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Pressurized Steam Reforming of Bio-Derived Liquids for Distributed Hydrogen Production

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U.S. Department
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DOE Hydrogen Program

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Overview

Timeline

- Start FY05
- On-hold FY06
- Continued: FY07, FY08
- End: Open

Barriers

- (A) Fuel Processor Capital Costs
- (E) Greenhouse Gas Emissions
- (H) System Efficiency

Budget

- FY08: 400K
- Total: 825K (3 years)

Partners / Interactions

- Other Argonne divisions
- Interactions: REB Research and Consulting

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 H₂)
- High pressure reforming is advantageous for subsequent separations and hydrogen purification

Objective

- Develop a distributed hydrogen production process
 - From hydrated ethanol and other bio-derived liquids
 - Using a pressurized steam reforming reactor
 - To develop an efficient hydrogen production / purification process by reducing the H₂ compression penalty

DOE FY12 Efficiency Cost Target	72%
DOE FY12 Cost Target	\$3.8 / gge

Milestones

July 2007	Complete catalyst performance studies in high pressure microreactor
September 2007	Model micro-reactor to evaluate membrane reactor performance
April 2008	Go / No-Go on High Pressure Ethanol Reforming Using H ₂ Extraction
September 2008	Define suitable reforming conditions for alternative bio-liquid
September 2008	Initiate tests in alternative (O ₂ or CO ₂) membrane reactor

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

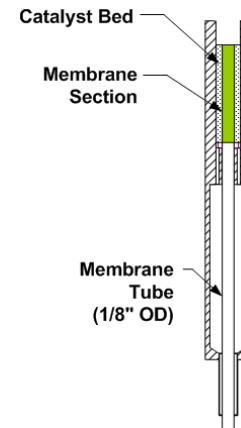
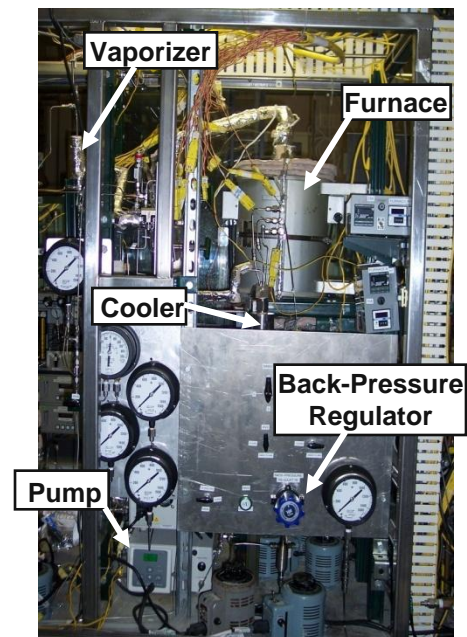
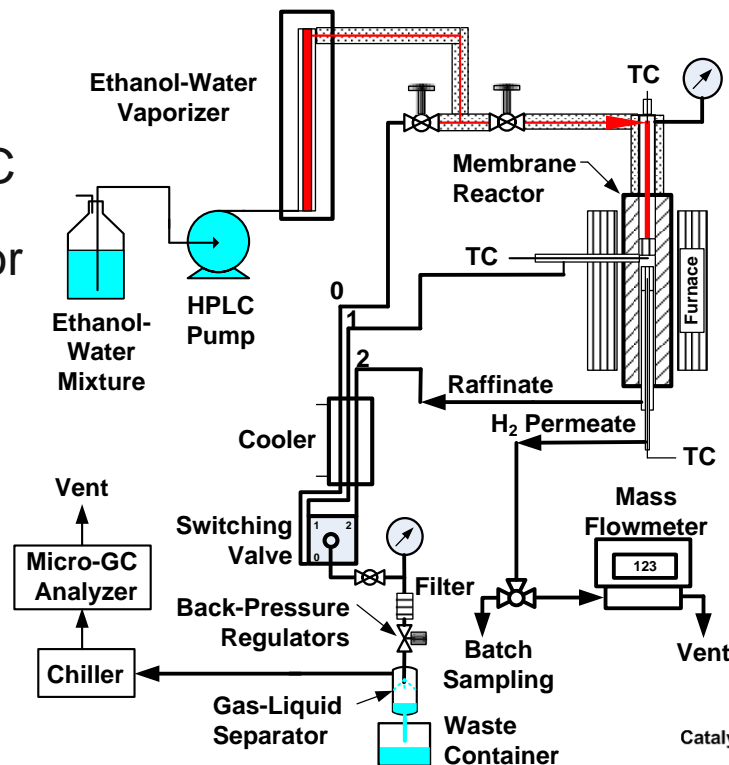
- Near Term – focus on individual process steps
 - Generate technical data, e.g., kinetics, flux, etc.
 - Quantitative measure: Efficiency (evaluate by modeling)
 - Qualitative indicator: Feasibility (evaluate experimentally)
 - *e.g., operating conditions, such as T and P combinations*
- Mid Term – focus on multiple process steps
 - Generate engineering-scale data, e.g., yields, durability, etc.
 - Determine (simulations) process efficiency and cost projections
- Longer Term – in consultation with early adopters (industry partners)

Reforming at high pressures increases methane and reduces hydrogen yields

- Options to overcome challenges
 - Higher temperature
(high T & P combinations increase materials costs)
 - Higher steam-to-carbon (S/C) ratio
(excess steam generation may lower process efficiency)
 - Hydrogen removal to increase conversion and yield pure H₂
(may increase coke formation tendency; product hydrogen is at lower pressure)
 - CO₂ removal to improve CH₄ conversion and yield higher purity H₂
- Oxygen provided through an O₂-transport membrane can provide the heat for the endothermic reforming reaction without introducing N₂
 - Potentially replace combustion zone with air zone?

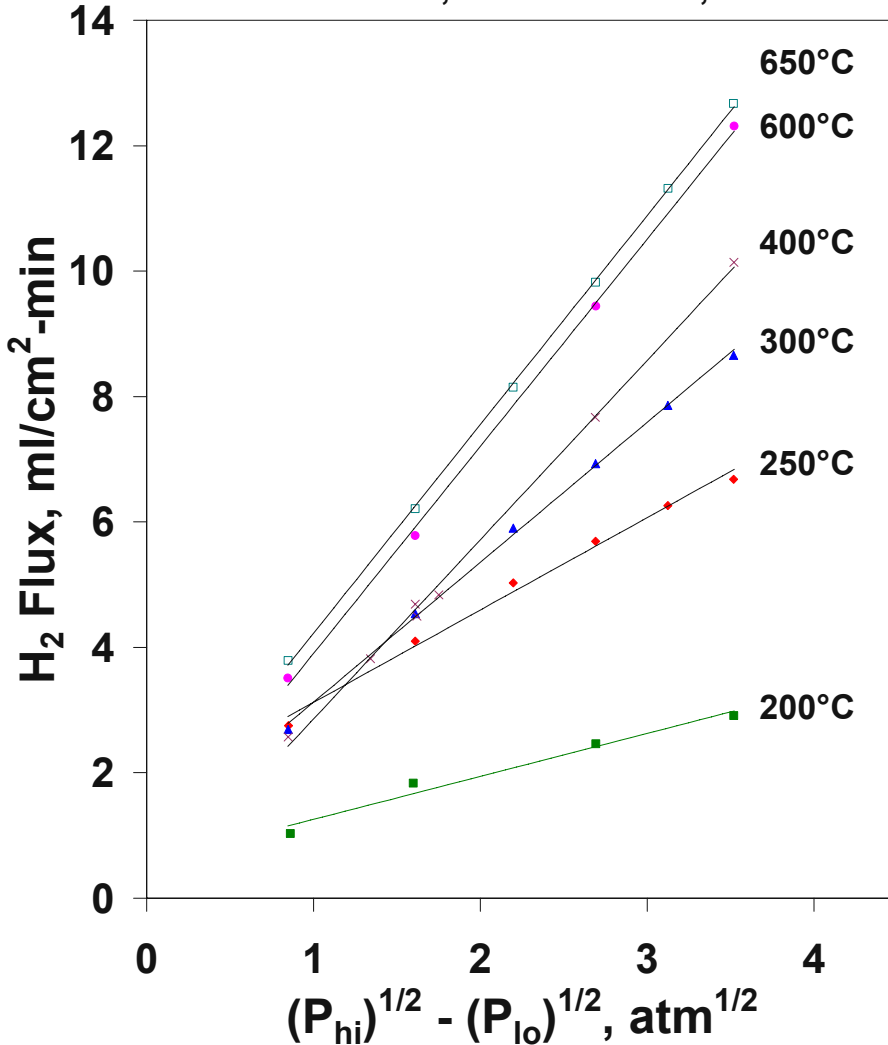
A micro-membrane reactor was built and tested

- 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

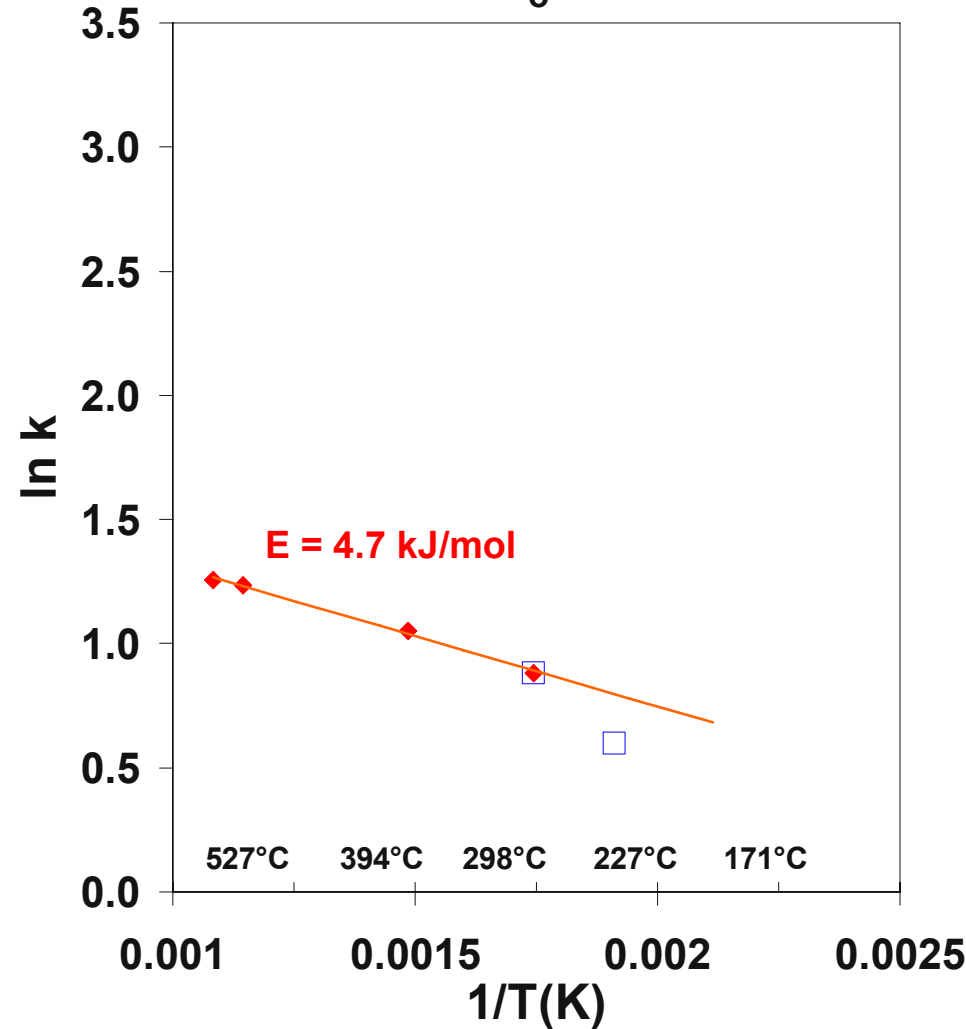


The measured hydrogen transport follows Sievert's and Arrhenius laws at the higher temperatures

$$F = k [(P_{H_2,hi})^{1/2} - (P_{H_2,lo})^{1/2}]$$

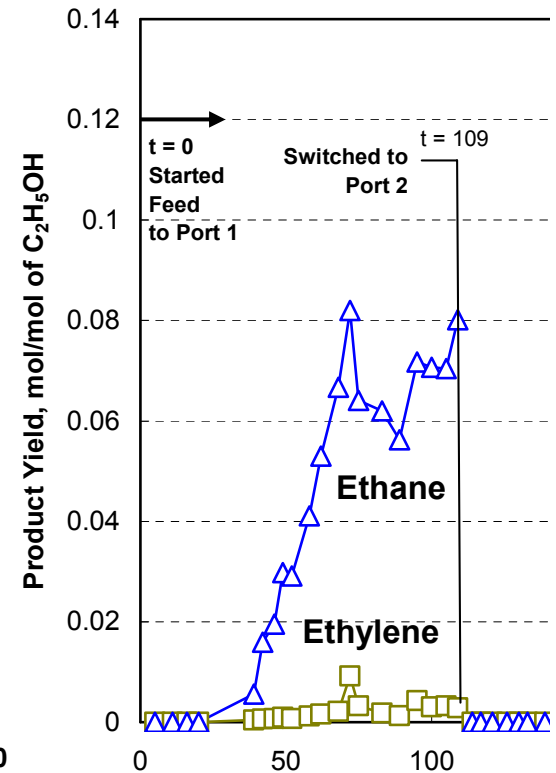
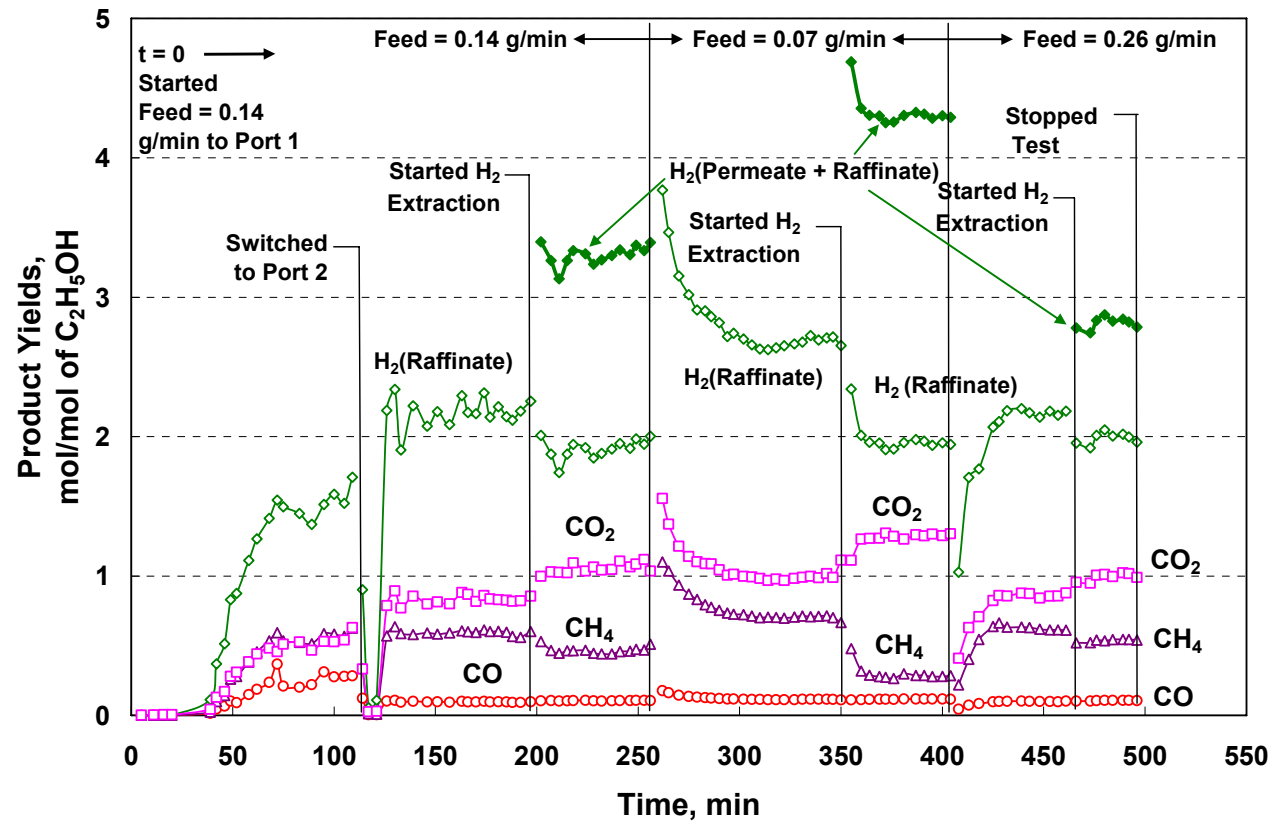


$$k = A_0 e^{-E/RT}$$



High pressure produced light HCs

H_2 permeation increased CH_4 conversion, H_2 yield



- The catalyst bed effectively reforms ethane and ethylene

Reactor Inlet: Gas analysis indicated reactions were initiated within the vaporizer and feed preheat zones

Pressure, psig	100 psig		
Temperature, °C	600°C	650°C	700°C
S/C=6	Exp.	Exp.	Exp.
H ₂ , mol/mol EtOH	0.89	1.40	1.96
CH ₄ , mol/mol EtOH	0.25	0.39	0.51
CO+CO ₂ , mol/mol EtOH	0.38	0.66	0.97
Pressure, psig	1000 psig		
Temperature, °C	600°C	650°C	700°C
S/C=6	Exp.	Exp.	Exp.
H ₂ , mol/mol EtOH	1.16	1.46	1.52
CH ₄ , mol/mol EtOH	0.54	0.42	0.57
CO+CO ₂ , mol/mol EtOH	0.62	0.61	0.79

- C₂s were detected at the inlet of the catalyst bed
- Higher boiling point and vaporizer temperatures may be causing the reactions (C₂H₆O = C₂H₄ + H₂O; C₂H₆O = CH₃CHO + H₂)

Reforming without H₂ separation: Higher temperatures and lower pressure favor hydrogen yields

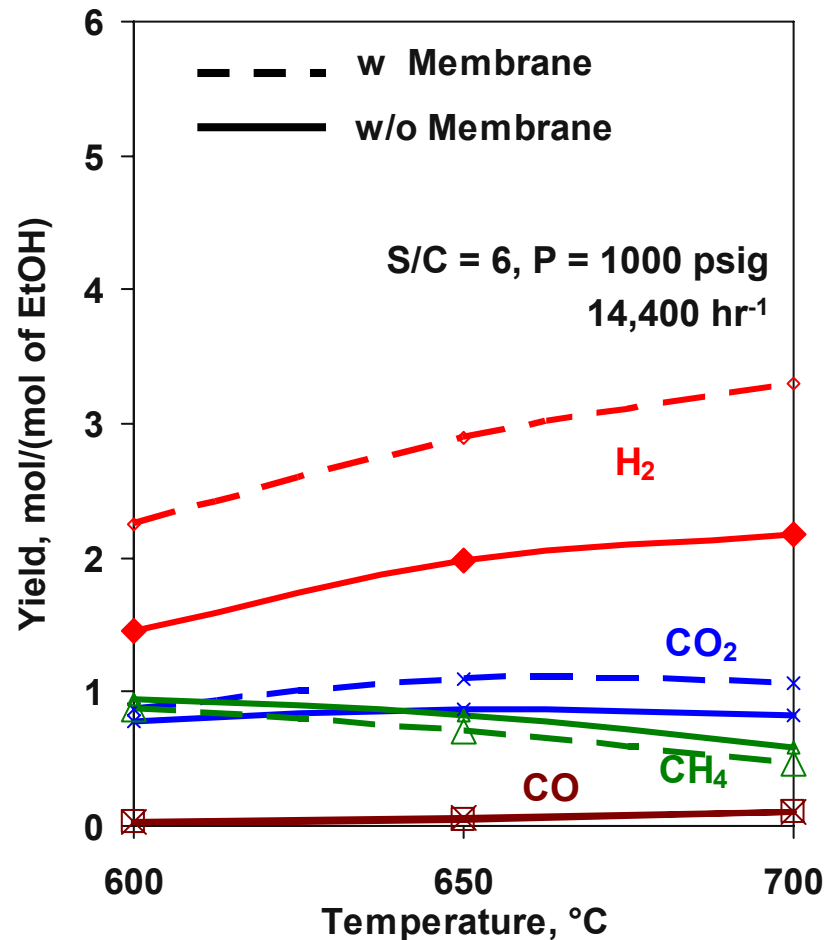
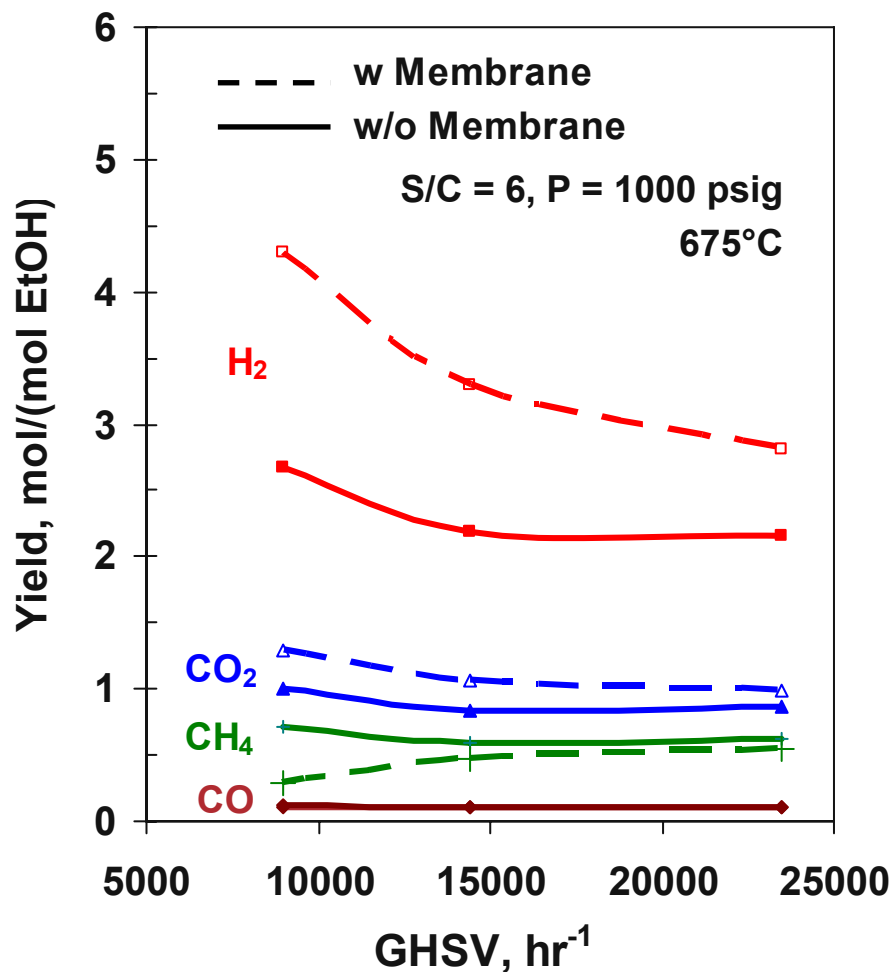
Pressure, psig	100 psig					
Temperature, °C	600°C		650°C		700°C	
S/C=6	Exp.	Equil.	Exp.	Equil.	Exp.	Equil.
H ₂ , mol/mol EtOH	3.63	3.97	4.38	4.71	4.60	5.14
CH ₄ , mol/mol EtOH	0.52	0.46	0.24	0.24	0.12	.095
CO _x Selectivity, %	69	77	80	88	83	96
Pressure, psig	1000 psig					
Temperature, °C	600°C		650°C		700°C	
S/C=6	Exp.	Equil.	Exp.	Equil.	Exp.	Equil.
H ₂ , mol/mol EtOH	1.46	1.73	1.98	2.30	2.18	2.91
CH ₄ , mol/mol EtOH	0.95	1.05	0.82	0.90	0.59	0.72
CO _x Selectivity, %	38	47	46	55	47	64

$$\text{CO}_x \text{ Selectivity, \%} = \frac{(\text{Mols of CO} + \text{CO}_2 \text{ in product})}{(\text{Mols of Ethanol Feed}) \times 2} \times 100$$

Reforming with H₂ separation: Higher pressures increase hydrogen permeation, lower CO_x selectivity

	S/C = 6					
Temperature, °C	600°C		650°C		700°C	
Pressure, psig	100	1000	100	1000	100	1000
H ₂ , mol/mol EtOH	3.64	2.25	4.24	2.89	4.45	3.30
Permeate	0.03	0.87	0.09	1.11	0.14	1.39
Raffinate	3.61	1.37	4.15	1.78	4.31	1.91
CH ₄ , mol/mol EtOH	0.49	0.87	0.22	0.7	0.10	0.47
CO _x Selectivity, %	69	45	78	58	80	58

The hydrogen yield increases with decreasing GHSV and with increasing temperature



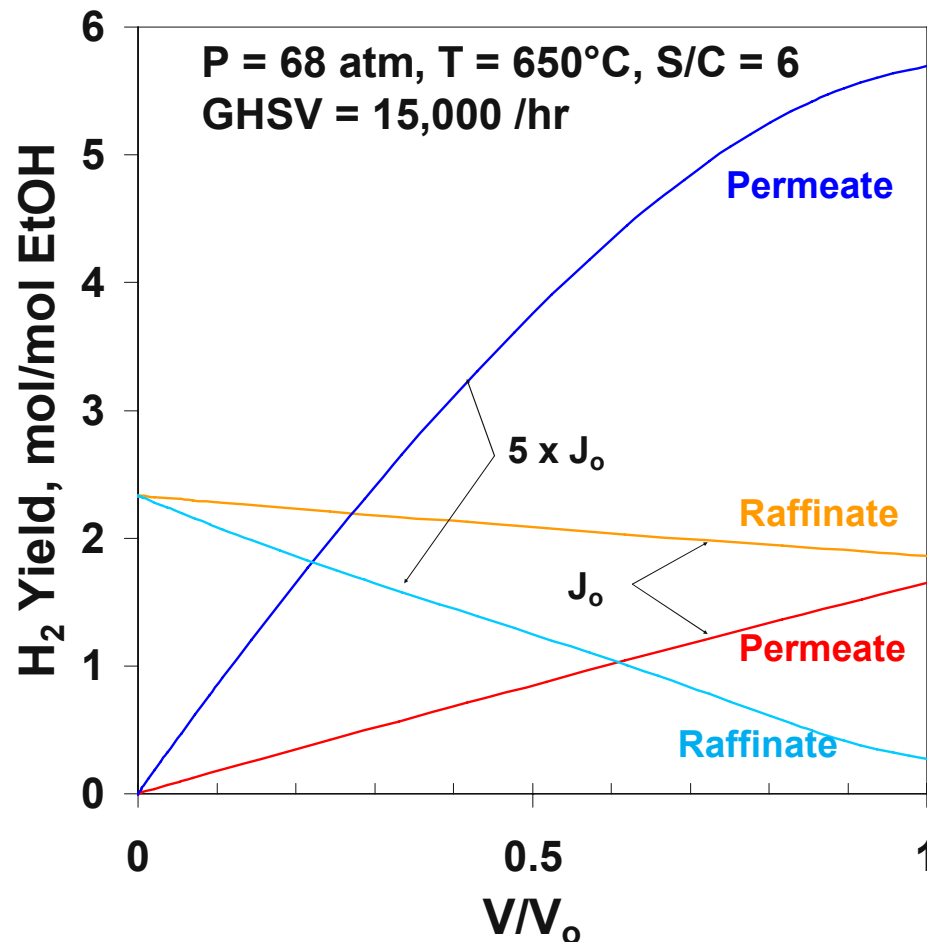
H₂ w/ membrane is the combined yield in the permeate and raffinate streams

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)
 - $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} = 2\text{CO} + 4\text{H}_2$ (Ethanol SR)
 - $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$ (Methane SR)
 - $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ (WGS)
 - no gas-phase mass-transfer limitations in the reactor
 - membrane follows Sievert's and Arrhenius laws

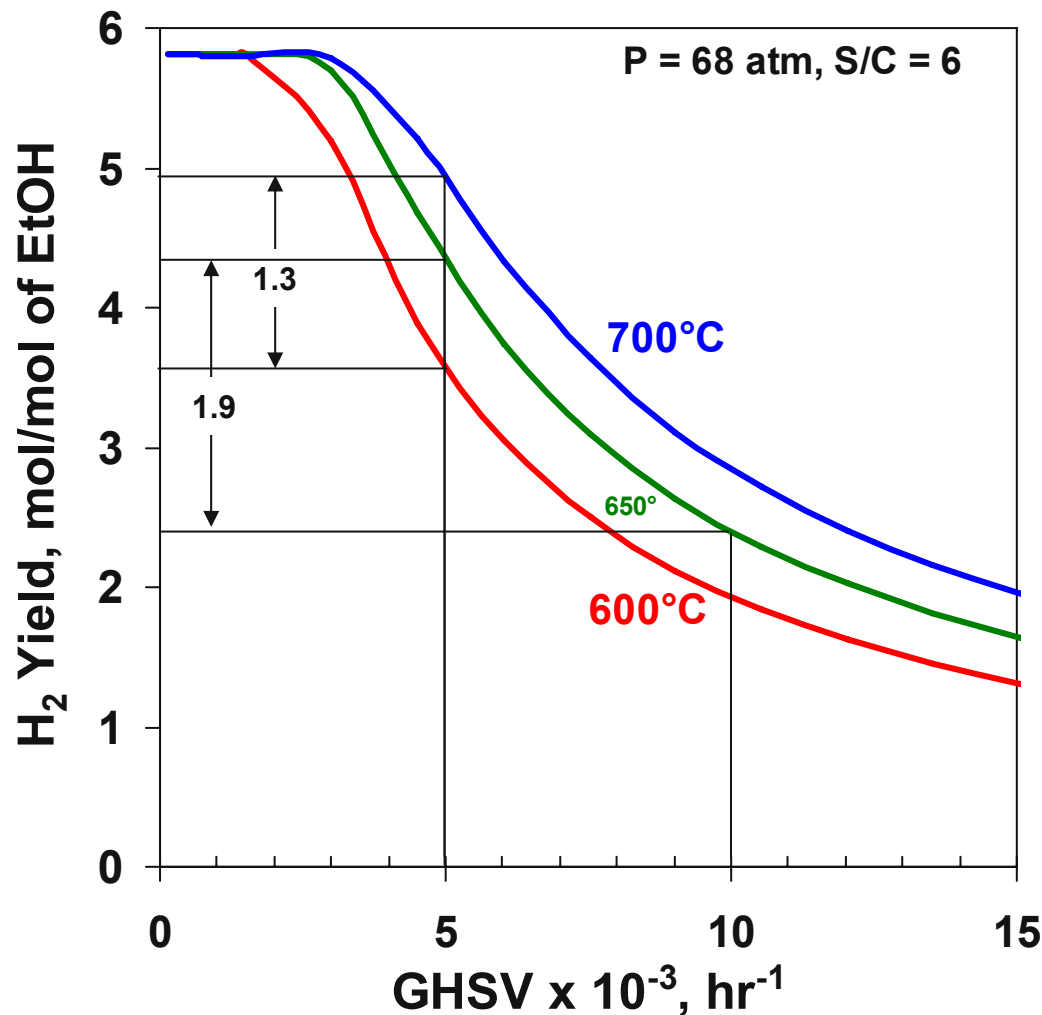
Hydrogen flux across the membrane is lower than desired

- With current flux (J_0), only 1.7 moles of H_2 can be extracted
- A 5-fold increase in flux could extract 5.6 moles of H_2
- This compares favorably to the theoretical maximum achievable of 6 moles of H_2 per mole of ethanol
 - $C_2H_5OH + 3H_2O = 2CO_2 + 6H_2$

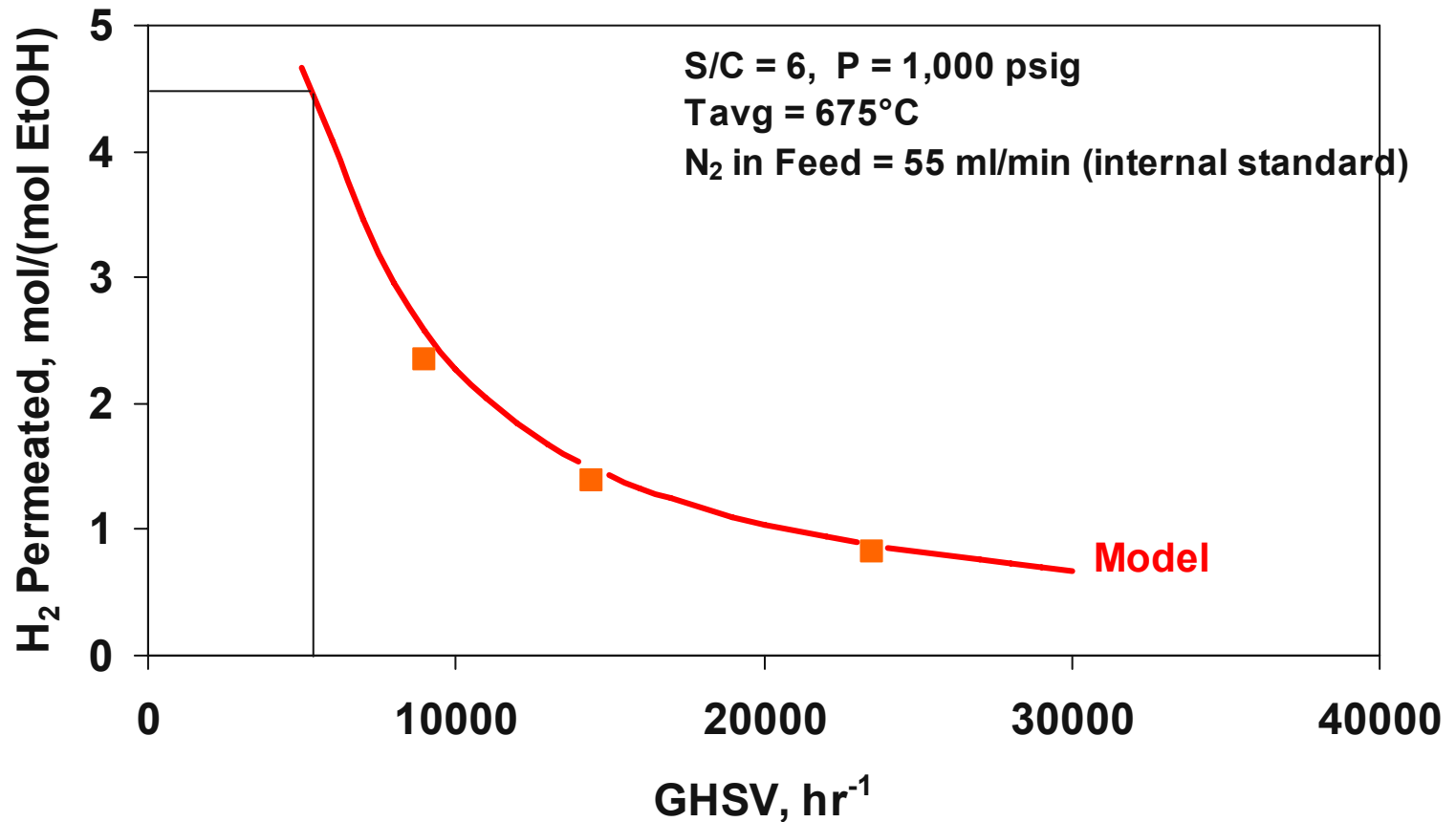


The hydrogen extracted can be improved by varying GHSV and temperature

- Lower GHSV improves H₂ yield across membrane
- Higher T improves H₂ 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



The model suggests that reducing the space velocity may be sufficient



- 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

Future work

- Make a go/no-go decision on the use of Pd-based H₂ transport membranes based on performance and cost
- Determine the influence of O₂ and CO₂ transport membranes on pressurized reforming (experimental with modeling support)
- Conduct systems analyses to evaluate the feasibility of alternative fuel processor designs using pressurized reforming
 - Based on experimental data generated

Summary

- We are pursuing an advanced reactor concept that will reduce the energy required to compress the product hydrogen
 - Steam reforming of bio-derived liquids is a promising approach
 - Membrane reactors provide in-situ separation and purification
- Experimental data on pressurized reforming of ethanol has been generated
 - Higher boiling point leads to decomposition in the vaporizer
- 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