BILIWG Meeting: High Pressure Steam Reforming of Bio-Derived Liquids

S. Ahmed, S. Lee, D. Papadias, and R. Kumar

November 6, 2007
Laurel, MD

Research sponsored by the Hydrogen, Fuel Cells, and Infrastructure Technologies Program of DOE's Office of Energy Efficiency and Renewable Energy

Rationale and objective

Rationale

- Steam reforming of liquid fuels at high pressures can reduce hydrogen compression costs
  - Much less energy is needed to pressurize liquids (fuel and water) than compressing gases (reformate or H_2)

- High pressure reforming is advantageous for subsequent separations and hydrogen purification

Objective

- Develop a reformer design that takes advantage of the savings in compression cost in the steam reforming bio-derived liquid fuels
  - Metric:
    - *Improved efficiency of the hydrogen production / purification process*
  - Constraint:
    - *Must be cost effective*

Approach

- Steam reform bio-derived liquids at high pressure
  - Define conditions suitable for reforming of bio-derived liquids
  - Define system concepts that can meet efficiency targets
  - Develop reactor concepts through simulations
    - *Incorporate membrane technology (O_2, H_2, CO_2)*
    - *Incorporate developments in catalysis*
  - Validate concepts at successive scales
    - *micro-reactor, bench-scale, tech transfer*

- Analytically and experimentally evaluate
  - Elevated-pressure steam reforming, potentially combined with
  - Membrane separations

Evaluation metrics

- Near Term – focus on individual process steps
  - Generate technical data, e.g., kinetics, flux, etc.
  - Quantitative measure : Efficiency (evaluate by modeling)
  - Qualitative indicator: Feasibility (evaluate experimentally)
    - *e.g., operating conditions, such as T and P combinations*

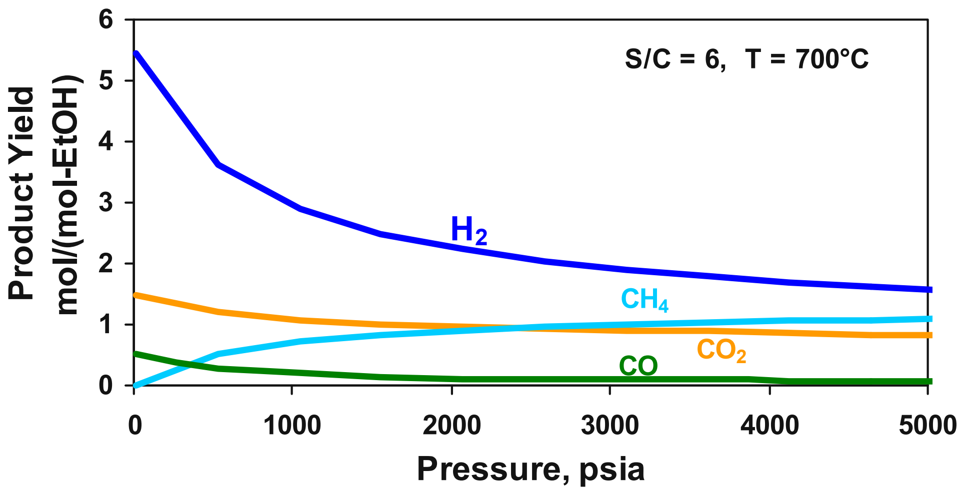
- Mid Term – focus on multiple process steps
  - Generate engineering-scale data, e.g., yields, durability, etc.
  - Determine (by simulations) process efficiency and develop cost projections

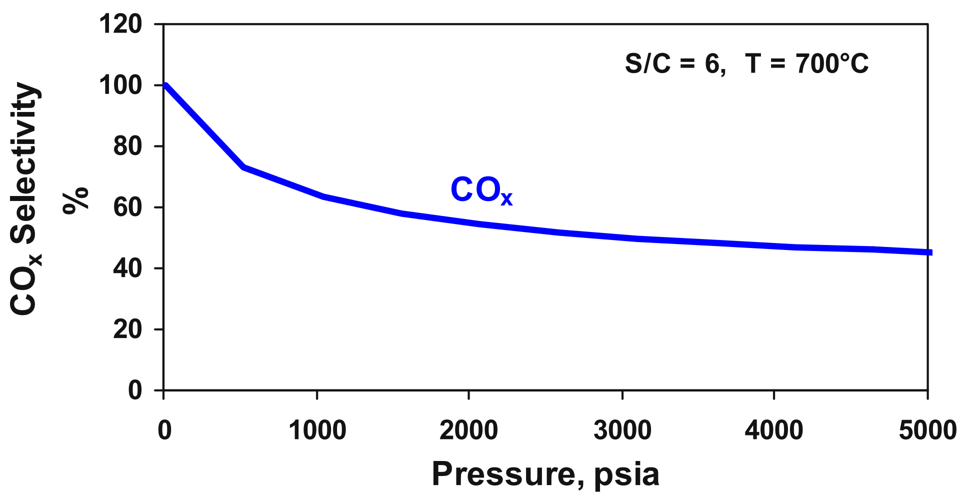
- Longer Term – in consultation with early adopters (industry partners)

Reforming at high pressures yields more methane, less hydrogen at thermodynamic equilibrium

- Coke formation tendency increases with increasing pressures

- Coking tendency can be lowered by using excess steam or higher temperatures





$$CO_x \text{ Selectivity, \%} = \frac{\text{moles of } CO+CO_2 \text{ Produced}}{\text{g-atoms of C in Feed}} \cdot 100$$

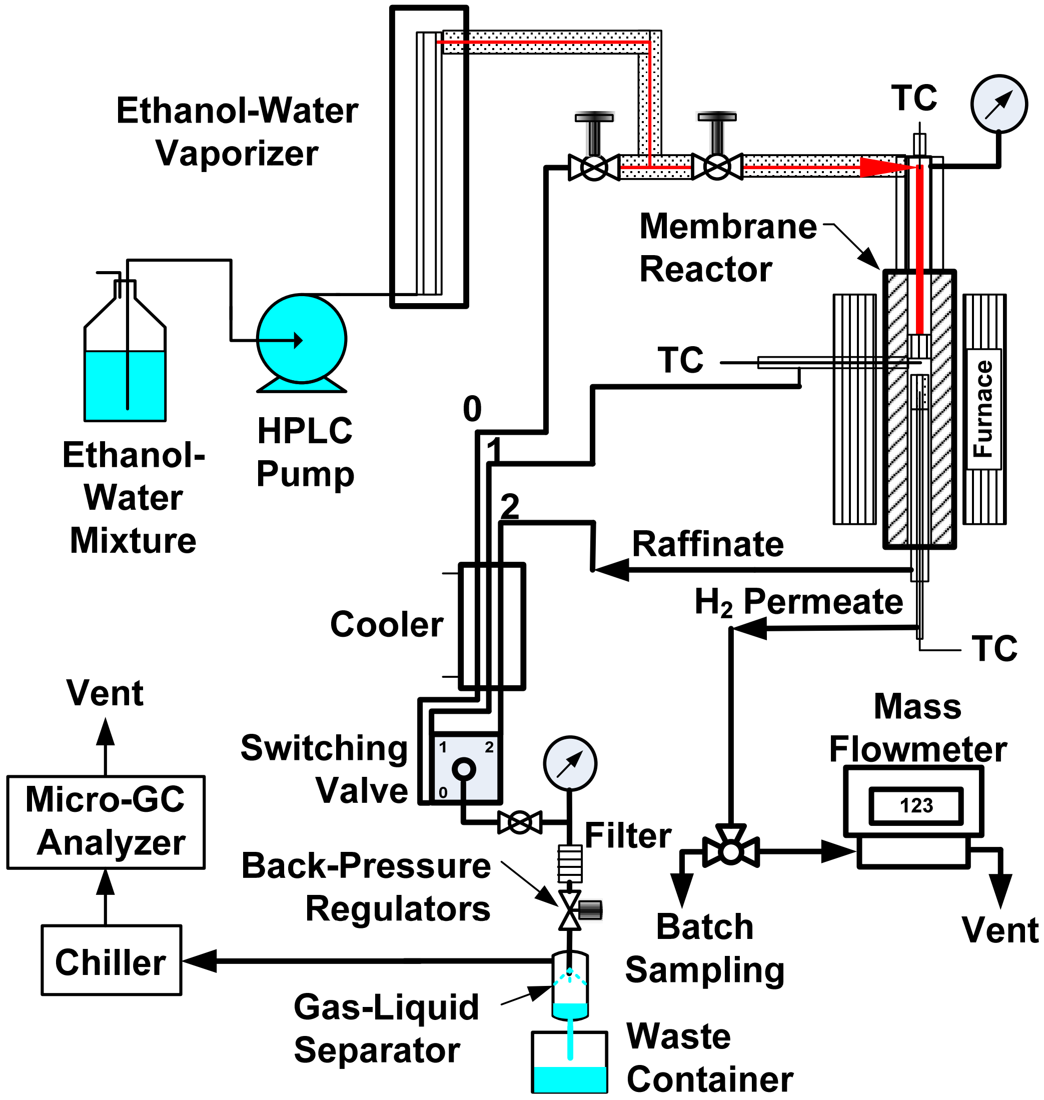
Challenges in high-pressure reforming and options to address them

- Higher pressures increase CH_4 yields and decrease H_2 yields
  - Options to overcome challenges
    - *Higher temperature*
      (but high T & P combinations increase materials costs)
    - *Higher steam-to-carbon (S/C) ratio*
      (but excess steam generation may lower process efficiency)
    - *Hydrogen removal to increase conversion and yield pure H_2*
      (may increase coke formation tendency; product hydrogen is at lower pressure)
    - *CO_2 removal to improve CH_4 conversion and yield higher purity H_2*

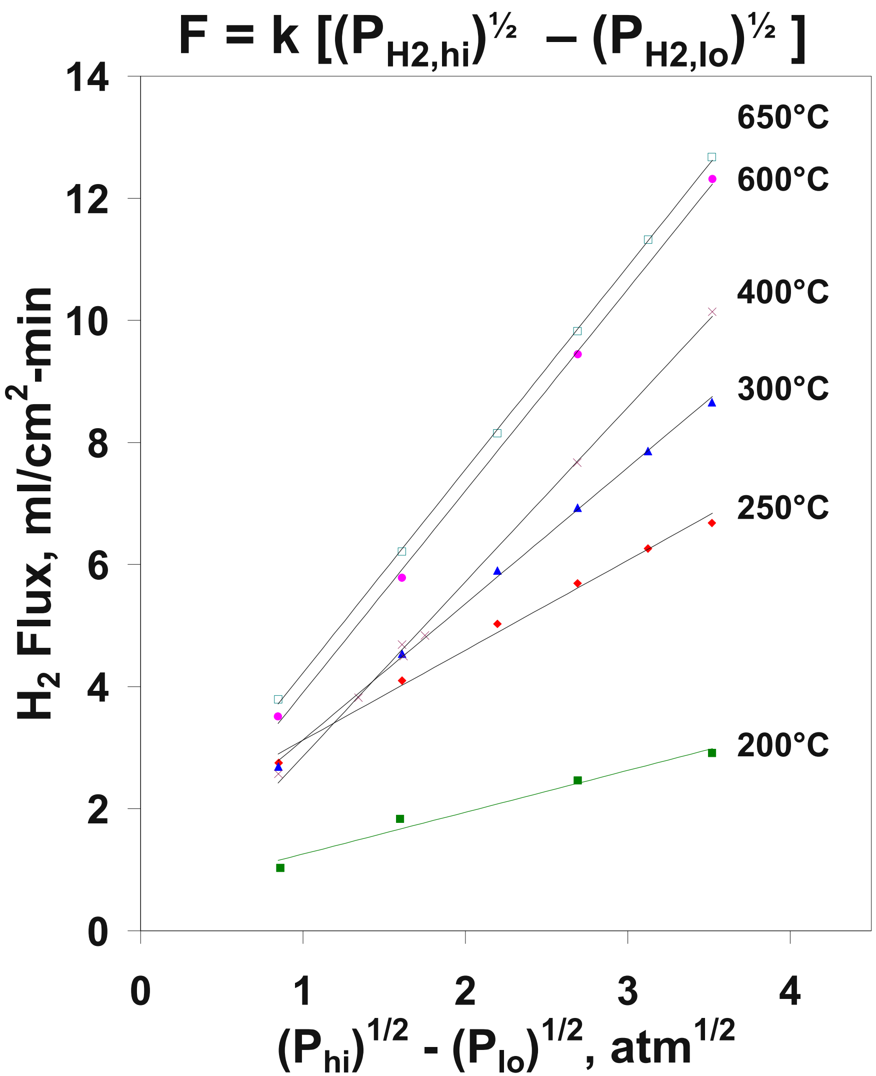
- Oxygen provided through an O_2-transport membrane can provide the heat for the endothermic reforming reaction without introducing N_2
  - Potentially replace combustion zone with air zone?

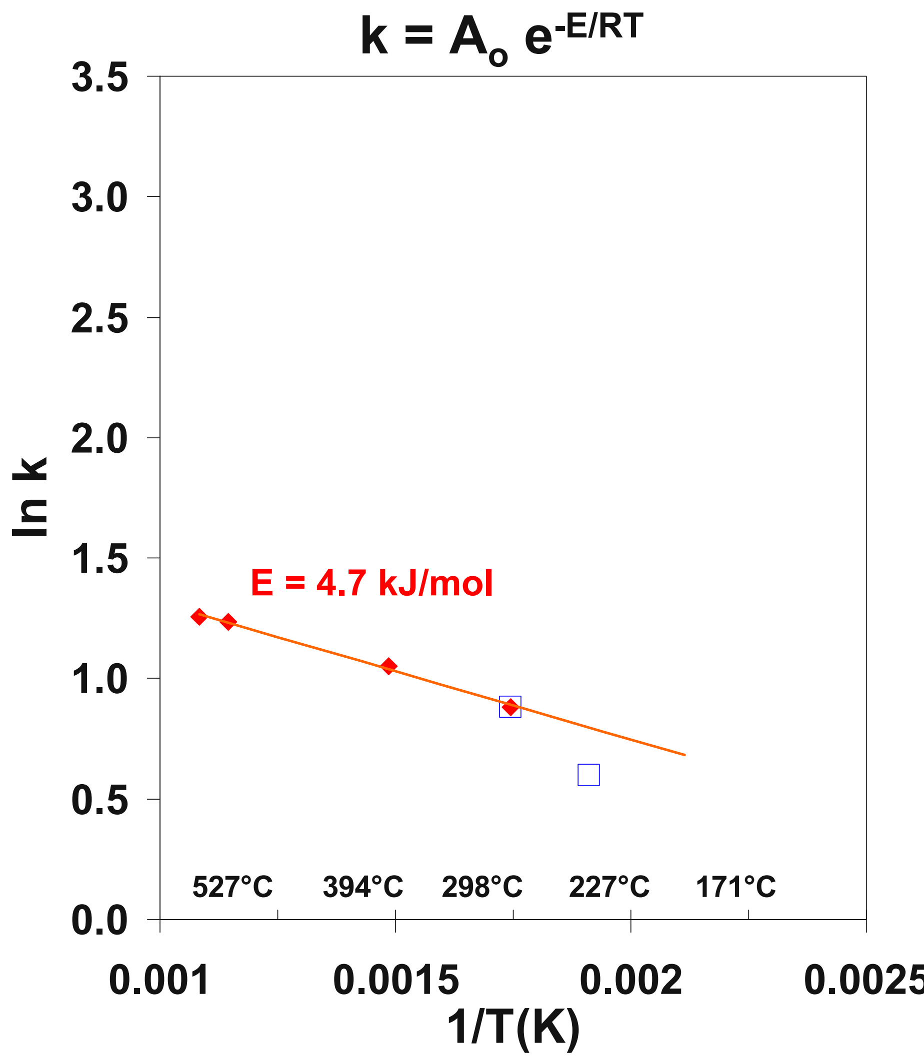
Membrane reactor testing apparatus

- Rated for 1,000 psi, 800°C
- 6.4 mm (0.25 in) ID reactor tube
- 4 wt% Rh/ La-Al2O3
- Powder, 150-250 µm
- 0.45 g of catalyst
- 35 mm long catalyst bed
- Pd-alloy membrane tube: 3.2 mm OD, 25.4 mm long, 30 µm thick

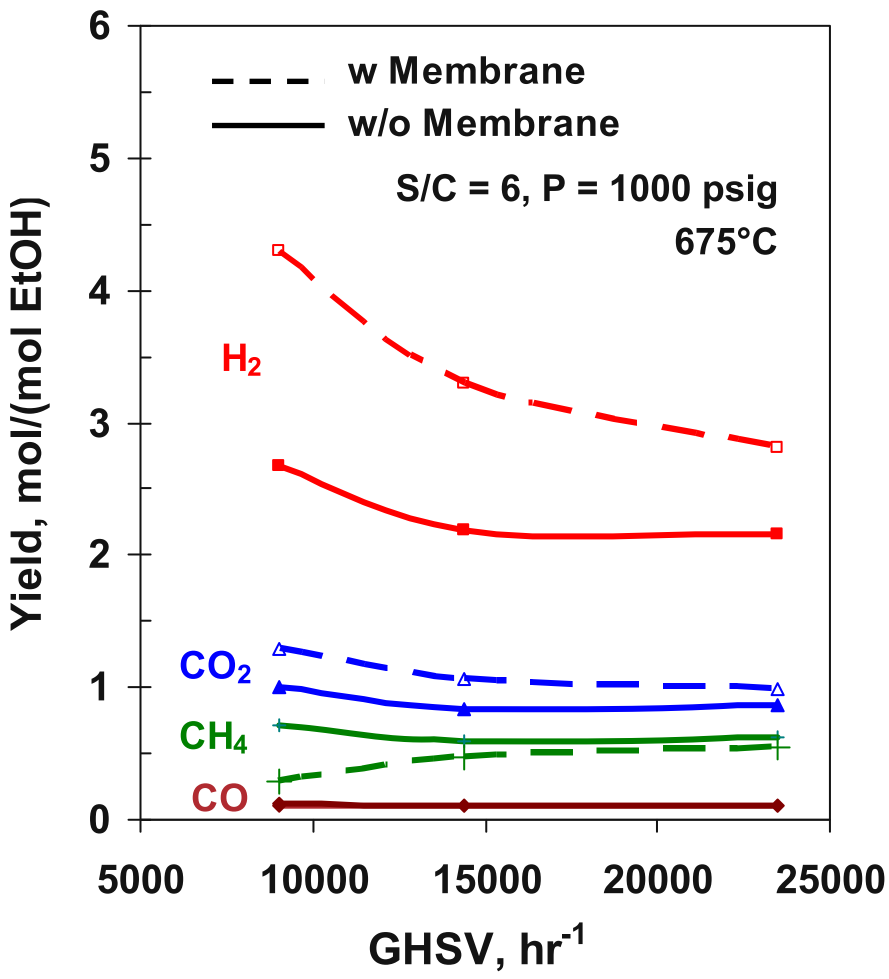


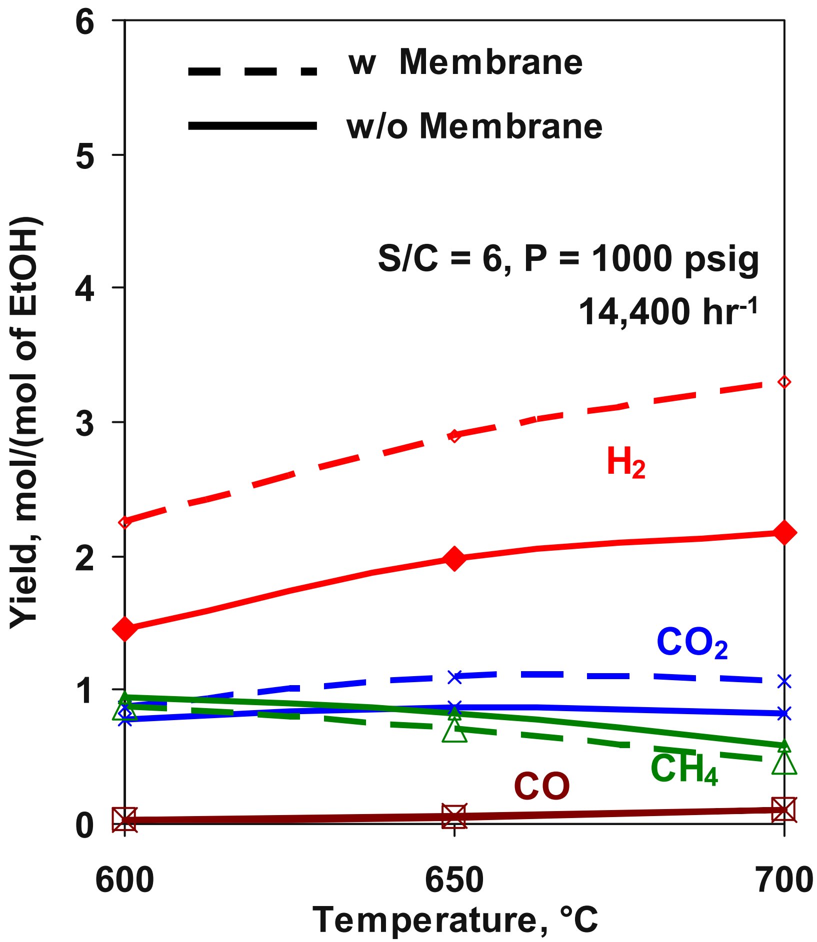
Hydrogen transport follows Sievert's and Arrhenius laws





The hydrogen yield increases with decreasing GHSV and with increasing temperature





H_2 w/ membrane is the combined yield in the permeate and raffinate streams

Argonne NATIONAL LABORATORY

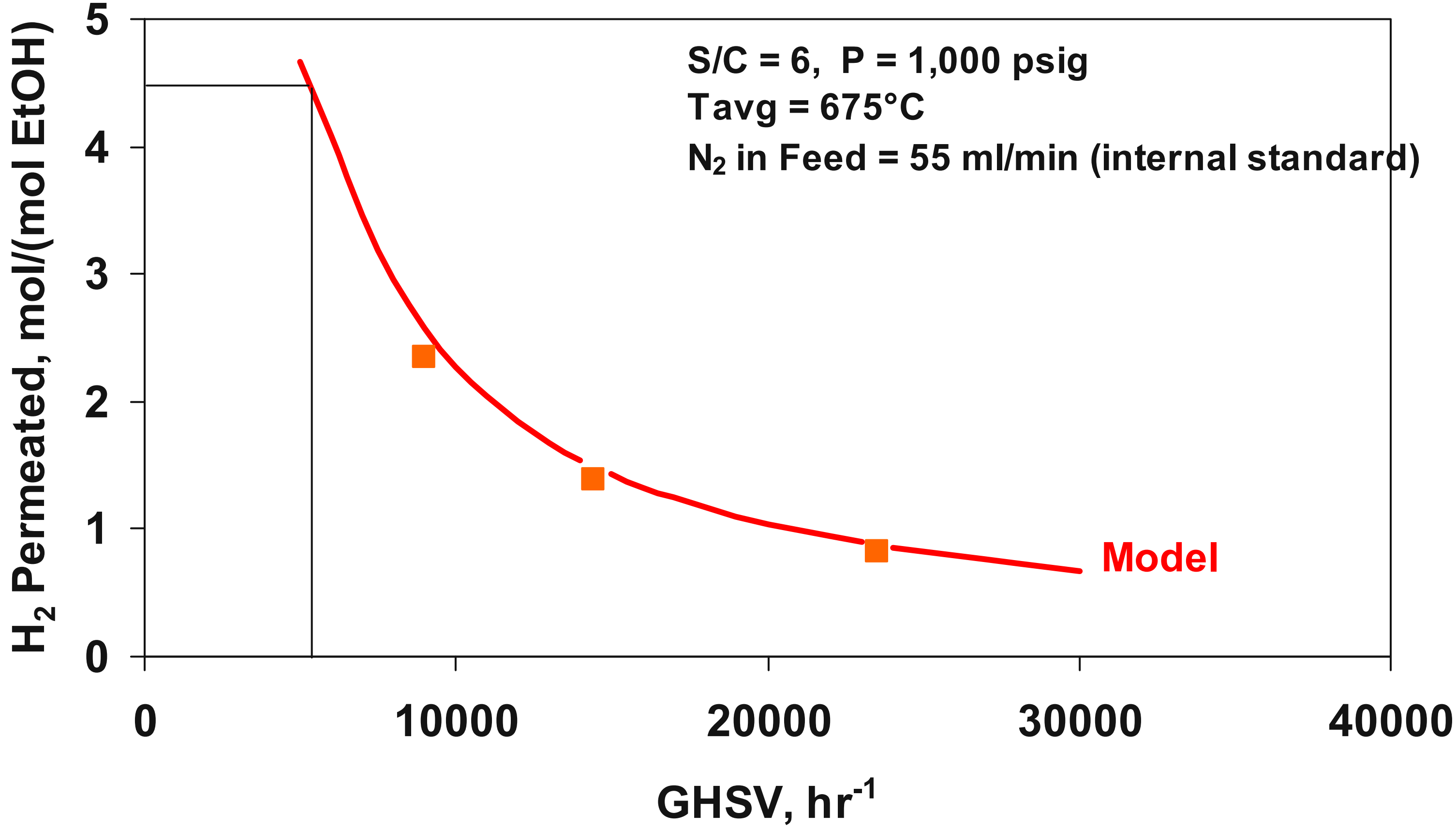
A mathematical model of the membrane reactor has been set up

- Evaluates effect of hydrogen extraction across a membrane in the steam-reforming reactor

- Provides ideal case scenario (upper bound) for reactor performance

- Assumes:
  - fast chemical reaction kinetics (equilibrium limited reactions)
  - $C_2H_5OH + H_2O = 2CO + 4H_2$ (Ethanol SR)
  - $CH_4 + H_2O = CO + 3H_2$ (Methane SR)
  - $CO + H_2O = CO_2 + H_2$ (WGS)
  - no gas-phase mass-transfer limitations in the reactor
  - membrane follows Sievert's and Arrhenius laws

Measured permeate hydrogen yields are consistent with model predictions

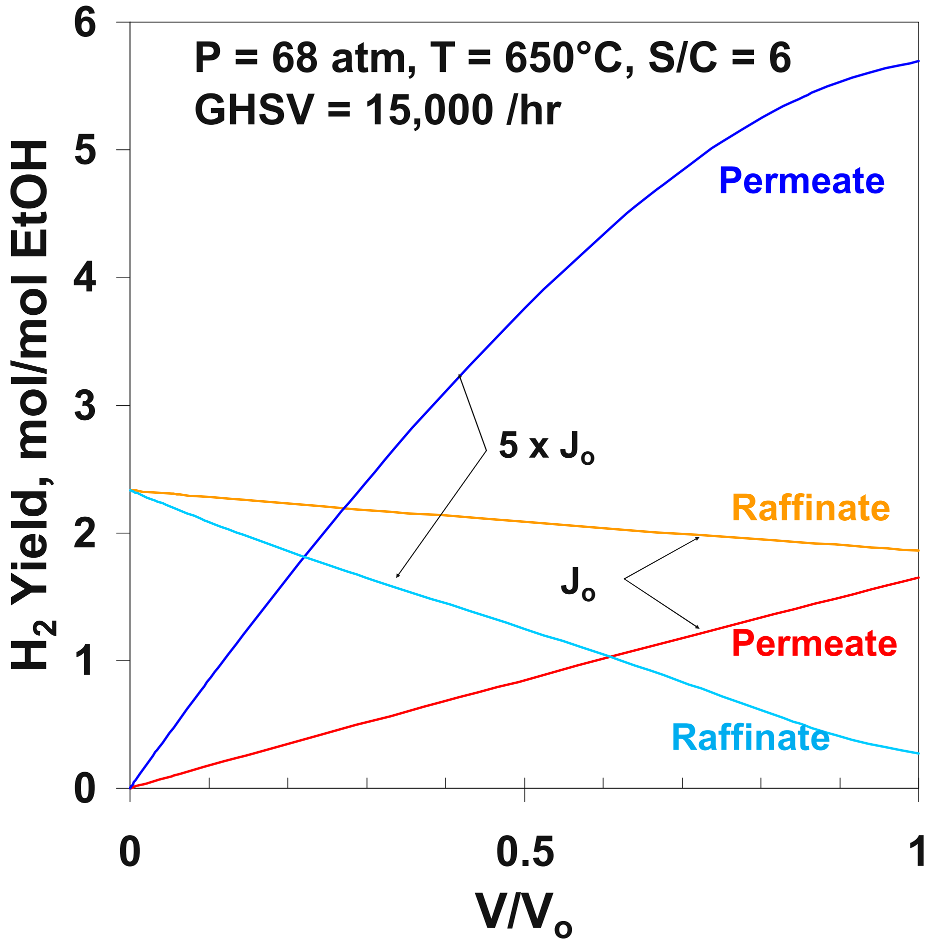


- The model predicts that 4.5* moles of hydrogen (per mole of ethanol) should be achievable at GHSV of ~5000 hr^{-1}

***75% of theoretical H2 yield of 6 moles/mole of ethanol**

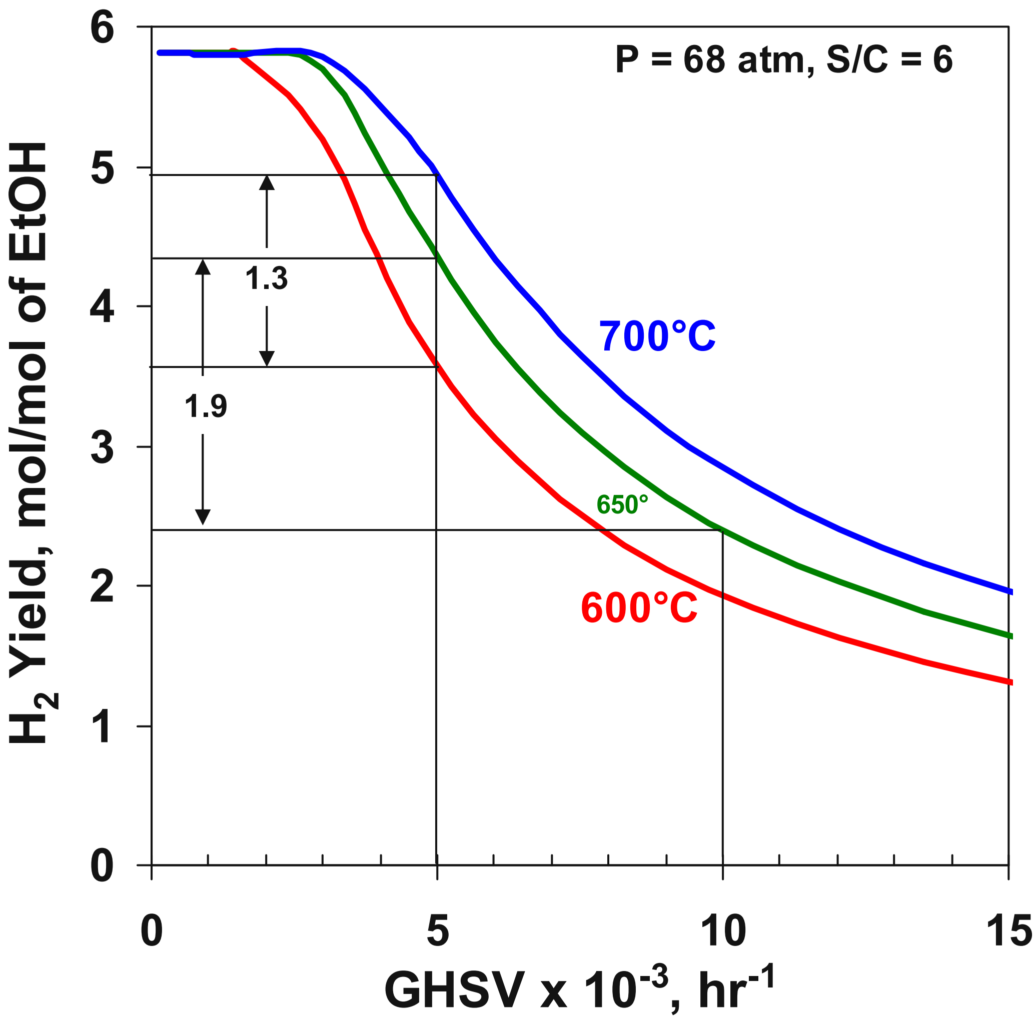
Hydrogen flux across the membrane is lower than desired

- With current flux (J_o), only 1.7 moles of H_2 can be extracted
- A 5-fold increase in flux could extract 5.6 moles of H_2
- The flux can be increased with thinner membranes



The hydrogen extracted can be improved by varying GHSV and temperature

- Lower GHSV improves H_2 yield across membrane
- Higher T improves H_2 yield across membrane
- For energy balance (heat needed to support endothermic reaction), 70-75% of theoretical yield (4.2-4.5 moles) may be sufficient



Summary

- We are pursuing an advanced reactor concept that reduces significantly the energy required to compress the product hydrogen
  - Steam reforming of bio-derived liquids can be a feasible option
  - Membrane reactors provide in-situ separation and purification
- Experimental membrane reactor studies are being guided by a reactor model
  - Preliminary results indicate that acceptable hydrogen yields may be possible even with thick Pd-alloy membrane/support layers
    - *Easier to fabricate, but involves higher materials costs*
- Appropriate combination of temperature, space velocity, and membrane improvements could make this reactor concept cost effective

Future work

- Conduct systems analyses to evaluate the feasibility of alternative fuel processor designs using pressurized reforming
  - Based on experimental data generated
- Make a go/no-go decision on the use of Pd-based H_2 transport membranes based on performance and cost
- Verify experimentally the influence of O_2 and CO_2 transport membranes on pressurized reforming