Aqueous Phase Catalyzed Biomass Gasification

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David L. King and Yong Wang
Pacific Northwest National Laboratory
2004 DOE OHFCIT Peer Review
May 25, 2004

Objective of Work

- Develop a cost-effective method for the conversion of biomass feedstocks to hydrogen
  - Ethanol, PG, EG, glycerol
  - Sugars, sugar alcohols (xylitol, sorbitol, glucose)
  - Less refined starting materials such as cellulose, hemicellulose
- Provide technical and economic comparison with alternate biomass conversion approaches

Project Budget

- New start FY2004
- Two separate projects consolidated into single project for total of $100K funding
  - Aqueous phase gasification ($50K)
  - Microchannel reforming ($50K)

Technical Targets and Barriers

- Cost and efficiency targets as defined by DOE
  - 2010 central hydrogen from biomass, total: \$2.90/kg H_2
  - 2010 reforming cost ~\$1.90/kg H_2
  - Combined gasification plus reforming efficiency = 67%
- Hydrogen production from biomass barriers (3.1.4.2.2)
  - "F" Feedstock cost and availability
    - Improved technology for production, collection, transportation, storage and preparation of feedstocks
  - "G" Efficiency of gasification, pyrolysis and reforming technology
    - Catalysts, heat integration, reactor configuration, feedstock handling, gas cleanup

Aqueous Phase Reforming Has Potential Advantages Over Conventional Reforming

- Compatible with wet or water-soluble feedstocks
  - Conventional steam reforming incompatible with sugars and sugar alcohols
- Eliminates need to vaporize water for reformation
- Improved capability to reform without concomitant reactant decomposition and carbon formation
- Low CO byproduct due to facilitated water gas shift
- High pressure operation compatible with subsequent hydrogen purification

Challenges of Aqueous Phase Reforming

- Reactor volumetric productivity must be competitive with other biomass conversion technologies
- Selectivity toward hydrogen production is challenging
  - H_2, CO thermodynamically unstable relative to CH_4, alkanes
  - Reactor configuration can have impact on selectivity
- Catalyst deactivation and reactor fouling must be minimized

Steam Reforming Using Microchannel Reactors Complements Aqueous Phase Reforming

- Improved heat and mass transfer significantly enhances reactor productivity
- Efficient thermal management and unit integration
- May offer best approach for
  - Fermentation-derived aqueous ethanol
  - Glycerol (bio-diesel byproduct)
  - Partially processed black liquor – PG, EG

Recent Work Indicates Promise for Aqueous Phase Gasification[1]

- Catalysts and reactors
  - Precious metals Pt, Pd best for hydrogen production
  - Rh, Ru, Ni tend to form methane, alkanes
  - Raney Ni + Sn dopant—reduces methanation activity of Ni
- Feedstocks
  - Glucose, sorbitol, glycerol, ethylene glycol, methanol
  - Higher carbon number feedstocks have increased tendency for alkane formation
  - Fixed bed reactor to minimize series reactions
- Increasing temperature leads to greater production of alkanes, potential for undesirable side reactions

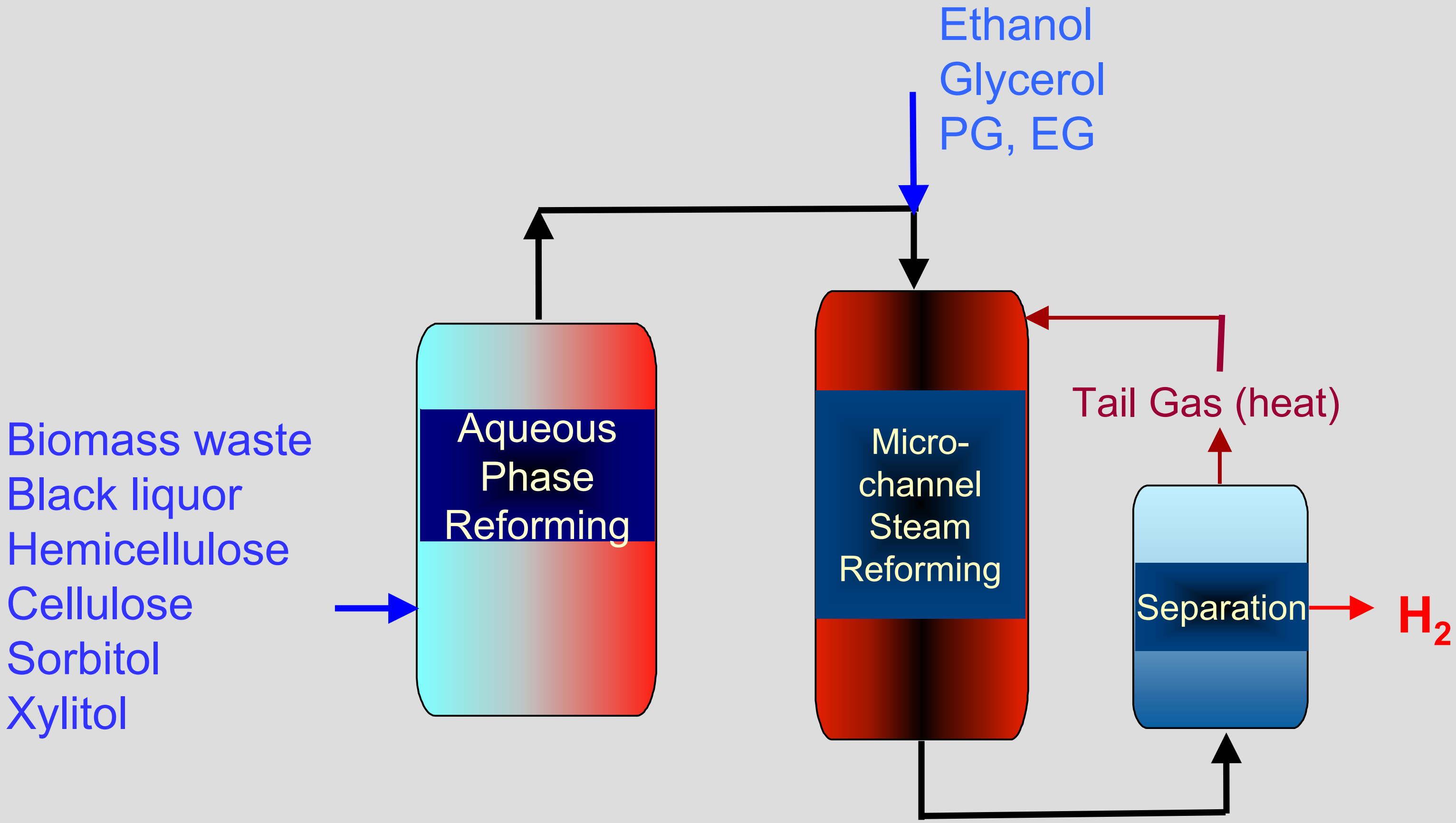
[1] R.D. Cortright et. al. Nature, vol 418, 29 August 2002; J.W. Shabaker et. al., J. Catalysis 215 (2003) 344; G.W. Huber et. al. Science vol 300, 27 June 2003.

Reactor Productivity

- “Weisz window” provides rule-of-thumb regarding required reactor productivity for chemical processes
  - Most chemical processes have reactor productivity $1x10^{-05}$ - $1x10^{-06}$ gmol reactant converted/cc-sec
    - Higher productivity limited by mass and heat transfer
    - Lower productivity may be uneconomic
  - Recently reported activity of Pt/Al_2O_3 with sorbitol
    - ~$1x10^{-07}$ mol sorbitol converted / cc-sec at 383K
    - ~$1.24x10^{-6}$ mole H_2 produced /cc reactor-sec <u>at low conversion</u>
    - An order of magnitude increase in activity may be necessary for an economic aqueous phase gasification process

Technical Concept

- Synergistic aqueous-phase reforming and microchannel steam reforming to produce hydrogen from biomass
  - Feedstock flexibility with aqueous phase reforming
  - Efficient steam reforming with microchannel reaction technology



Technical Approach

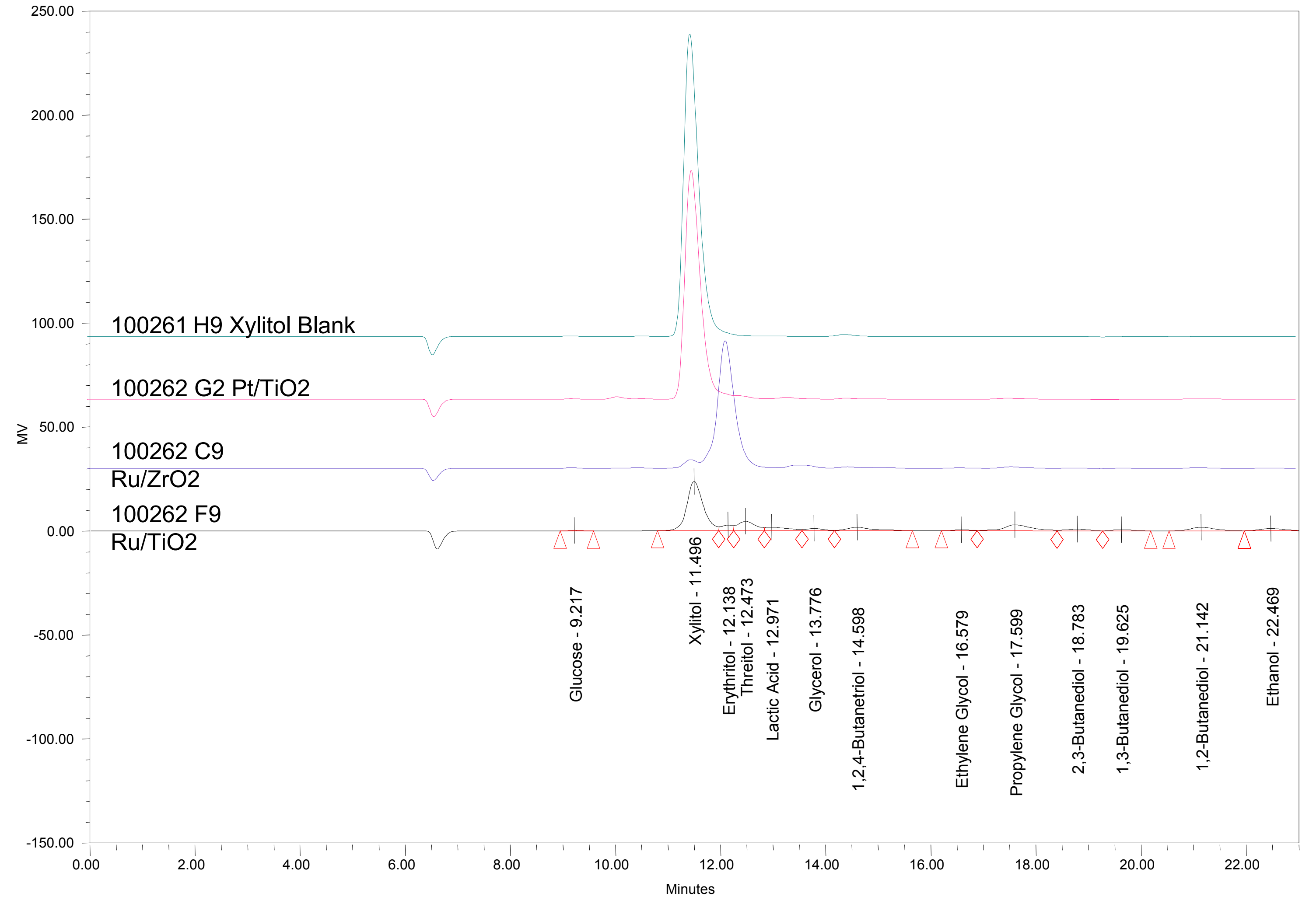
- Aqueous phase gasification
  - Select xylitol as model feedstock which is difficult to steam reform
  - Evaluate catalyst candidates via combinatorial/high throughput screening approach
  - Maximize activity toward useful gas phase products: H_2 plus hydrocarbons
  - Select best catalysts for further reactor studies
- Microchannel steam reforming
  - Demonstrate the efficient steam reforming of the effluent from aqueous phase gasification of xylitol
  - Compare microchannel vs. conventional steam reforming of ethanol
- Combine aqueous gasification with microchannel steam reforming

Combinatorial-High Throughput Screening of Aqueous Phase Gasification Catalysts

- Current equipment provides qualitative comparisons of catalyst performance
  - Liquid phase analysis (no gas phase sampling)—activity based on depletion of starting material
- Xylitol gasification: testing protocols
  - 200^{o}C (maximum temperature of operation)
  - 5% xylitol in water
  - Catalyst charge: 5 wt.%
  - Metal loading on support: 3 wt.%
  - Gas overhead: 5%H_2/95%N_2 at 500 psi (initial)
  - Reaction duration: 4 hours
  - Analysis: hplc
- Preliminary findings
  - Ru most active of group VIII metals
  - TiO_2 (rutile), carbon most effective supports for gasification

Combinatorial/High Throughput Screening Facilitates Identification of New Catalysts

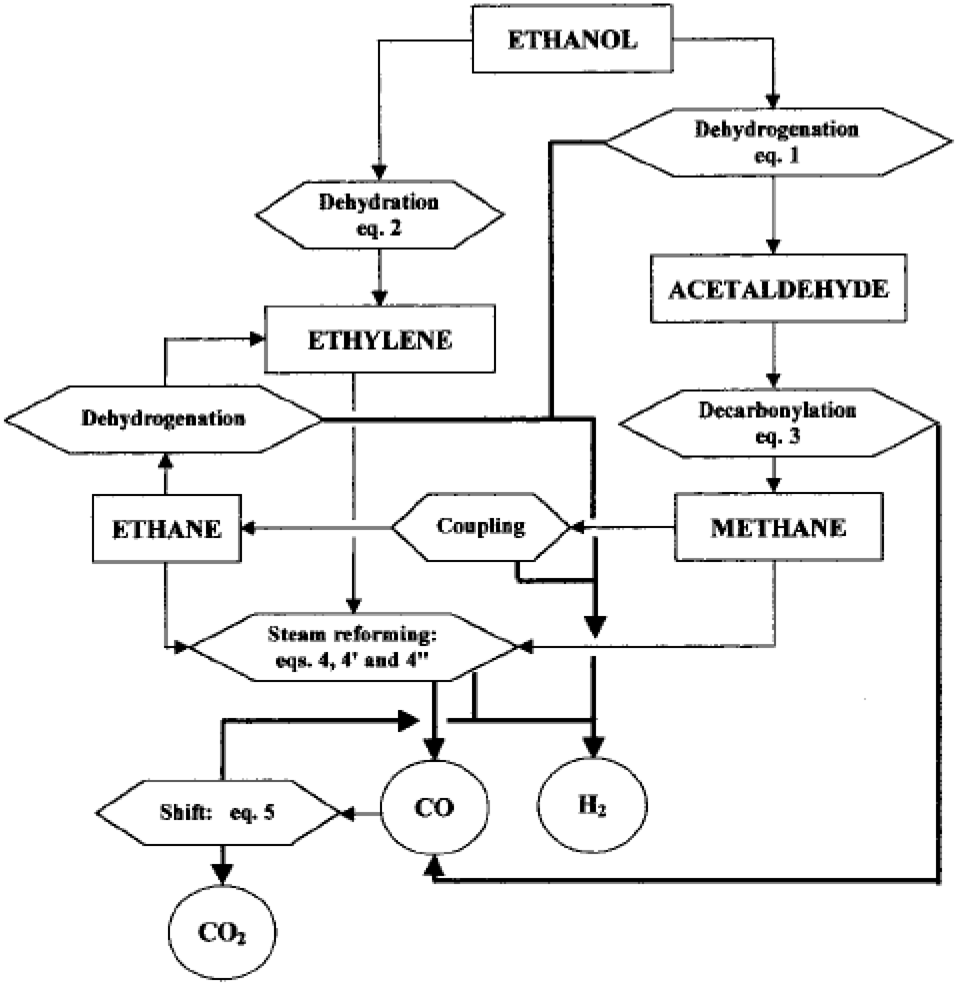
Combinatorial/High Throughput Screening Shows Catalyst Differences



Microchannel Steam Reforming

- Steam reforming of methane (primary aqueous phase product) has been demonstrated
- Steam reforming of aqueous ethanol and glycerol
  - Fermentation derived ethanol has the potential to meet the H_2 cost target ($1.50/kg)
  - Bio-diesel byproduct glycerol has potential to be cost competitive ($0.10/lb)
- Demonstrate the advantage of microchannel reactors

Ethanol Steam Reforming



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

$C_2H_5OH = CH_3CHO + H_2$ (1)

$C_2H_5OH = C_2H_4 + H_2O$ (2)

$CH_3CHO = CO + CH_4$ (3)

$CH_4 + H_2O = CO + 3H_2$ (4)

$C_2H_4 + 2H_2O = 2CO + 4H_2$ (4')

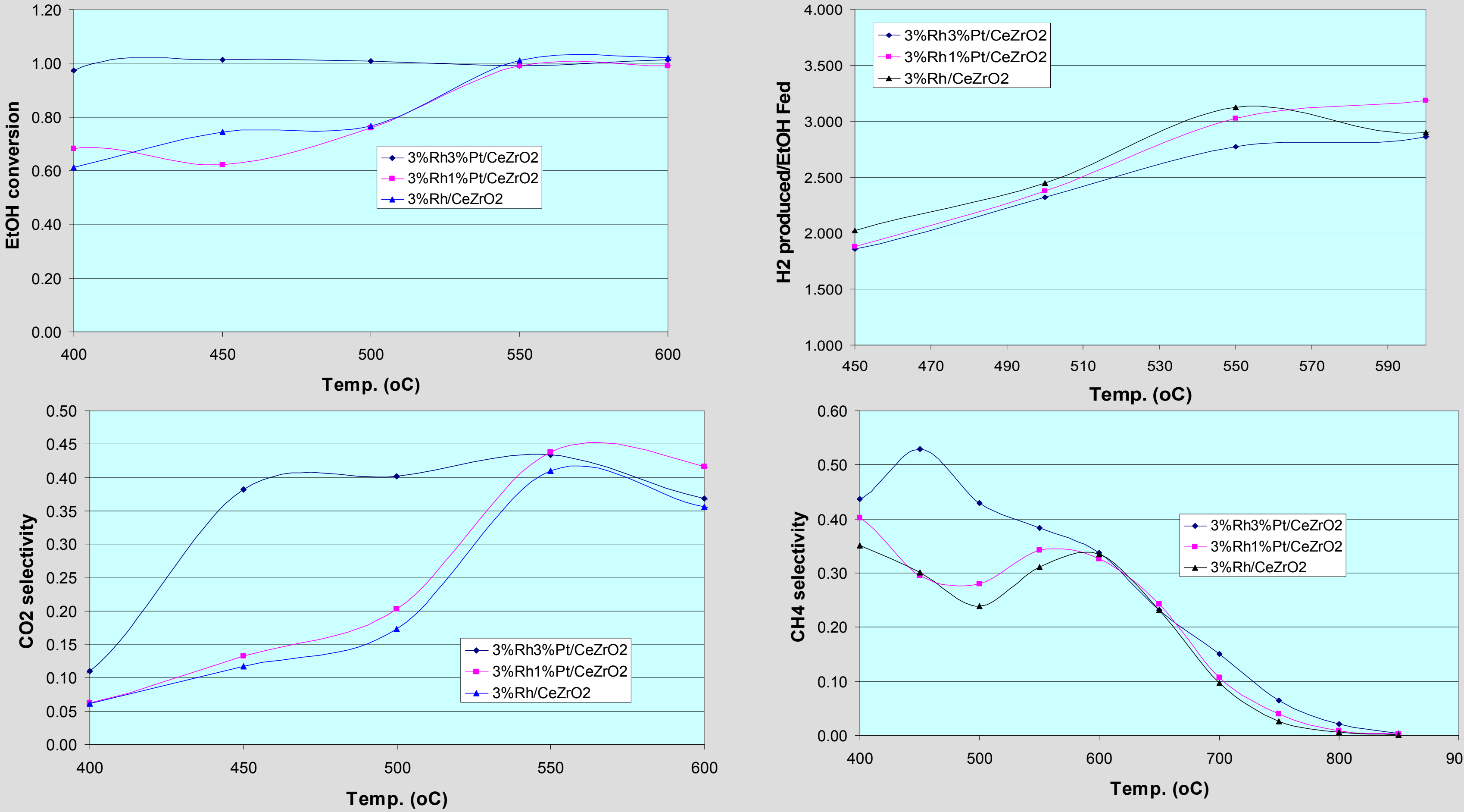
$CH_3CHO + H_2O = 2CO + 3H_2$ (4'')

$CO + H_2O = CO_2 + H_2$ (5)

- **Pathways for the steam reforming of ethanol are complex**
- **Ethylene and methane are the potential intermediates**
- **Efficient ethanol steam reforming depends on the control of intermediate formation and their efficient reforming.**

Effect of Pt Addition on Rh/CeO_2-ZrO_2 Reforming of Ethanol

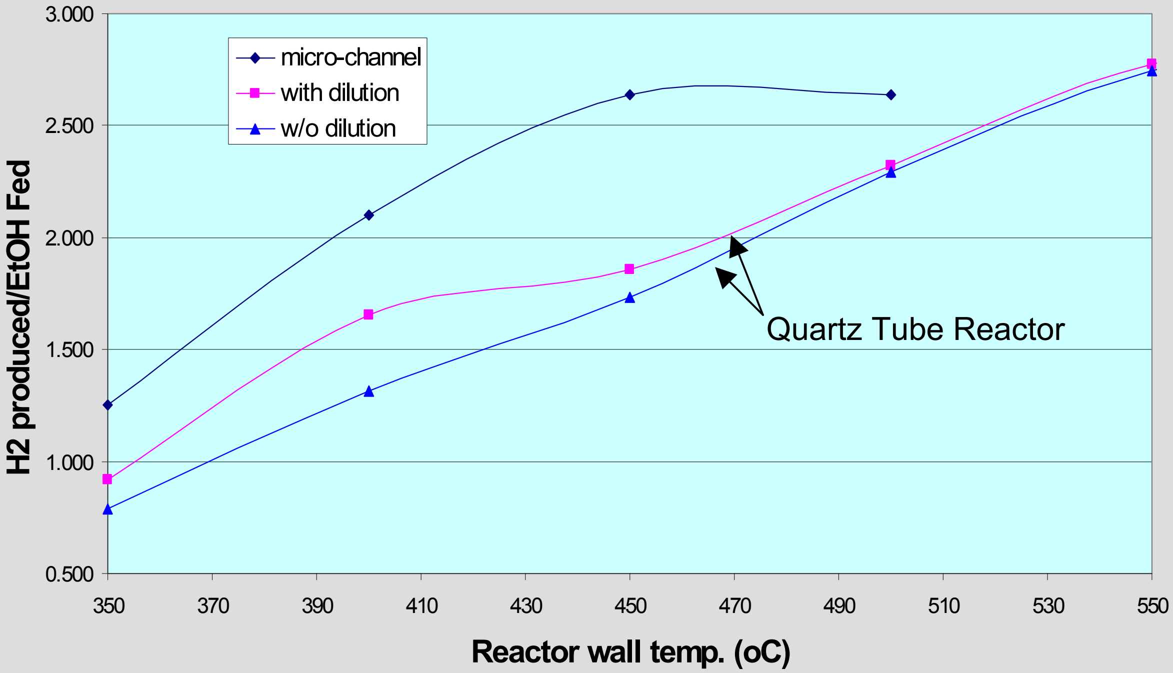
Reaction conditions: GHSV = 75,660 cm^3/gh, $H_2O/EtOH/N_2$ = 3.0/1.0/1.8



- **Pt enhances EtOH conversion and selectivity to CO_2, likely due to enhanced WGS.**
- **Pt also increases the selectivity to CH_4, likely due to increased decarbonylation**
- **Further improvement in catalysts to minimize CH_4 formation is needed.**

Reforming of Ethanol Shows Advantage of Microchannel Reactor

Catalyst: 3%Rh-3%Pt/CeO_2-ZrO_2



Reaction conditions: GHSV = 75,660 cm^3/gh, $H_2O/EtOH/N_2$ = 3.0/1.0/1.8
Quartz tube fixed bed reactor vs. microchannel reactor

H_2 productivity at low temperatures can be enhanced using micro-channel reactor due to efficient heat transfer.

Conclusions

- Aqueous phase gasification provides attractive alternative for generation of hydrogen from biomass feedstocks
- Preliminary screening of catalysts indicate ruthenium as attractive candidate for production of gas phase products
- Steam reforming of ethanol indicates two possible pathways:
    - Via ethylene
    - Via methane
- Addition of Pt to Rh/CeO_2-ZrO_2 catalyst increases undesirable methane formation
    - More acidic supports will favor desired ethylene pathway

Future Work

- Scaled-up tests of most active aqueous phase gasification catalysts in slurry and fixed bed reactors
  - Process variable study with xylitol, sorbitol
  - Determine advantages, disadvantages of each reactor approach
- Continue microchannel steam reforming studies of EtOH and glycerol
- Verify that conventional steam reforming of sorbitol and xylitol not feasible due to reactant instability
- Demonstrate efficient steam reforming of aqueous phase effluent in microchannel hardware
- Develop process economics for combined aqueous phase gasification/ steam reforming approach
  - Compare with alternate approaches based on pyrolysis + reforming

Safety Aspects

- Aqueous gasification work to date limited to small volume, high throughput mini-reactors
  - Each run employs 96 vials containing water, sorbitol, and catalyst
  - Overhead pressure for some runs of 200 psig of 5%H2 in N2, total H2 volume (stp)~50 cc
    - Total combustion of H2 in system would lead to less than 200 psig increase in overall pressure
  - Reactor encasing rated at 1500 psig
  - System enclosed in vented canopy
  - System appears safe
- No safety-related events or issues encountered