

Production of Hydrogen by Biomass Reforming



David King, Yong Wang, James Cao, Gordon Xia,
Hyun-Seog Roh, Alexander Platon

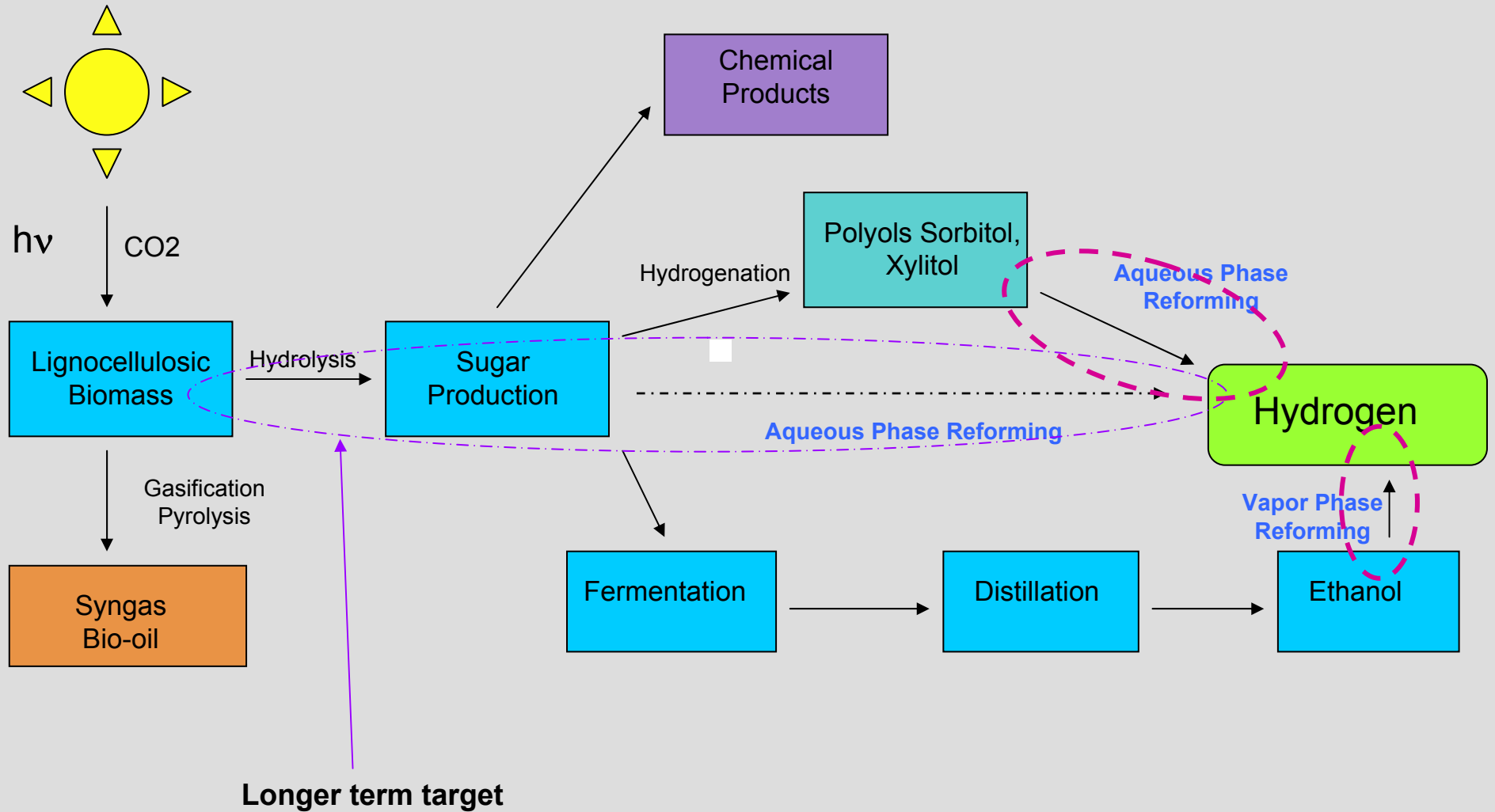
Pacific Northwest National Laboratory

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Production of Hydrogen in the Bio-refinery



Project Background

▶ Timeline

- Project start date: FY04
 - Aqueous phase gasification
 - Ethanol steam reforming
- Project consolidation: March 04

▶ Budget (consolidated)

- FY04: \$100,000
- FY05: \$500,000

▶ Barriers

- F: Feedstock cost and availability
- G: Efficiency of gasification, pyrolysis and reforming technology
- Z: Catalysts—durability, efficiency, and impurity tolerance in reforming and water gas shift

▶ Collaborations

- Collaboration underway with Virent Energy Systems
- Collaboration with ethanol producers under discussion

Reforming Project Objectives

Assist DOE in evaluating alternatives to gasification and pyrolysis of biomass for hydrogen production

- ▶ Identify and develop advanced catalysts for hydrogen production from:
 - Aqueous phase gasification of sugars and sugar alcohols (sorbitol) and less processed feedstocks to hydrogen and CO₂; near term objectives:
 - Minimize formation of alkanes: product ratio H₂/CH₄ >3
 - Productivity >75 l H₂/l reaction vol-h
 - Steam reforming of ethanol at low temperatures
 - Potential integration with membrane
 - Eliminate separate wgs reaction
 - GHSV > 100,000 h⁻¹
 - Methane selectivity < 30% @ S/C < 4/1

- ▶ Identify key chemical structural elements that impact reforming and thermal chemistry
 - Feedstock composition
 - Amount of pre-processing required

- ▶ Carry out experimental and modeling studies to determine preferred reactor configuration(s) for improved efficiency and productivity

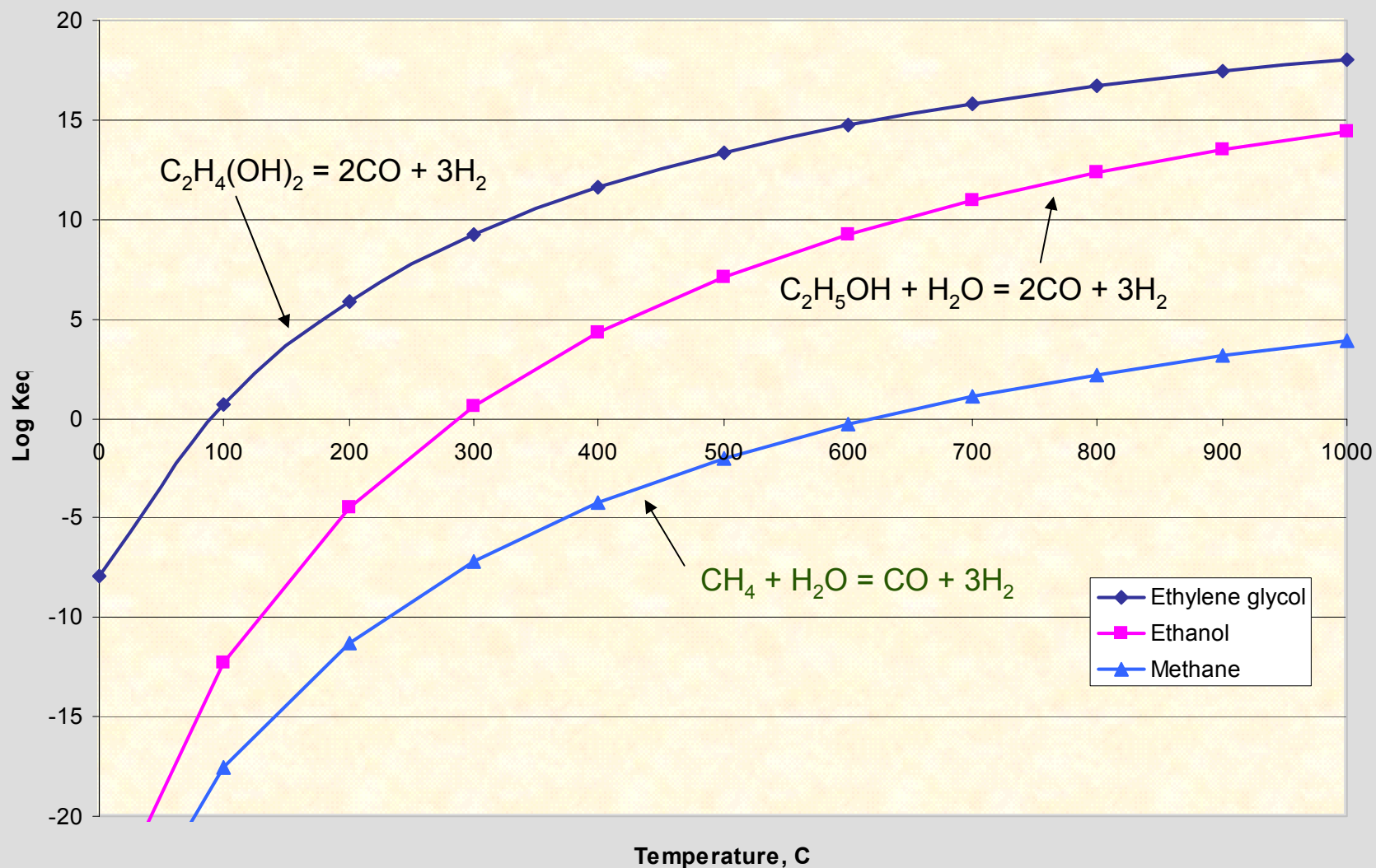
Project Status

| Project Milestones | Task Completion Date | | |
|--|----------------------|------------------|-------------|
| | Plan | Percent Complete | Progress |
| Construct test stand for catalyst evaluation, | Dec. | 100% | Complete |
| Identify catalyst(s) producing H ₂ from xylitol or sorbitol that meet productivity and selectivity targets | July | 50% | On track |
| Complete initial study of catalyst stability | May | 40% | On track |
| Compare performance in fixed bed and slurry batch reactors | May | 70% | On track |
| Design and construct best test reactor for microchannel based aqueous gasification | Sept | 0% | Not started |
| Preliminary report summarizing feed cost/availability and projections | Sept | 10% | On track |
| Report on performance of various catalysts and supports for steam reforming of ethanol | July | 70% | On track |
| Report summarizing design and deployment of an efficient single channel testing reactor for steam reforming of ethanol | July | 50% | On track |

Hydrogen Potential From Different Feedstocks

| Feedstock | Formula | MW feedstock | moles/kg | moles H ₂ / mol feed | g H ₂ / kg feed | g H ₂ /kg feed w/wgs |
|-----------------|---|-----------------|----------|------------------------------------|-------------------------------|------------------------------------|
| Methanol | CH ₃ OH | 32 | 31.3 | 2 | 125 | 188 |
| Ethanol | C ₂ H ₅ OH | 46 | 21.7 | 4 | 174 | 261 |
| Ethylene glycol | C ₂ H ₆ O ₂ | 62 | 16.1 | 3 | 97 | 161 |
| Glycerol | C ₃ H ₈ O ₃ | 104 | 9.6 | 4 | 77 | 135 |
| Glucose | C ₆ H ₁₂ O ₆ | 180 | 5.6 | 6 | 67 | 133 |
| Sorbitol | C ₆ H ₁₄ O ₆ | 182 | 5.5 | 7 | 77 | 143 |
| Hexane | C ₆ H ₁₄ | 86 | 11.6 | 13 | 302 | 442 |
| Methane | CH ₄ | 16 | 62.5 | 3 | 375 | 500 |

Thermodynamic Considerations in the Generation of H₂ and CO From Different Feedstocks



Aqueous Phase Reforming



Advantages of Aqueous Phase Reforming

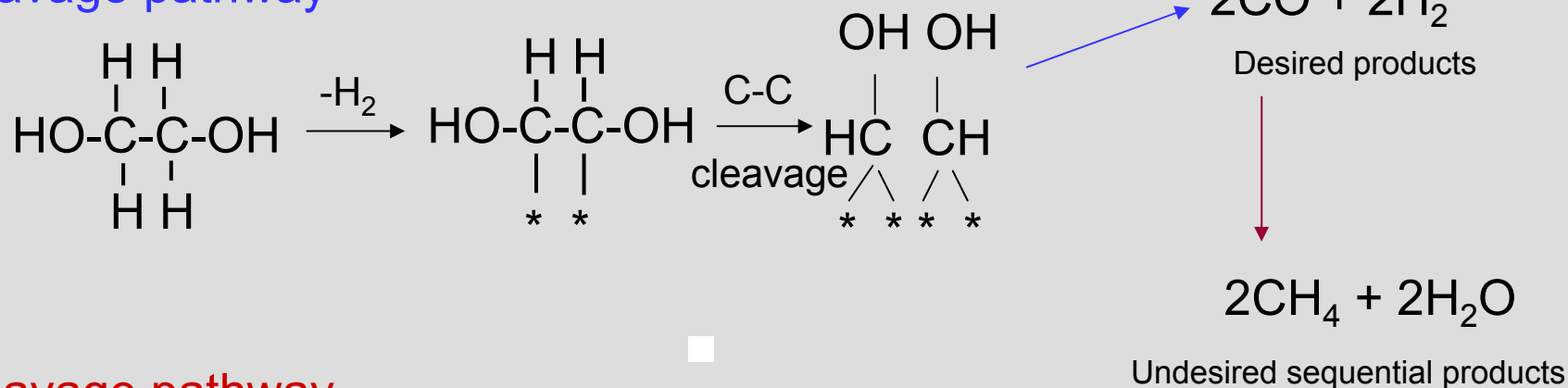
- ▶ Eliminates energy required to vaporize water
- ▶ Allows processing of bioproducts that cannot be vaporized without decomposition
- ▶ Compatible with processing wet feedstocks, avoiding need for an initial dehydration step
- ▶ Operates at low temperatures compared with conventional reforming, reducing energy costs
- ▶ Water gas shift reaction occurs simultaneously with reforming
- ▶ Pressurized product is compatible with membrane or pressure swing H₂ purification

Approach

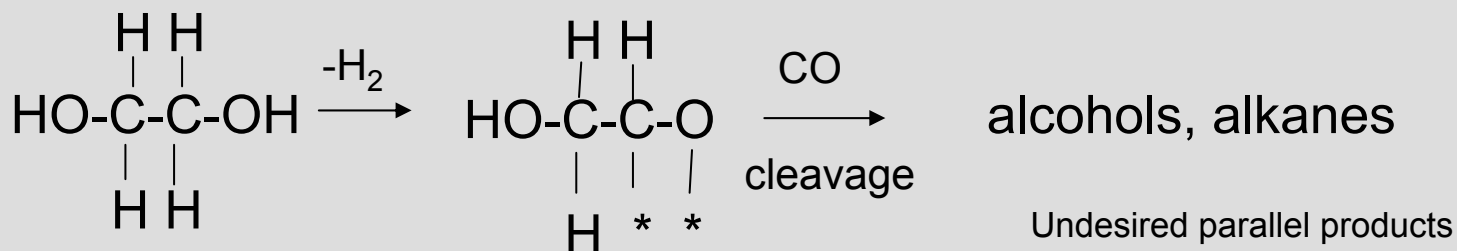
- ▶ FY04 work: high throughput evaluation of catalysts for total conversion of xylitol
- ▶ Construct fixed bed and slurry batch reactors for catalyst testing
- ▶ Prepare candidate catalysts identified from high throughput screening and other leads
- ▶ Measure activity and product selectivity of most promising catalyst systems
- ▶ Compare catalyst performance in fixed bed and batch reactors
- ▶ Develop feedstock structure/reactivity relationships
- ▶ Determine catalyst life and stability
- ▶ Determine potential benefits of microchannel reactors

Kinetic Control of Reaction Pathways* is Essential For Good Hydrogen Production

C-C cleavage pathway



C-O cleavage pathway

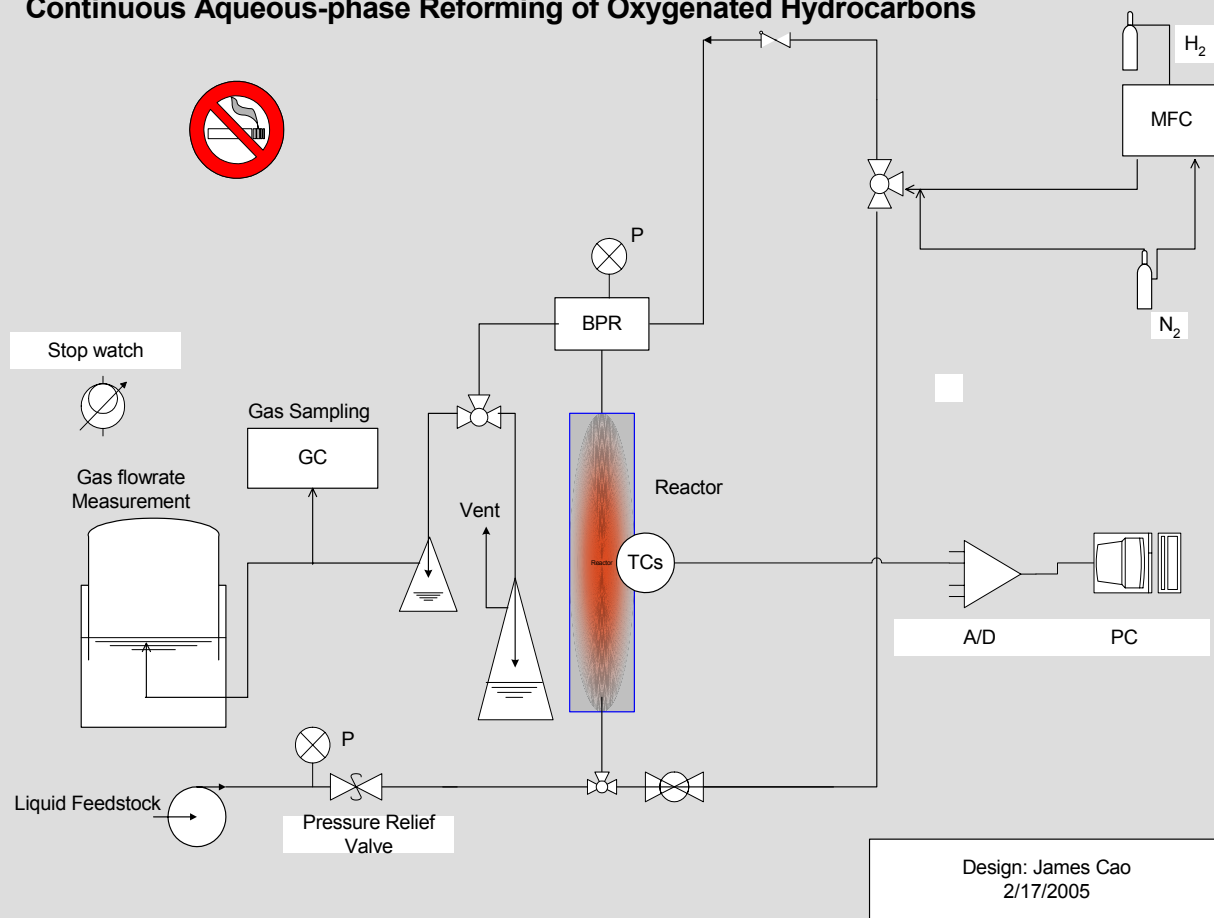


Good catalyst should have good C-C cleavage and water gas shift activity, low C-O bond cleavage and methanation activity

* Adapted from Davda et. al., Appl. Catal. B, **56** (2005), 171-186

Technical Progress: Continuous Aqueous-phase Reforming Unit

Continuous Aqueous-phase Reforming of Oxygenated Hydrocarbons

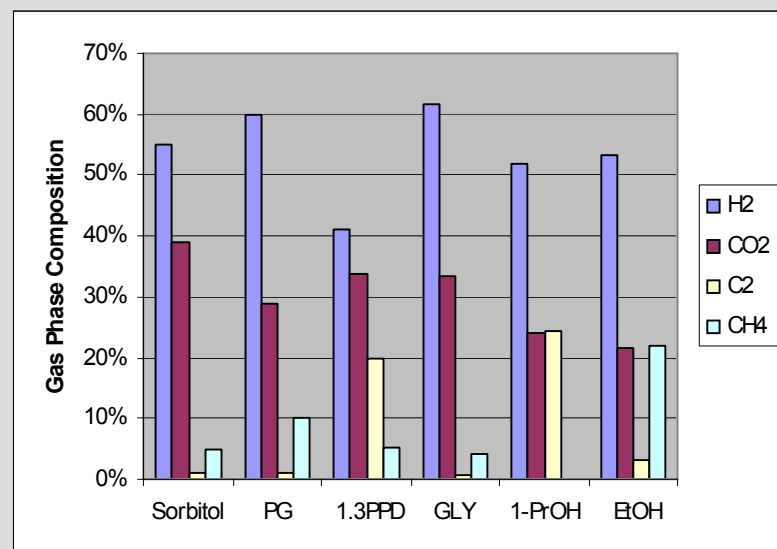
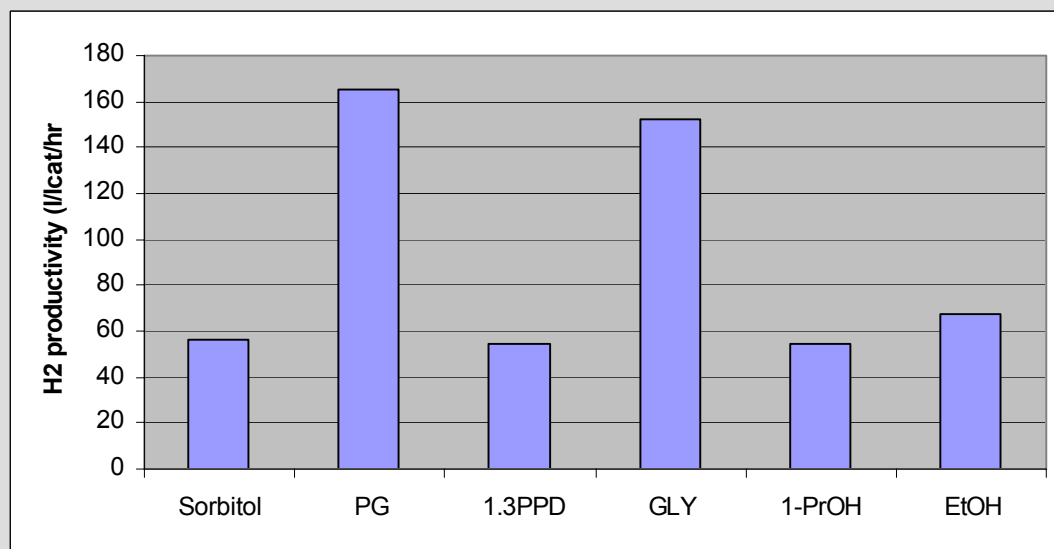
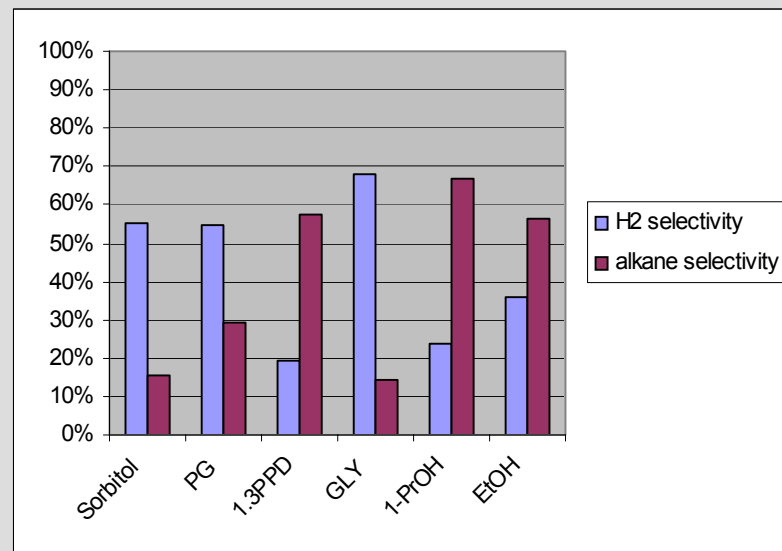
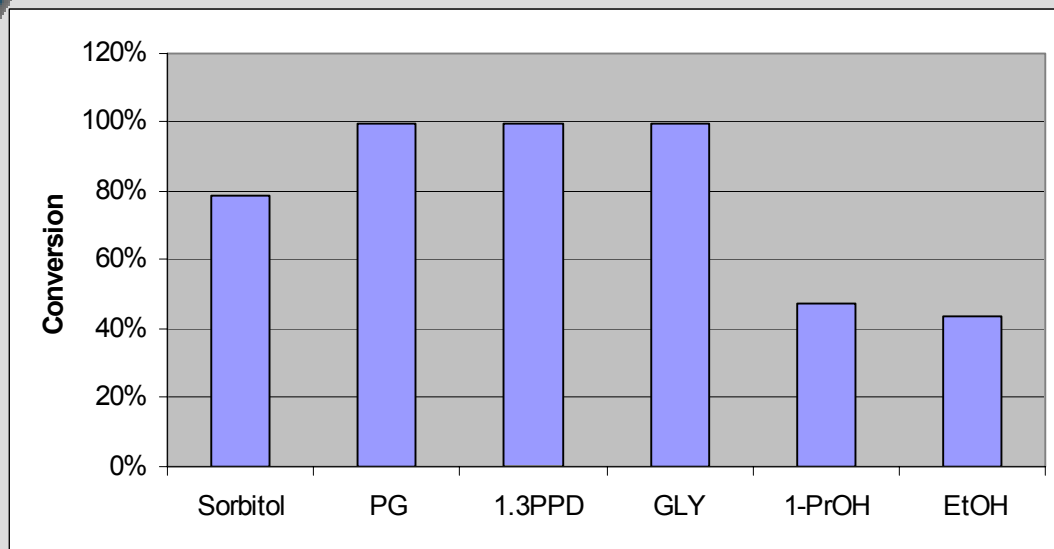


Technical Progress: Aqueous Phase Reforming of Sorbitol in Continuous Plug Flow Reactor

| | Run#1 | Literature | Run#2 | Literature | Run#3 |
|---|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| Catalyt | 3%Pt/Al ₂ O ₃ | 3%Pt/Al ₂ O ₃ | 3%Pt/Al ₂ O ₃ | 3%Pt/Al ₂ O ₃ | 3%Pt/Al ₂ O ₃ |
| Liquid feed | 10% Sorbitol | 1% Sorbitol | 10% Sorbitol | 1% Sorbitol | 10% Sorbitol |
| T | 225 | 225 | 265 | 265 | 225 |
| P | 471 | 425 | 835 | 812 | 475 |
| WHSV(gSorbitol/gcat/hr) | 0.08 | 0.008 | 0.08 | 0.008 | 0.14 |
| Contact time(min) | 70 | 94 | 70 | 94 | 42 |
| Sorbitol Conversion | 88.3% | | 99.88% | | 74.2% |
| % Carbon in gas-phase effluent | 58.3% | 61.0% | 95.7% | 90.0% | 40.6% |
| % Carbon in liquid-phase effluent | 41.7% | 39.0% | 4.3% | 12.0% | 59.4% |
| H ₂ productivity (l/l catalyst/hr) | 91.3 | | 140.9 | | 86.0 |
| <i>Gas phase composition (mol%)</i> | | | | | |
| H ₂ | 58.9% | 61.0% | 57.0% | 54.0% | 49.2% |
| CO ₂ | 35.5% | 35.0% | 33.8% | 36.0% | 47.9% |
| C ₂ | 0.9% | 0.7% | 2.2% | 2.3% | 0.7% |
| CH ₄ | 4.7% | 2.5% | 7.2% | 6.0% | 2.2% |
| H ₂ /CO ₂ | 1.66 | 1.74 | 1.69 | 1.50 | 1.03 |
| H ₂ selectivity | 64.8% | 66.0% | 58.3% | 46.0% | 44.1% |
| alkane selectivity | 15.4% | 15.0% | 25.2% | 32.0% | 7.0% |
| H ₂ /CH ₄ | 12.5 | 24.4 | 8.1 | 9.0 | 22.8 |

Primary liquid phase products include: propylene glycol, glycerol, ethanol, ethylene glycol, butane-diols, propanols

Technical Progress: Reactivity of Sorbitol and C₃ Feedstocks Over 3% Pt/Al₂O₃ Catalyst



Technical Progress: Batch Reactor Catalyst Screening

| Catalyst | 5%Ru/TiO ₂ | 5% Pt/C | 3%Pt/Al ₂ O ₃ |
|---------------------------------|-----------------------|---------|-------------------------------------|
| Gas Product (mmol) | 60.68 | 117.56 | 48.55 |
| H ₂ Selectivity | 23.7% | 16.85% | 39.39% |
| Alkane Selectivity | 17.8% | 19.91% | 9.08% |
| H ₂ /CO ₂ | 0.64 | 0.46 | 0.94 |

Technical Progress: Comparison of Batch and Fixed Bed Flow Reactor Results

| Reactor Type | Batch Reactor | PFR |
|---|---------------|-------|
| <u>Process Conditions</u> | | |
| T (°C) | 225 | 225 |
| WHSV(gorbitol/gcat/hr) | 14 | 0.165 |
| P (psi) | 921 | 425 |
| <u>Reforming Results</u> | | |
| Sorbitol Conversion | 78% | 64% |
| H ₂ productivity (l/l catalyst/hr) | 95 | 36 |
| <u>Gas phase composition (mol%)</u> | | |
| H ₂ | 58.6% | 53.3% |
| CO ₂ | 39.6% | 41.2% |
| C ₂ H ₆ | 0.1% | 1.0% |
| CH ₄ | 0.7% | 4.5% |
| CO | 1.0% | 0.0% |
| H ₂ selectivity | 65.2% | 51.7% |
| Alkane selectivity (gas phase) | 2.1% | 13.5% |
| H ₂ /CH ₄ | 89 | 12 |
| H ₂ /C ₂ | 550 | 55 |
| H ₂ /CO ₂ | 1.5 | 1.3 |
| Peclet Number (uL/D) based on sorbitol | ∞ | 155 |
| Peclet Number(uL/D) based on H ₂ | ∞ | 46 |

Ethanol reforming



Advantages of Low Temperature Steam Reforming

- ▶ Potentially lower capital cost by using low cost metals for reactor and heat exchanger hardware.
- ▶ Minimize the heat loss and improve overall thermal efficiency, particularly for small scale distributed hydrogen product (<1,500kg/day).
- ▶ Allow integration with membrane separation for potential process intensification.
- ▶ Favor WGS equilibrium or eliminate a separate WGS unit
- ▶ Produce high pressure hydrogen without excess and expensive gas compression

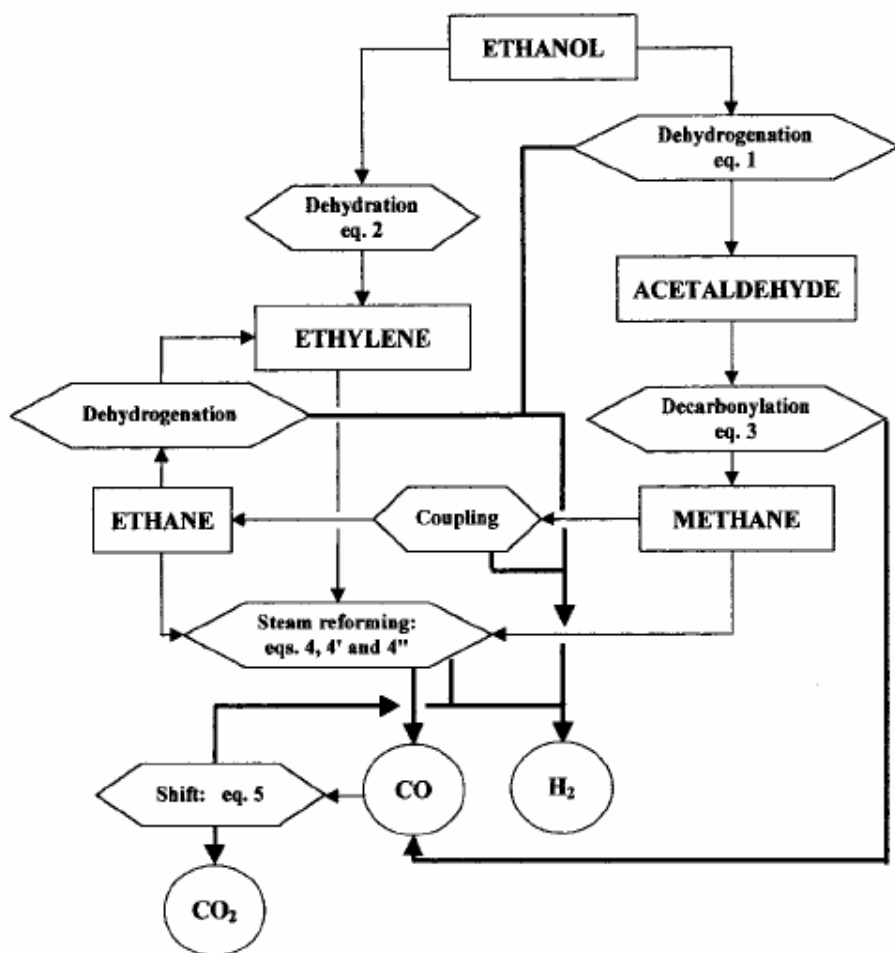
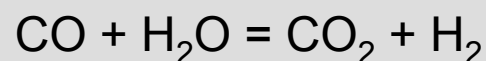
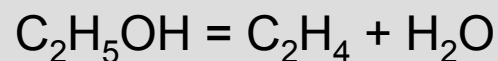
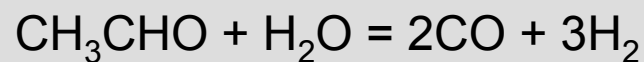
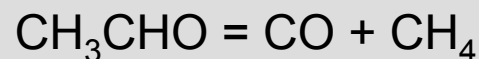
Approach

- ▶ Optimize catalyst compositions, supports, and pretreatment to reduce the selectivity to methane while improving the activity.
 - GHSV > 100,000 h⁻¹ @ S/C < 4
 - CH₄ selectivity < 30%
- ▶ Identify the potential challenges associated with low temperature reforming, and develop relevant strategies by synergistically improving catalyst, reaction engineering, and process conditions.
- ▶ Determine catalyst life and stability
- ▶ Measure kinetics of most promising catalyst systems
- ▶ Evaluate the potential advantages of novel reaction engineering, i.e., microchannel reactor, for process intensification.

Suggested Pathways For Steam Reforming of Ethanol over Rh/Al₂O₃ Catalysts

Reaction pathways appear to be complicated

Possible pathways:



C-C bond cleavage
facilitated by Rh



Steam reformation with
CeO₂-ZrO₂ to produce
CO/CO₂ + H₂

* Cavallaro, *Energy & Fuels*, 14 (2000) 1195

Supports Examined in This Work

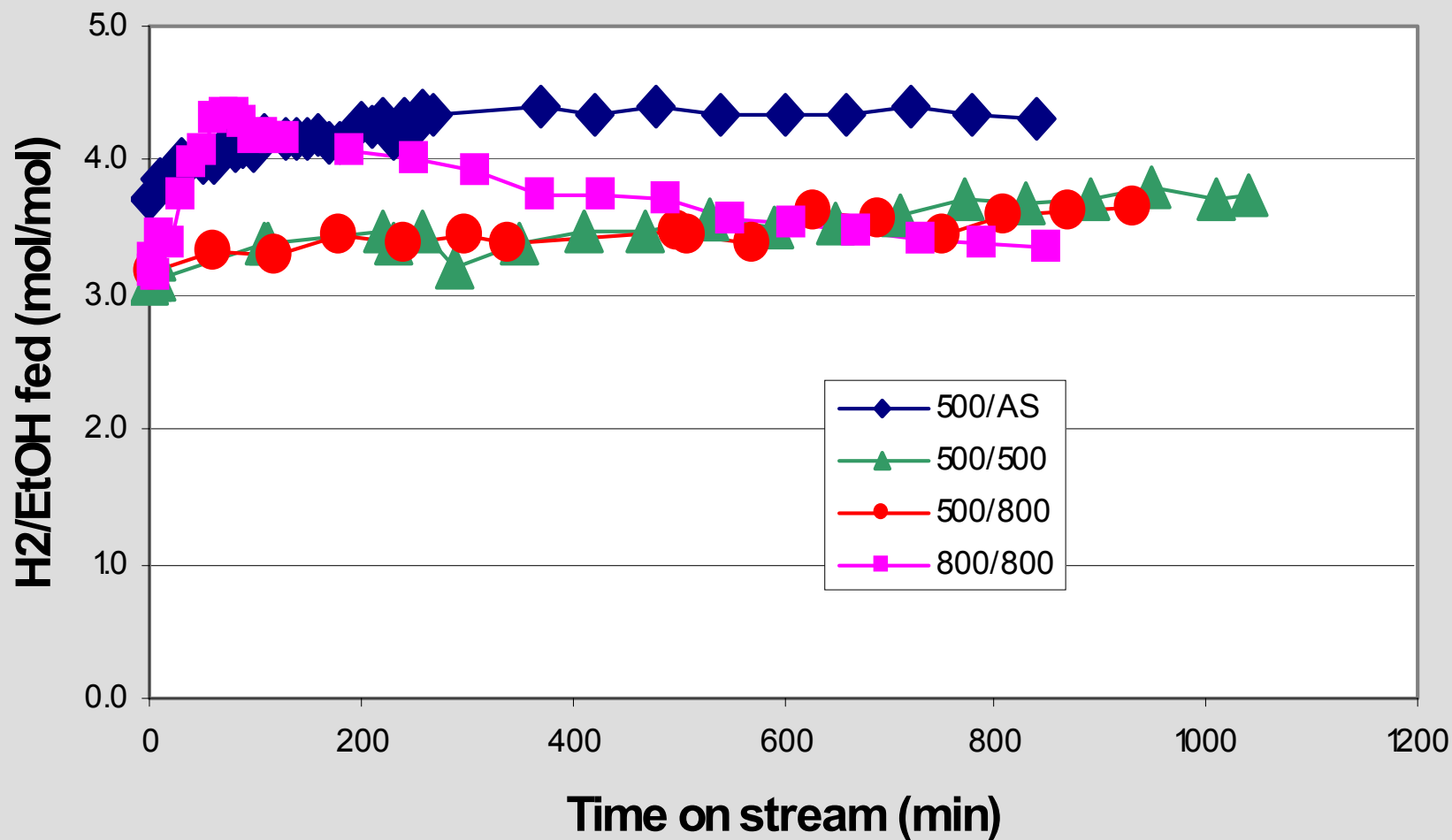
- ▶ Al_2O_3
 - High surface area
 - Acidic surface properties
- ▶ ZrO_2
 - Stable under oxidizing and reducing atmospheres
 - Moderate surface area
- ▶ $\text{CeO}_2\text{-ZrO}_2$
 - Incorporates unique properties of CeO_2
 - Redox and oxygen storage capability
 - Key component in precious metal-based water gas shift catalyst
 - ZrO_2 component facilitates stability and maintenance of surface area
- ▶ $\text{MgO-Al}_2\text{O}_3$
 - Neutralizes acidity of Al_2O_3 while maintaining high surface area

Comparison of product yields at 450°C

| | Y_{H_2} | Y_{CH_4} | Y_{CO} | Y_{CO_2} |
|---|-------------|-------------|-------------|-------------|
| 1%Rh/Ce-ZrO₂ | 3.50 | 0.63 | 0.33 | 1.05 |
| Thermodynamic equilibrium | 2.40 | 0.89 | 0.05 | 1.06 |
| 1%Rh/Al₂O₃ | 1.17 | 0.06 | 0.48 | 0.03 |

Reaction conditions: WHSV = 85,320 cm³/gh, H₂O/EtOH/N₂ = 8.0/1.0/3.5

Effect of Calcination Temperature on Hydrogen Yield at 450°C



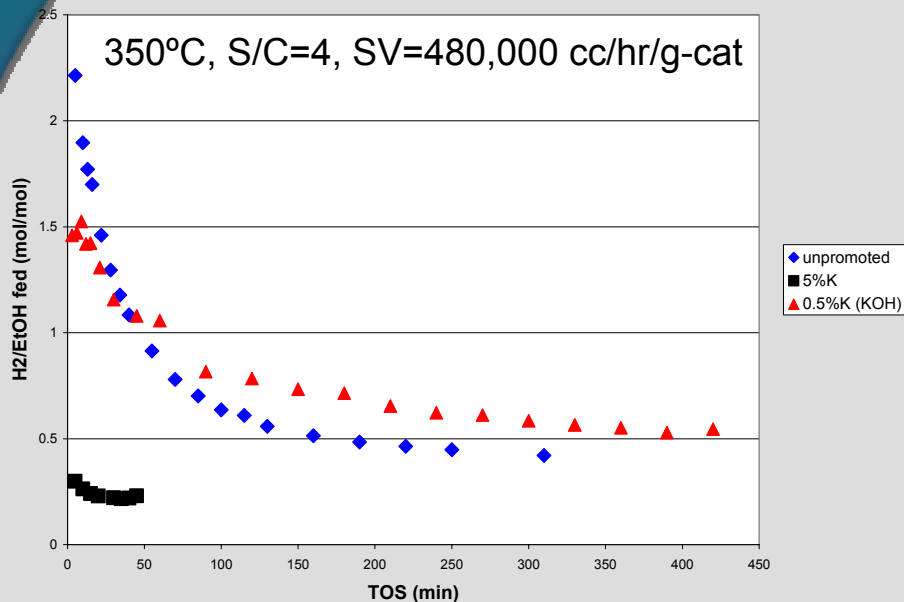
Catalyst Comparison of Hydrogen Yield From Ethanol Steam Reforming at 450°C

$\text{H}_2\text{O}/\text{EtOH} = 8$

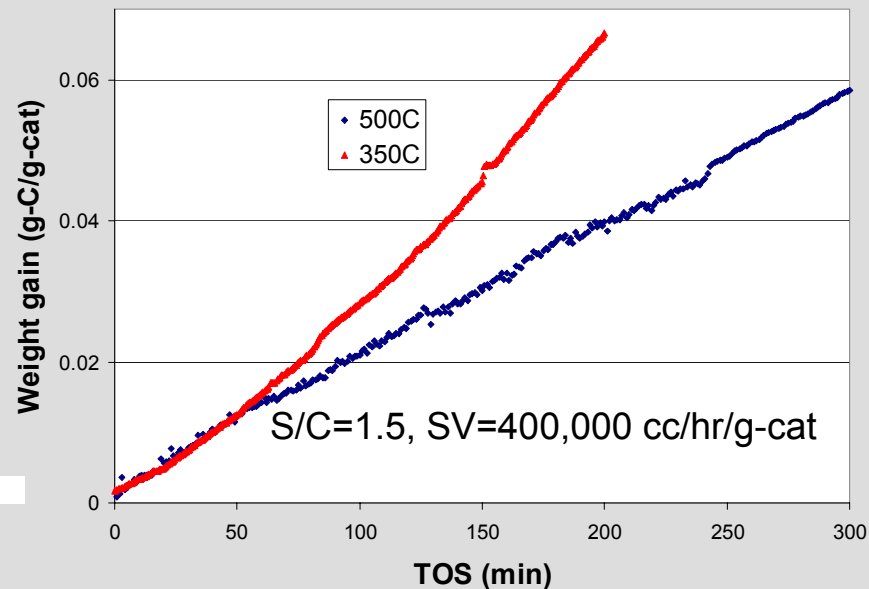
| <u>Catalyst</u> | <u>Moles H_2/Mole EtOH Fed</u> |
|--|--|
| 1%Rh/Al ₂ O ₃ | 1.2 |
| 1%Rh/MgO-Al ₂ O ₃ | 1.8 |
| 1%Rh/ZrO ₂ | 1.4 |
| 1%Rh/Ce-ZrO ₂ (13 %Ce tet, 500/800) | 3.5 |
| 3%Rh/Ce-ZrO ₂ | 2.5 |
| 10%Rh/Ce-ZrO ₂ | 2.1 |
| 3%Pt/Ce-ZrO ₂ | 1.1 |
| 1%Rh/Ce-ZrO ₂ (80%Ce cub, 500/AS) | 4.4 |

Potential Challenges with Low Temperature Reforming

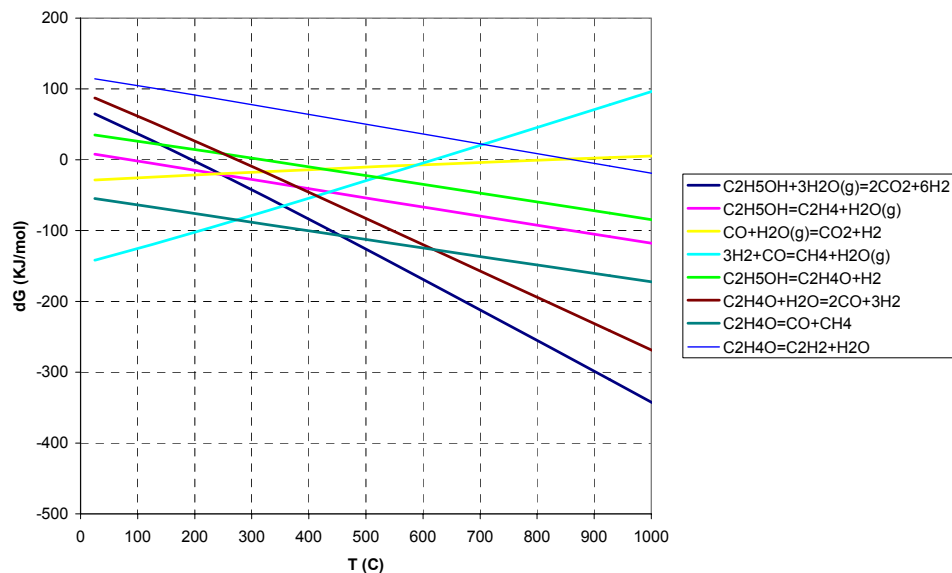
EtOH steam reforming activity



TGA measurement of coke formation

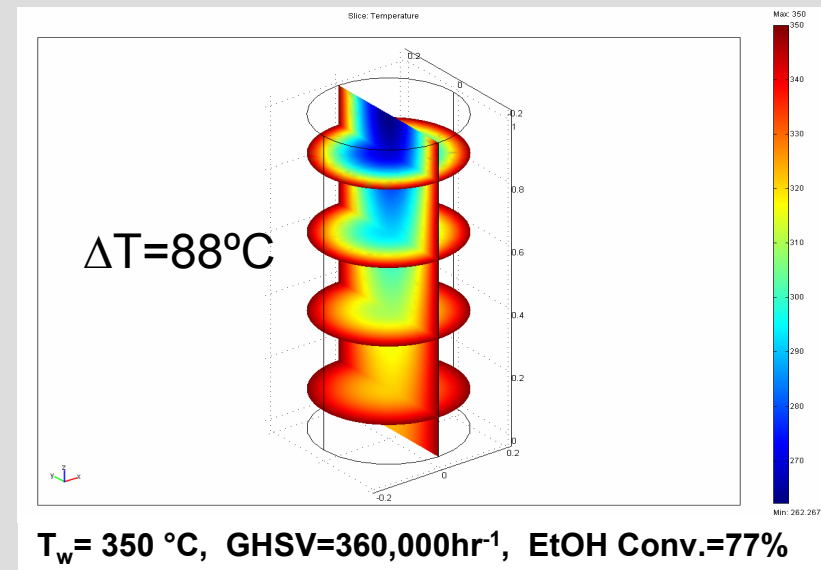
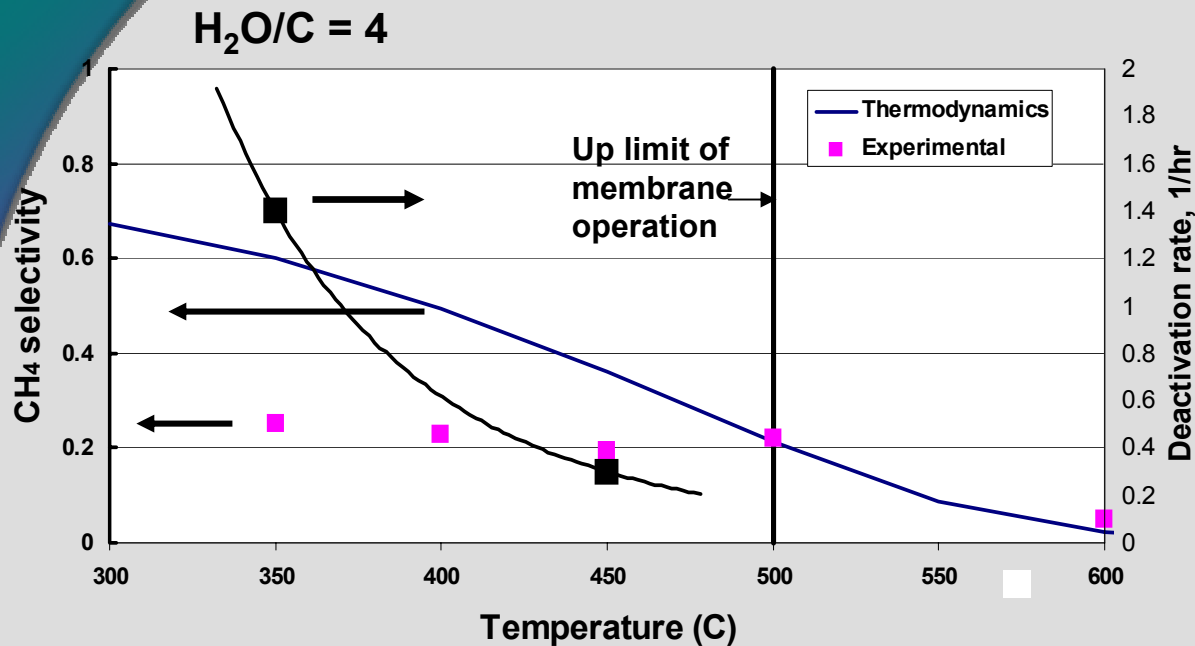


Gibbs Free Energy Change



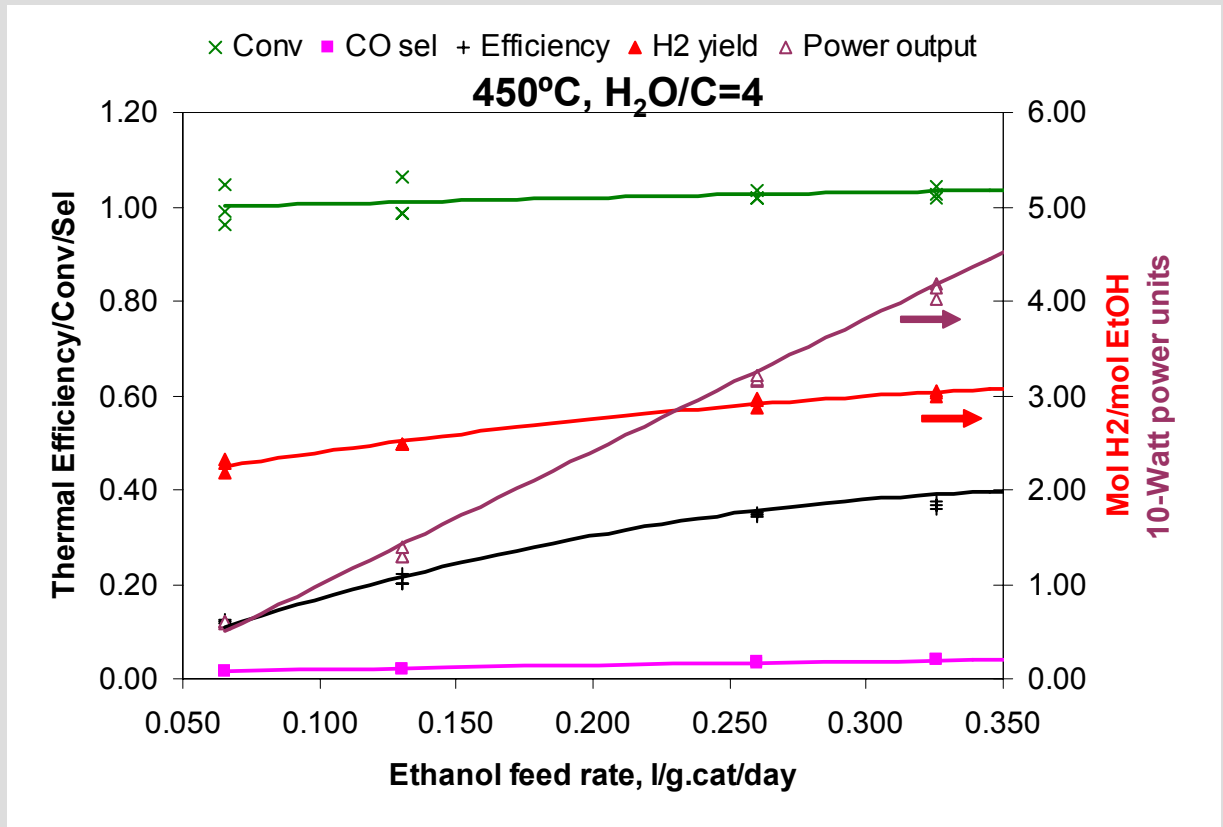
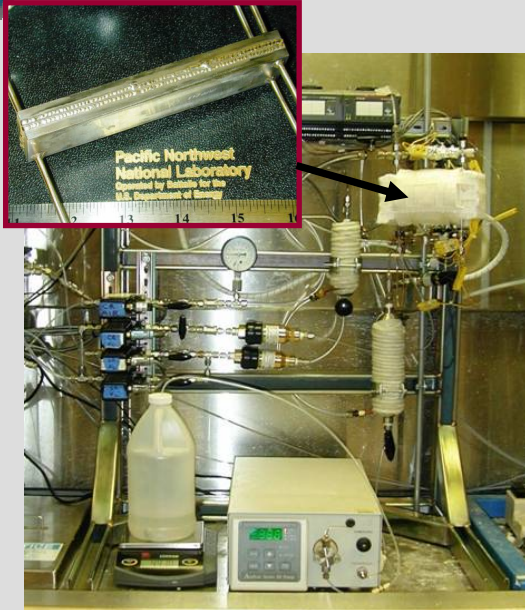
- ▶ Catalyst deactivates more rapidly at low temperatures, as confirmed by TGA experiments
- ▶ Thermodynamically, low temperature favors ethylene formation vs reforming
- ▶ Addition of K mitigates the deactivation but also reduces the activity

Potential Challenges and Proposed Approaches



- ▶ Selectivity to methane is favored at low temperatures which reduces hydrogen yield
- ▶ Membrane separation requires temperature $< 500^\circ\text{C}$
- ▶ Large temperature gradients present even in a $\frac{1}{4}$ " microtubular reactor – potentially higher deactivation rate and methane selectivity
- ▶ More efficient heat transfer and precise temperature control required—microchannel reactors offer one approach
 - DOE-OHFCIT has supported development of such reactors for reforming

Preliminary Results



- ▶ Demonstrated single channel ethanol steam reformer with integrated combustion, vaporization, and heat recuperation
- ▶ Stainless steel laminate construction with dimensions of 5" x 1" x 0.7" (volume: 60 ml)
- ▶ Power output of up to 40We, power density up to 0.6We/cc
- ▶ Thermal efficiency of about 40% (can be dramatically improved with larger scale)
- ▶ Flow sheet calculations indicate thermal efficiency can be as high as 82% (compare with DOE target of 70%--2010)

Summary and Conclusions

▶ Aqueous phase reforming

- Higher feed concentration decreases H₂ selectivity slightly but increases productivity significantly
- Increase in productivity is observed at higher temperature at expense of hydrogen selectivity
- Shorter residence time decreases methane make (higher H₂/CH₄ ratio)
- Reaction intermediates are important for product selectivity
- Comparison of product selectivity from fixed bed vs. slurry batch reactor tests suggests importance of reactor engineering component
- Microchannel technology is one potential approach to improved heat and mass transfer

▶ Ethanol reforming

- Catalyst is highly active and selective at low temperatures
- Low temperatures favor methane selectivity and catalyst deactivation
- Further catalyst development is necessary and ongoing
- Precise temperature control is desired for optimal performance
- Microchannel reactors provide attractive approach

Reviewers' Comments

- ▶ Feedstock: availability, purity—should focus on less pure feedstocks
 - Program aims to focus on less pure feedstocks in the future
 - Much catalytic work and reaction pathway understanding needed with more pure feedstocks to understand feedstock structure and reactivity
- ▶ Activity may be too slow to be economically viable
 - Recent advances show that may not be the case
 - Reactivity within Weiss Window ($>1 \times 10^{-06}$ gmol glycerol converted/cc-sec)*
- ▶ Goals for achievement need to be set: done
- ▶ Need better links to industry
 - Collaboration established with Virent Energy Systems
 - Collaboration with ethanol producers under discussion

*R. Cortright, private communication, 1300h test, 10% glycerol feed, precious metal catalyst

Future Work

▶ Aqueous phase reformation

- Structure-reactivity studies (FY05)
 - Evaluate potential advantages of converting sorbitol to more selective intermediates
 - Build on PNNL's strength in selective aqueous hydrogenolysis of sorbitol
- Explore approaches to glucose rather than sorbitol (FY06)
- Explore less pure feedstocks such as hemicellulose (FY06)
- Evaluate best reactor types for improved heat and mass transfer (FY06)
- *Go/no go decision*: economic analysis demonstrates potential to meet DOE targets (FY06)

▶ Ethanol reformation

- Continue catalyst development for improved longevity (>100h at steady state performance) (FY05-06)
 - *Go/no go decision* for continued low temperature approach
- Reactor development and demonstration (FY06)
 - Improve thermal efficiency (target 70%)
 - Reduce production costs (to meet 2010 target)
 - Leverage PNNL development in microchannel reactors for reforming

Publications and Presentations

Publications:

- ▶ H.Roh, Y.Wang, D.L.King, “Highly selective and active Rh based catalysts for ethanol steam reforming”, to be submitted to *Catal.Today* (invited publication)
- ▶ H.Roh, Y.Wang, D.L.King, “Selective Production of H₂ from Bio-Ethanol at Low Temperatures over Rh/CeO₂-ZrO₂ Catalysts”, Proc. Of 19th North American Catalysis Society Meeting, 2005 (in press).
- ▶ H.Roh, D.L.King, and Y.Wang, “Hydrogen Production from Biomass Feedstocks”, *Prepr. - Am. Chem. Soc., Div. Pet. Chem.*, 49 [2] 912-913 (2004).

Presentations:

- ▶ H.Roh, Y.Wang, D.L.King, “Hydrogen Production from Biomass”, 228th ACS Meeting, Philadelphia, Aug. 22-26, 2004
- ▶ D.L. King, “Bio-derived Liquid Reforming”, presented to Hydrogen Production Tech Team, Jan. 13, 2005, NREL.
- ▶ Y.Wang, H.Roh, A.Platon, D.L.King, “Selective Production of Hydrogen from Bio-Ethanol at Low Temperatures over Rh/CeO₂-ZrO₂ Catalysts,” accepted for oral presentation in 19th North American Catalysis Society Meeting, Philadelphia, May 21-25, 2005.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Aqueous phase reforming:

- ▶ Possible failure of the reforming reactor, fittings, or tubing at high pressure (420psig) could lead to the release and explosion of hydrogen.

Vapor phase reforming of ethanol:

- ▶ Possible failure of the reforming quartz tube reactor can lead to the release of hydrogen into the heated furnace, which could cause explosion.

Hydrogen Safety

Our approach to deal with this hazard is:

Aqueous phase reforming:

- ▶ A testing reactor is designed with a safety factor of at least 10 and has a small volume (about 7cm^3). Reactor is operated in a hood so that any emitted flammable gas is vented and the hydrogen concentration is diluted to below flammable limit. A rigorous helium leak test is performed before each experiment. A rupture disc is installed to prevent over pressurization. A minor deviation in temperature or pressure activates either a high- or low- alarm, and shuts down the feeding and heating source automatically.

Vapor phase ethanol steam reforming:

- ▶ A testing reactor with a small system volume (less than 10cm^3) is used to test less than 50mg catalyst. The maximum hydrogen production rate is about 10sccm. The reactor is operated in a hood so that any emitted flammable gas is vented to far below flammable limit. Leak test is performed before each experiment to prevent any release of hydrogen through the unsealed fittings. A pressure gauge is installed in upstream of the reactor to monitor the system pressure. If pressure builds up to a certain level, the control system will shut down the experiment. The temperature malfunction of the reactor system would lead to the shut down of furnace automatically.