Capital Investment	$M	150	170 (117–304)
Energy Efficiency	%	43	**51.1**

Carbon neutral mode (grid independent, 44.1 psia H_2)

Characteristics	Units	2012 Target	2000 tpd Plant Design
Hydrogen Cost (Plant Gate)	$/gge	1.60	**1.54** (1.31–2.11)
Total Capital Investment	$M	150	164 (117–283)
Energy Efficiency	%	43	**46.1**

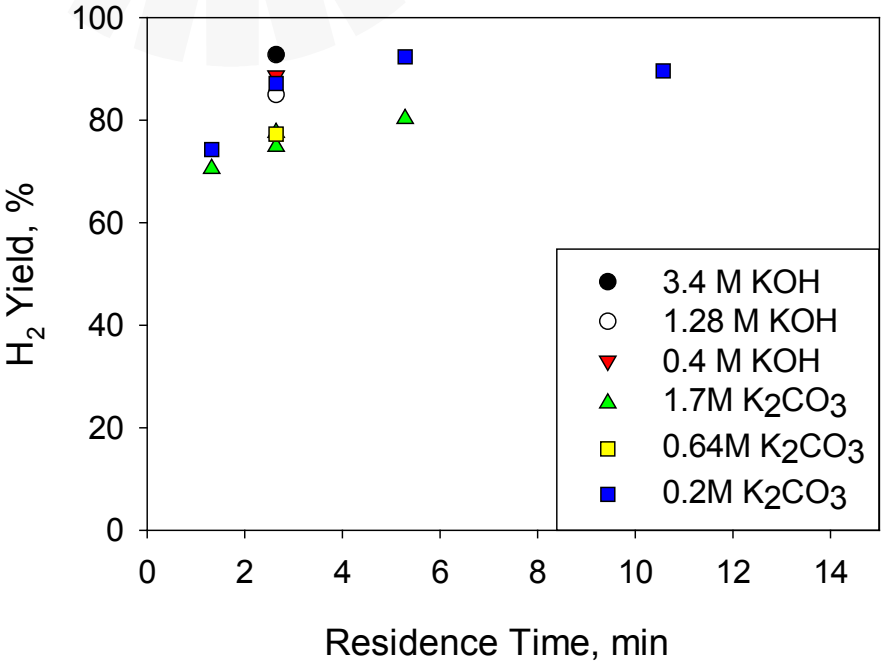
Liquid Phase Reforming of Raw Biomass (2010 Technical)

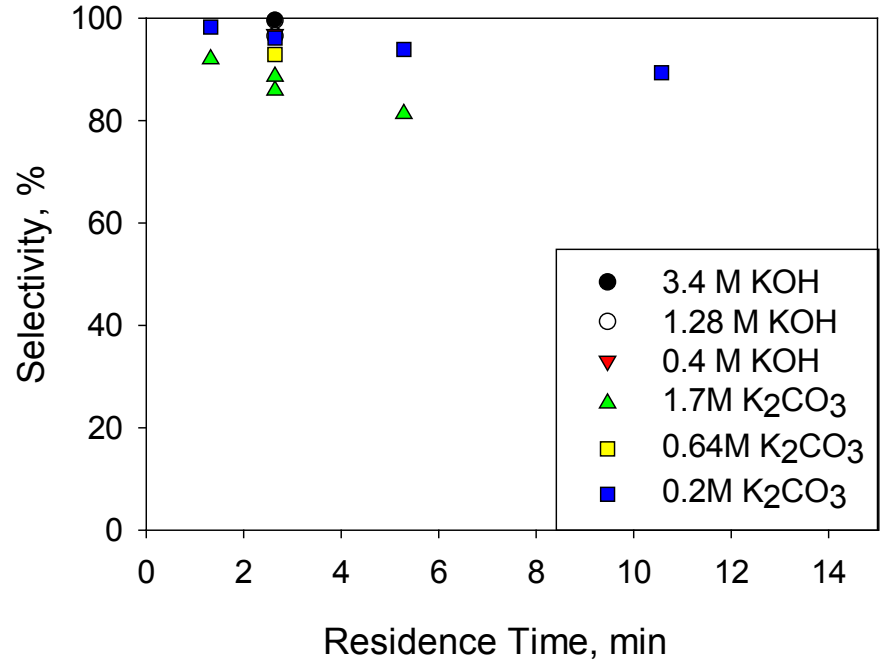
Demonstrated complete conversion of up to 5 wt% wood to gas species

- Liquid phase reforming of raw biomass over Ni or Pt
  - 310 °C, 120 atm
- Commercially available wood flour
  - Hardwood mixture, 100 mesh
- Pt-based catalysts (2005-2009)
  - 1 wt% wood, 0.1 M K_2CO_3
  - **≈100%** conversion of wood, **≈74%** H_2 selectivity
- Ni-based catalysts (2009-2011)
  - 5 wt% wood
  - 0.2 M KOH: **≈100%** conversion of wood, **≈15%** H_2 selectivity
  - 2.0 M KOH : **≈75%** conversion of wood, **≈60%** H_2 selectivity
- Increased base concentrations increased H_2 selectivity
- Increased base leads to high levels of intractable organic acids

Promoted Ni Removes Need for High Base Levels (2010 Technical)

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



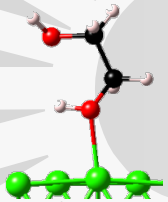


Promoted Raney Ni, 2.5% Ethylene Glycol, 310 °C, 120 atm

$$H_2\ \text{Yield} = \frac{\text{H in product gas stream}}{\text{Theoretical H from reforming}} \times 100 = \frac{[H_2] + 4 \times [CH_4]}{5 \times [C_2H_6O_2]} \times 100$$

$$H_2\ \text{Selectivity} = \frac{2 \times H_2 \text{ in product gas stream}}{\text{Total H in product gas stream}} \times 100 = \frac{2 \times [H_2]}{2 \times [H_2] + 4 \times [CH_4]} \times 100$$

Reforming of Ethylene Glycol over Ni (2010 Technical)



Ethylene glycol

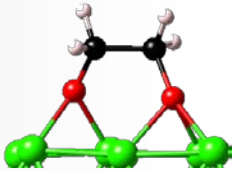
$HOH_2CCH_2OH + * \rightarrow HOH_2CCH_2O*H$

E_{ads}=-0.29 eV

dehydrogenation

$HOH_2CCH_2OH \rightarrow *OH_2CCH_2O* + *H_2$

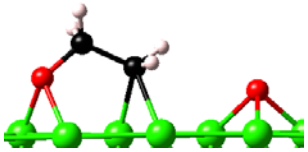
ΔH_1=-0.57 eV; ΔH_2=-0.75 eV



C-O bond scission

$HOH_2CCH_2OH \rightarrow *OH_2C*CH_2 + O* + H_2$

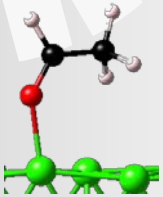
ΔH=-0.85 eV



Rearrangement

$*OH_2C*CH_2 \rightarrow *OHCCH_3$

ΔH=-0.15 eV

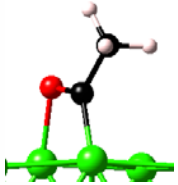


Acetaldehyde

dehydrogenation

$CH_3CHO \rightarrow CH_3CO + H*$

ΔH=-0.79 eV

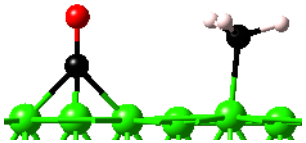


Acetyl

C-C bond scission

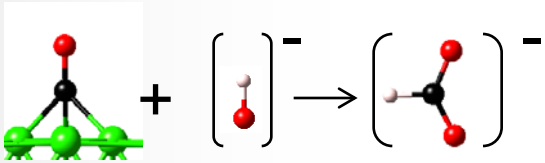
$CH_3CO \rightarrow *CH_3 + *CO$

ΔH=-1.188 eV



CO + methyl

base

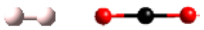


Hydrophilic attack from base produces formate ion

*CO +OH- (base)→ HCOO- (solution)

ΔH=-0.88 eV

shift



$CO + H_2O \rightarrow CO_2 + H_2$

ΔH=-0.23 eV

hydrogenation

CH3+H →CH4

ΔH=-0.45 eV

Ni C O H

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

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

With base

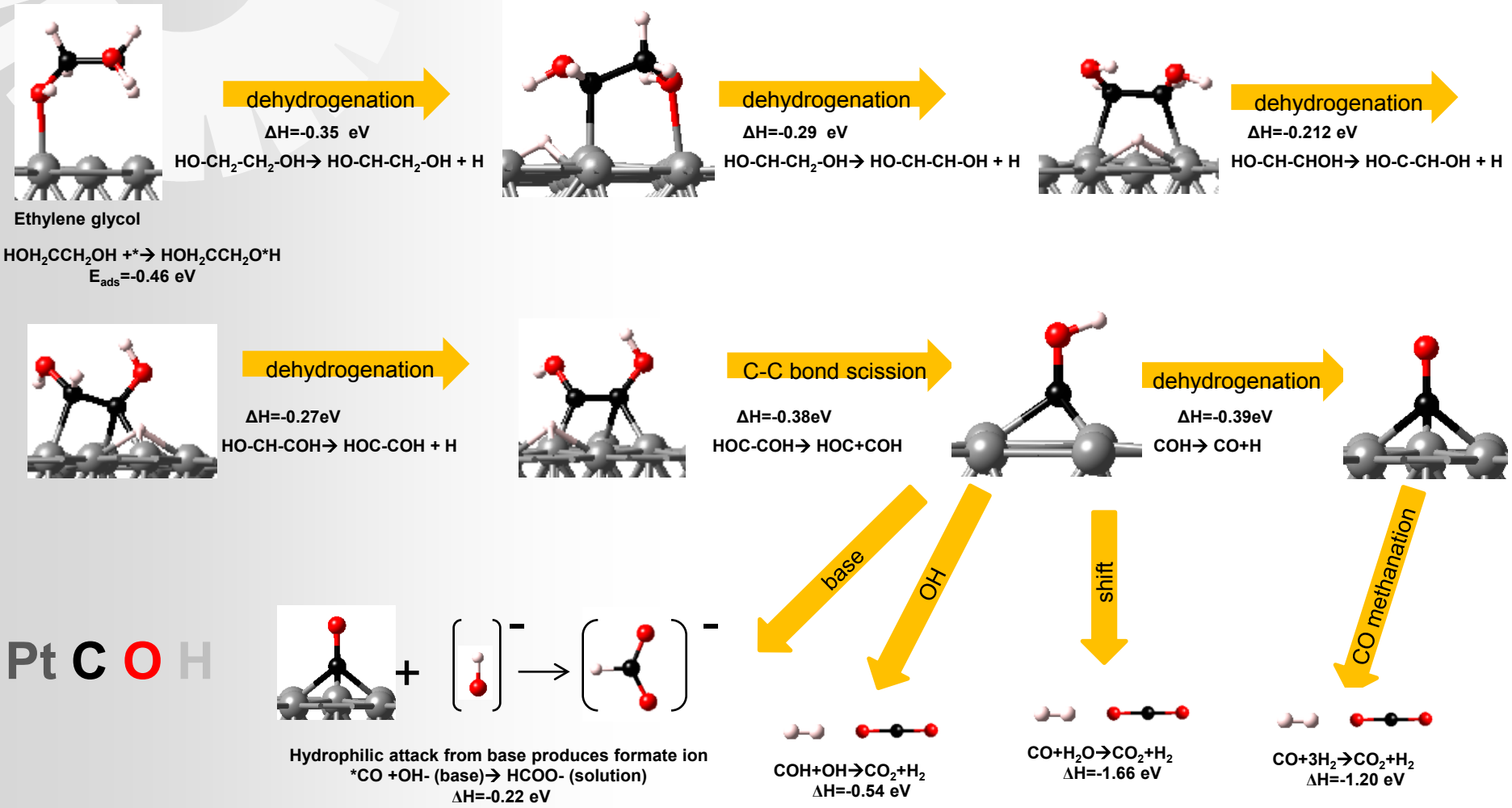
$$C_2H_6O_2 + H_2O \longleftrightarrow H_2CO_3 + CH_4 + H_2 \quad \Delta G_{300°C} = -179 \text{ kJ/mol}$$

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

Without base

Reforming of Ethylene Glycol over Pt (Technical)

Ni attacks C-O bonds first, resulting in CO & CH3 groups on surface; Pt attacks C-C bonds first, resulting in only CO groups (higher H_2 selectivity)



Complete reforming: $C_2H_6O_2+2H_2O \rightarrow 2CO_2+5H_2$

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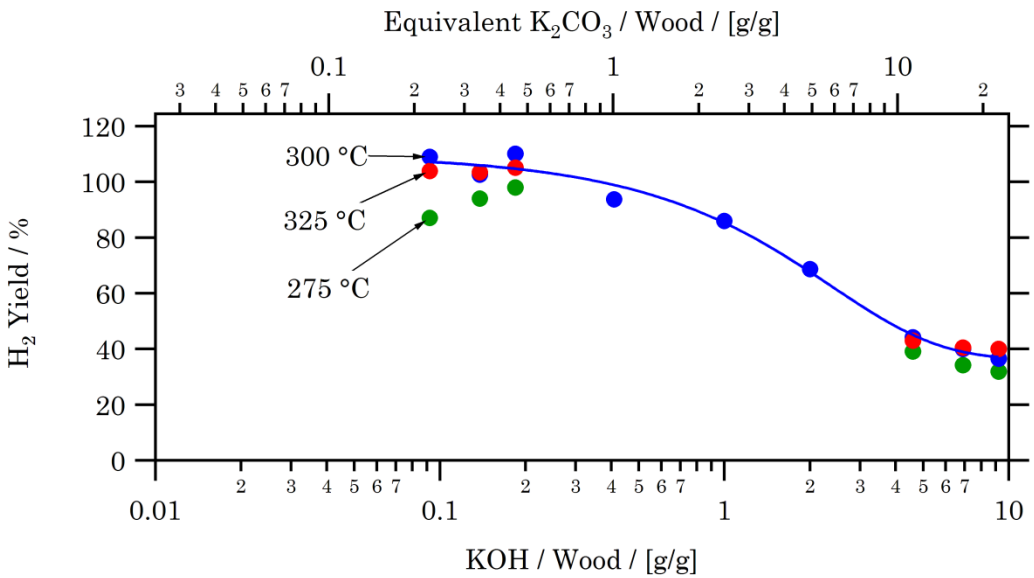
EERC Batch Reforming of Wood with Raney Ni (Technical)

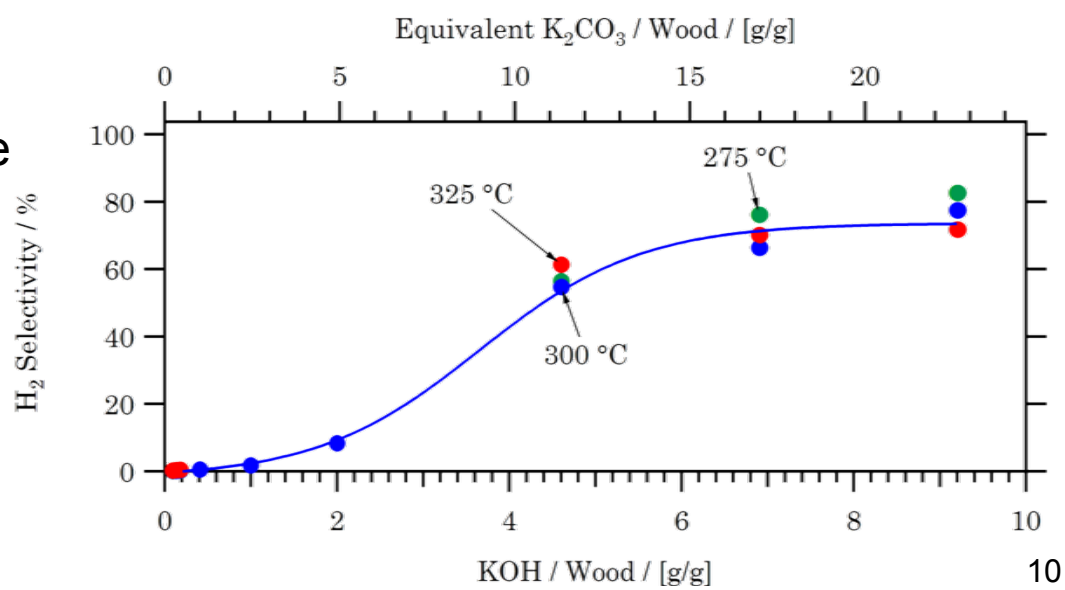
Consistent with UTRC observations, increasing base increases H_2 selectivity while decreasing H_2 yield

- Experimental Conditions
  - Batch 7.6 L autoclave
  - Unmodified Raney Ni
  - 8 wt% wood
  - KOH/Wood (g/g) = 0.184 to 9.2
  - Ni/Wood = 1/1
  - T = 275 °C to 325 °C
- Optimal H_2 Yield with low base
  - KOH/Wood = 0.1 to 0.5
- Optimal H_2 Selectivity with high base
  - KOH/Wood > 7

$$H_2\ \text{Yield} = \frac{\text{H in product gas stream}}{\text{Theoretical H from reforming}} \times 100$$

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

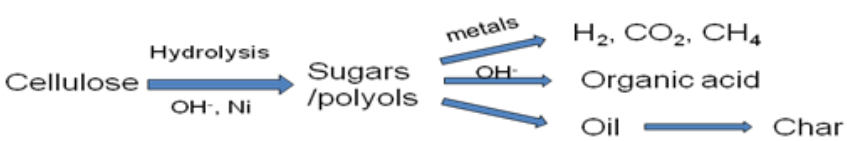


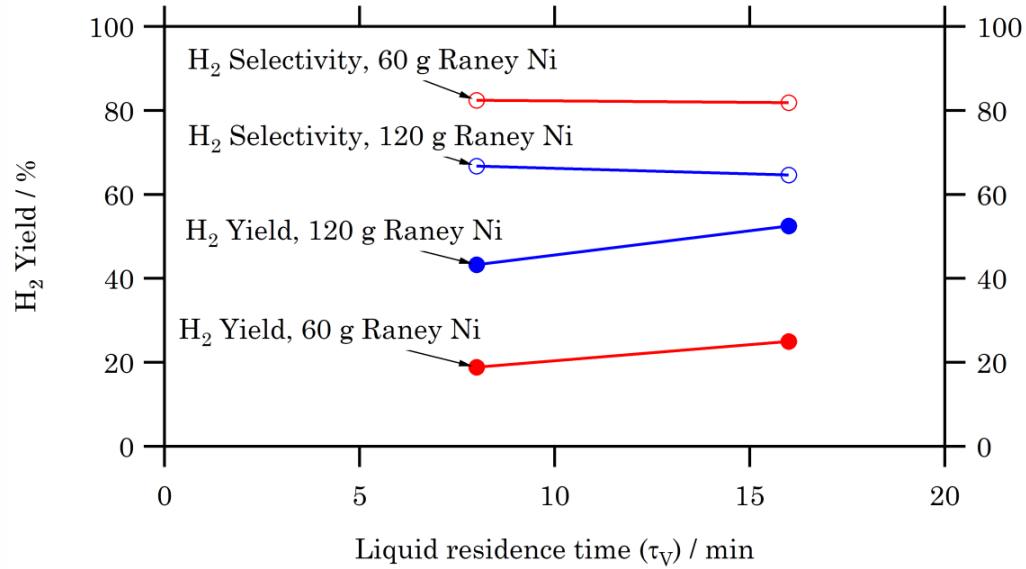


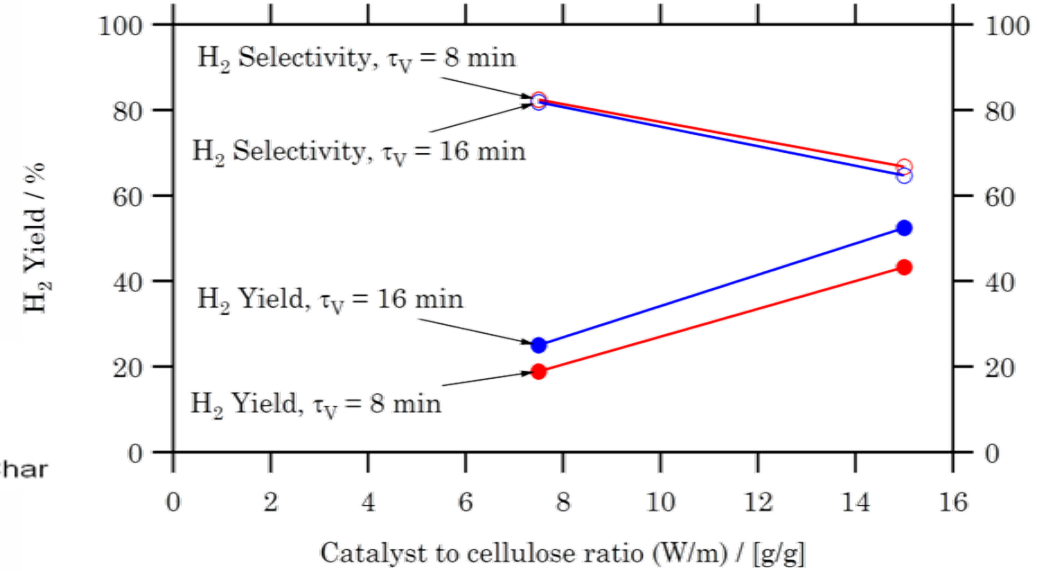
Wood Component Design Studies with Raney Ni (Technical)

Reforming is the rate determining step, not base hydrolysis

- Investigated cellulose reforming in a continuous stirred tank reactor (CSTR)
- Cellulose reforming significant at T > 275 °C
- Liquid residence time (τ_V)
  - Small impact on yield and selectivity
  - Hydrolysis of cellulose very fast
- Catalyst to cellulose ratio (W/m)
  - Doubling catalyst doubles the yield
  - Doubling catalyst decreases selectivity
  - Cellulose catalytic reforming determines reactor performance







Construction of Demonstration System (Technical)

Continuous liquid phase reforming of woody biomass

Caustic Solution Pump
•K_2CO_3

High Pressure Reactor
•310 °C, 120 atm

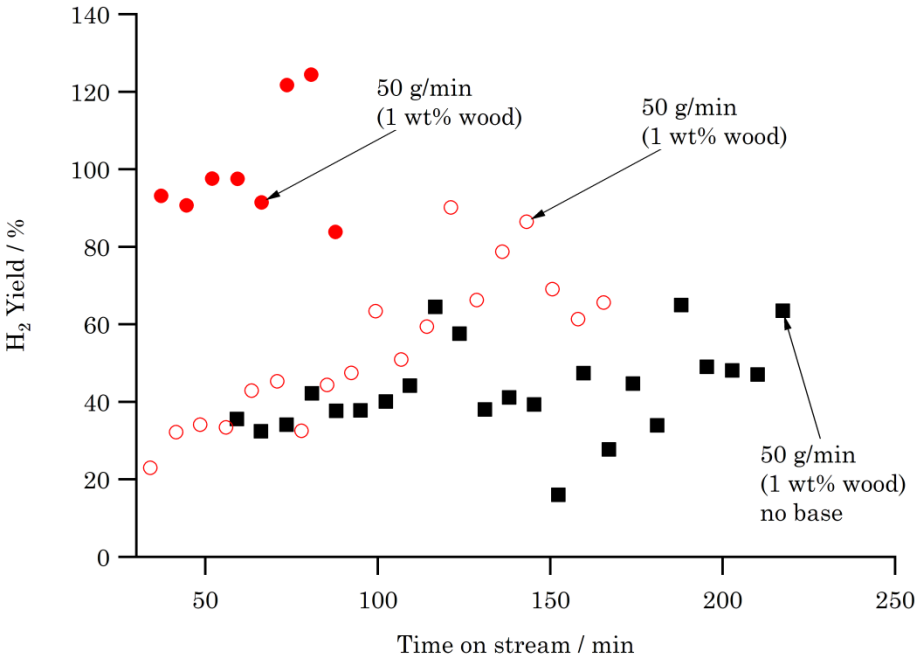
High Pressure Reactor
•240 °C, 120 atm

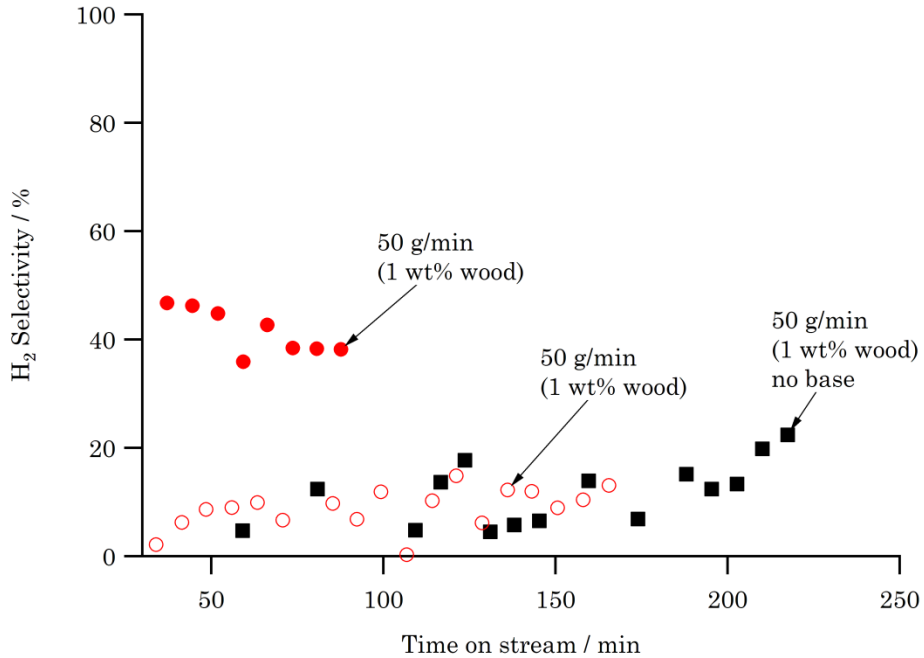
High Pressure Wood Slurry Pump
•≤10% Slurry
•25-200 mL/min

- Not shown: gas-liquid separator & particulate trap

Fixed Bed Raney Ni Catalyst Results (Technical)

Demonstrated continuous flow slurry system for woody biomass;
Fixed bed Raney Ni mitigates particulate issues, but suffers deactivation





- 1 wt% wood at 50 g/min in demonstrator setup
- Unmodified fixed bed Raney Ni catalyst to avoid particulate issues
- Fixed bed Raney Ni has lower surface area than conventional Raney Ni
- Base addition increases yield and selectivity
- Repeat runs with base show decreased yield and selectivity
- Potential degradation of fixed bed Raney Ni requires further investigation

Fixed Bed Raney Ni Catalyst Result Summary (Technical)

Fixed bed Raney Ni not active enough for >50 g/min flows in demonstrator

Feed	Slurry feed rate (g/min)	Feed concentration (%)	K_2CO_3/Feed (g/g)	H_2 yield (%)	H_2 selectivity (%)	Carbon yield (%)
Wood flour	50.0	1	1.35	**103.8**	38.7	**81.1**
Wood flour	50.0	1	0	43.8	1.2	48.6
Wood flour	40.1	1	1.676	69.2	10.0	71.7
Wood flour	97.3	1	1.38	**25.2**	40.4	**44.0**

Note: the numbers are all based on average value obtained from the runs.

- Conventional Raney Ni powder has a high surface area (≈80 m^2/g) but can cause downstream plugging
- Fixed Bed Raney Ni "chunks" have a lower surface area (≈10 m^2/g) and a lower packing density
- Fixed Bed Raney Ni does not have enough activity for the volume of the UTRC reactor to effectively reform higher flows (>50 g/min) of wood slurry
- Unreacted wood either converts to organic acids or results in <20 μm particulates that can also cause downstream plugging

Future Work

- Follow on projects need to focus on developing technology further
- Design new reactors to further investigate sizing kinetics
- Demonstrate >90% base recycle
- Investigate catalyst durability and higher activity base metal catalysts
- Slurry pump development
- Integrate burner unit with reformer
- Demonstrate system on a larger scale
- Demonstrate system with power generation (fuel cell, turbine, or ICE)

Collaborations

- 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

Project Summary

Demonstrated continuous flow slurry system for woody biomass;

Liquid phase reforming can achieve a lower H_2 production cost at a higher efficiency than biomass gasification

Characteristics	Units	2012 Target	Current Status
Hydrogen Cost (Plant Gate)[a]	$/gge	1.60	1.54 (1.31–2.11)
Total Capital Investment	$M	150	170 (117–304)
Energy Efficiency[b]	%	43	51.1

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

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

- 2000 dry ton wood per day H_2 plant
- Assumes carbon neutral operation (burn product gas for heat)
- Electricity grid used to power pumps and other equipment
- Capital costs lowered without H_2 purification (Pd membranes)

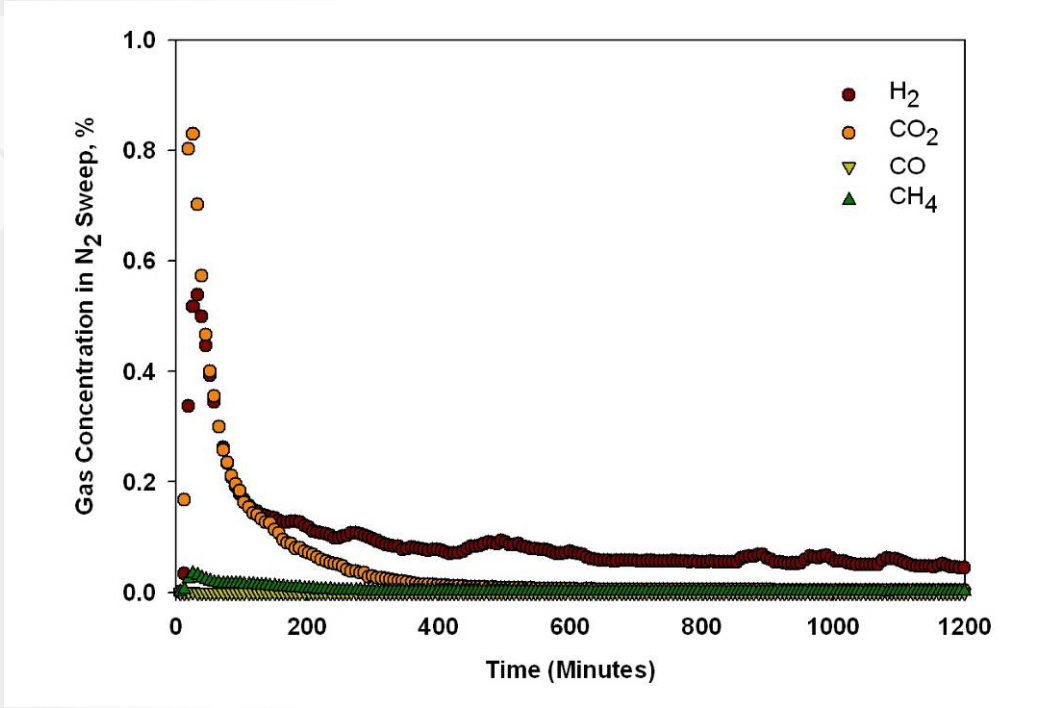
This research used resources of the National Center for Computational Sciences at Oak Ridge National Laboratory, which is supported by the Office of Science of the Department of Energy under Contract DE-AC05-00OR22725.

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.

Technical Back-Up Slides

2009 Accomplishment: Total Reforming of Yellow Poplar

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

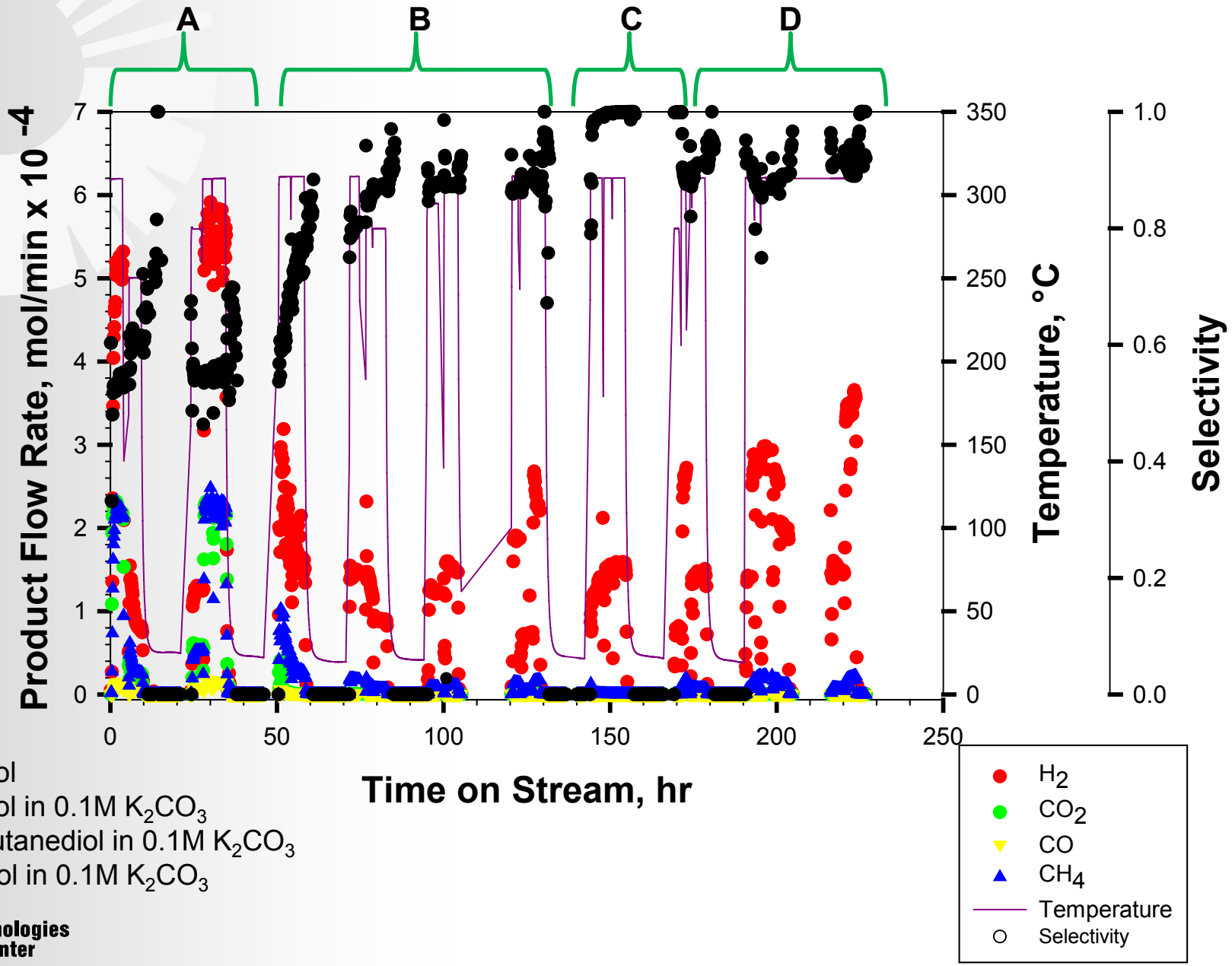


Effluent product profiles from the hydrolysis and liquid phase reforming of 1 wt% yellow poplar at 310 °C in 0.1M K_2CO_3 with a 0.5 L/min N_2 sweep gas.

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

Reforming Catalyst Durability Testing with 1% Ethanol (>250 h)



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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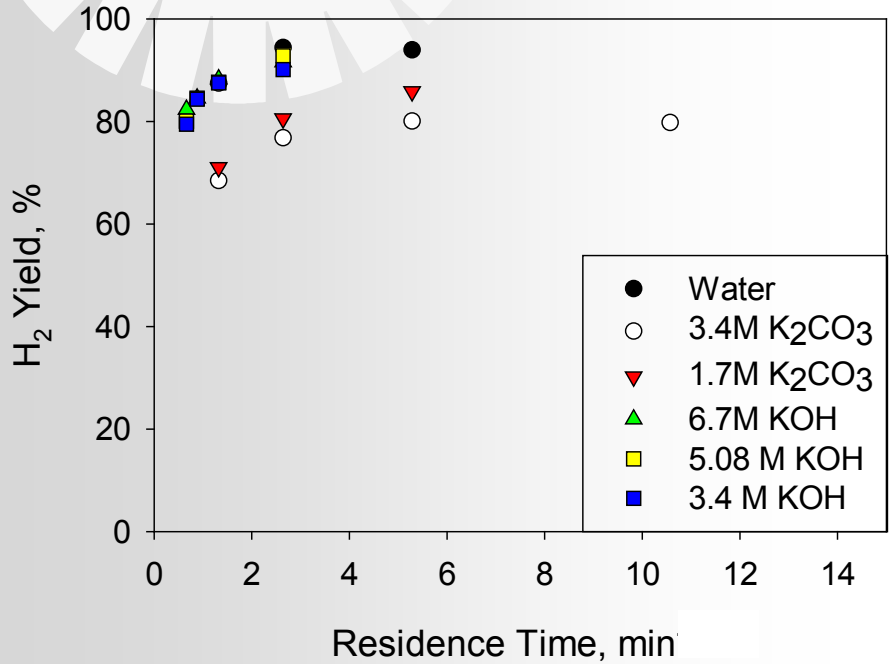
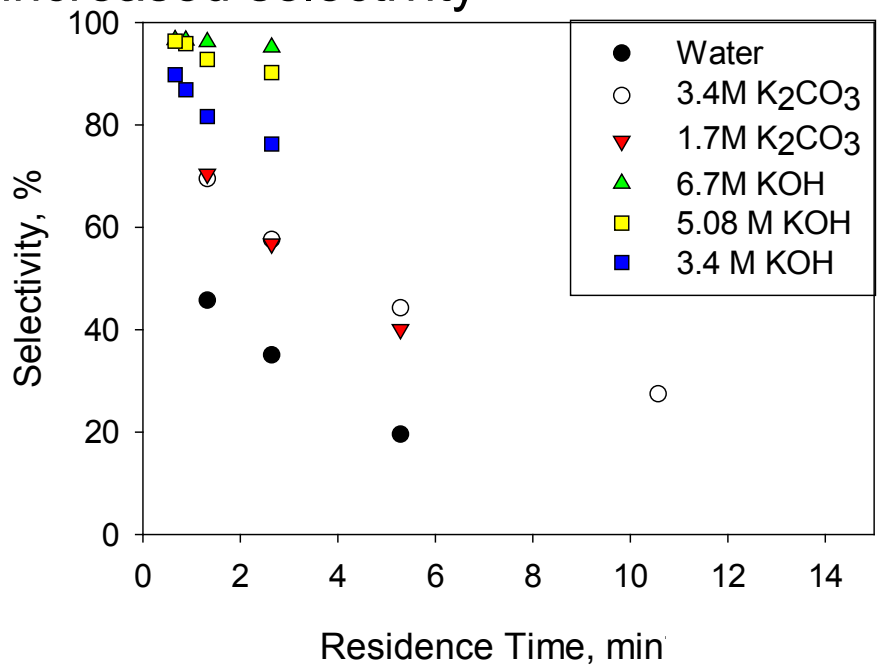
High pH Increases H_2 & Decreases CH_4 (Technical)

- *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% Ethylene Glycol, 310 °C, 120 atm

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$$H_2\ \text{Selectivity} = \frac{2 \times H_2\ \text{in product gas stream}}{\text{Total H in product gas stream}} \times 100 = \frac{2 \times [H_2]}{2 \times [H_2] + 4 \times [CH_4]} \times 100$$