A Novel Slurry Based Biomass Reforming Process

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United Technologies Research Center, East Hartford, CT

Project ID #PD31

Overview

Timeline

- Start – May 2005
- End – March 2009
- ≈50% Complete

Budget

- Total Project Funding
  - DOE share - $2.9M
  - Contractor share - $737k
- Funding Received in FY07
  - $650k from DOE
- Funding for FY08
  - $800k (projected)

Barriers

- Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan
  - S. Feedstock Cost and Availability
  - T. Capital Costs and Efficiency of Biomass Gasification/Pyrolysis Technology

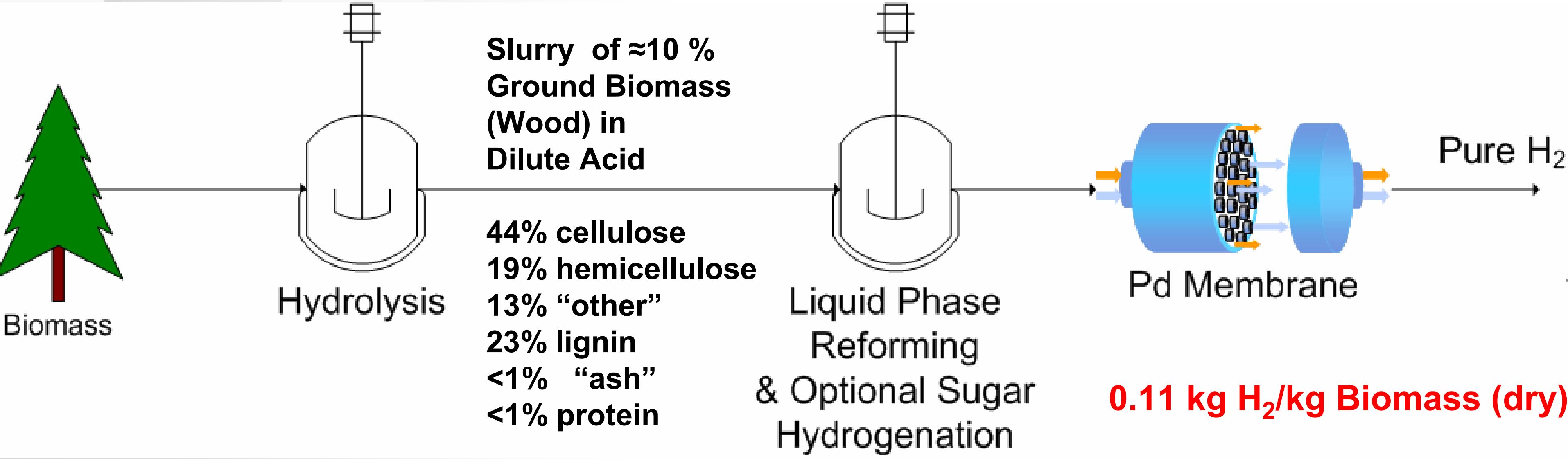
Partners

- University of North Dakota Environment Energy Research Center

Objectives

- (2007) 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**).
- (2008) Demonstrate, through preliminary results, that an acid tolerant, model sugar solution reforming catalyst with acceptable kinetics has been synthesized and that a viable technical path for scale up (mass production) of this catalyst in a cost-effective way exists.
- (2008) Identify hydrolysis conditions for a simulated biomass system and a viable technico-economical path towards the achievement of the hydrolysis of the real biomass system.
- (2008) Demonstrate, through extensive test results, an acid tolerant, long life, cost-effective biomass hydrolysis product reforming catalyst.

Approach: Biomass Slurry to Hydrogen Concept



Biomass

Hydrolysis

Slurry of ≈10 %
Ground Biomass
(Wood) in
Dilute Acid

44% cellulose
19% hemicellulose
13% "other"
23% lignin
<1% "ash"
<1% protein

Liquid Phase
Reforming
& Optional Sugar
Hydrogenation

Pd Membrane

Pure H_2

0.11 kg H_2/kg Biomass (dry)

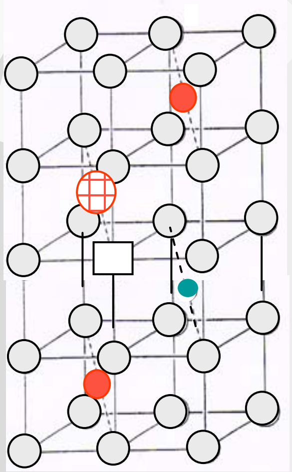
- Fuel flexible, using raw, ground biomass such as wood or switch grass
- Carbon neutral means of producing Hydrogen
- H_2 separation: Leverage experience with Advanced Pd membranes

Hydrogen from Biomass

UTRC Catalyst Discovery Approach

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

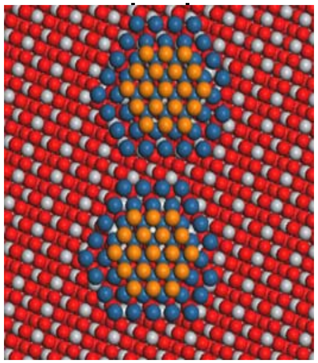
Conceptual Catalyst Design



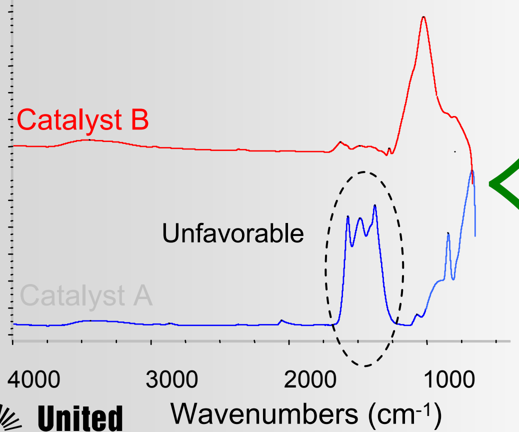
Catalyst Synthesis

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

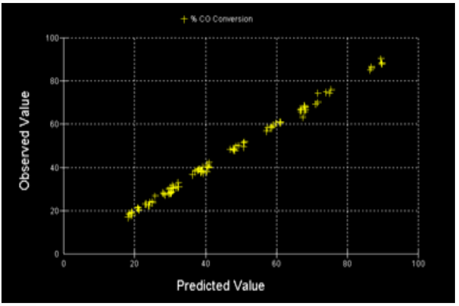
Quantum Mechanical Atomistic Modeling for advanced catalysts



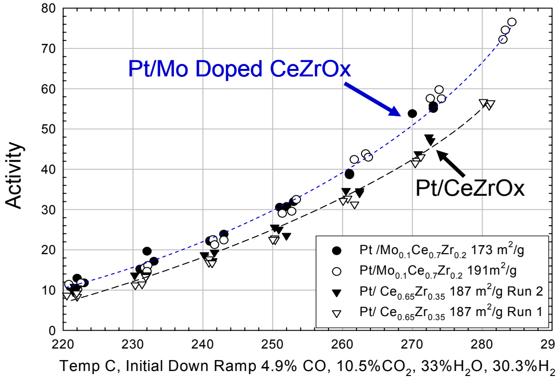
Characterization



Kinetic Expressions Derived From Reaction Data



Superior Performance



Higher Activity Catalyst with Similar Pt & Surface Area

Simplified 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

$$SO_2 + 0.5O_2 \rightarrow SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

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

Key Features of Proposed Biomass Reforming Plant

- Sulfur/acid 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

United Technologies Research Center

Summary from 2007

- 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.

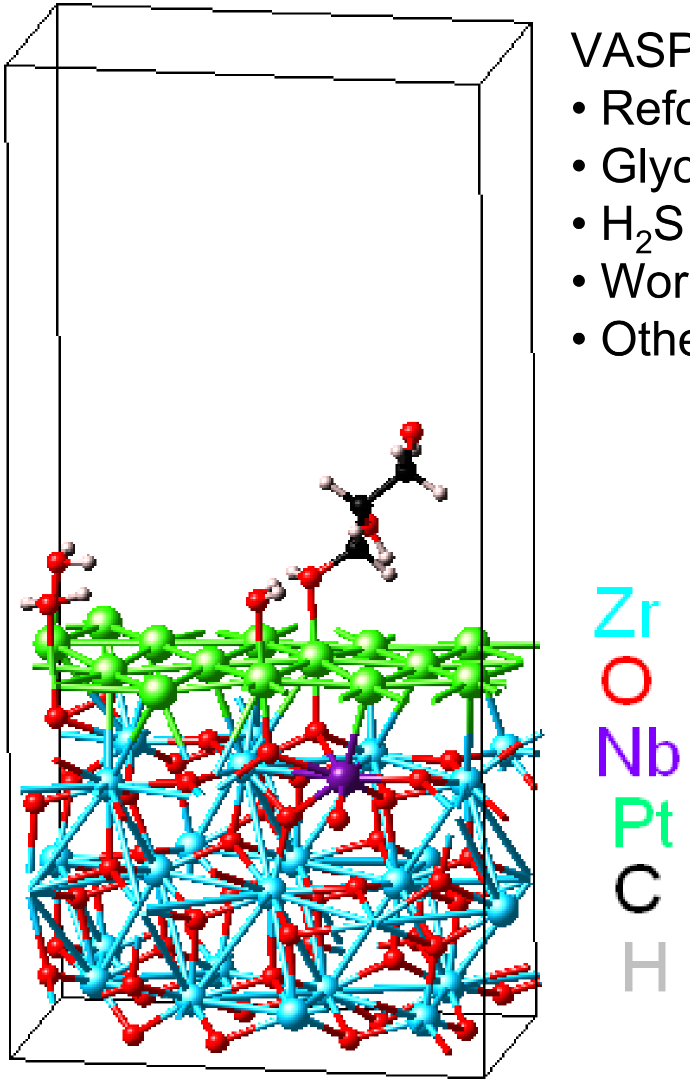
- Major drivers on the efficiency were identified in parameter sensitivity studies.

- > 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.

Explore Oxide Doping to Impact Reactant–Pt Binding Energies



VASP DFT Calculations; Assumptions:

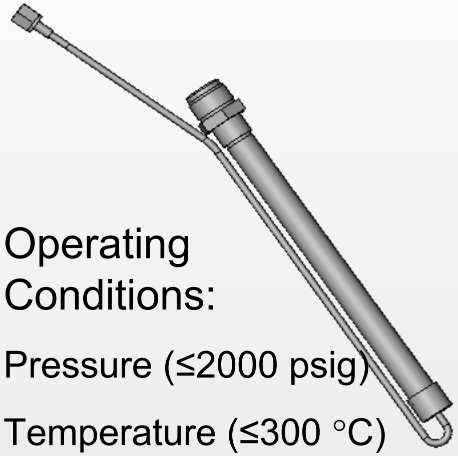
- Reforming reaction requires at least some Pt Sites
- Glycerol reacts on Pt
- H_2S as a surrogate for other poisons; competes for sites
- Work is continuing
- Other deactivation mechanisms not yet considered

Calculated binding energies, E, for H_2O, glycerol, and H_2S molecules on hydrated oxide surfaces and hydrated Pt monolayer on pure and doped oxides.

Material Surface	E_{H_2O} (eV)	$E_{glycerol}$ (eV)	E_{H_2S} (eV)
TiO_2 (wet)	-0.72	-0.93	-0.37
Pt/TiO_2	-1.086	-1.076	-1.658
Pt/(Al)TiO_2	-1.105	-1.180	-1.634
Pt/(Zr)TiO_2	-1.069	-1.013	-1.606
Pt/(V)TiO_2	-0.75	-0.93	-1.25
ZrO_2(wet)	-0.80	-0.48	-0.13
Pt/ZrO_2	-0.848	-0.645	-1.207
Pt/(Nb)ZrO_2	-1.147	-1.558	-1.495

Upgraded Testing Reactor to Improve Reproducibility

Move to Stirred Zirconium Autoclave

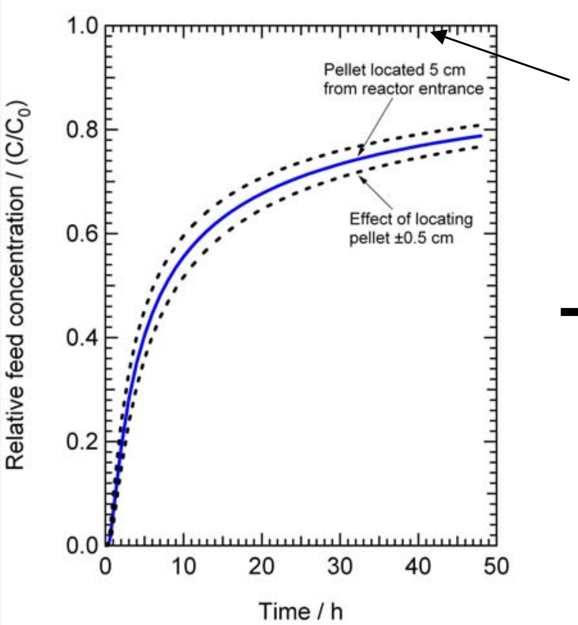


Operating Conditions:

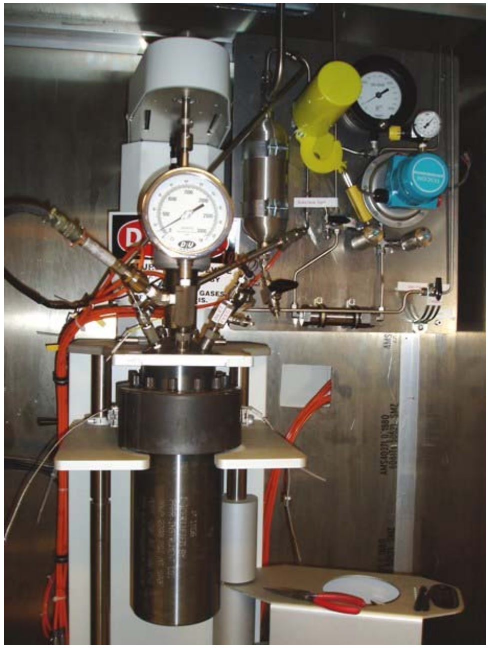
Pressure (≤2000 psig)

Temperature (≤300 °C)

Titanium Batch Reactor



Stirred autoclave operates at constant C/Co=1.0 fot t≥0

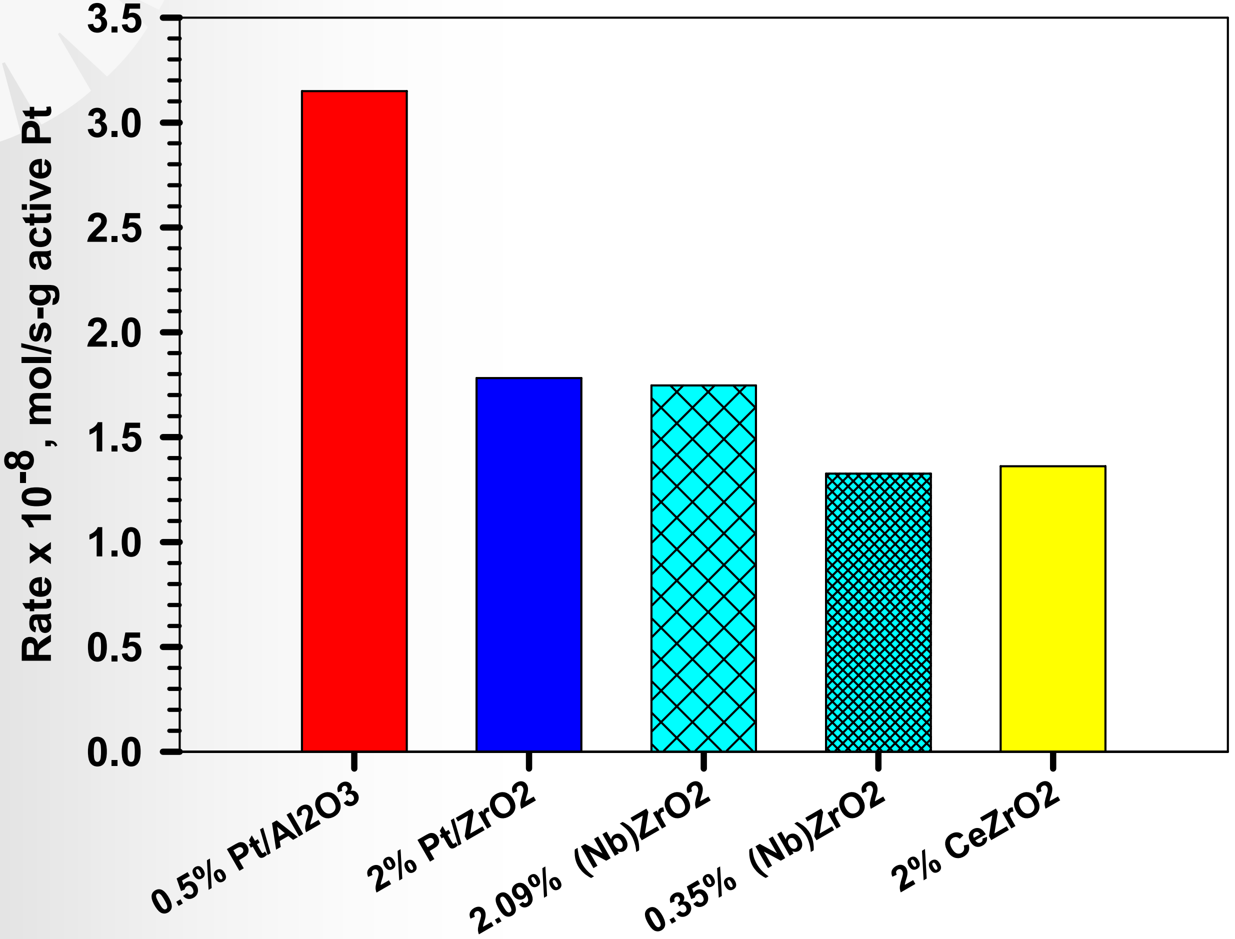


Stirred Zirconium Autoclave

- Reproducibility of Pt/alumina reference motivated reactor switch
  - **Pt-dissolution** from vendor catalyst
- Introduction of feed into batch reactor contributed to variability
  - **Low diffusivity of glycerol**
  - No significant agitation for convective mixing (N_2 sweep gas only)
  - Small variability in catalyst pellet placement complicates diffusion resistance

Glycerol to Hydrogen Rate for Various Catalysts

240 °C, 2.5 wt% (0.283 M) Glycerol (0.283 M)

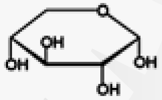


Sugar / Sugar Alcohol Reaction Conditions

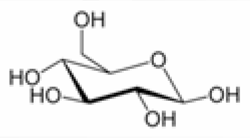
Temperature and concentrations ranges set based on charring studies

Candidate Sugars

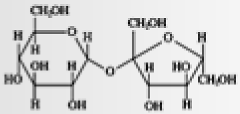
Xylose (cyclic)



Glucose (cyclic)

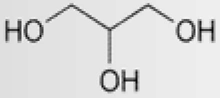


Sucrose (cyclic)

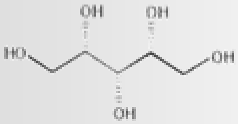


Candidate Sugar Alcohols

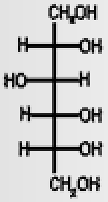
Glycerol (C3)



Xylitol (C5)



Sorbitol (C6)



Glucose (cyclic)

	1%	2.5%	5%	10%
300°C				
250°C				
225°C	🟧			🟥

Xylose (cyclic)

	1%	2.5%	5%	10%
300°C				
250°C				
225°C	🟧			🟥

Glycerol (C3)

	1%	2.5%	5%	10%
300°C				🟧
250°C	X			
225°C	🟩			🟨

Xylitol (C5)

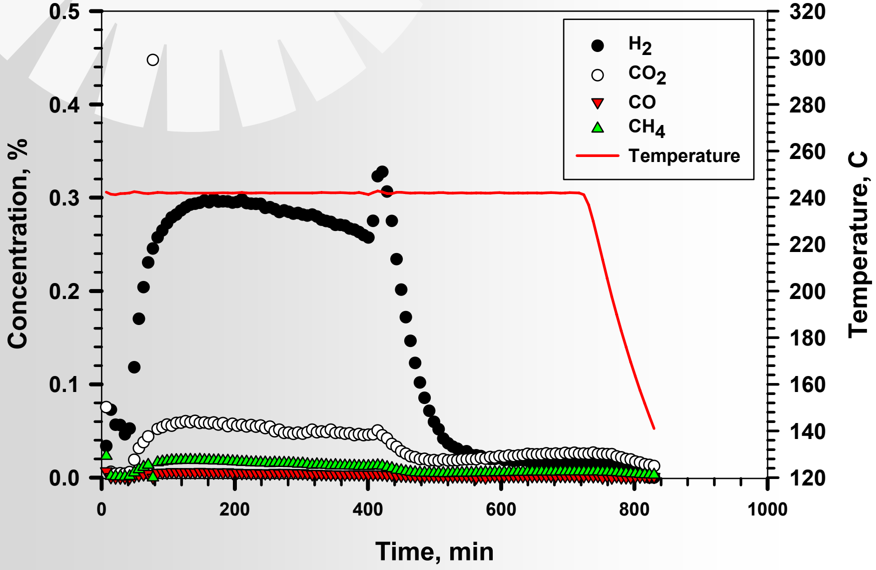
	1%	2.5%	5%	10%
300°C				🟨
250°C				
225°C				🟩

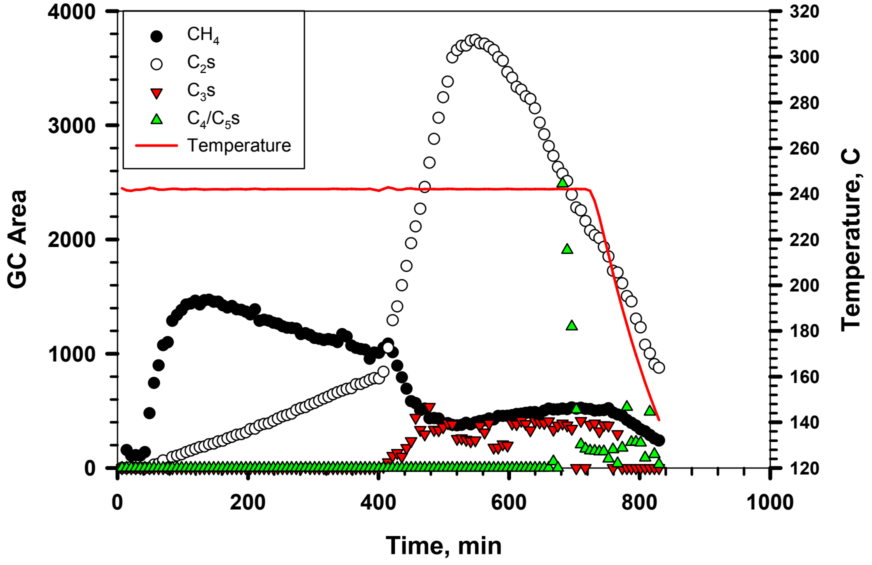
Sorbitol (C5)

	1%	2.5%	5%	10%
300°C				🟥
250°C	🟨			
225°C				

🟥 char, severe
🟧 char, moderate
🟨 char, minor
🟩 no char

0.5% Pt/Al_2O_3 Testing- $KHSO_4$ Addition Terminates H_2 Production

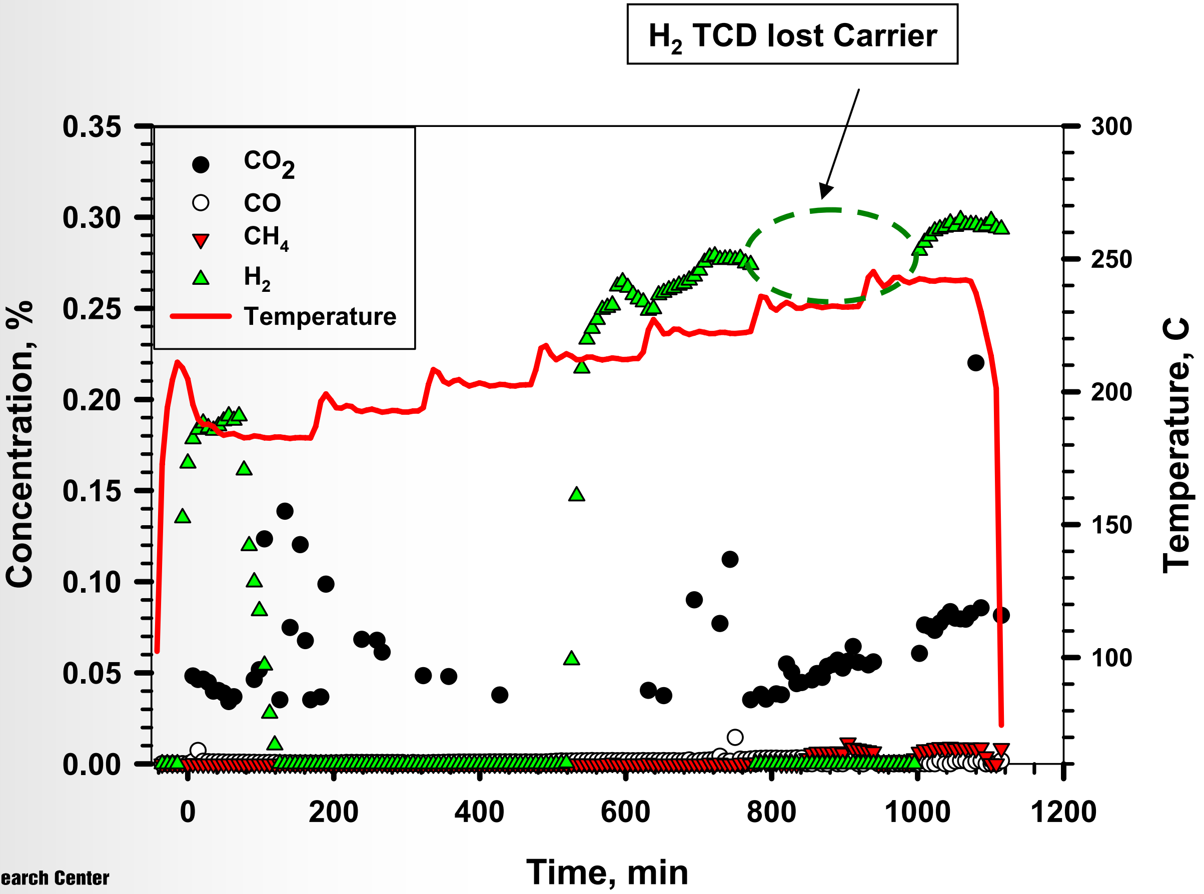




- 2.5 wt% Glycerol (0.283M); 0.1M $KHSO_4$ addition at 400 min
- Immediate termination of H_2 production
- Increased production of C_2 and C_3+ Species

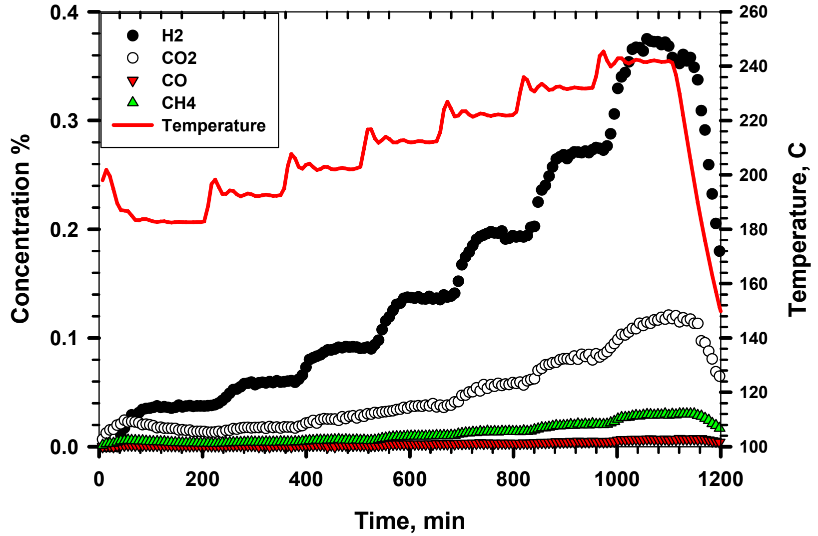
0.5% Pt/Al_2O_3 Testing- Temperature Ramp

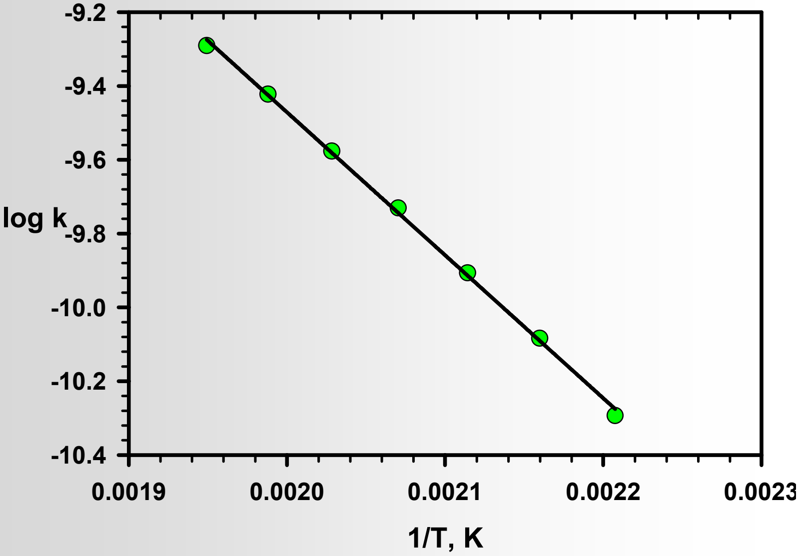
- Temperature ramped from 180 °C to 240 °C
  - 2.5 wt% (0.283 M) Glycerol
  - No H_2 production below 210 °C
  - Initial H_2 production due to temperature overshoot

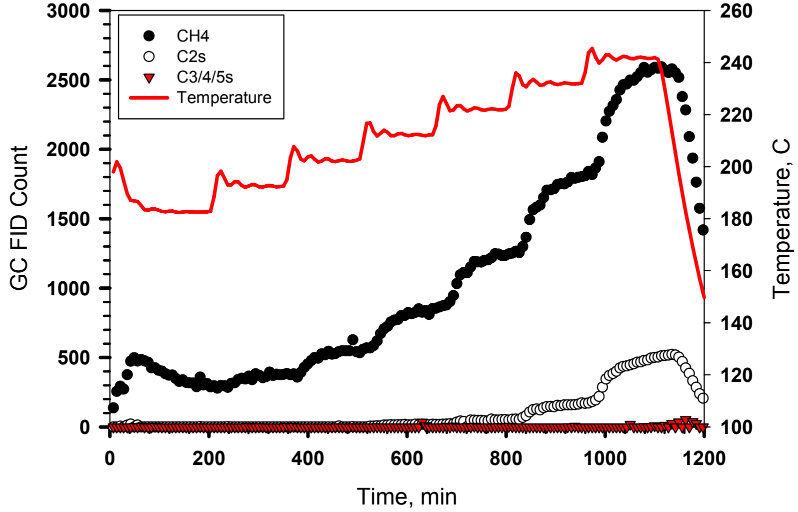


2% Pt/$Ce_{0.6}Zr_{0.4}O_2$ Testing — H_2 Production at <190 °C

- 2.5 wt% (0.283 M) Glycerol
- 93% selectivity towards H_2 through the entire temperature range
- E_{act} = 74.2 kJ/mol
- Vendor prepared UTRC mixed metal oxide
- $KHSO_4$ Addition Tests underway







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Work For 2008-2009

- (2008) Demonstrate, through preliminary results, that an acid tolerant, model sugar solution reforming catalyst with acceptable kinetics has been synthesized and that a viable technical path for scale up (mass production) of this catalyst in a cost-effective way exists.
- (2008) Identify hydrolysis conditions for a simulated biomass system and a viable techno-economical path towards the achievement of the hydrolysis of the real biomass system.
- (2008) Demonstrate, through extensive test results, an acid tolerant, long life, cost-effective biomass hydrolysis product reforming catalyst.
- Pending future funding, further 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.

Status: Experimental effort now carried out in 2 liter stirred autoclave, earlier catalyst results called into question.

- Pt/Al_2O_3 outperforms uniformly loaded Pt/ZrO_2 family at 240 °C on a per site basis without $KHSO_4$
- $Pt/CeZrO_x$ catalyst active at 180 °C without $KHSO_4$.
- $KHSO_4$ addition shuts down H_2 production while increasing ethane production
- Retest of $Pt/CeZrO_x$ Water Gas Shift Catalyst with $KHSO_4$ underway