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Fuel Processor R&D

*2005 DOE Hydrogen, Fuel Cells & Infrastructure
Technologies Program Review
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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

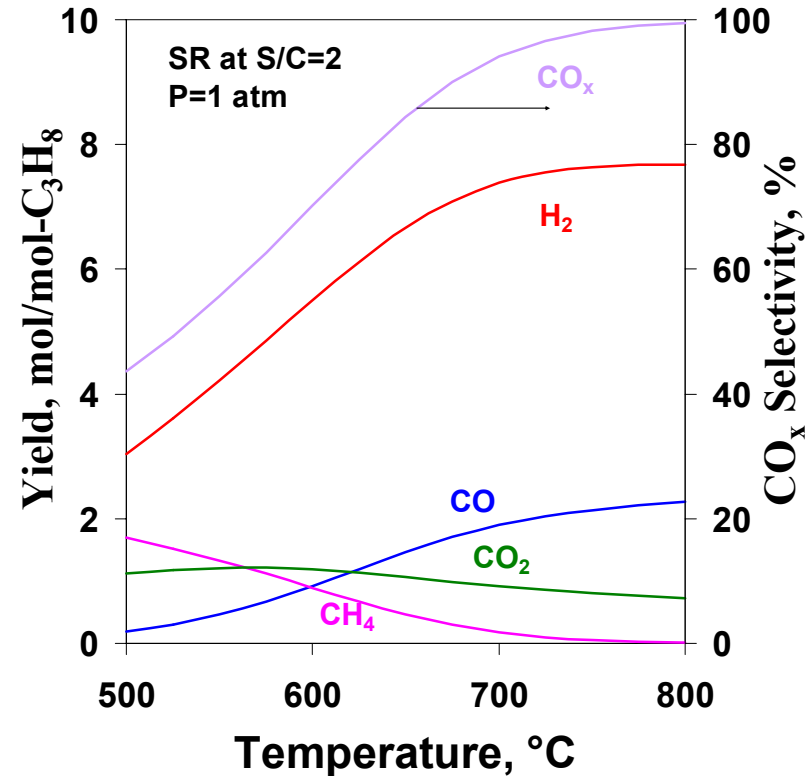
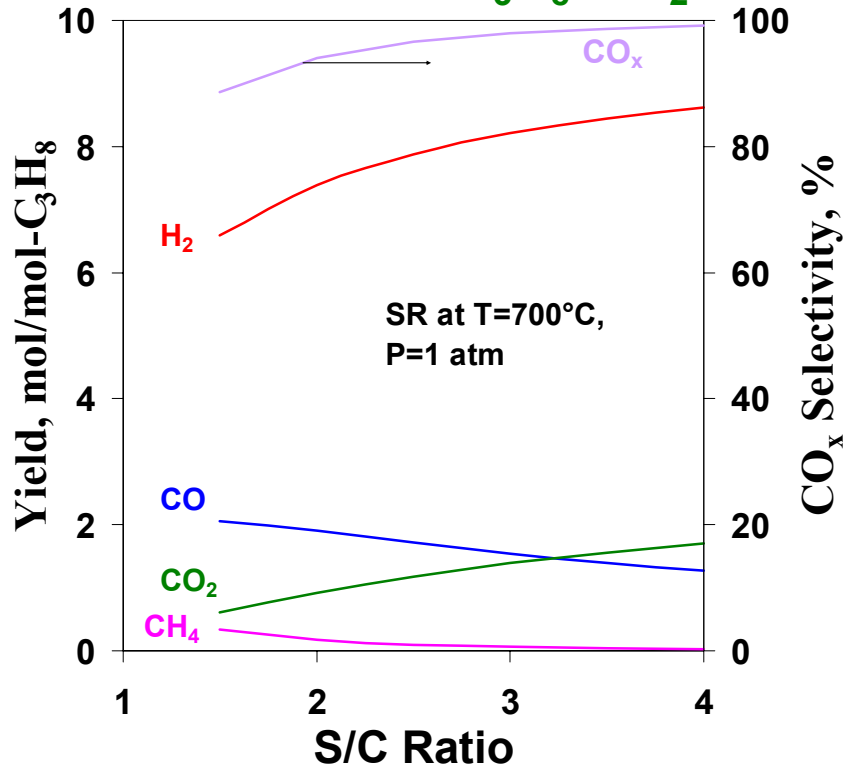
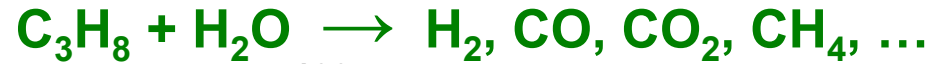
Objectives

- **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

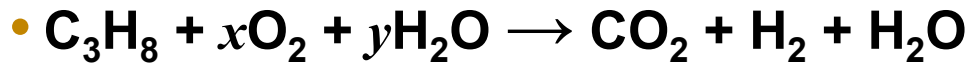
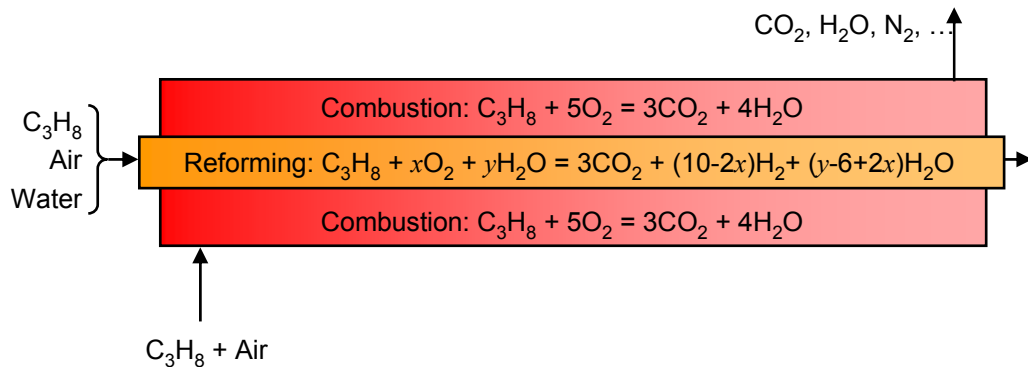
- **Study thermodynamic equilibria**
 - Effect of temperature, pressure, O:C, and H₂O:C ratio
- **Establish reforming kinetics through experiments and models**
 - Experiments conducted at micro-reactor (<1 g of catalyst) level

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

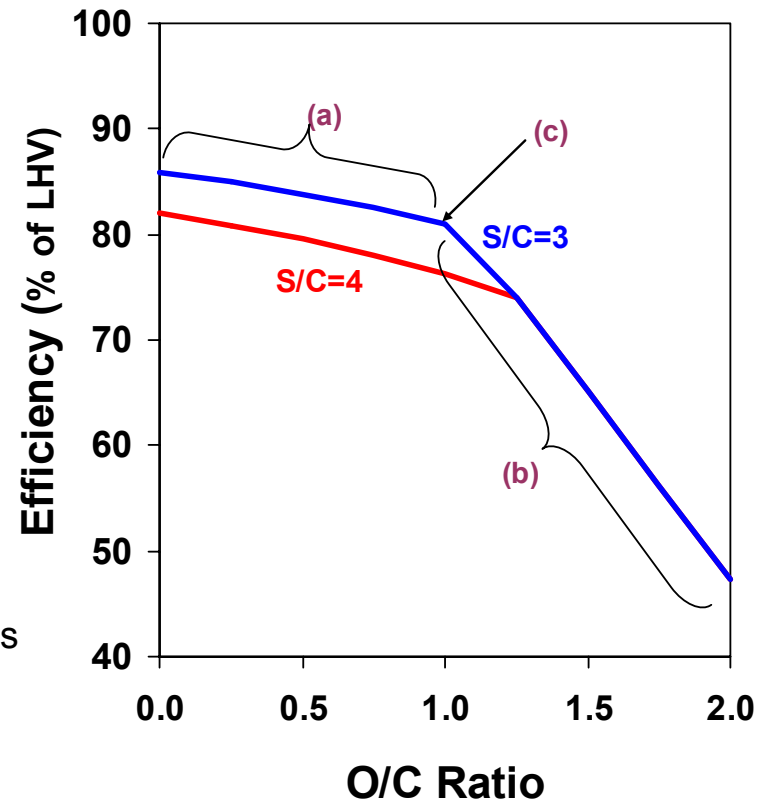


- At $S:C > 2$ and $T > 500^\circ C$, carbon formation is not predicted
- 90% CO_x selectivities are anticipated at $S/C=2$, $675^\circ C$ and 1 atm.

Fuel processing efficiency depends on the O:C and H₂O:C ratios



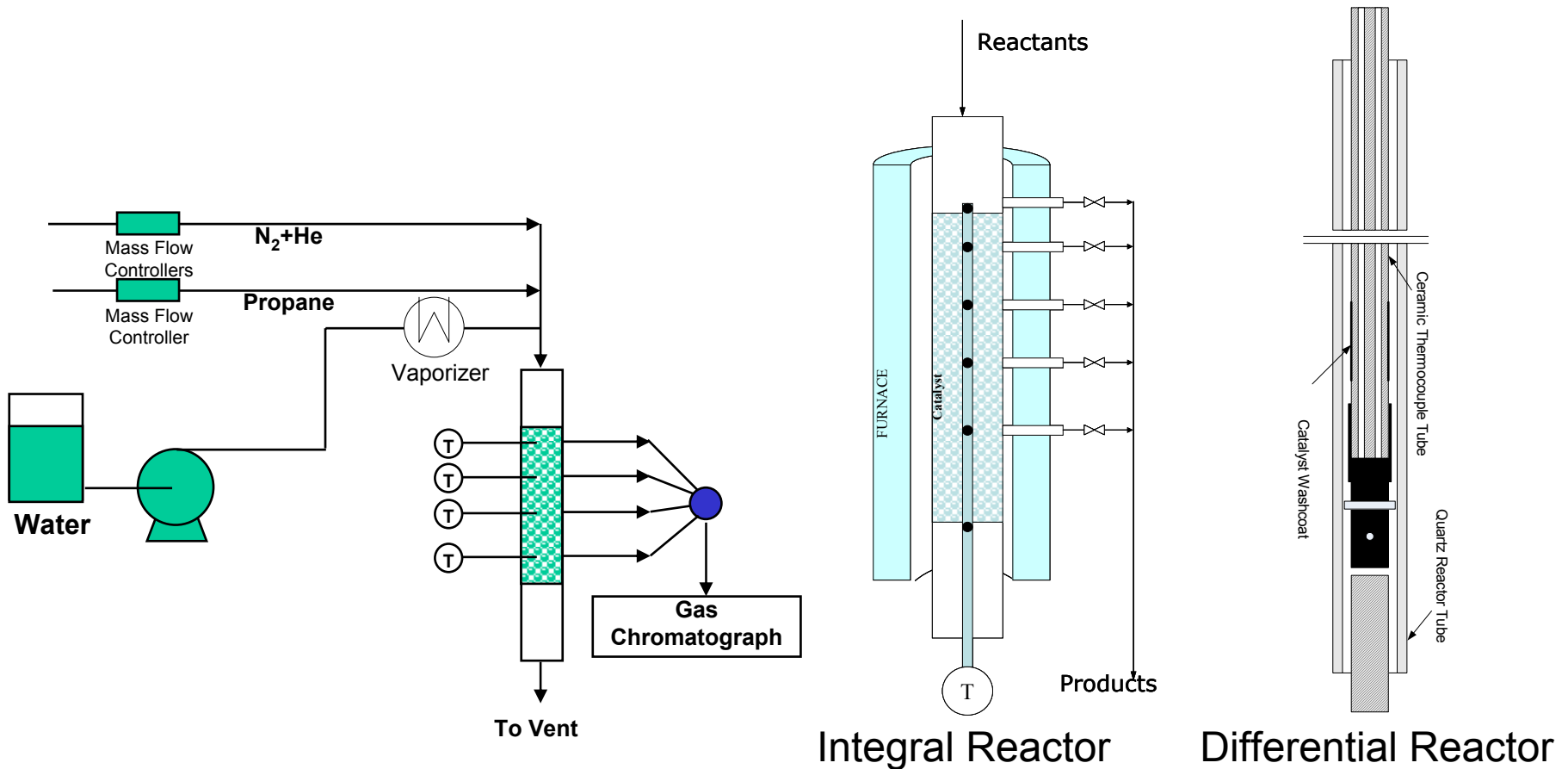
- (a): Fuel combustion needed to maintain energy balance
- (b): Reforming is exothermic, sensible heat lost with products
- (c): Combustion not needed, no sensible heat loss with products



- 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

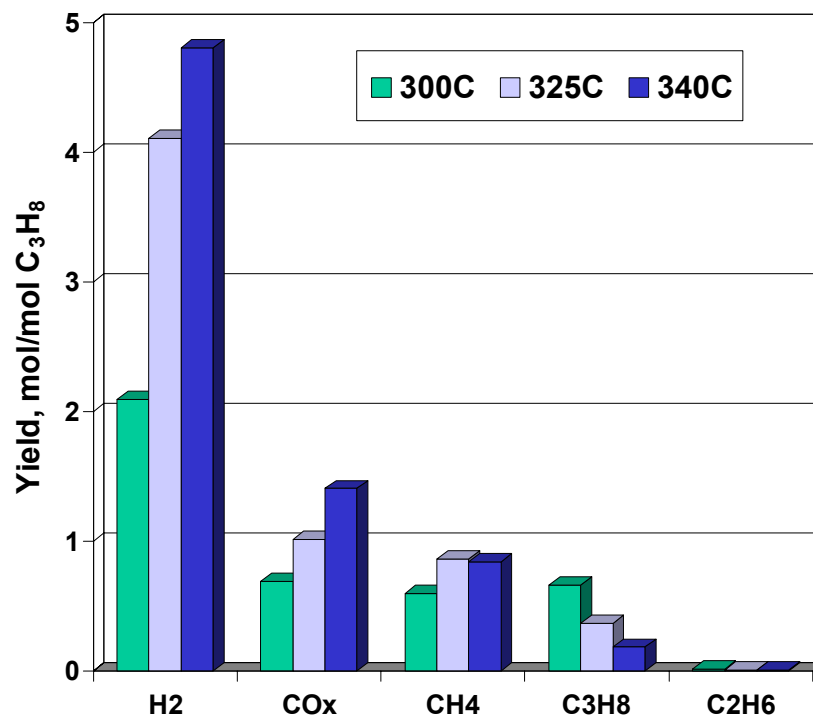


The catalyst is active at temperatures as low as 340°C

- **Propane Concentration in Feed:**
 - C₃H₈: 0.5% (wet); 1.7% (dry)
- **Propane Feed Rate:**
 - 20 ml/min (STP)
- **P = 1 atm**
- **H₂O:C Molar Ratio = 45**
- **GHSV = 122,000 per hour**
- **Catalyst : Rh/La-Al₂O₃**

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 ₂ H ₆	0.009	± 0.002	0.003	± 0.002
C ₃ H ₈	0.659	± 0.126	0.181	± 0.073

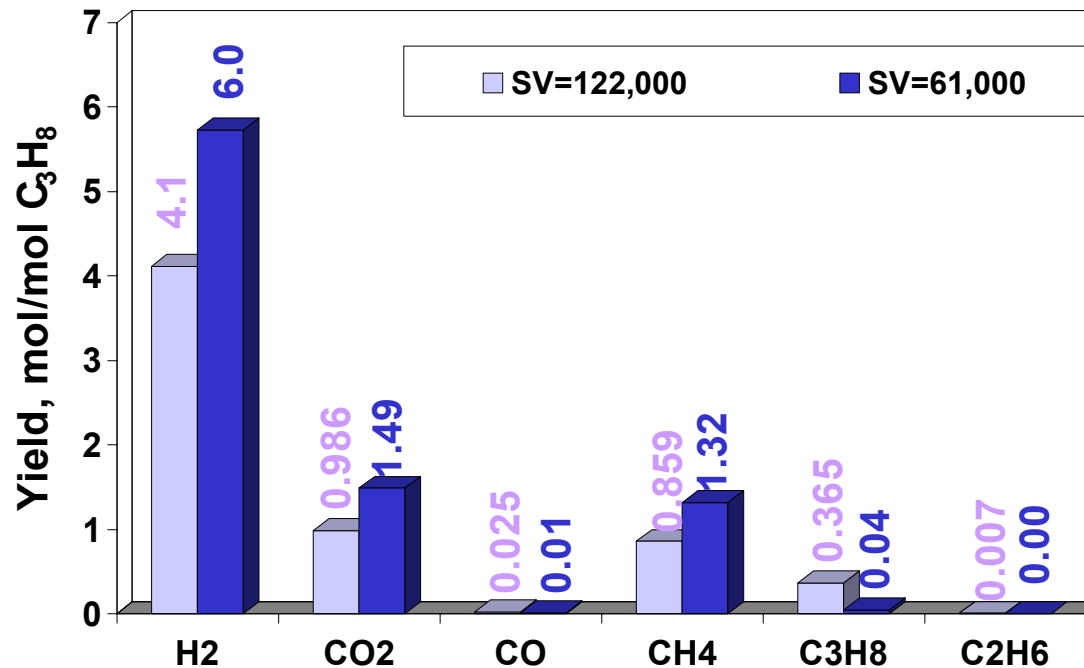
* Mol/(Mol of C₃H₈ Feed)



7

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

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- H₂O:C Molar Ratio = 45
- Catalyst : Rh/La-Al₂O₃



* Mol/(Mol of C₃H₈ 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

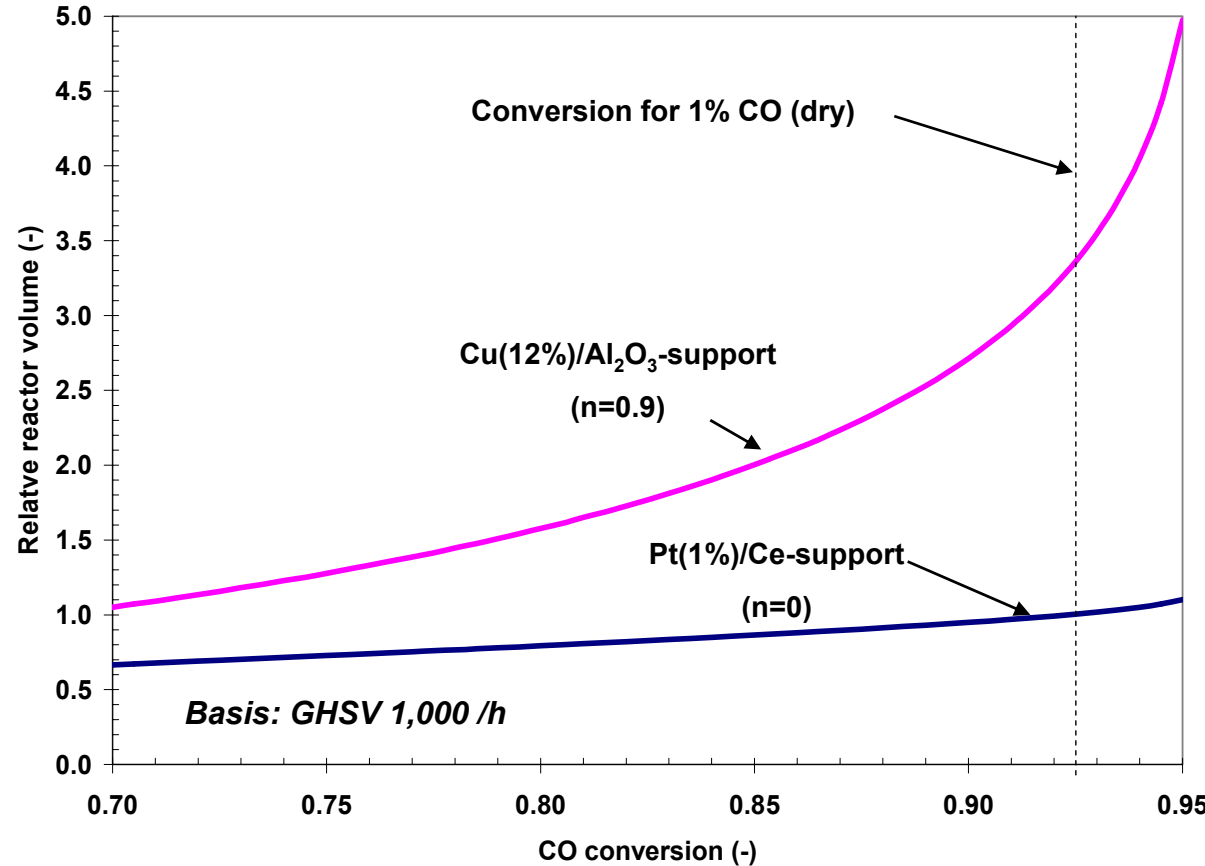
- I
 - Select a suitable WGS catalyst and establish its kinetics
 - Model the shift reactor under adiabatic, isothermal, and other temperature profiles
 - Design a laboratory reactor for experimental verification
 - Without membrane separation
 - Fabricate and test with temperature control to validate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

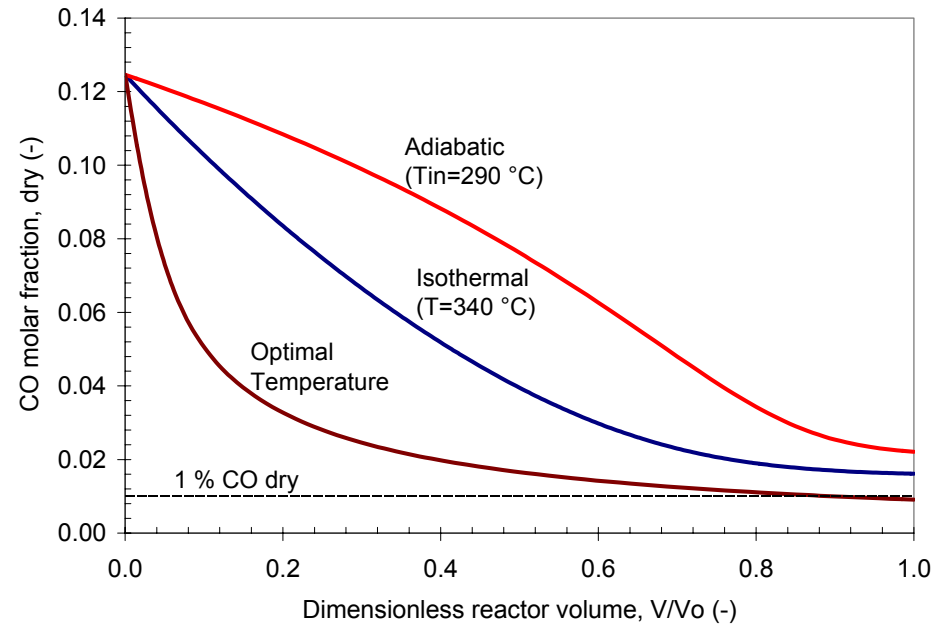
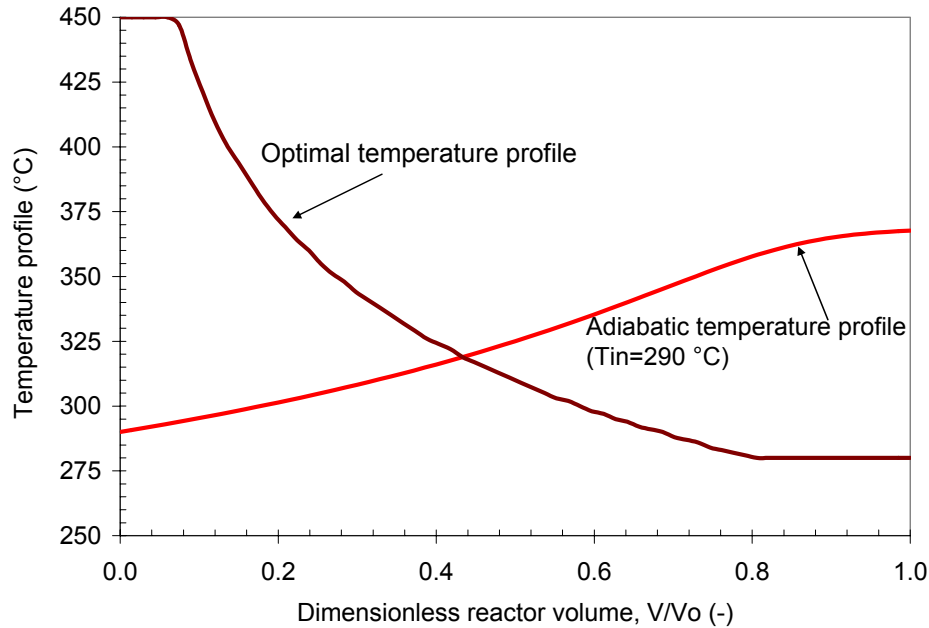
- Established kinetics for a catalyst: Pt-Re/Ce_{0.46}Zr_{0.54}O₂
CO order = 0

Case (S/C=3): CO₂ (5.7%), H₂O (27.6%), CO (10.9%), H₂ (55.8%)



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

A combination of reaction/heat exchange enhances WGS rates



Parameters:

Catalyst: Pt-Re/Ce (1% Pt)

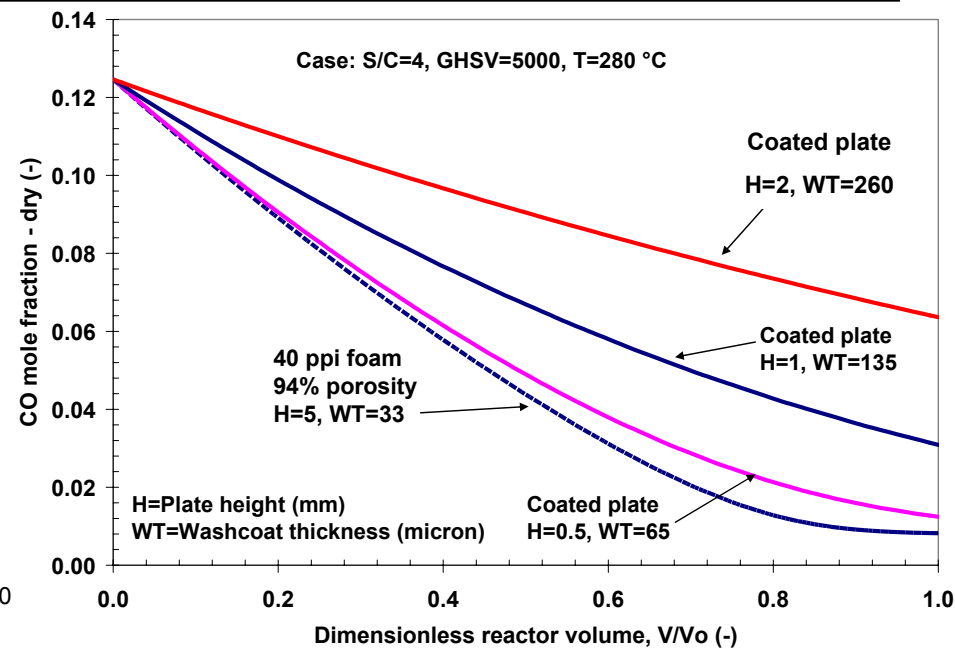
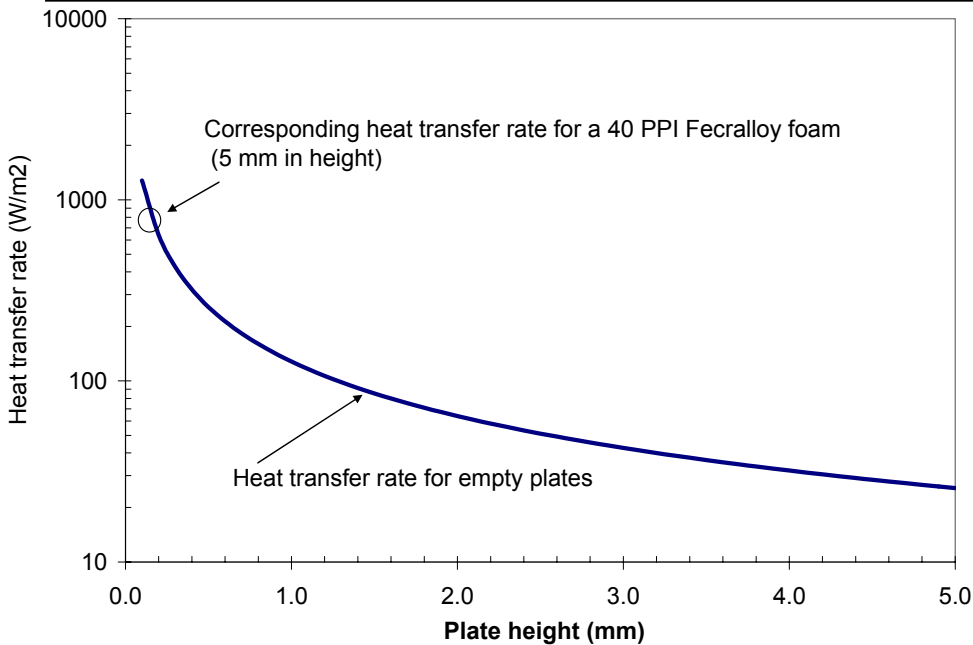
GHSV: 30,000 h⁻¹

S/C: 4.0

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

Case (S/C=4): CO₂ (6.3%), H₂O (36.3%), CO (7.9%), H₂ (49.2%)

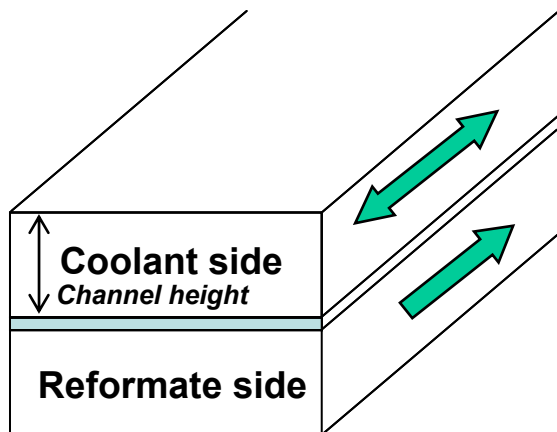
Foam support enhances heat transfer rates and reduces transport limitations



Foam support offers several advantages:

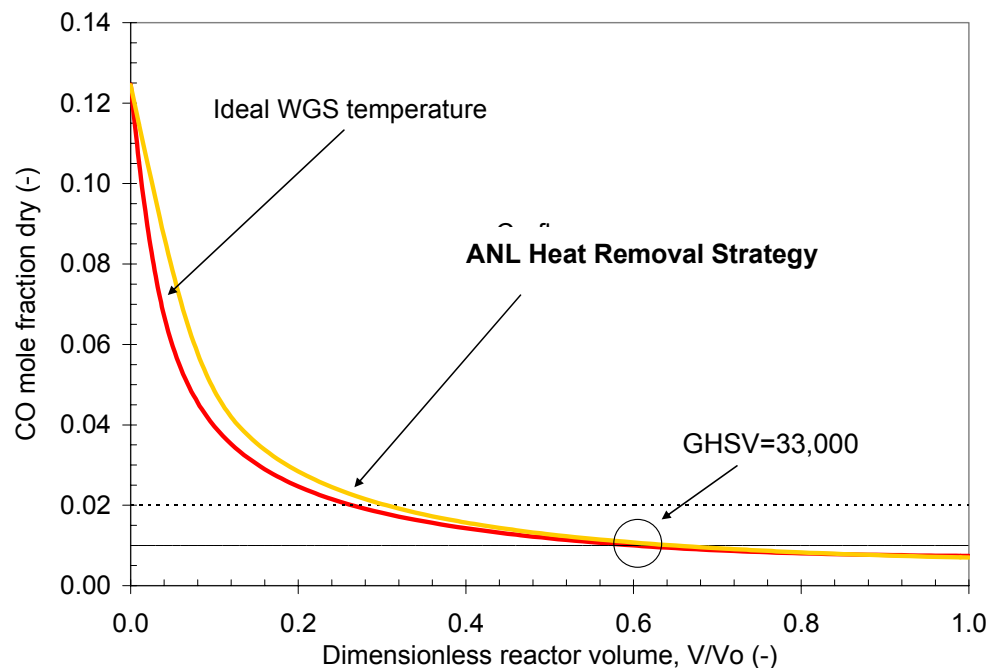
- Increases heat transfer rates between coolant/WGS sides
- Minimizes transport limitations for the WGS reaction by dispersing the washcoat into a high surface area support
- Can be co-sintered into different geometries if needed

A parallel plate geometry is advantageous for temperature control



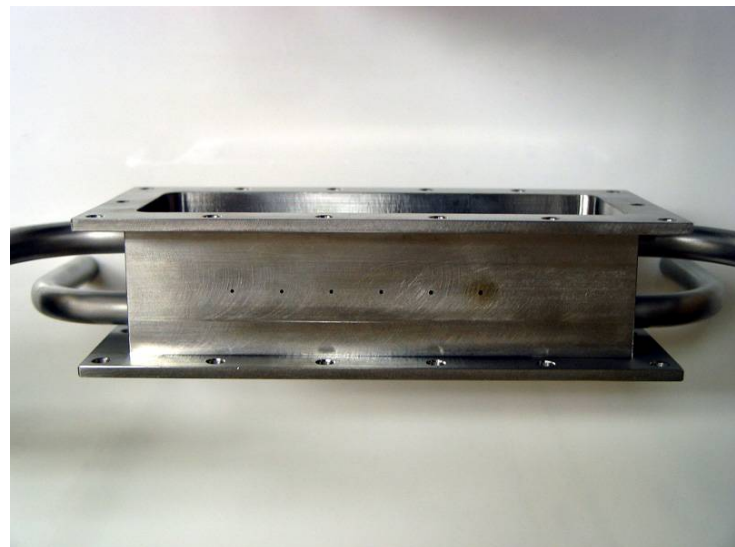
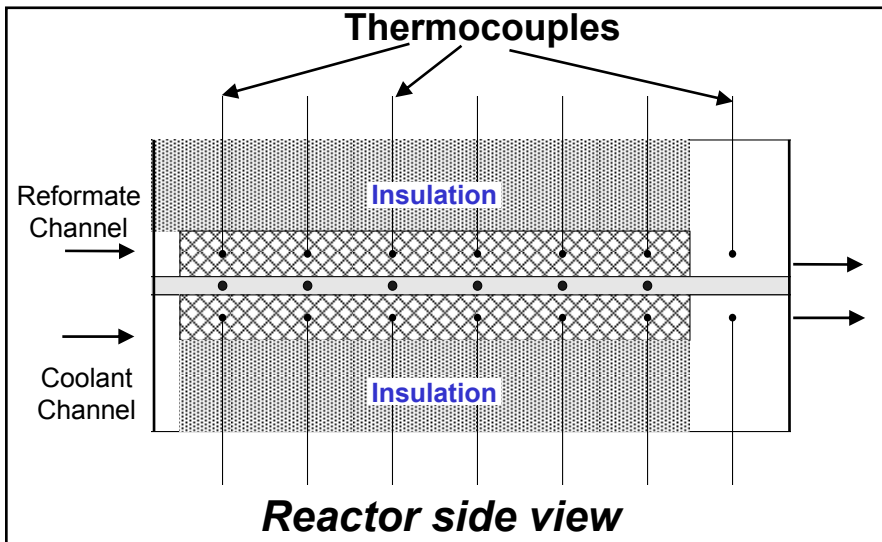
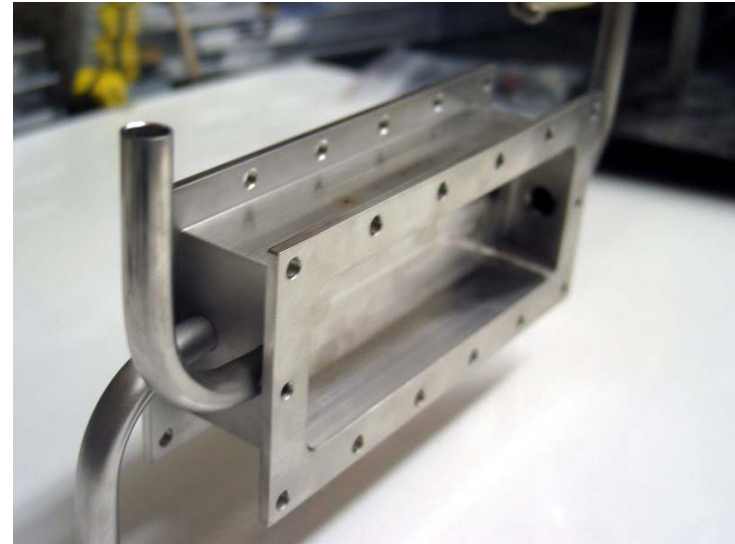
➤ A plate type reactor is a suitable reactor geometry to achieve an integrated reactor/heat exchanger

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

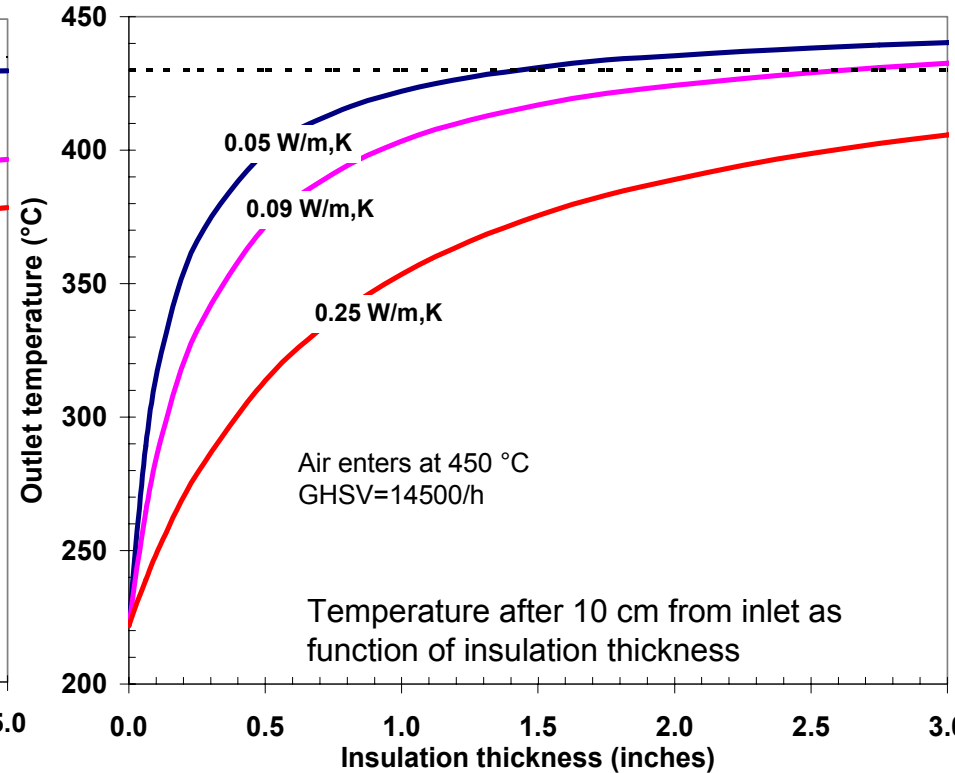
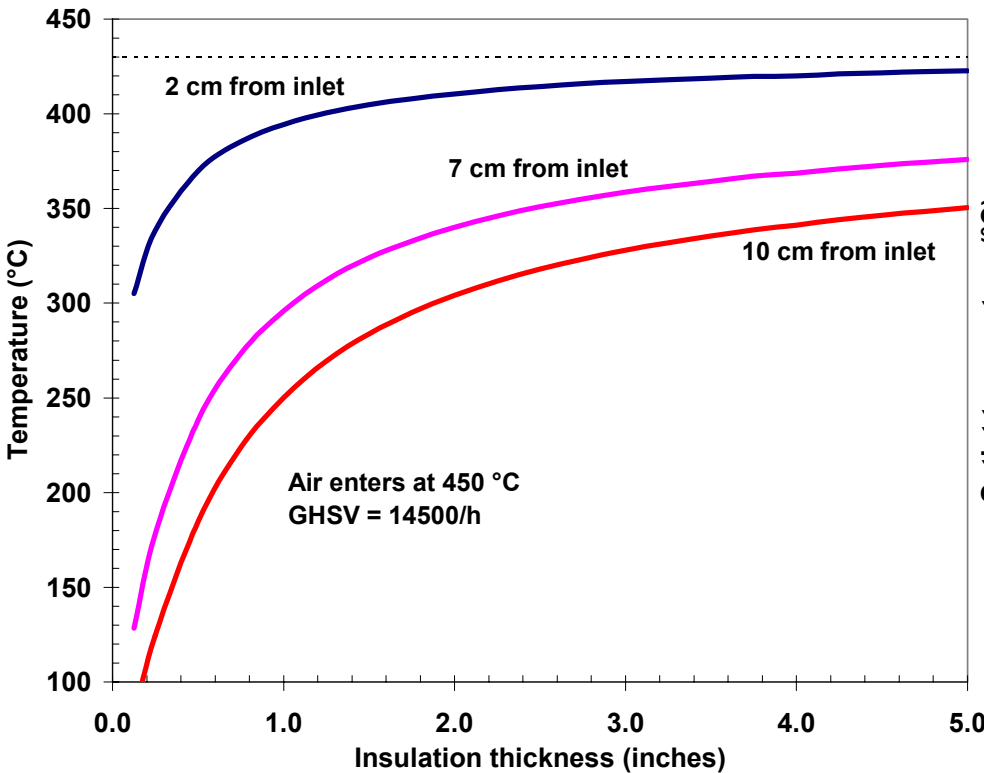


Catalyst:	Pt-Re/Ce (1% Pt)
GHSV:	20,000 hr ⁻¹
S/C:	4.0
WGS:	T _{in} =375°C
Coolant:	Air at 25°C

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



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

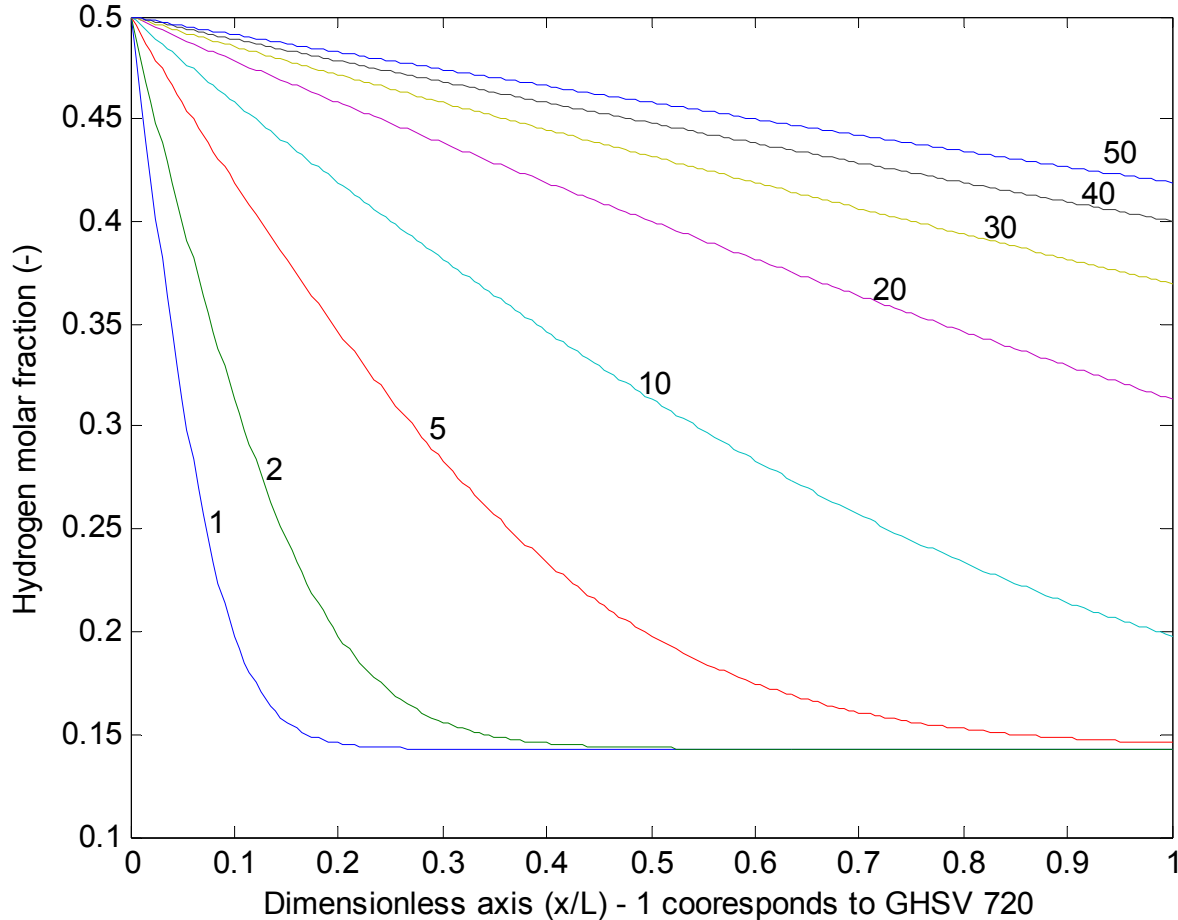


➤ The microreactor can lose heat despite good insulation. Heat losses must be compensated for with less flow of coolant

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

Thin membranes favor H_2 removal

H₂ permeation as function of membrane thickness (micron)



- Flux not limited by bulk diffusion

Reaction side:

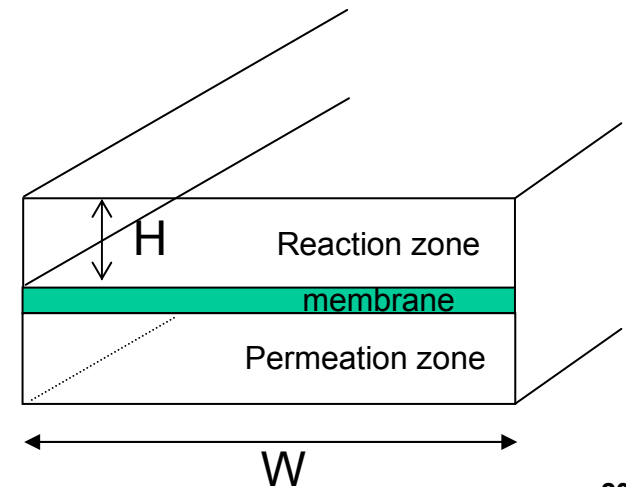
N_2 (0.5) H_2 (0.5), $L=10$; $W=2.54$;
 $H=0.5$ cm, $P=1$ atm
 $U_0=2$ cm/s, $m=0.0934$ g/min

Membrane:

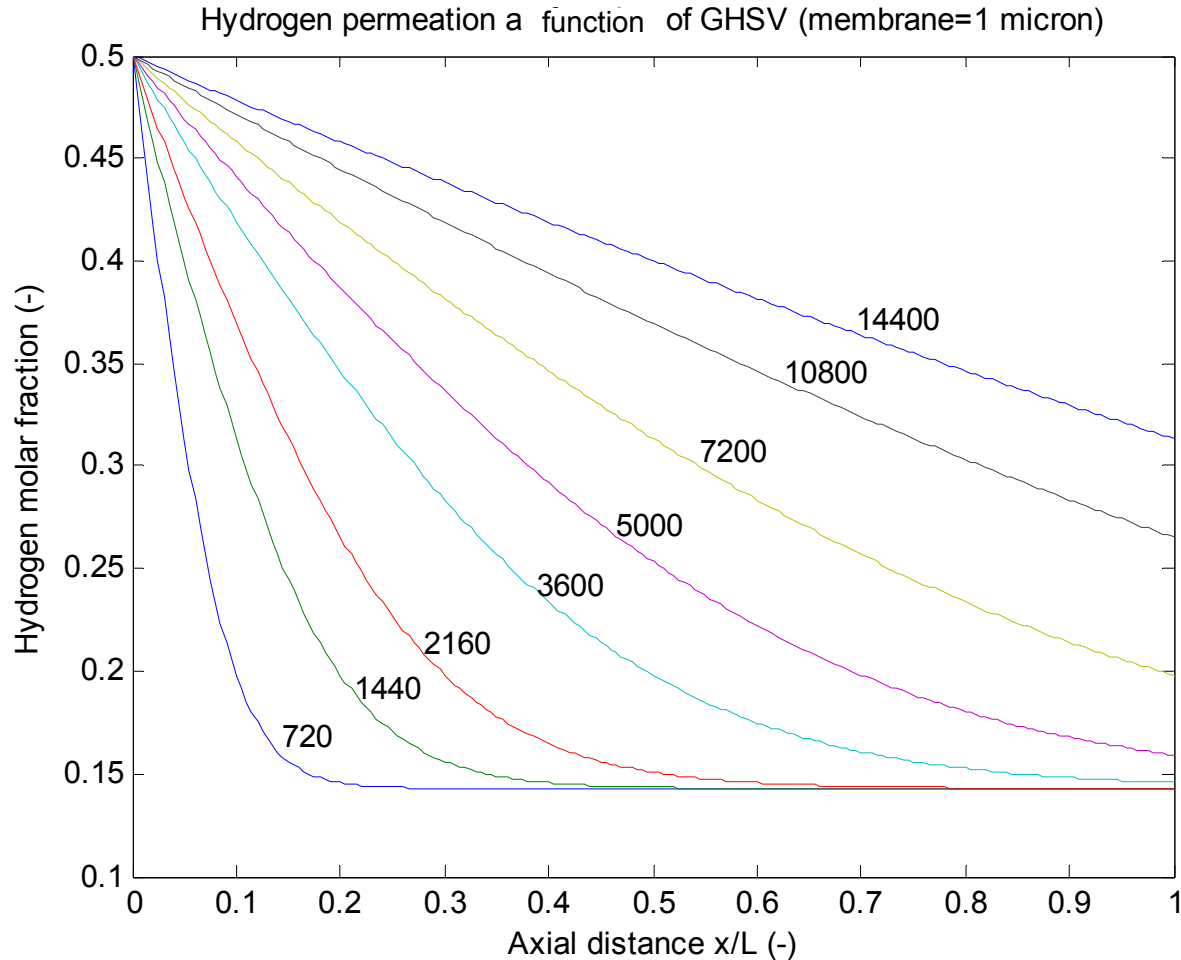
Pd (Basile et al), P_e (68 micron)
 $2.56e-5$ mol/($m^2, s, Pa^{0.5}$)

Permeation side:

N_2 (0.436 g/min), $L=10$; $W=2.54$;
 $H=0.5$ cm, $U_0=5$ 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,
 $U_0=2-40$ cm/s, $P=1$ atm

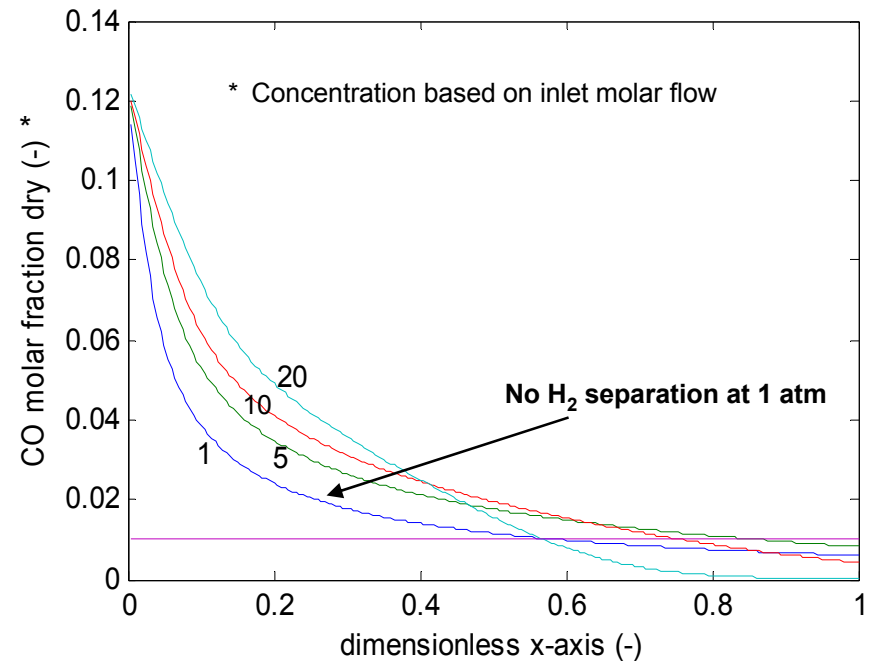
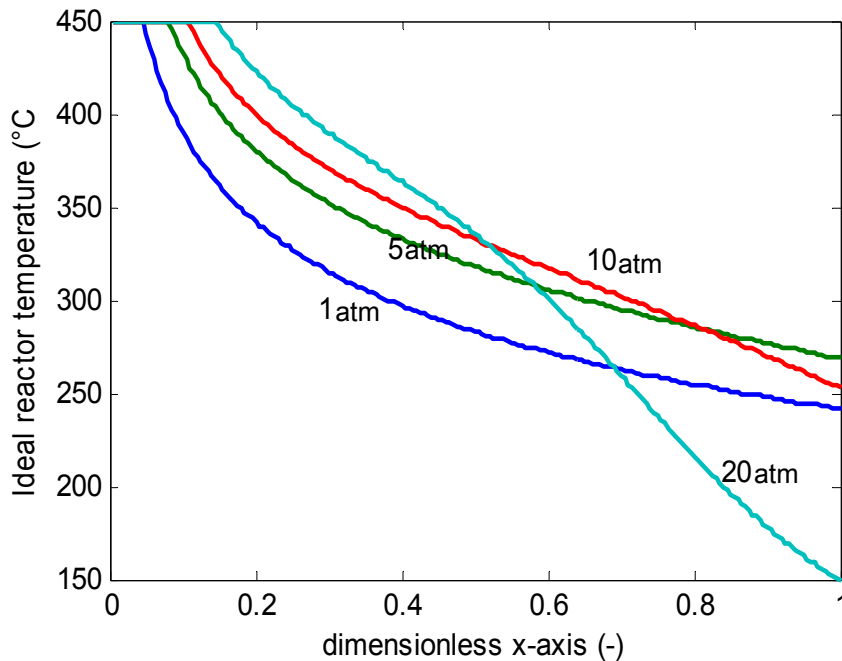
- **Membrane:**

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, $U_0=5-100$ cm/s, $P=1$ atm

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



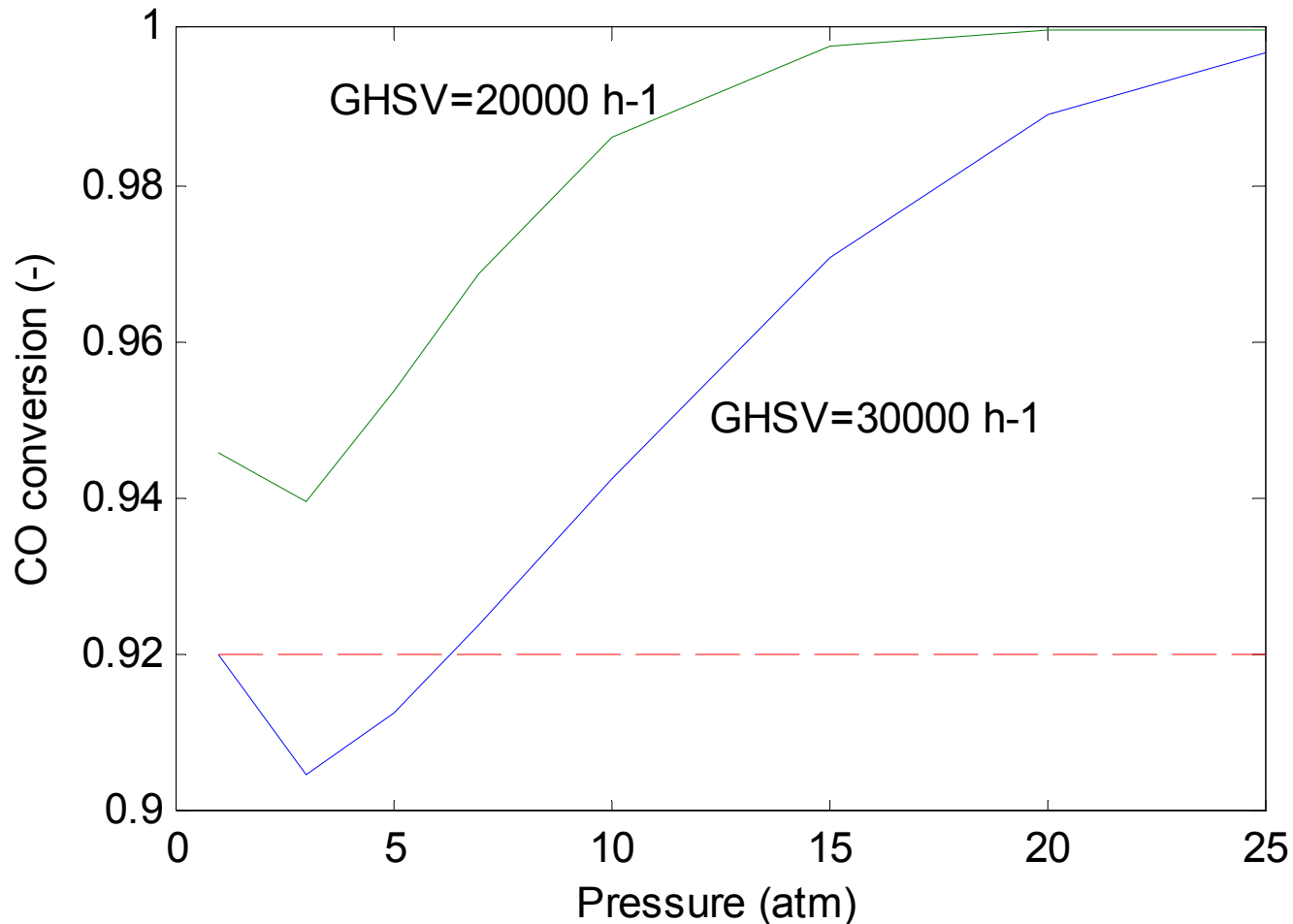
WGS reactor results with temperature control and membrane separation (Pd, 1 micron).
Dimensionless axis corresponds to a GHSV of 20000 h⁻¹.

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**
 - H₂ 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
 - *H₂ diffusion to membrane becomes predominant.*
 - Increasing pressure slows WGS kinetics due to inhibition of CO₂ and H₂
 - Due to slow hydrogen permeation, a membrane can worsen reactor performance without separation unless the pressure is high enough to compete with the CO₂ and H₂ 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