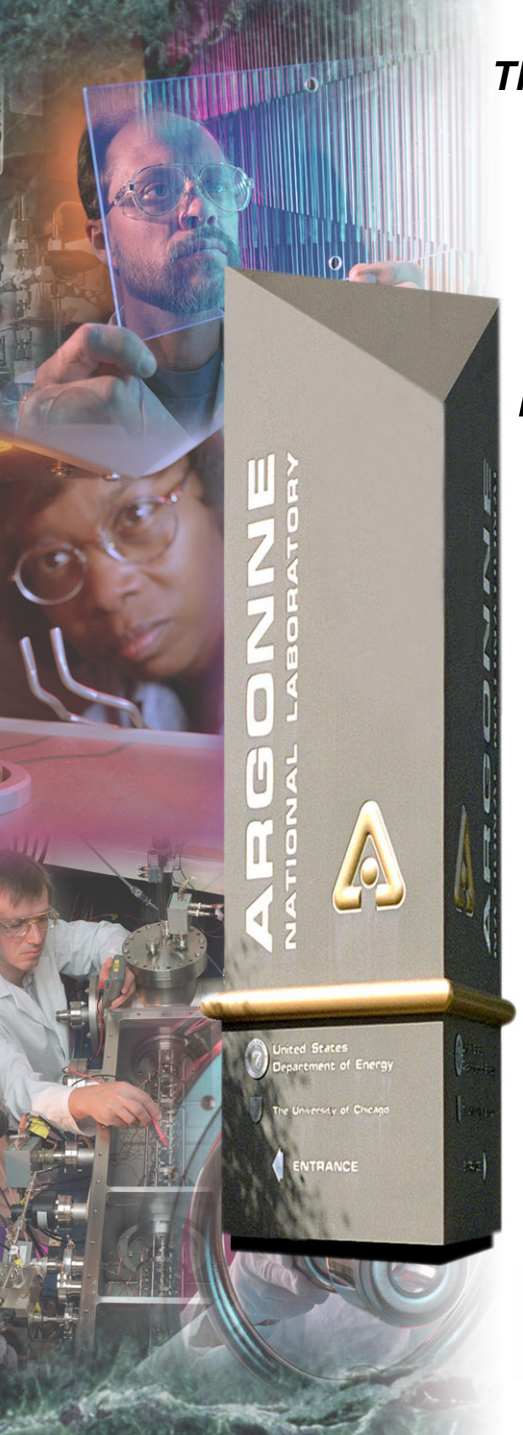

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Fuel Processor R&D

2005 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review
Arlington, VA, May 23-26, 2005

D. Papadias, L. Miller, S. Ahmed, D. Applegate, S. Lee

Argonne National Laboratory ***Project ID# FCP25***

U.S. Department of Energy
Energy Efficiency and Renewable Energy

Overview – Reforming of LPG

Timeline

- Project start: October, 2004
- Project end: September, 2007

Barriers addressed

- Efficiency
- Cost

Budget

- DOE share: 100%
- FY05 funding: $400K

Relevance

- LPG is widely available in urban and rural settings, and is attractive for distributed fuel cell power

Objectives and Approach

Objectives

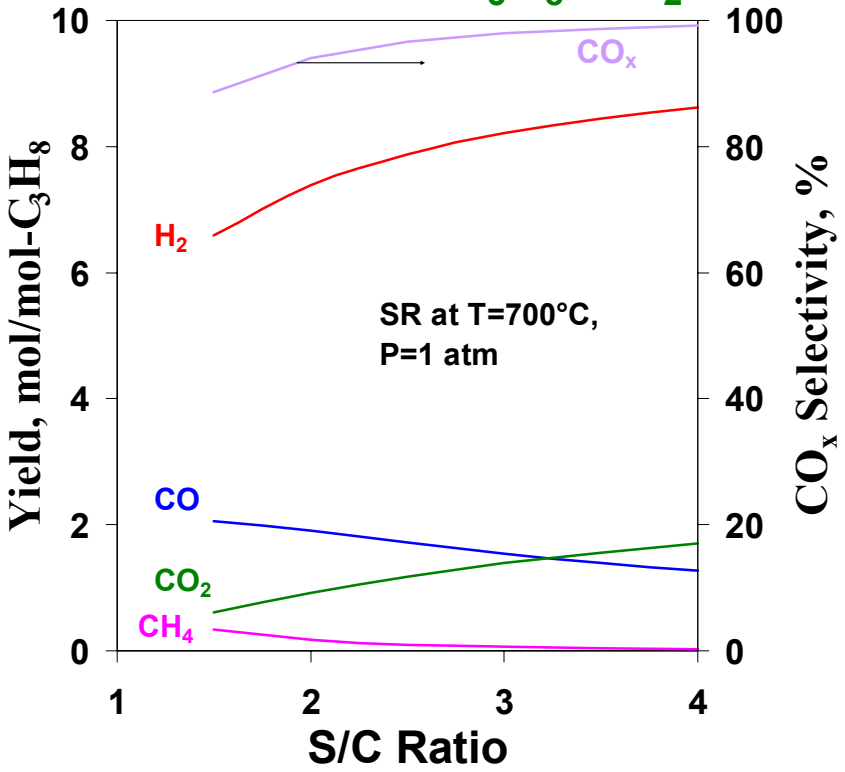
- **Study reforming of liquefied petroleum gas**
  - Establish kinetics of propane reforming
    - *Steam reforming and autothermal reforming*
  - Address LPG reforming challenges
    - *Effect of propylene on reforming*
    - *Sulfur in LPG*

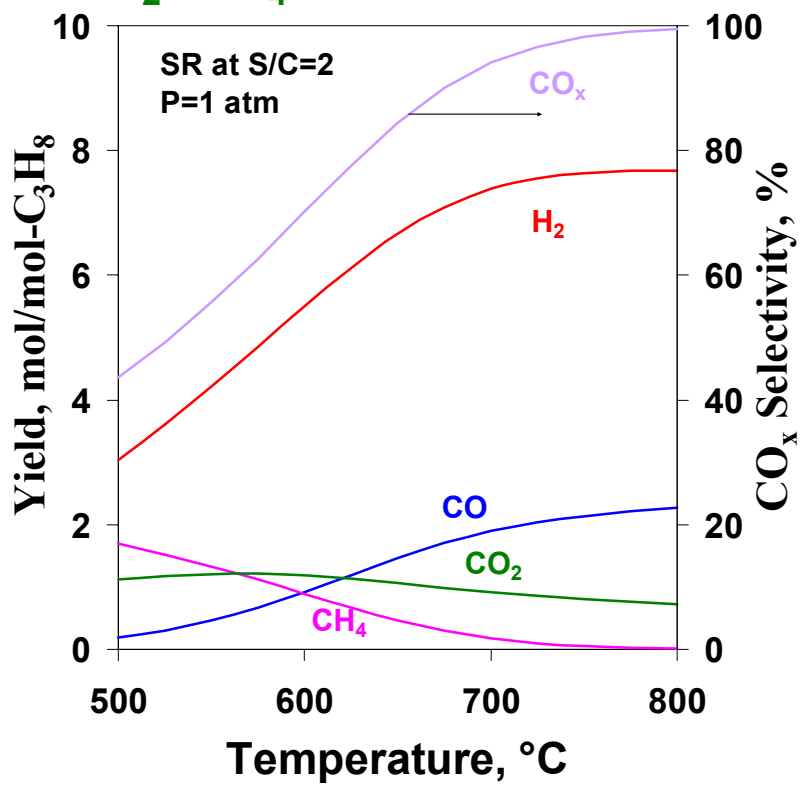
Approach

- **Study thermodynamic equilibria**
  - Effect of temperature, pressure, O:C, and H_2O:C ratio
- **Establish reforming kinetics through experiments and models**
  - Experiments conducted at micro-reactor (<1 g of catalyst) level

Higher H_2O:C and temperatures favor higher hydrogen yields at equilibrium

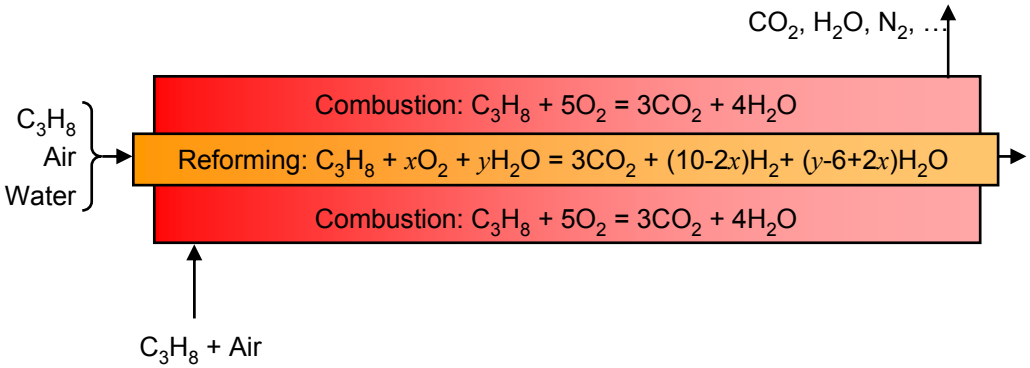
$$C_3H_8 + H_2O \rightarrow H_2, CO, CO_2, CH_4, \ldots$$

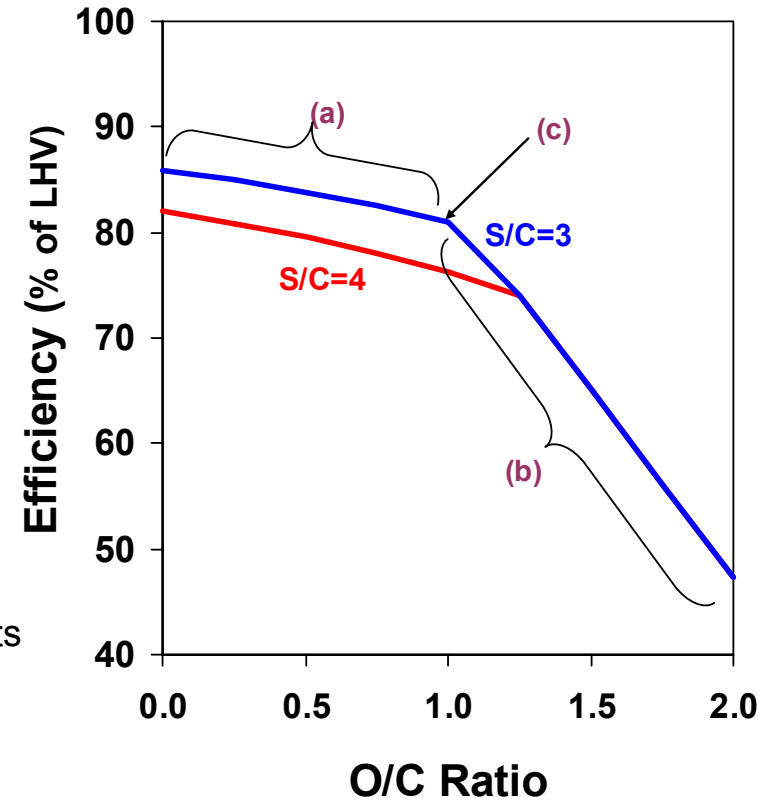




- At S:C>2 and T>500°C, carbon formation is not predicted
- 90% COx selectivities are anticipated at S/C=2, 675°C and 1 atm.

Fuel processing efficiency depends on the O:C and H_2O:C ratios





- $C_3H_8 + xO_2 + yH_2O \rightarrow CO_2 + H_2 + H_2O$

(a): Fuel combustion needed to maintain energy balance

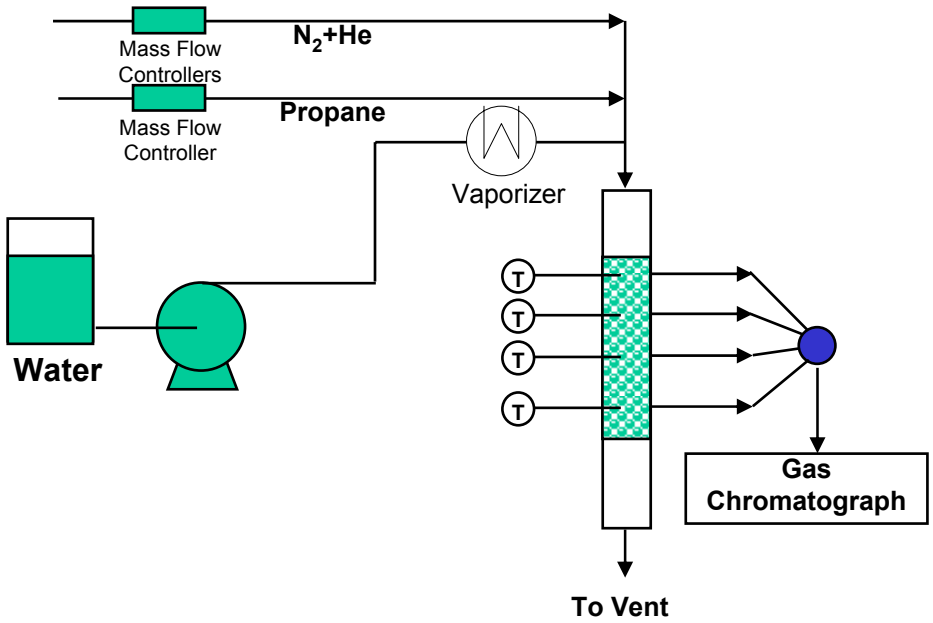
(b): Reforming is exothermic, sensible heat lost with products

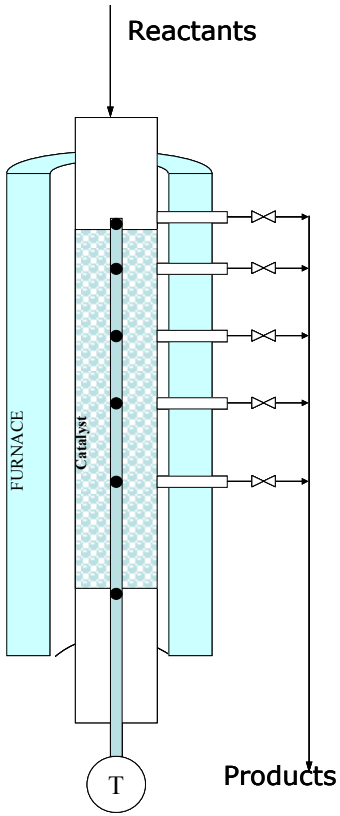
(c): Combustion not needed, no sensible heat loss with products

- **Efficiency decreases with increasing O/C and S/C**

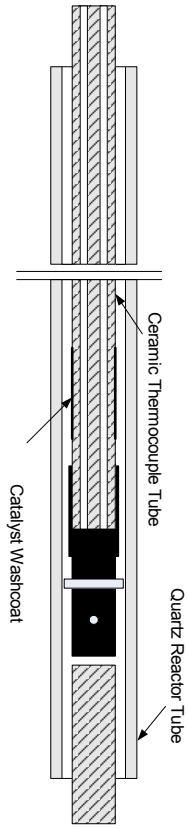
Experiments with two micro-reactors will help define kinetics, mechanism, and suitable operating conditions

- **Effect of temperature, pressure, space velocity**
- **Kinetic parameters, reaction pathways**





Integral Reactor



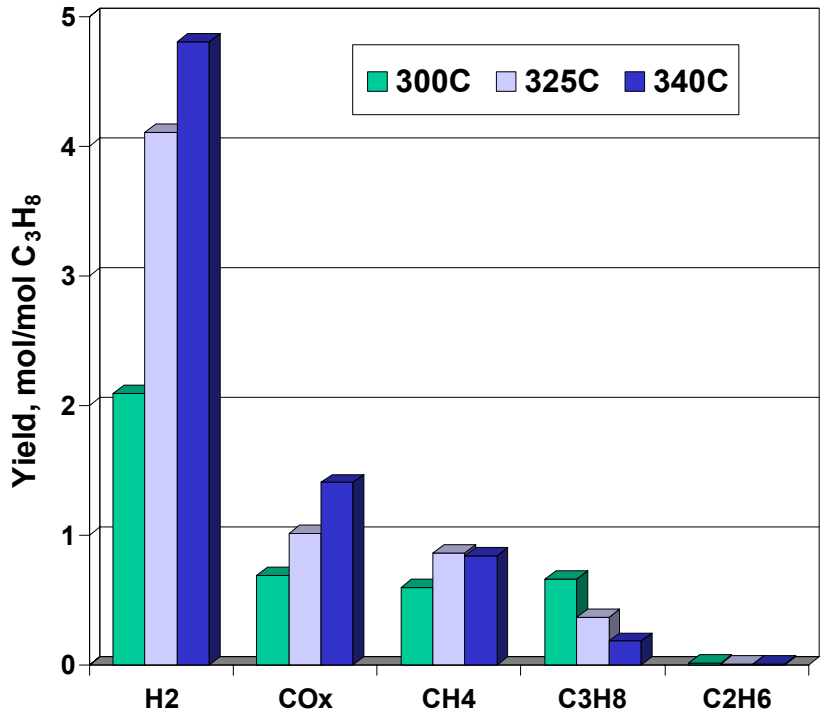
Differential Reactor

The catalyst is active at temperatures as low as 340°C

- **Propane Concentration in Feed:**
  - C_3H_8: 0.5% (wet); 1.7% (dry)
- **Propane Feed Rate:**
  - 20 ml/min (STP)
- **P = 1 atm**
- **H_2O:C Molar Ratio = 45**
- **GHSV = 122,000 per hour**
- **Catalyst : Rh/La-Al_2O_3**

Temperature	300°C		340°C	
	Yield*	Std. Dev.	Yield*	Std. Dev.
H_2	2.092	± 0.135	4.811	± 0.315
CH_4	0.597	± 0.093	0.838	± 0.177
CO	0.016	± 0.005	0.018	± 0.007
CO_2	0.670	± 0.071	1.387	± 0.046
C_2H_6	0.009	± 0.002	0.003	± 0.002
C_3H_8	0.659	± 0.126	0.181	± 0.073

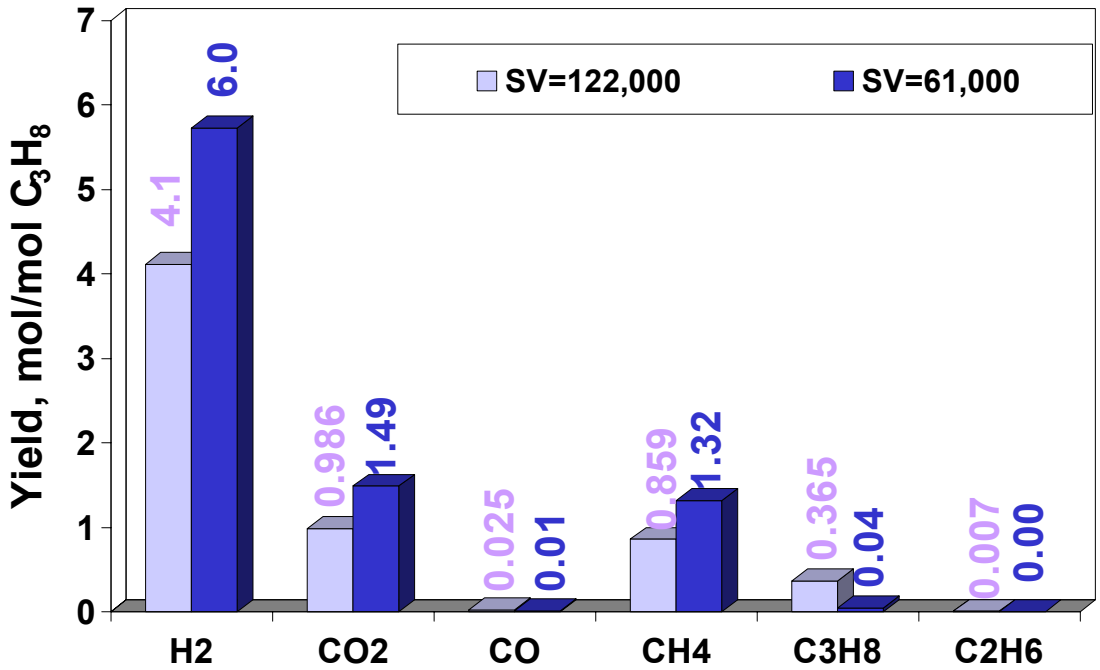
* Mol/(Mol of C_3H_8 Feed)



Essentially complete conversion of propane is achievable at 325°C, space velocity of 61,000 per hr

- **Propane Concentration in Feed:**
  - C_3H_8: 0.5% (wet); 1.7% (dry)
- **Propane Feed Rate:**
  - 20 ml/min (STP)

- **P = 1 atm**
- **T = 325°C**
- **H_2O:C Molar Ratio = 45**
- **Catalyst : Rh/La-Al_2O_3**



* Mol/(Mol of C_3H_8 Feed)

Accomplishments

- Thermodynamic equilibrium analysis has been done
- Experimental apparatus has been assembled
  - **Apparatus has been safety reviewed**
  - **Steam reforming experiments have started**
- A partial oxidation reactor has been designed
  - **Fabrication in progress**

Future Work

- **Reaction data will be used in model to establish kinetic parameters**
  - Effect of propylene and sulfur species during LPG reforming will be studied to resolve any detrimental effect
- **Reactor model will be set up to explore alternative designs**

Overview – Single Stage Water Gas Shift Reactor

Timeline

- **Project start: October, 2004**
- **Project end: September, 2007**

Barriers addressed

- **Efficiency**
- **Cost**

Budget

- **DOE share: 100%**
- **FY05 funding: $450K**

Relevance

- **Single stage water gas shift reactors offer**
  - more compact fuel processors (desired in distributed fuel cell systems)
  - lower costs due to reduced catalyst loading

Objectives

- **Achieve water-gas shift conversion in a single-stage reactor using**
  - Catalyzed reaction, enhanced by temperature control and selective product removal
  - Convert CO from ~10% to <1% (dry)
  - Space velocity > 20,000 h^{-1}

Approach

I
- Select a suitable WGS catalyst and establish its kinetics
- Model the shift reactor under adiabatic, isothermal, and other temperature profiles
- Design a laboratory reactor for experimental verification
  - Without membrane separation
- Fabricate and test with temperature control to validate model
- Simulate reactor operation with membrane separation

II
- Evaluate potential membrane materials for WGS use

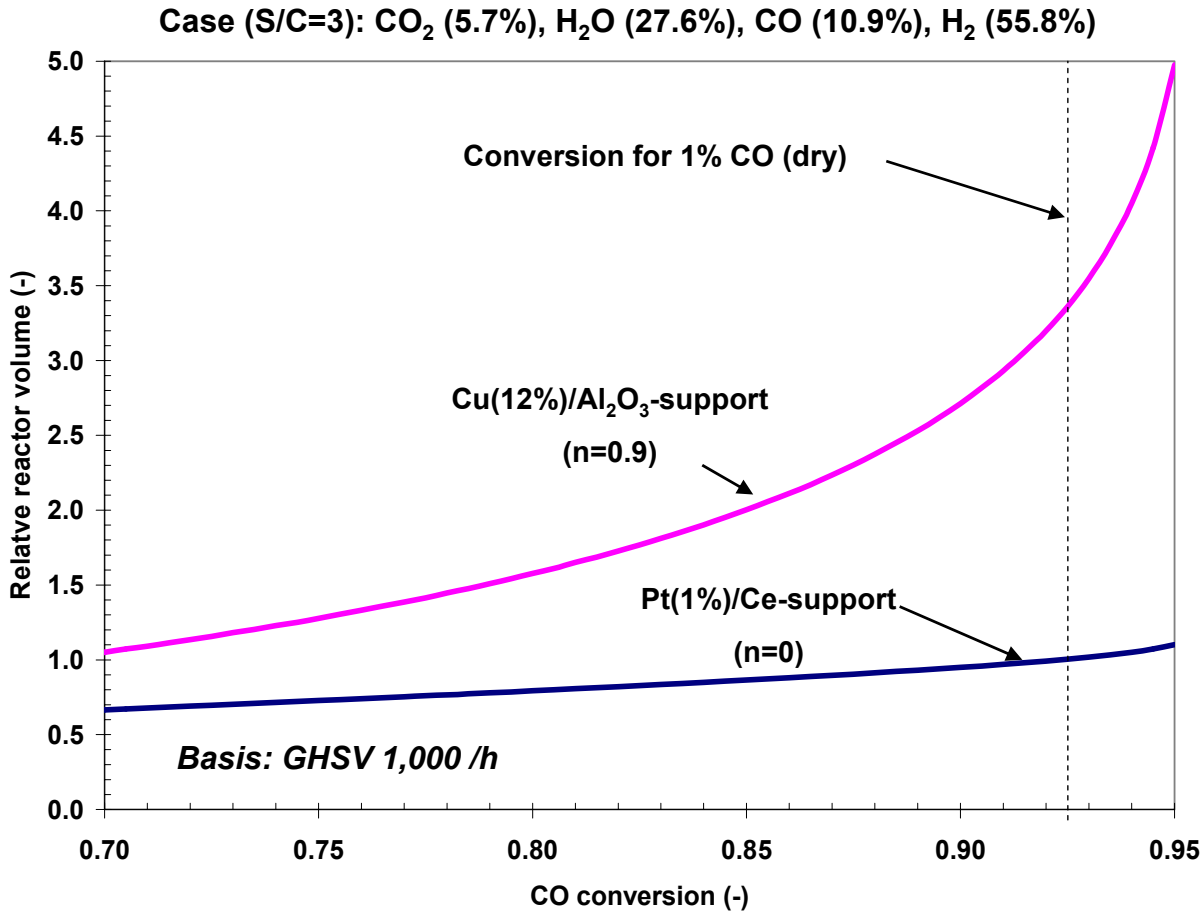
III
- Continue WGS simulations using temperature control with anticipated membrane flux
- Confirm a compact WGS reactor – simulation and experimental

Kinetics with a zero-order in CO favor compact reactors achieving high conversions

- The WGS reactor volume (V_{WGS}) as function of conversion and constant flow rate depends on the reaction order, n, of the CO concentration:

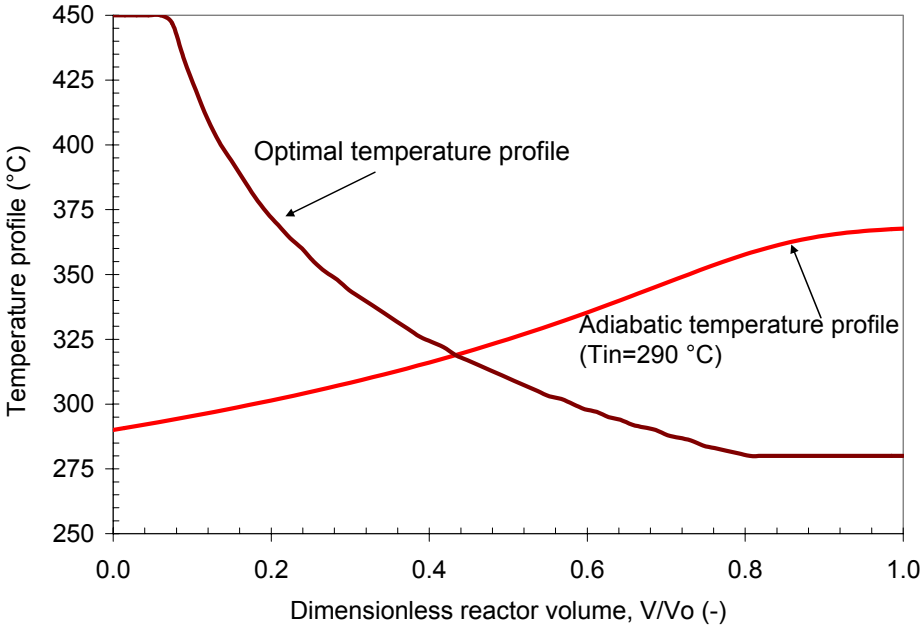
- Established kinetics for a catalyst: Pt-Re/$Ce_{0.46}Z_{r0.54}O_2$

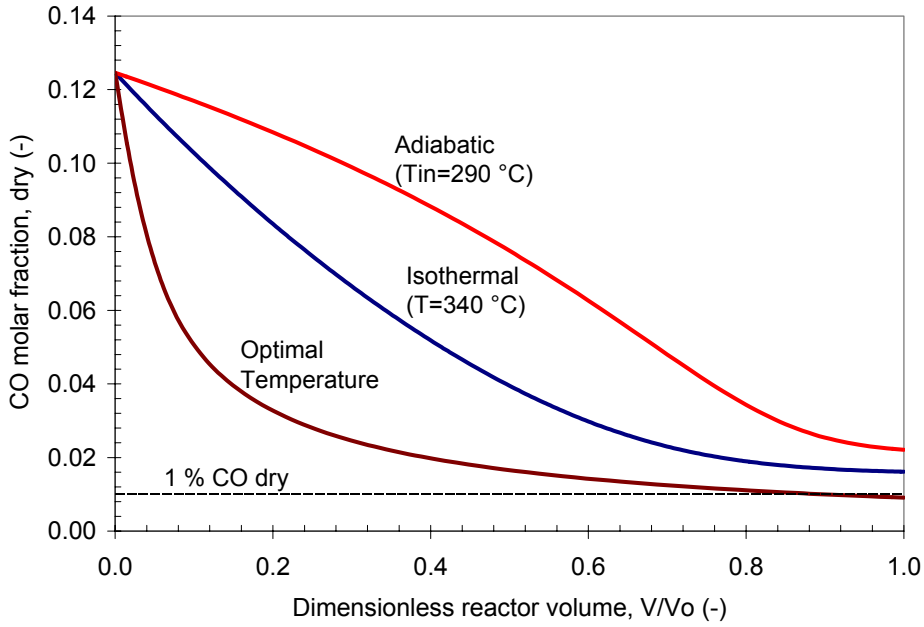
CO order = 0



$$R = A \times e^{-16000/RT} \times \frac{(C_{CO})^0 \times (C_{H_2O})^{0.4}}{(C_{CO_2})^{0.18} \times (C_{H_2})^{0.58}}, \quad \left(\frac{mol}{cm^3, s}\right)$$

A combination of reaction/heat exchange enhances WGS rates





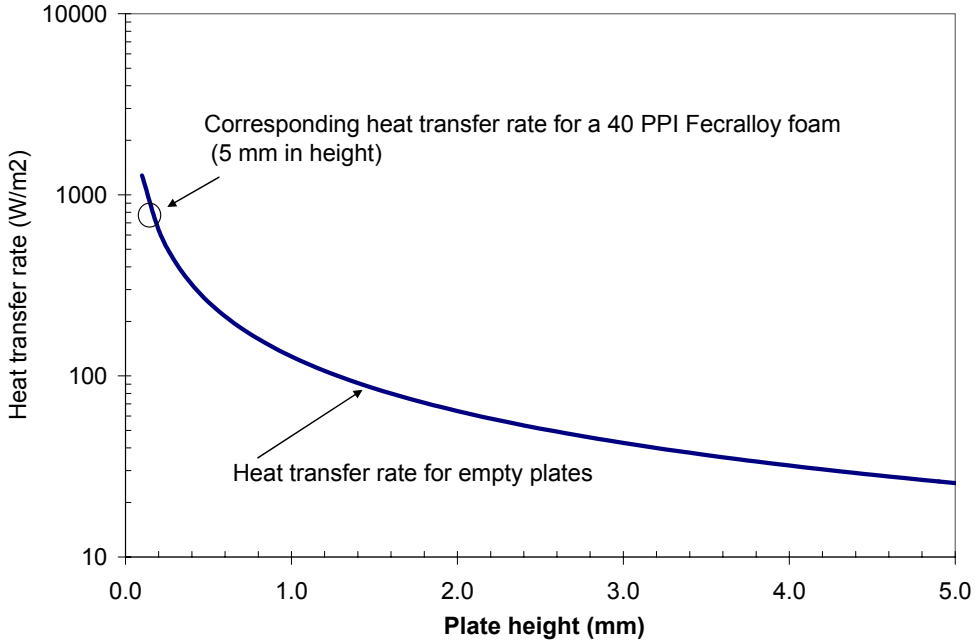
A WGS reactor with an optimal temperature profile maximizes the conversion within a given volume

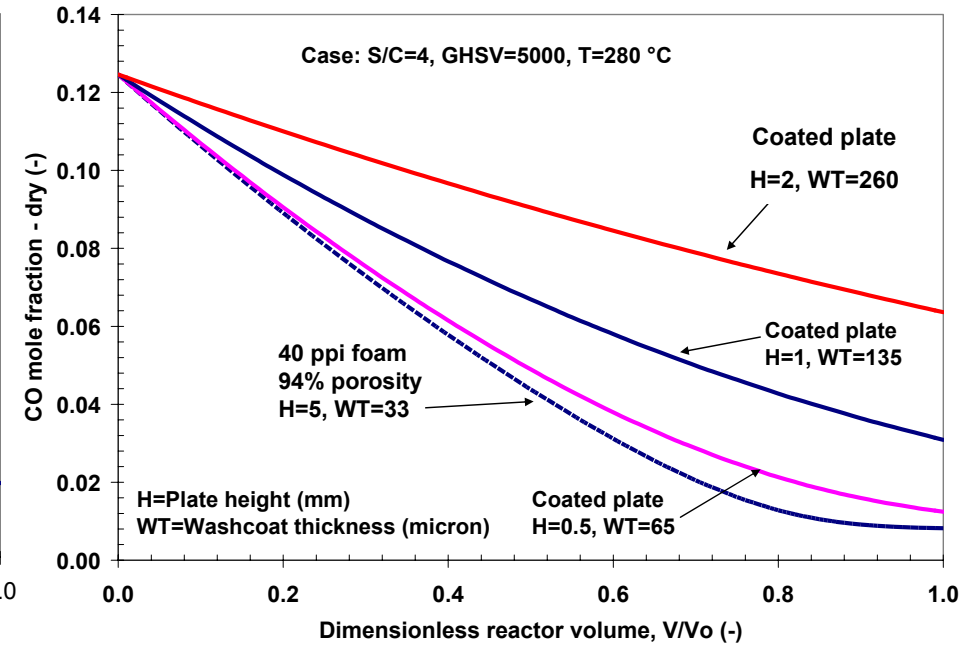
Parameters:

Catalyst: Pt-Re/Ce (1% Pt)
GHSV: 30,000 h-1
S/C: 4.0

Case (S/C=4): CO_2 (6.3%), H_2O (36.3%), CO (7.9%), H_2 (49.2%)

Foam support enhances heat transfer rates and reduces transport limitations

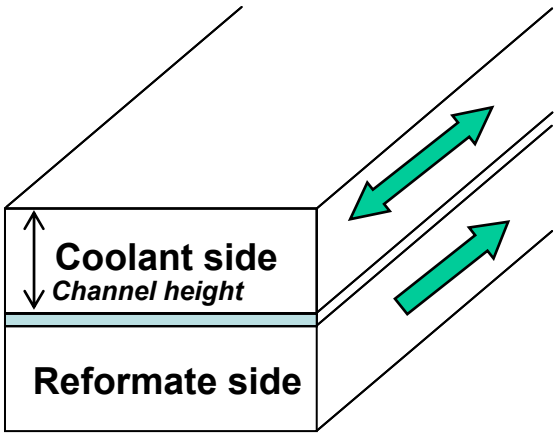


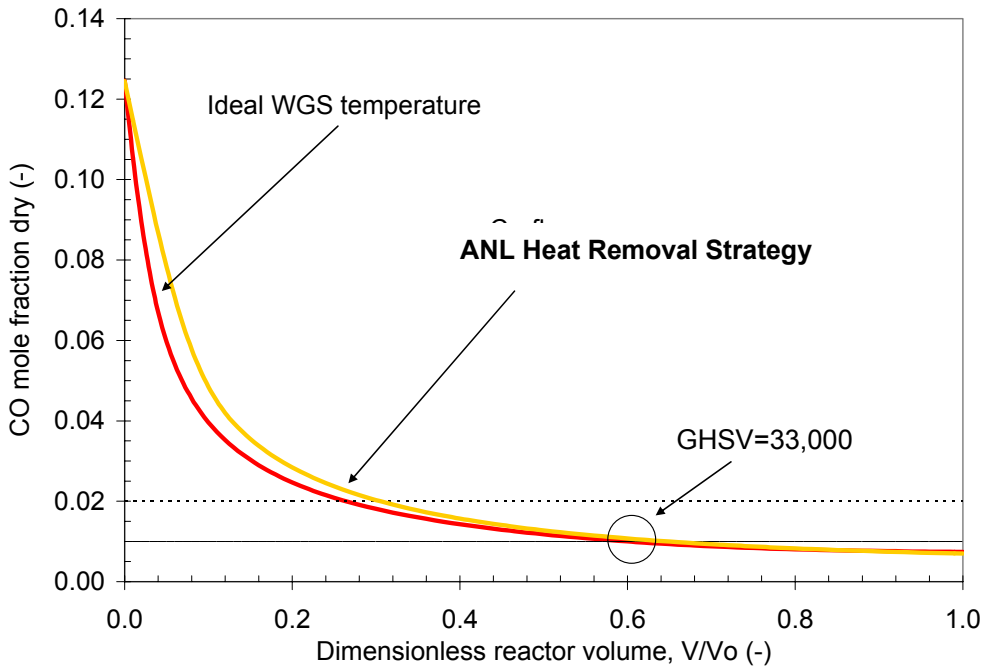


Foam support offers several advantages:

- **Increases heat transfer rates between coolant/WGS sides**
- **Minimizes transport limitations for the WGS reaction by dispersing the washcoat into a high surface area support**
- **Can be co-sintered into different geometries if needed**

A parallel plate geometry is advantageous for temperature control



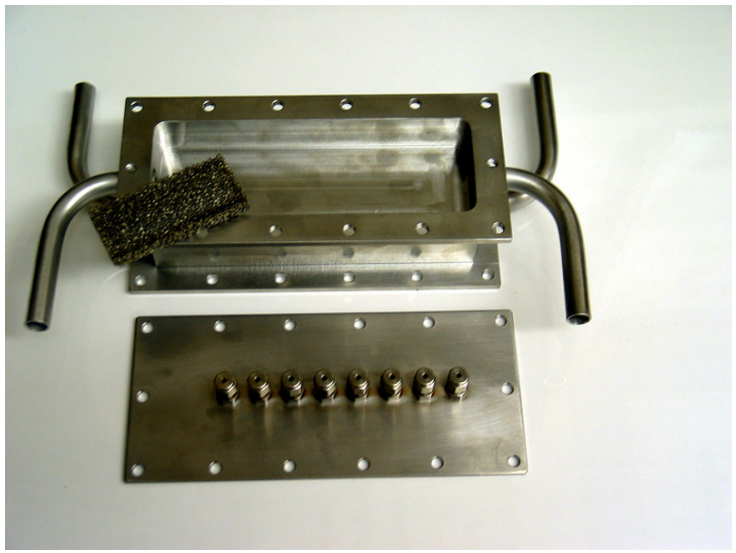


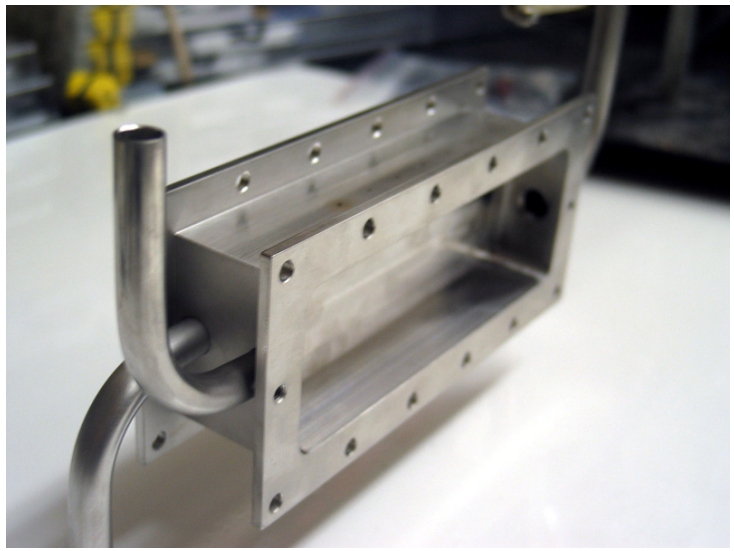
- **A plate type reactor is a suitable reactor geometry to achieve an integrated reactor/heat exchanger**

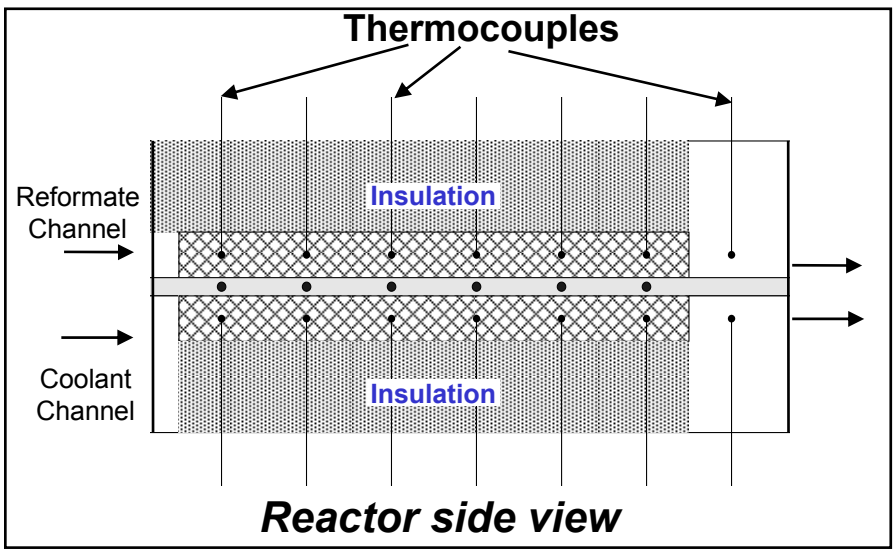
- **Heat exchange can be obtained using *co-, counter- or cross-flow*, whichever reproduces the ideal temperature profile best**

Catalyst:	Pt-Re/Ce (1% Pt)
GHSV:	20,000 hr^{-1}
S/C:	4.0
WGS:	Tin=375°C
Coolant:	Air at 25°C

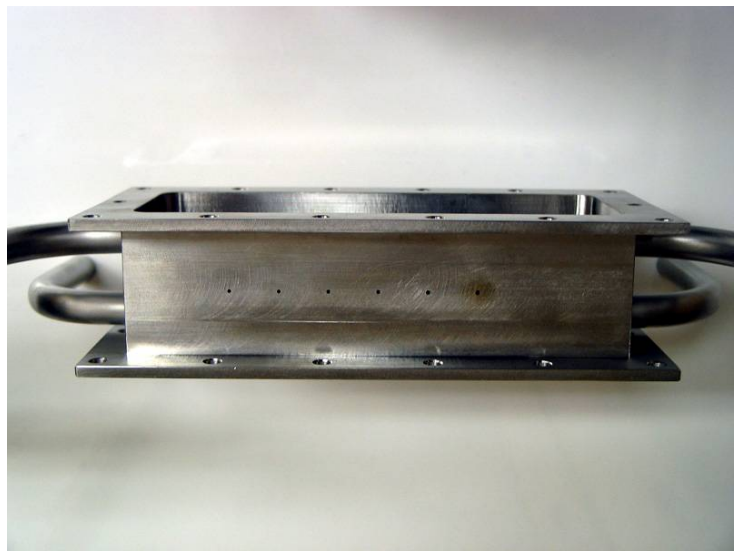
The experimental reactor has been fabricated and installed in the test apparatus



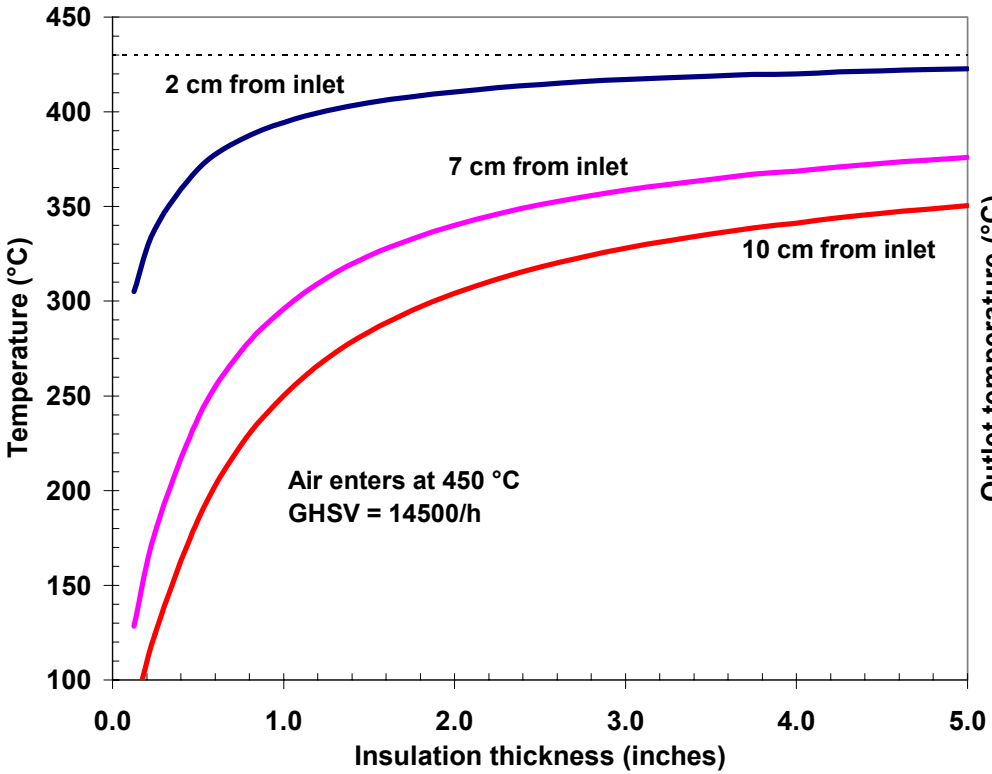


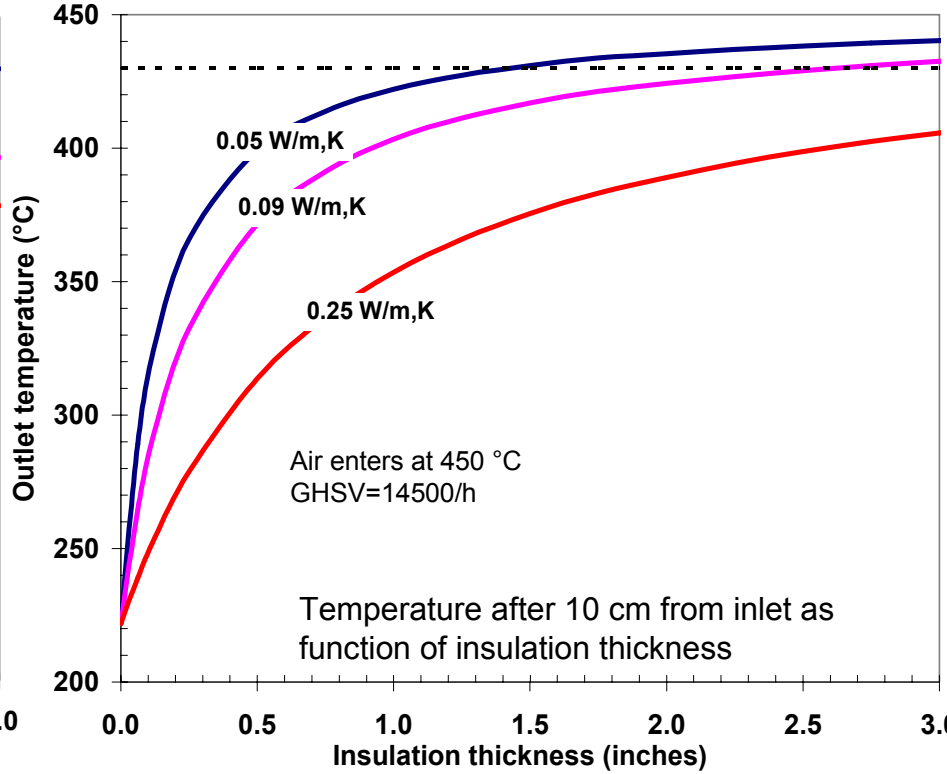


Reactor side view



Heat losses in the present reactor (width = 2.5 cm) are significant after a length of 2 cm

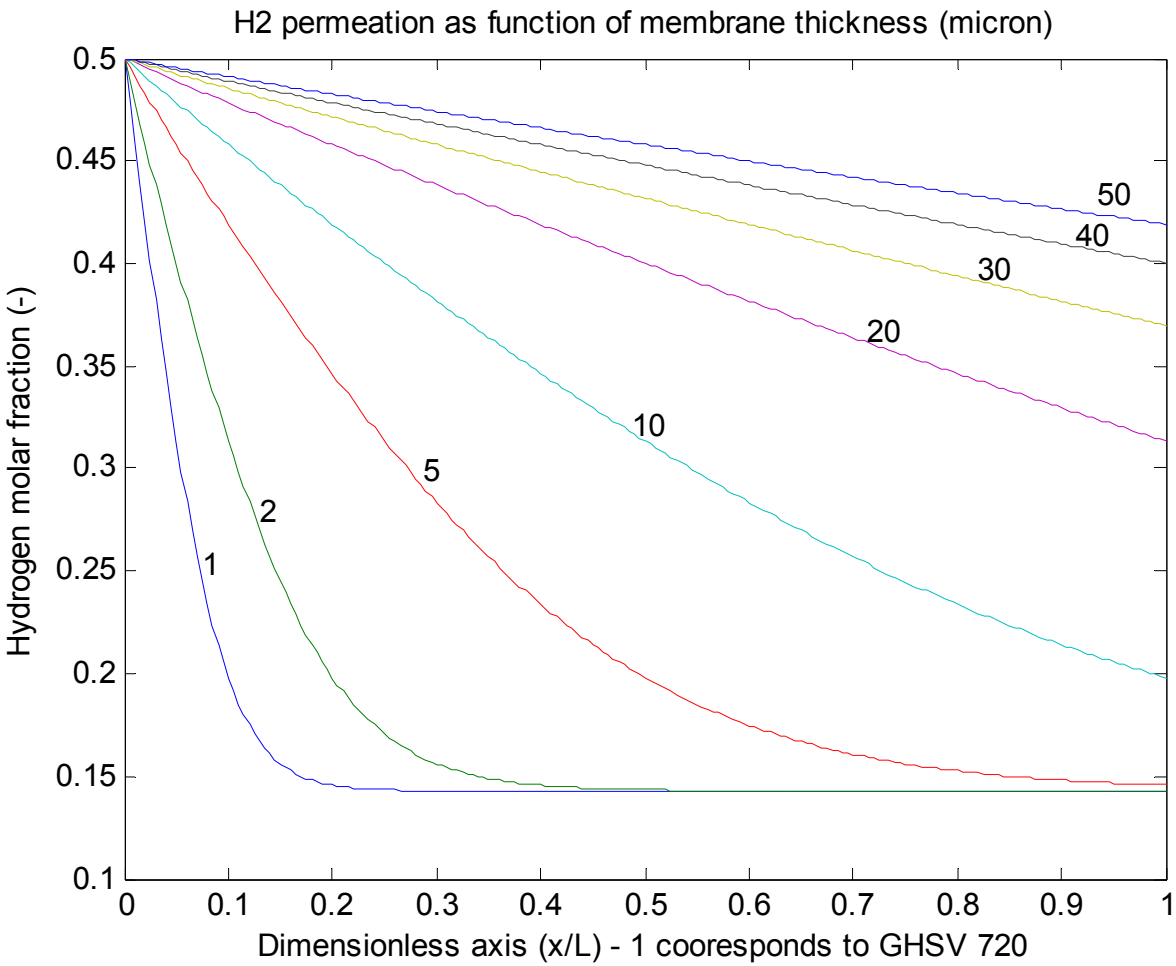




- The microreactor can lose heat despite good insulation. Heat losses must be compensated for with less flow of coolant

- A plate reactor with a width of 10 cm, or a stacked WGS, is almost adiabatic

Thin membranes favor H_2 removal



- Flux not limited by bulk diffusion

Reaction side:

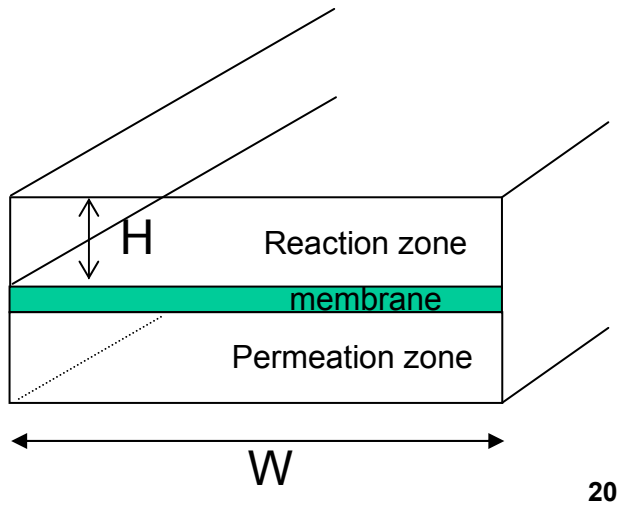
N_2 (0.5) H_2 (0.5), L=10; W=2.54;
H=0.5 cm, P=1 atm
U0=2 cm/s, m=0.0934 g/min

Membrane:

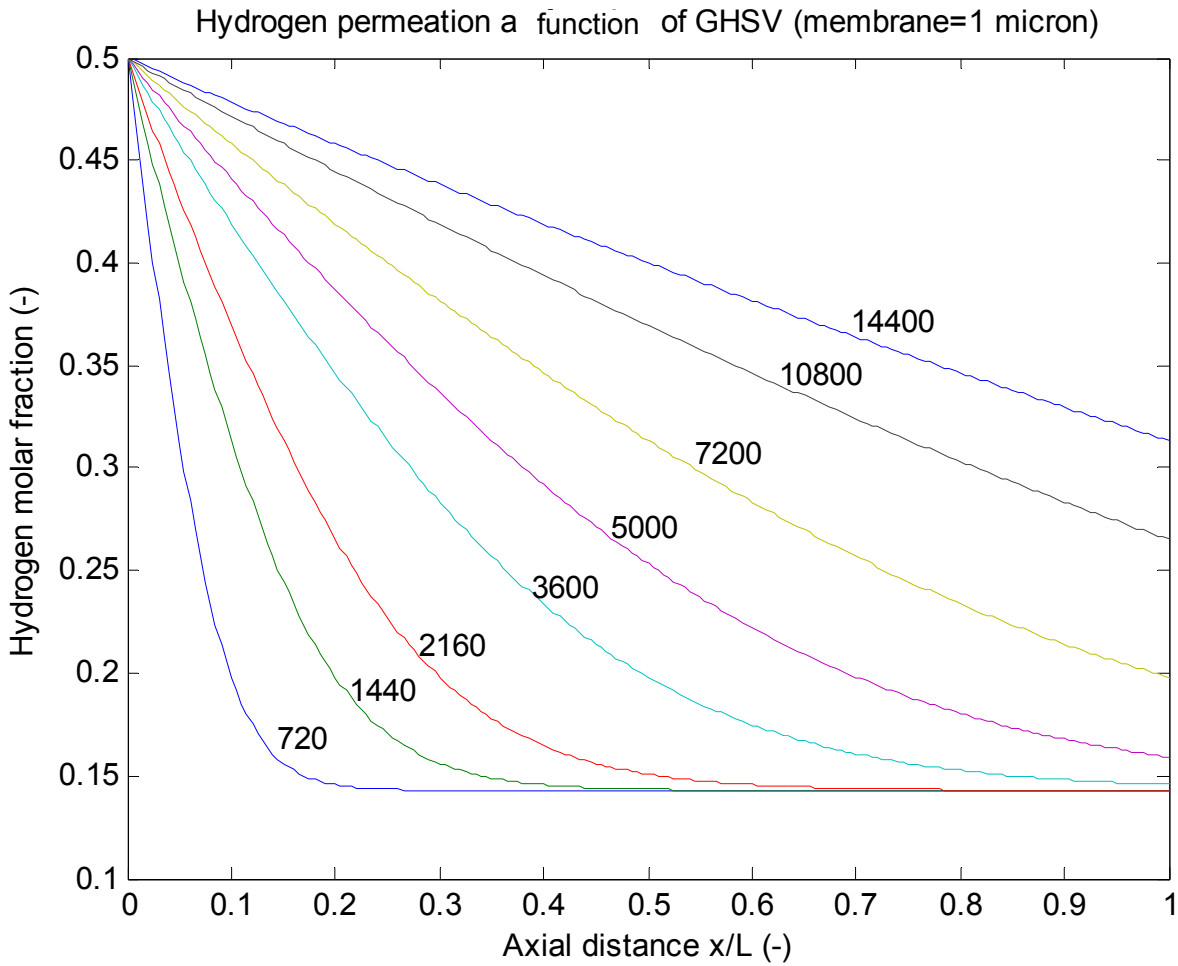
Pd (Basile et al), Pe (68 micron)
2.56e-5 mol/(m^2,s, $Pa^{0.5}$)

Permeation side:

N_2 (0.436 g/min), L=10; W=2.54;
H=0.5 cm, U0=5 cm/s, P=1 atm



Hydrogen removal is limited by residence time in the reactor



- Flux not limited by bulk diffusion
- ***Reaction side:***

N_2 (0.5) H_2 (0.5), L=10; W=2.54; H=0.5 cm,
U0=2-40 cm/s, P=1 atm

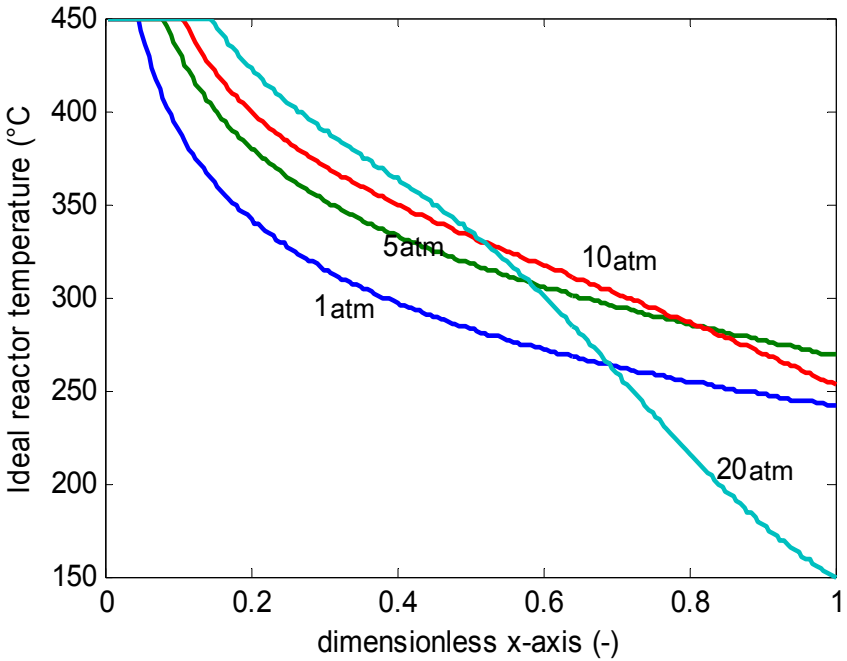
- ***Membrane:***

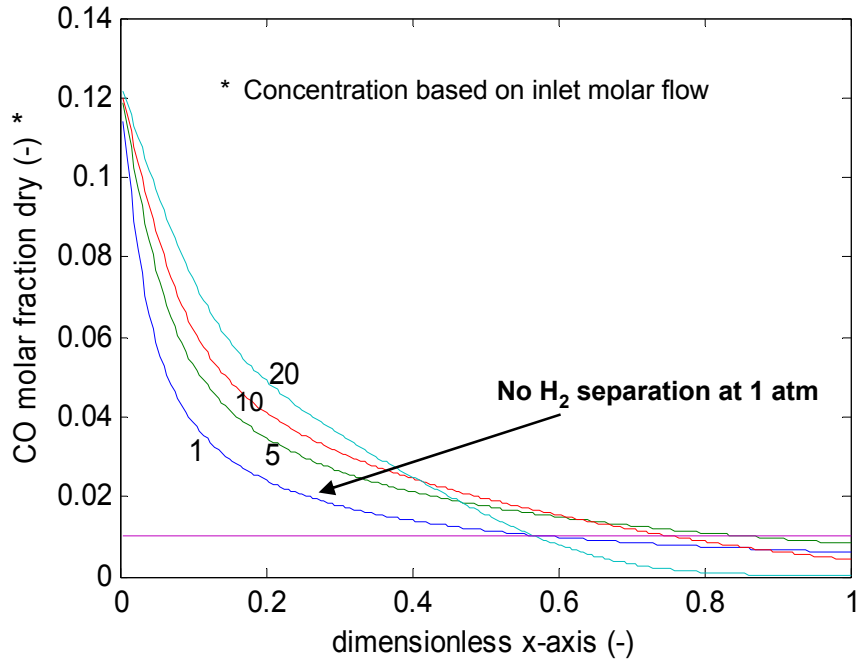
Pd (Basile et al), Pe (68 micron)
2.56e-5 mol/(m^2,s, $Pa^{0.5}$)

- ***Permeation side:***

N_2 (0.436 g/min), L=10; W=2.54; H=0.5 cm, U0=5-100 cm/s, P=1 atm

A pressure > 5 atm is needed to benefit from selective product removal





WGS reactor results with temperature control and membrane separation (Pd, 1 micron).

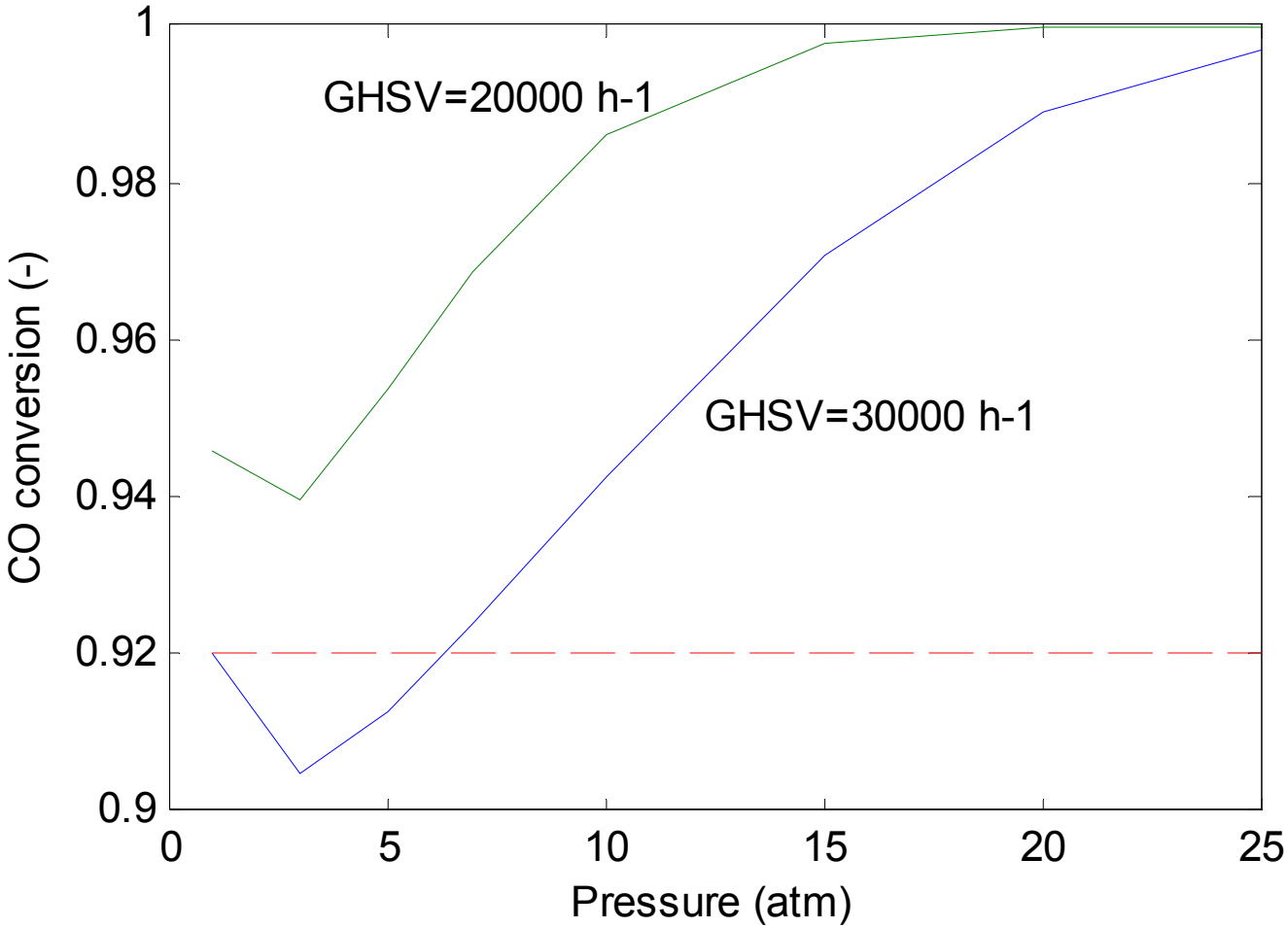
Dimensionless axis corresponds to a GHSV of 20000 h^{-1}.

WGS Parameters:

S/C=4 (CH4 reforming, CO2=6.3%, H2O=36.6%, CO=7.9%, H2=49.2%)

Foam (40 ppi), Catalyst=Pt/Ce (250 g/L)

Depending on membrane flux, there is a pressure threshold to benefit from H_2 separation



Assumptions: S/C=4, 1 μm Pd membrane

Accomplishments

- **Developed a shift reactor model using parallel plate geometry**
  - Includes kinetics of Pt-Re/Ce catalyst
  - Designed reactor with an optimized temperature profile
    - *Outlet CO of ~1% at a space velocity of 33,000 hr^{-1}*
    - *CFD was used to predict flow, temperature, heat loss*
  - Fabricated experimental reactor to validate model
- **Used 1D model to analyze membrane performance**
  - H_2 separation is limited by membrane at low pressures (P<10 atm)
  - Low pressures limit GHSV
    - *Performance can be improved with sweep gas (preferably counter flow), thin membranes (less than 1 μm), high membrane surface area*
  - At high pressures membrane flux increases
    - *H_2 diffusion to membrane becomes predominant.*
  - Increasing pressure slows WGS kinetics due to inhibition of CO_2 and H_2
  - Due to slow hydrogen permeation, a membrane can worsen reactor performance without separation unless the pressure is high enough to compete with the CO_2 and H_2 inhibition effect

Future Work

- **Validate model with data from experimental reactor**
  - Explore alternative (cross, counter) flow patterns and geometries
- **Expand model to design reactor that combines heat transfer and separation**
- **Demonstrate laboratory-scale single-stage water gas shift reactor**

Hydrogen Safety

- **The most significant hazard of these experiments is the possibility of leakage of hydrogen and carbon monoxide**

- **The hazard has been addressed by**
  - Locating apparatus within a vacuum-frame hood
  - Automated shutdown triggered by hood exhaust failure
  - Laboratory is equipped with a CO sensor