

Bio-Derived Liquids Reforming

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June 9, 2008

Overview

Timeline

- Project start date: Oct. 1, 2004
- Two projects consolidated in 2007
 - Aqueous phase reforming of sugar and sugar alcohols
 - Vapor phase reforming of ethanol
- Project end date: on-going
- Percent complete: 25%

Budget

- Funding received in FY04: \$100K
- Funding received in FY05: \$500K
- Funding received in FY06: \$0K
- Funding for FY07: \$550K
- Funding for FY08: \$1,000K

Barriers

- A: Reformer Capital Cost
- C: Operation & Maintenance
- D: Feedstock Issues
 - Better catalysts to improve yield
 - Handle cheaper, less-refined feedstocks

Collaborations

- Virent Energy Systems – catalyst characterization
- DTI - process economics

Objectives

- Overall: Evaluate and develop bio-derived liquid reforming technologies for hydrogen production that can meet the DOE 2017 cost target of <\$3.00 /gge
- Ethanol steam reforming
 - Identify at least one catalyst having necessary activity, selectivity, and life at moderate temperatures to justify scale up
 - Provide input for H2A analysis to determine potential economic viability and provide guidance to R&D effort
- Aqueous phase reforming
 - Identify and control the reaction pathways to enhance hydrogen selectivity and productivity as well as catalyst life
 - Provide preliminary data for H2A analysis

Why Bio-derived Liquids?

- Biomass-derived liquids can be produced at moderate scale at centralized facilities located near the biomass source
- The liquids have a high energy density and can be transported with minimal new delivery infrastructure
- CO₂-neutral distributed production of hydrogen from bio-derived liquids can contribute to near-term hydrogen supply and delivery

Project Milestones

| Ethanol Steam Reforming | |
|---|------------|
| Complete elevated pressure studies of catalyst productivity and product selectivity for both Rh and Co catalysts | 9/30/2008 |
| Provide data for H2A comparative analysis of Rh and Co catalyst systems at best identified operating conditions and catalyst formulations | 9/30/2008 |
| Down-select catalyst for subsequent process development and scale-up. Update costs to produce H ₂ at 1500 kg/day with best catalyst system and conditions. Identify sensitivities to guide R&D effort to meet 2017 targets | 12/31/2008 |

| Aqueous Phase Reforming | |
|--|-----------|
| Report summarizing kinetic data, catalytic and non-catalytic reaction pathways, and pH effects with glycerol feedstock | 9/30/2008 |
| Demonstrate catalyst performance showing no greater than 20% H ₂ productivity decline over 100 hours | 9/30/2008 |
| Provide preliminary performance data to H2A Analysis | 12/31/08 |

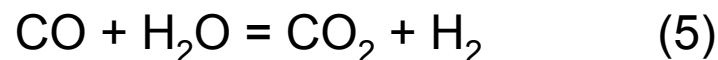
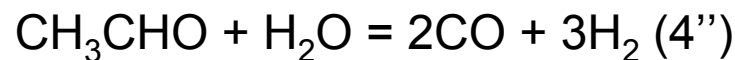
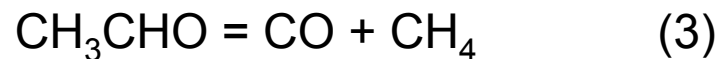
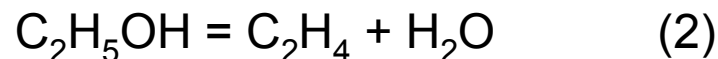
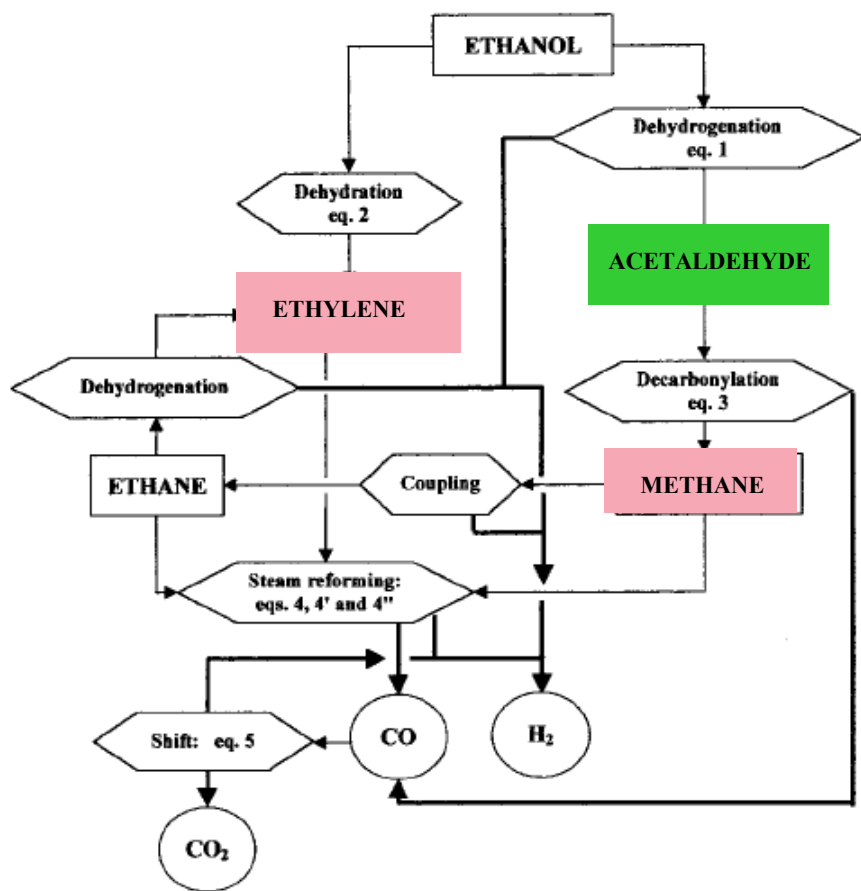
Ethanol Steam Reforming

- Approach
 - Test two separate and distinctly different catalyst systems for ethanol steam reforming (Rh-based and Co-based) for activity, selectivity, life
 - Provide results to H2A model in order to
 - Quantify economic advantages and disadvantages of each catalyst system
 - Assist in down-selecting preferred system for follow-on work
 - Identify performance improvements required to meet 2017 target
- Technical Accomplishments
 - Improved the life of Rh based catalysts by a factor of 4 by adjustment of pretreatment protocols and support promotion
 - Quantified the performance of Co/ZnO catalyst over a range of conditions with realistic feed concentrations and conversion levels
 - Provided test results from Rh/CeO₂-ZrO₂ catalyst to H2A analysis

Steam Reforming of Ethanol

- $\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 6\text{H}_2 + 2\text{CO}_2$ $\Delta H_{298\text{K}} = 173.7 \text{ kJ/mol}$
- Low temperature SR (<550°C)
 - Cheaper materials of construction
 - More efficient integration with water gas shift
 - Challenges: catalyst activity and deactivation
- High temperature SR (>550°C)
 - More expensive materials of construction
 - Increased probability of undesired methane formation
 - Less efficient integration with water gas shift
 - Catalyst deactivation may be masked by excess activity for runs of short duration
- Candidate catalysts
 - Non-precious metals: Ni, Co, Ni-Cu
 - Precious metals: Rh, Pt, Pd
 - Supports: Al_2O_3 , $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$, $\text{CeO}_2\text{-ZrO}_2$, ZnO
 - Promoters: alkali, alkaline earth

Proposed Pathways for Ethanol Steam Reforming

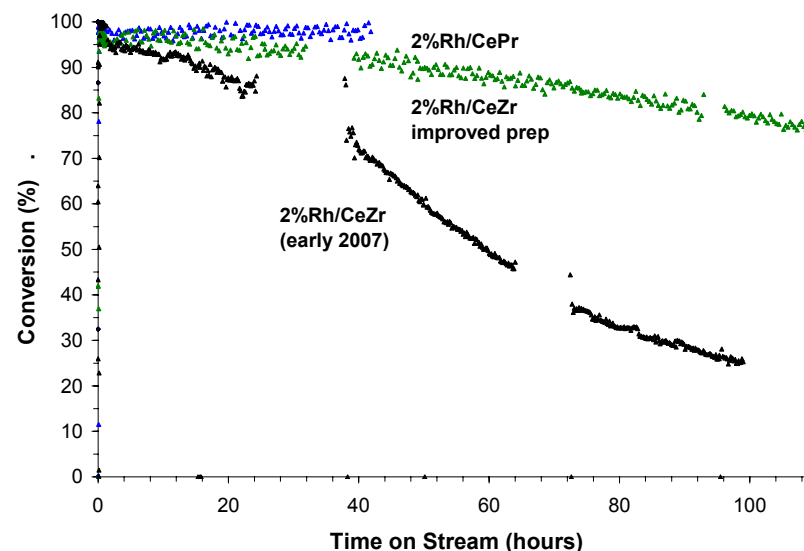
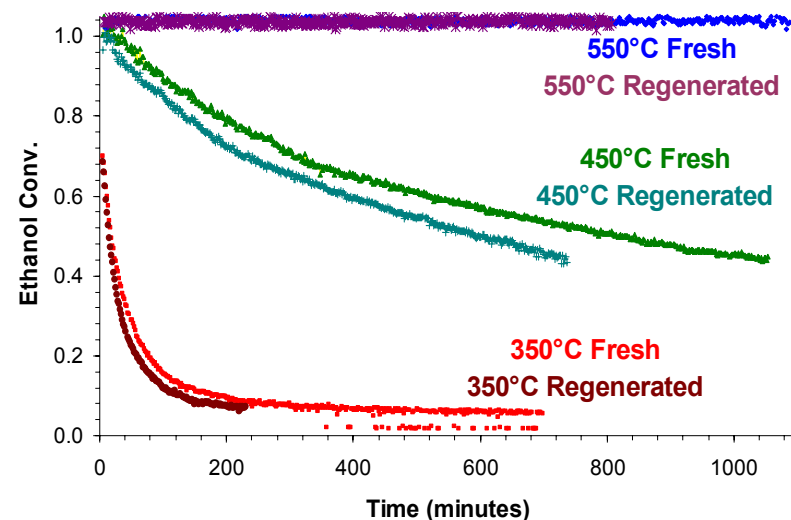


Ethylene and methane are undesired products

Target is high CO₂ (and H₂) selectivity

Performance of Rh-Based Catalyst (Rh/Ce_{0.8}Zr_{0.2}O₂ and Rh/Ce_{0.8}Pr_{0.2}O₂)

- Catalyst preparation: incipient wetness impregnation
- Test conditions
 - Fixed bed reactor, 25 mg catalyst 60-100 mesh diluted 10x with SiC)
 - GHSV (total) = 493K; EtOH SV = 1.2 mol/gcat-h
 - Analysis of both liquid and gas phase products
- Operate at high space velocities to accelerate catalyst deactivation
- High activity with ~60% CO₂ selectivity
 - Methane selectivity ~10-20% of total C
 - Catalyst will deactivate, even at high temperatures, but more slowly
 - Catalyst durability increased by use of PrO₂
- Catalyst Regeneration
 - Removal of detrimental carbon via air oxidation
 - Catalyst does not require re-reduction, allowing for improved system design and efficiency



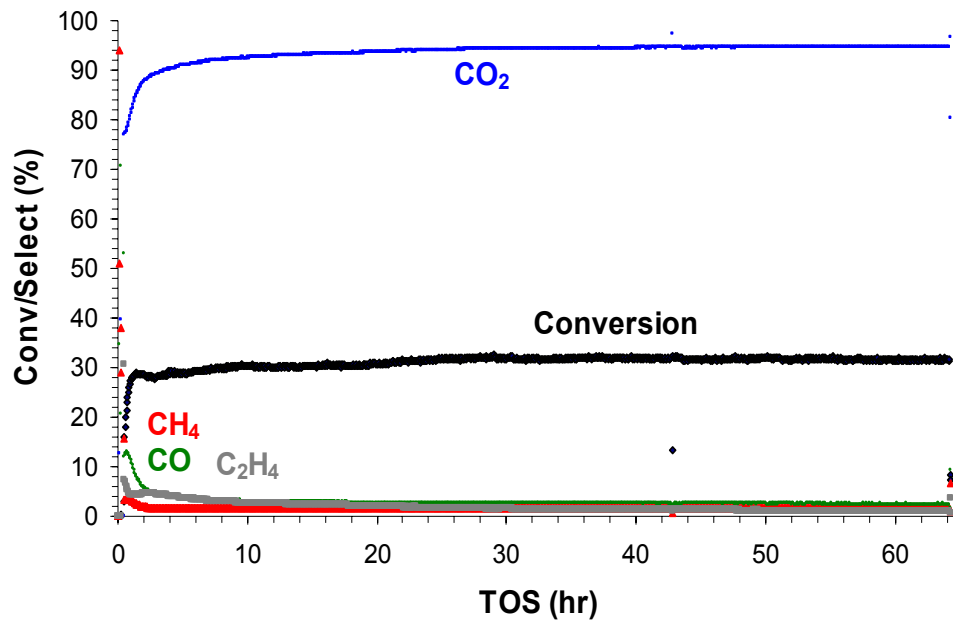
Alternate Catalyst: Co/ZnO(Na)

- Described in literature to produce highly selective catalysts for H₂ and CO₂ from ethanol steam reforming*
 - High conversions and H₂/CO₂ selectivity achieved with high steam feed concentrations and substantial Ar dilution (450°C, H₂O/EtOH/Ar = 13/1/70)
- PNNL approach
 - Examine catalyst system under realistic H₂O/EtOH ratios and without diluent
 - Quantify activity and long term stability
 - Understand conversion/selectivity tradeoffs vs. process conditions
 - Generate data allowing H₂A economic comparison between Co and Rh catalyst systems

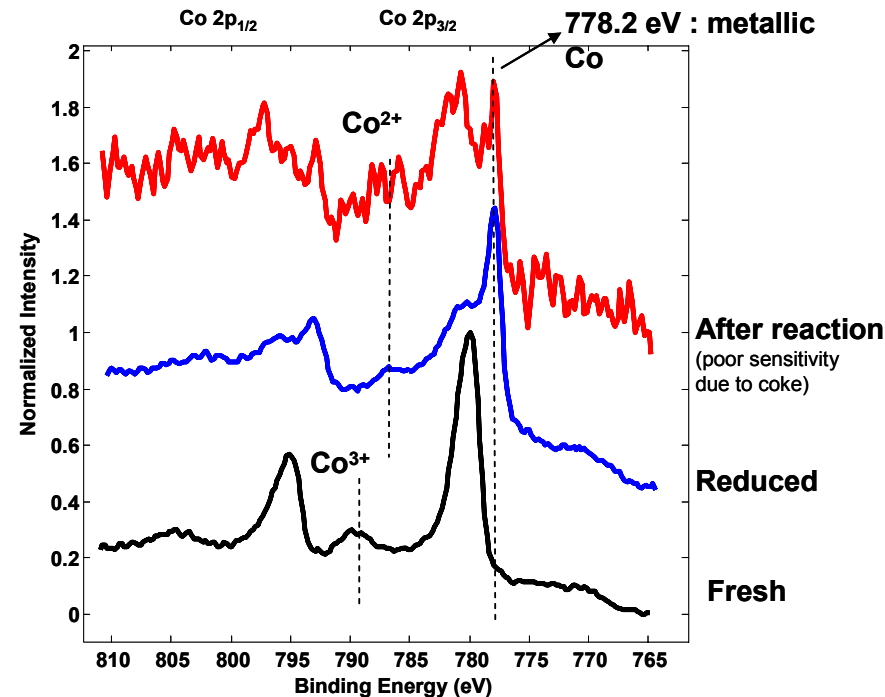
* Llorca et. al., J. Appl. Cat. B 43 (2003) 355; J. Catal. 222 (2004) 470

XPS Post-Reaction Characterization of Co/ZnO Catalyst for Co Speciation

SV=0.278mol EtOH/g-hr
S/C=4, T=450°C

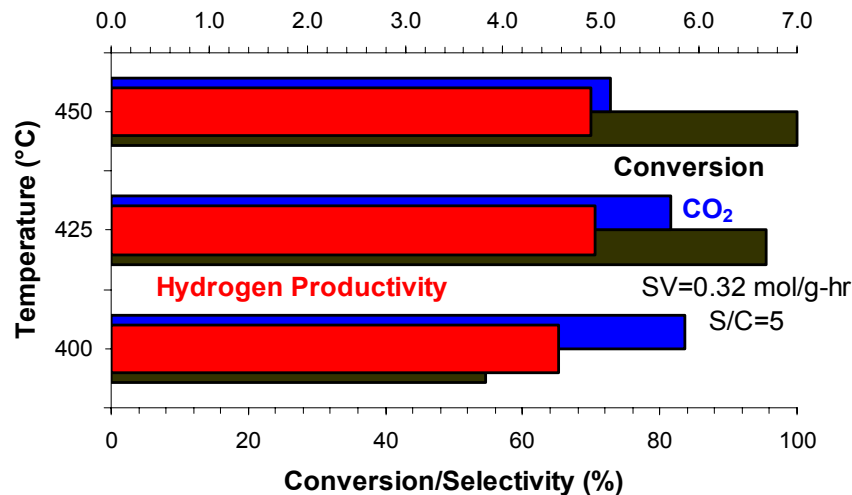
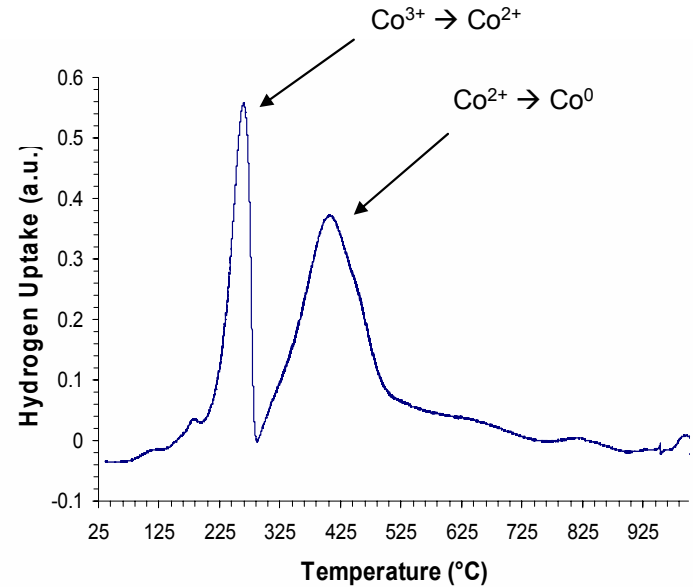
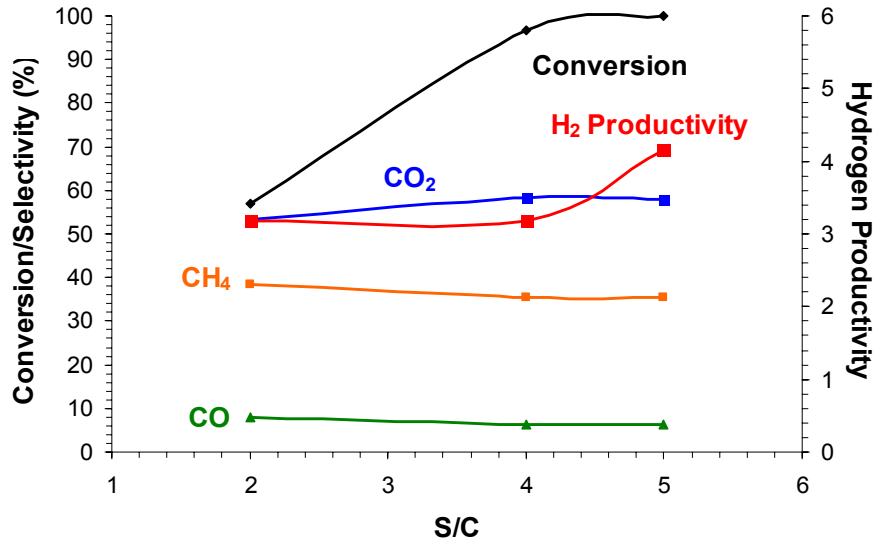


- High initial CH₄ selectivity: reduced cobalt metal, subsequently partially oxidized under operation



- Apparently stable catalyst shows significant carbon buildup on Co (not on ZnO)
- XPS data suggests possible key role of Co²⁺ and oxidation of Co⁰ during reaction

Increased Steam is Required to Provide Good H₂, CO₂ Selectivity at High Ethanol Conversions



- Operation at $T \geq 500^\circ\text{C}$ results in high methane make and carbon formation
- Operation at $T \sim 450^\circ\text{C}$ is near $\text{Co}^{2+} - \text{Co}^0$ transition
- Degree of reduction may be function of conversion level (H_2 , H_2O concentrations)

Rh and Co Catalyst Cost Comparison—Metals Basis

| <i>Catalyst</i> | <i>Temp, C</i> | <i>GHSV</i> | <i>S/EtOH</i> | <i>EtOH conv, %</i> | <i>CH4 select, %</i> | <i>CO select, %</i> | <i>H2/EtOH conv</i> |
|-----------------|----------------|-------------|---------------|---------------------|----------------------|---------------------|---------------------|
| Rh | 550 | 500K | 8 | 85 | 16.2 | 18.6 | 5 |
| Co | 450 | 56K | 4 | 17 | 5 | 5 | 6 |

| | <i>metal cost, \$/lb</i> | <i>Productivity, mole/H2/g-cat/hr</i> | <i>catalyst weight (kg), 1500kg-H2/day</i> | <i>Catalytic metal cost, \$</i> |
|----|--------------------------|---------------------------------------|--|---------------------------------|
| Rh | 100,000 | 7.905 | 3.95 | 17570 |
| Co | 30 | 0.047 | 665 | 887 |

Potential advantages of Co-based catalyst:

- A factor of ~20 lower catalyst inventory cost
- Stable performance (a few hundred hours) at H₂O/EtOH = 4 (stoichiometric = 3)
- Lower CO and CH₄ selectivities than Rh catalyst
- Higher H₂ yield per mole ethanol converted (stoichiometric = 6)

Potential disadvantages

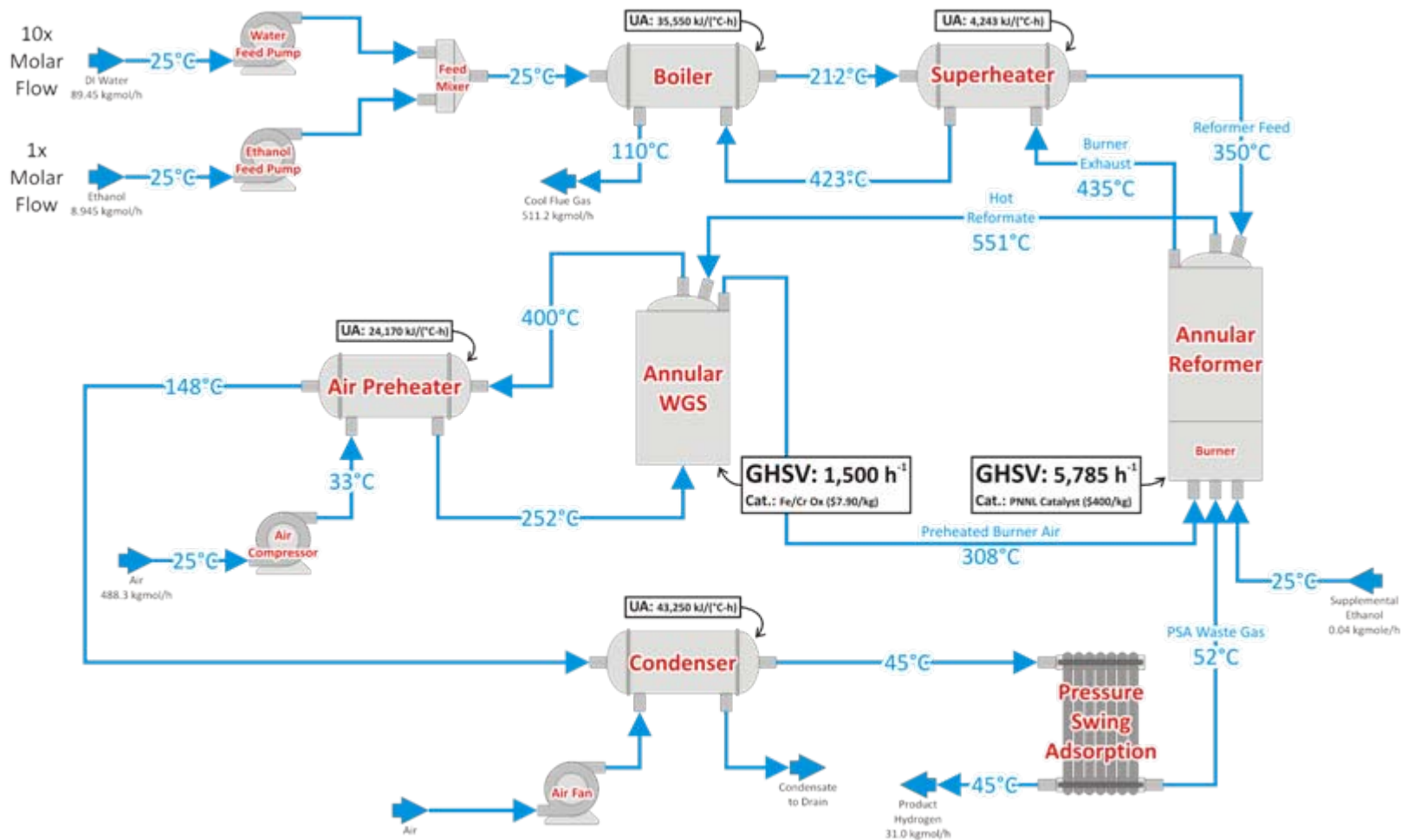
- Requirement for EtOH recycle and/or need to operate at high S/C ratio to increase conversion and minimize CH₄ yield
- Possible CH₄ increase with high pressure operation
- Larger catalyst reactor volume

Comparison and down-selection will be provided through H2A analysis

H2A Analysis

- Approach
 - Based on process simulation modeling conducted by Directed Technologies
 - 5:1 steam to carbon ratio; 550°C reformation
 - Sizing assumptions developed to translate process simulation results into equipment sizes.
 - Cost models developed for unit operations based on
 - Directed Technologies reports
 - AspenTech Icarus Process Evaluator
 - Chemical engineering cost estimating manuals
 - Hydrogen production cost calculated with H2A spreadsheet with mostly default assumptions
- Key Design Assumptions
 - Reformer space velocity based on total inlet flow at STP = 24,200 per hour
 - WGS space velocity based on total inlet flow at STP = 1500 h⁻¹
 - PSA H2 recovery = 75%

Ethanol Steam Reforming Process Flow Diagram (From Directed Technologies)



H2A Analysis Status: EtOH Steam Reforming

Key H2A Assumptions

- Ethanol cost = \$1.07/gallon
- 1500 kg H₂/day capacity
- 85.2% annual capacity factor
- No operating labor required
- Maintenance and repair cost = 5% of capital
- Replacement costs
 - 15% of capital in year 6
 - 50% of capital in year 11
 - 15% of capital in year 16

Caveats

- Low assumed cost of EtOH
- Catalyst regeneration not included
- Feedstock recycle not included
- Assumption that H₂ selectivity is unaffected by elevated pressure operation needs to be verified

| <i>Specific Item Cost Calculation</i> | |
|--|--|
| Cost Component | Hydrogen Production Cost Contribution (\$/kg) |
| Capital Costs | \$0.463 |
| Decommissioning Costs | \$0.000 |
| Fixed O&M | \$0.156 |
| Feedstock Costs | \$2.344 |
| Other Raw Material Costs | \$0.000 |
| Byproduct Credits | \$0.000 |
| Other Variable Costs (including utilities) | \$0.055 |
| Total | \$3.017 |

Aqueous Phase Reforming

- Approach
 - Summarize the undesired reaction pathways (glycerol as model) that can adversely affect H₂ productivity and yield
 - Correlate their importance as a function of catalyst, reaction medium, and test conditions.
 - Identify deactivation pathways and identify solutions to provide acceptable catalyst life

- Technical Accomplishments
 - Increased longevity of current best Pt-Re/C catalyst by 2x by support modification (based on a hypothesis on cause of deactivation)
 - Extended the study of KOH and alternate base addition with glycerol and quantified the concentration effects on life and selectivity

Distinguishing Between the Work of PNNL and Virent Energy Systems

Virent

- Has developed and demonstrated technology for production of hydrogen from sugars and sugar alcohols (see presentation PD6 this session)
- Recent work has expanded to the production of liquid transportation fuels through modifying the sugar/sugar alcohol conversion chemistry

PNNL

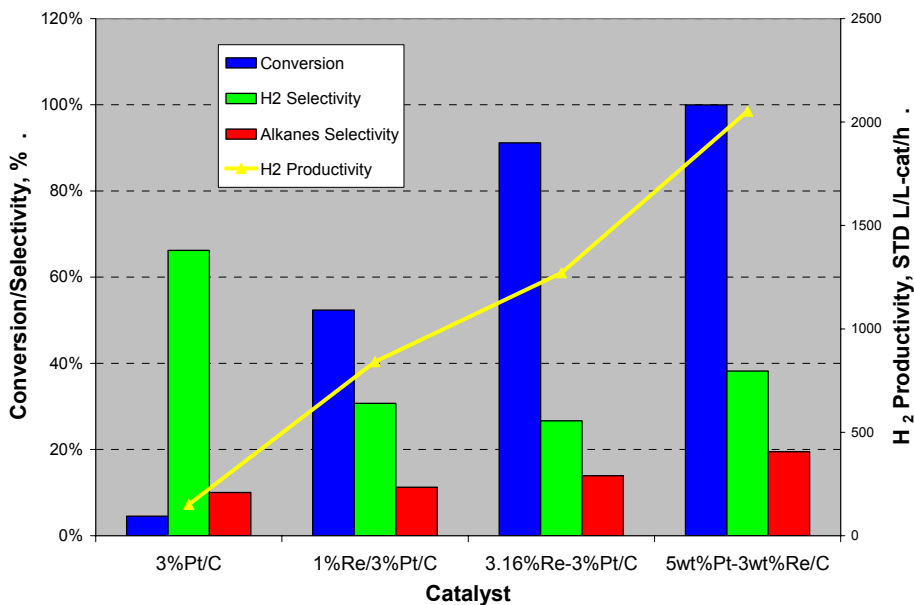
- Understand and quantify importance of desired and undesired reaction pathways for H₂ production
- Propose approaches to minimize undesired reactions
- Develop high activity and long lived catalysts
- Understand catalyst deactivation mechanisms and improve catalyst durability

Effect of Rhenium, Base Addition to Pt/C for Aqueous Phase Reforming

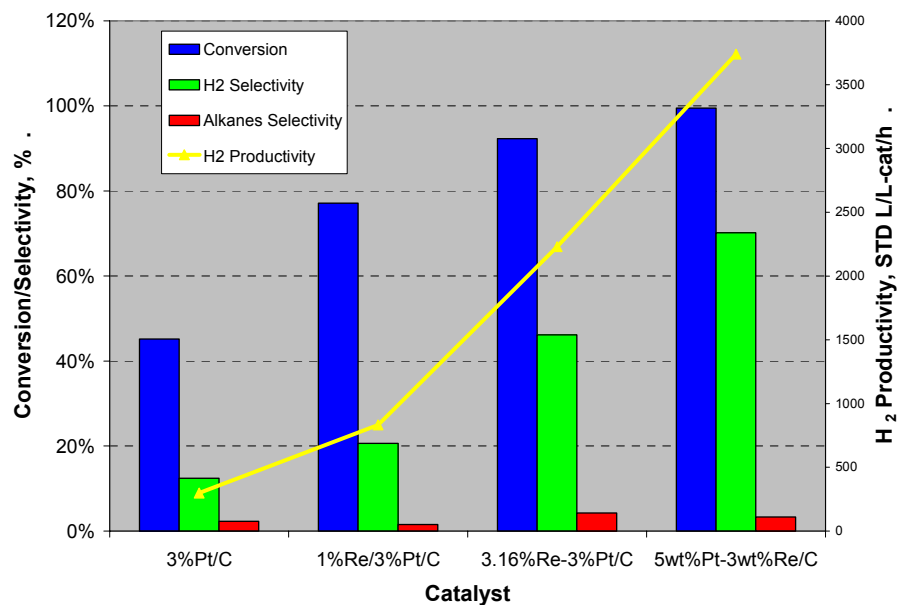
Catalyst testing

- Fixed bed microchannel reactor, 0.5 mm i.d., oil bath heated
- 200mg catalyst pre-reduced in H₂ at 270°C

No base addition

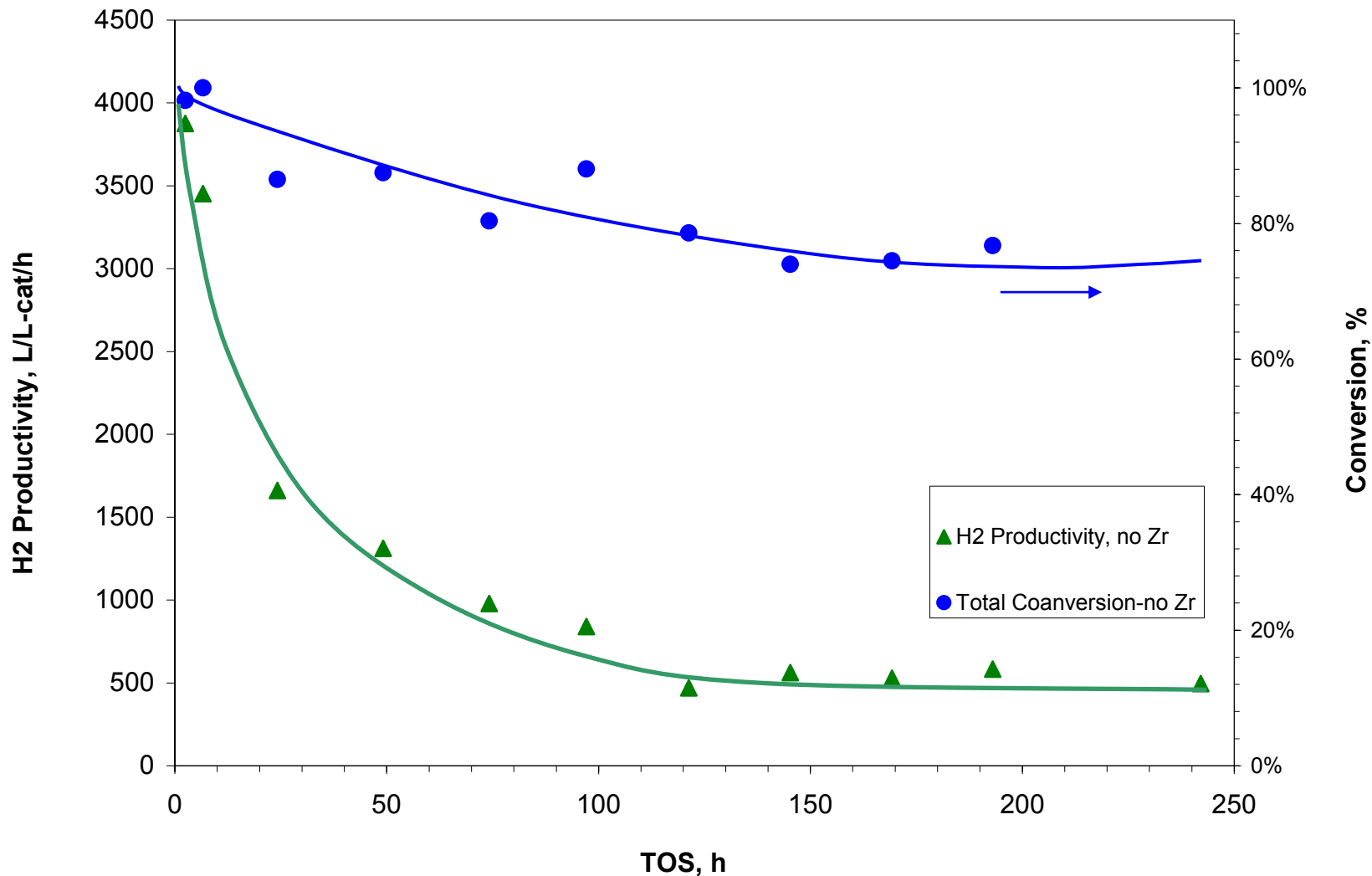


With KOH addition



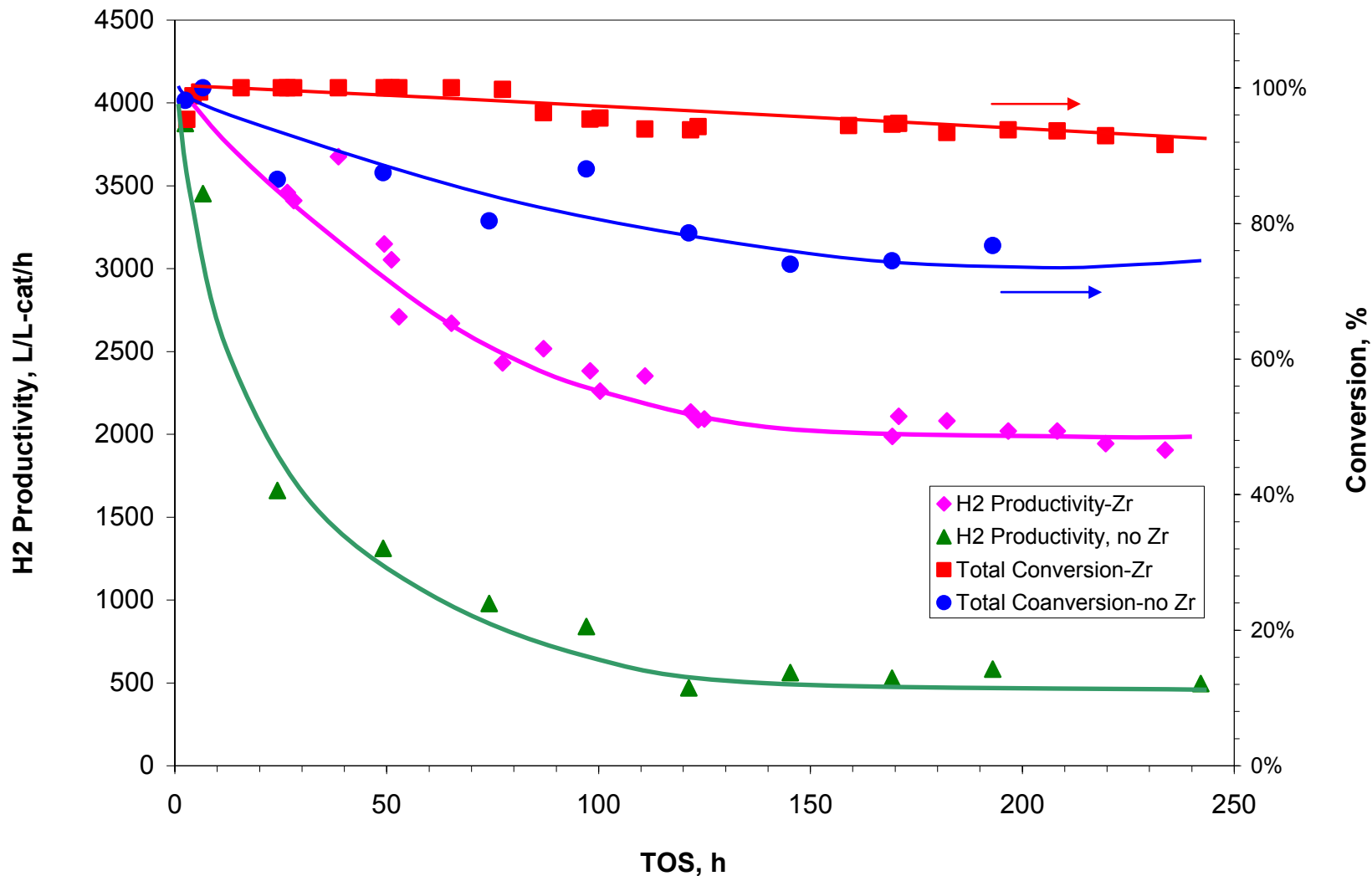
Stability of 5%Pt-3%Re/Carbon

10%Gly+1%KOH, Contact time= 2min, 225°C, 425psi



Stability of 5%Pt-3%Re/Carbon (Zr)

10%Gly+1%KOH, Contact time= 2min, 225oC, 425psi



Future Work

Ethanol Reforming

- Continue Co speciation studies (role and stability of oxidized Co)
 - Potential to increase conversion while maintaining high H₂/CO₂ selectivity
 - Develop stabilization methods through catalyst modification
- Quantify and determine the potential of carbon formation over Co/ZnO
- Determine and compare H₂ yield and selectivity for Co and Rh catalysts at elevated pressures (10 atm)
- Provide complete data for comparative H₂A analysis
- Downselect catalyst and use H₂A analysis to help guide process development

Aqueous Phase Reforming

- Study Pt-Re interactions using EXAFS and XANES (in collaboration with Virent)
- Continue studies on (alternate) base effects
- Continue catalyst modification studies to improve durability
- Implement combinatorial reactor to facilitate process variable effects with sorbitol
- Begin H₂A analysis of APR system

Summary

Ethanol Reforming

- Substantial progress made on increasing lifetime of Rh-CeO₂-MO₂ catalyst
- Generated good understanding of strengths and weaknesses of Co/ZnO catalyst system and proposed approaches for catalyst improvement
- Provided test results from Rh/CeO₂-ZrO₂ catalyst to H2A analysis

Aqueous Phase Reforming

- Improved catalyst life through modification of catalyst support
- Gained further insights into role of side-reactions leading to concepts to further improve hydrogen selectivity

H2A Analysis

- Established baseline using preliminary results with Rh catalyst
- Cost of feedstock highlighted as key driver to economics
- Ongoing work will compare Rh and Co catalyst performance to allow downselection