Composite Pd and Alloy Porous Stainless Steel Membranes for Hydrogen Production and Process Intensification

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June 8th, 2010

Project ID: PD007

Overview

Timeline

- ➔ Start : 5/7/2007
- ➔ Finish : 5/6/2010
- ➔ 100% Complete

Budget

- ➔ Total Project Cost: $ 1,602,922
  - DOE Share: $ 1,256,226
  - Recipient Share: $ 346,696
- ➔ Funding Received:
  - FY08: $ 442,785
  - FY09: $ 420,638
  - FY10: $ 392,803
- ➔ DOE Award #: DE-FC26-07NT43058
- ➔ DOE Project Manager: Dr. Daniel Driscoll

Subcontractor

- ➔ **Adsorption Research Inc. (ARI)**

Barriers

- ➔ **Barriers Addressed:**
  - Long-term selectivity stability & re-producibility
  - H_2 flux targets
  - Mixed gas & long-term WGS reaction studies
  - Steady-state & unsteady-state CMR modeling simulations
  - Process intensification analysis & process control strategies
  - Absorbent selection & PSA system build-up and testing
- ➔ **Technical Targets****

	H_2 Flux [scfh/ft^2] §	Temp. [°C]	ΔP max. [psi]	H_2 Purity	Sulfur Tolerance
2010	200	300-600	400	99.5%	20 ppm
2015	300	250-500	800-1000	99.9%	>100 ppm
§ @ 100 psi ΔP H_2 partial pressure					
CO Tolerance: Yes; WGS Activity: Yes					

** DOE-NETL Test Protocol v7 – 05/10/2008

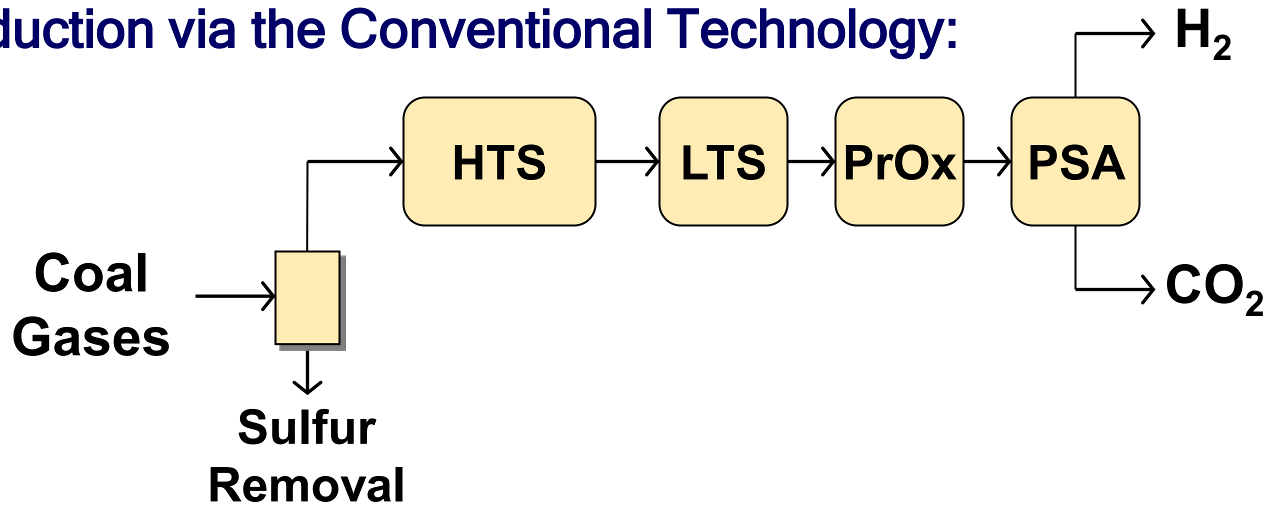
WPI

Project Objectives & Relevance

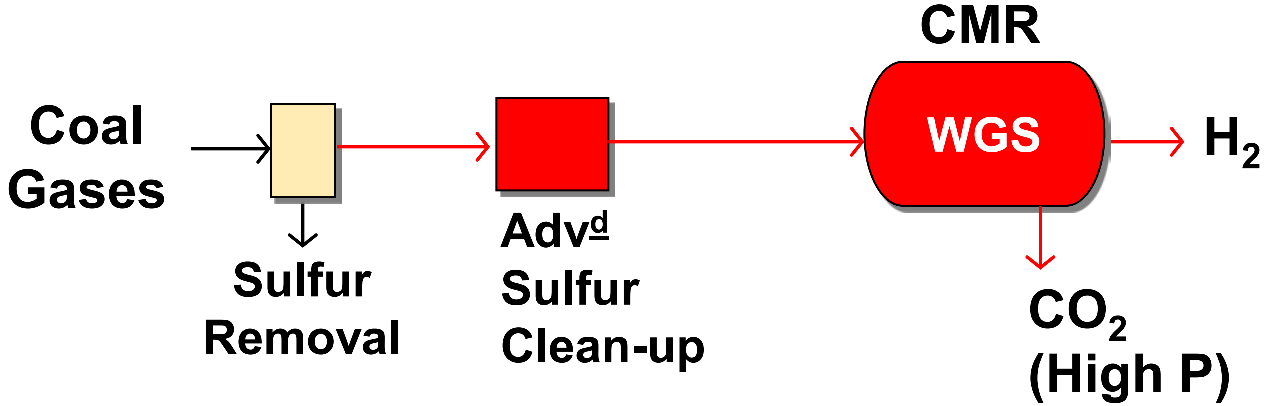
- Synthesis of composite Pd and Pd/alloy porous Inconel membranes for WGS shift reactors with long-term thermal, chemical and mechanical stability with special emphasis on the stability of hydrogen flux and selectivity
- Demonstration of the effectiveness and long-term stability of the WGS membrane shift reactor for the production of fuel-cell quality hydrogen
- Research and development of advanced gas clean-up technologies for sulfur removal to reduce the sulfur compounds to <2 ppm
- Development of a systematic framework towards process intensification to achieve higher efficiencies and enhanced performance at a lower cost
- Rigorous analysis and characterization of the behavior of the resulting overall process system, as well as the design of reliable control and supervision/monitoring systems
- Assessment of the economic viability of the proposed intensification strategy through a comprehensive calculation of the cost of energy output and its determinants (capital cost, operation cost, fuel cost, etc.), followed by comparative studies against other existing pertinent energy technologies

Approach: Coal Gasification & CMR

H_2 Production via the Conventional Technology:



Novel Catalytic Membrane Reactor (CMR):



Project Schedule & Milestones

Tasks	Year 1				Year 2				Year 3			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
	Months											
	3	6	9	12	15	18	21	24	27	30	33	36
Gas Clean-up & Fast PSA using Structured Adsorbent			M1 ✓		G1 ✓							
						M2 ✓						
										M3 ✓		
Membrane Synthesis		M4 ✓										
				M5 ✓				G2 ✓				
Membrane Characterization & Reactor Performance						M6 ✓						
										M7 ✓		
Membrane Reactor Modeling			M8 ✓									
Process Intensification					M9 ✓							
Process Control System; Design & Implementation								M10 ✓				
Process Monitoring System; Design & Implementation										M11 ✓		
Program Management & Reporting												

Membrane Properties & Permeation Test Set-up

- **Membrane:**

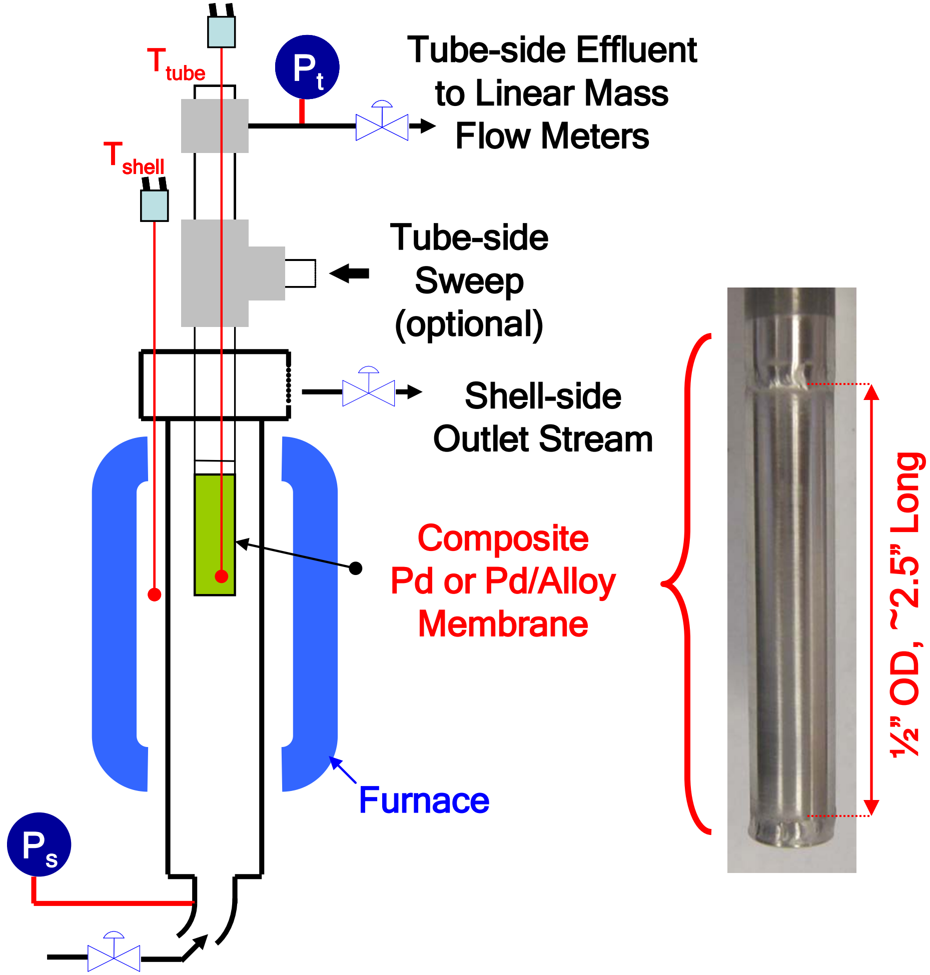
  Pd supported on porous Inconel (media grade 0.1 µm)

- **Method of Preparation:** Electroless Plating

- **Geometry:**

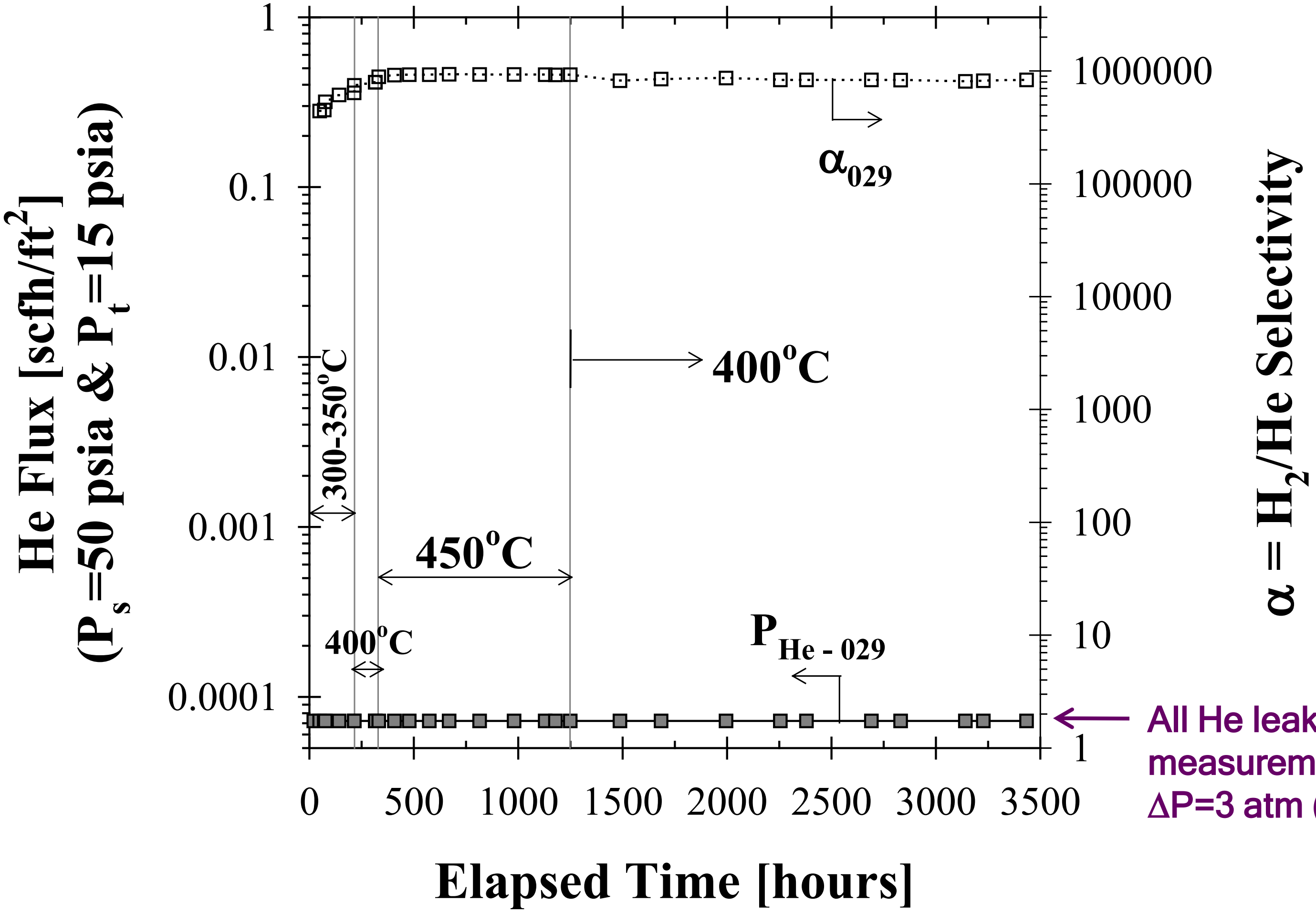
  Tubular (Plated on the outside of a tube)

- **Membrane Area ≈ 25 cm^2**



Similar setup equipped w/ pre-heater, mixer, cold trap & GC was utilized for the mixed gas & WGS reaction tests

Long-Term Selectivity Stability



All He leak measurements at ΔP=3 atm (P_t=1 atm)

Excellent long-term H_2/He selectivity stability was achieved over a total testing period of ~3550 hours (>147 days).

Membrane #029 7.6 μm Pd/Inconel

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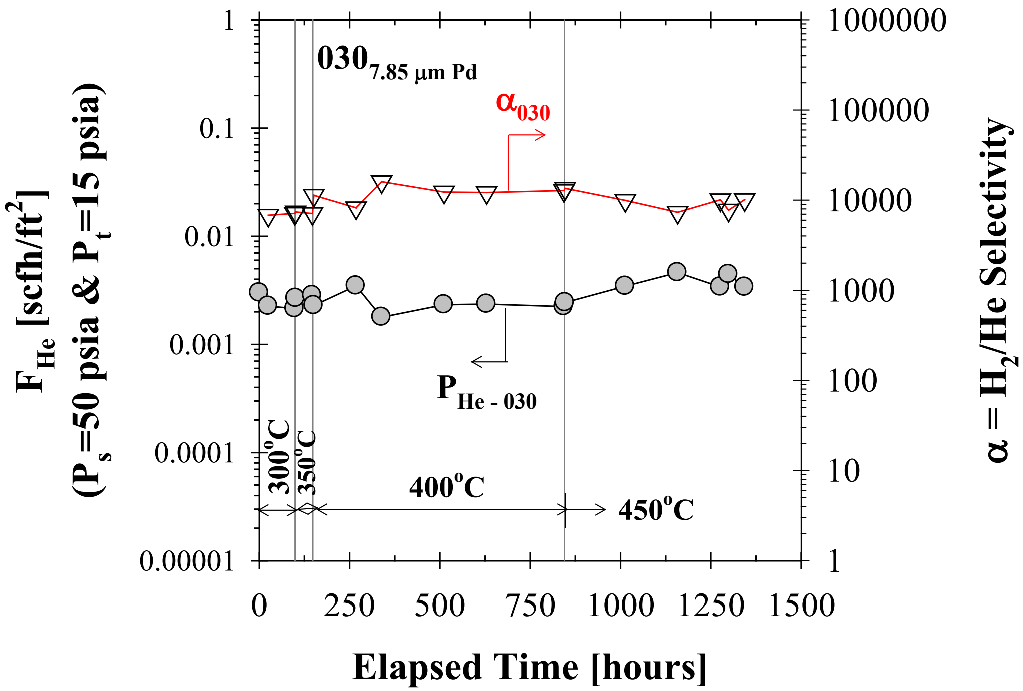
Reproducible Long-Term Selectivity Stability:

Membranes #030$_{7.9\ \mu m\ Pd}$, #031$_{7.0\ \mu m\ Pd}$ & #033$_{8.7\ \mu m\ Pd}$



#029$_{7.6\ \mu m}$	• H_2/He ≅ ∞ at 450°C • H_2 purity: ≥ 99.999% • 3550 hours (>147 days)
#030$_{7.9\ \mu m}$	• H_2/He ≅ 10000 at 450°C • H_2 purity: ≥ 99.99% • 1400 hours (>58 days)
#031$_{7.0\ \mu m}$	• H_2/He ≅ 4500 at 450°C • H_2 purity: ≥ 99.99% • 2200 hours (>90 days)
#033$_{8.7\ \mu m}$	• H_2/He ≅ 9725 at 450°C • H_2 purity: ≥ 99.99% • 800 hours (>32 days)

Excellent leak mitigation and <u>re-producible</u> long-term H_2/He selectivity stability via high temperature pre-Annealing (at 550°C/He/12h) and surface Polishing (pAP) treatments

➢ Also delivered a ½" OD, 12" long Pd/Inconel membrane for DoD-Ballards

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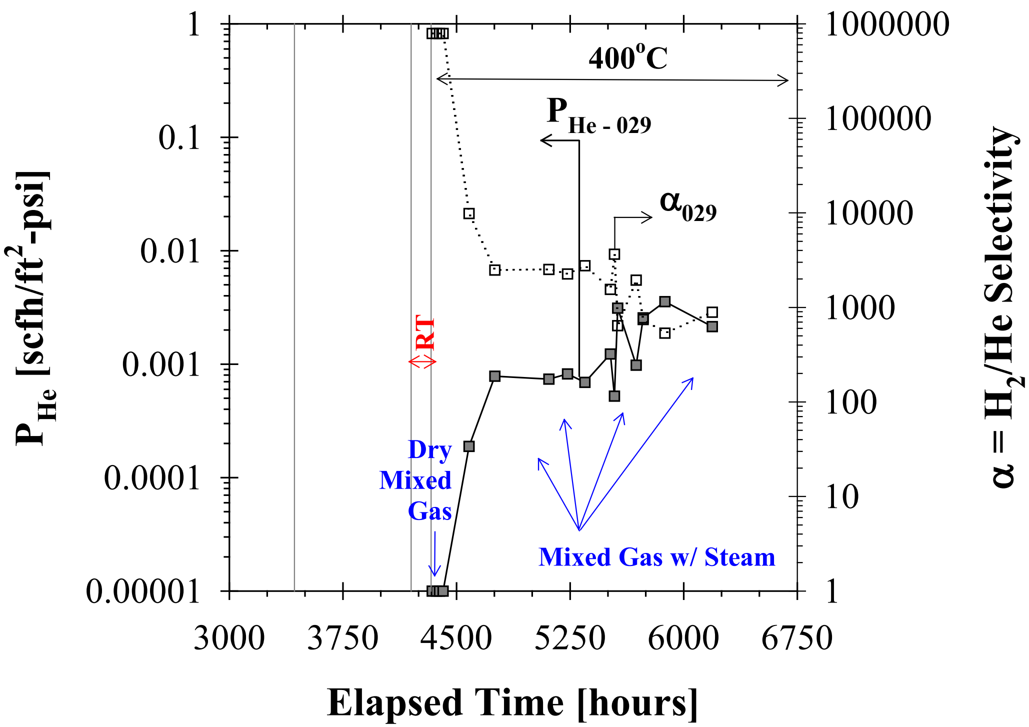
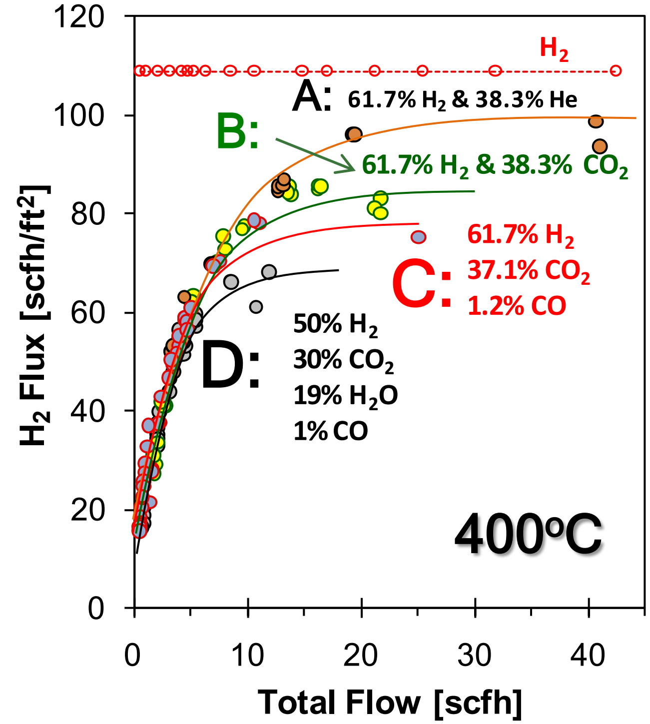
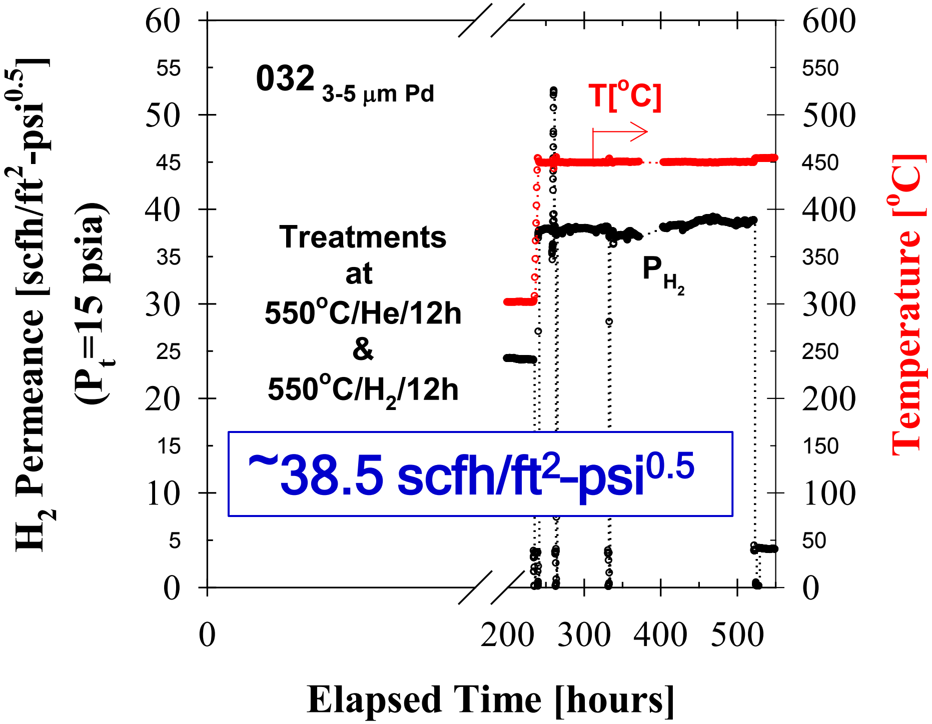
Mixed Gas Testing of Membrane #029$_{7.6\ \mu m\ Pd}$

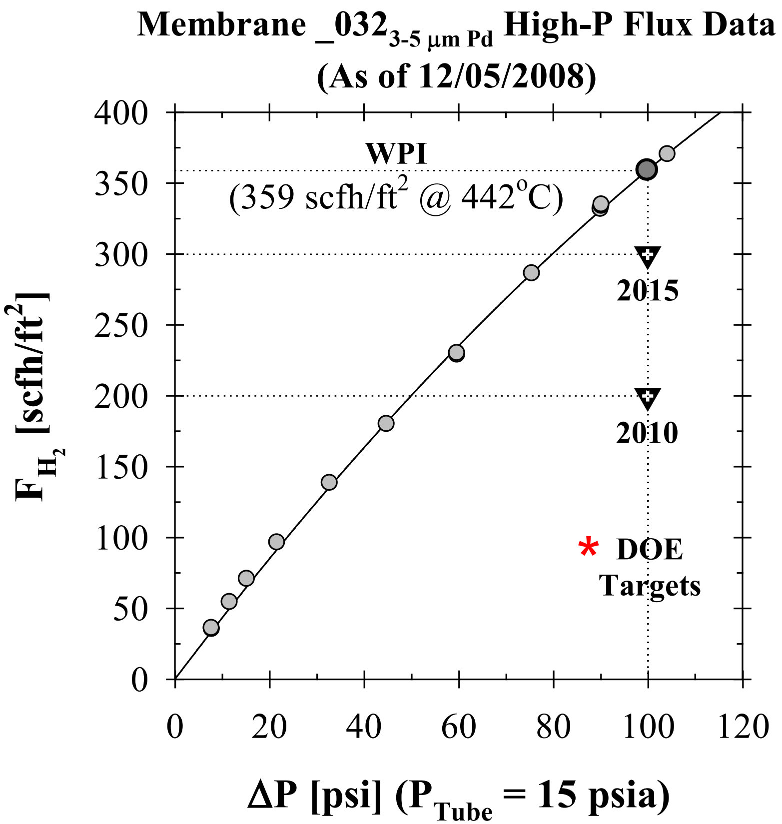




- Mixed gas permeation testing for an additional ~3000 hours at ~400°C & at a ΔP range of 1-14 atm (P_{Low}=1 atm) w/ stable H_2 Flux, H_2/He Selectivity & no significant increase in He leak after successive testing at 400°C
- Below 10 scfh, high recovery (> 90%) and no significant/additional inhibiting effect of ~19% steam or CO on H_2 flux
- Permeate: H_2 only, no other gases were detected
- Retentate: High-pressure CO_2 !!!

Progress Towards DOE H_2 Flux Targets



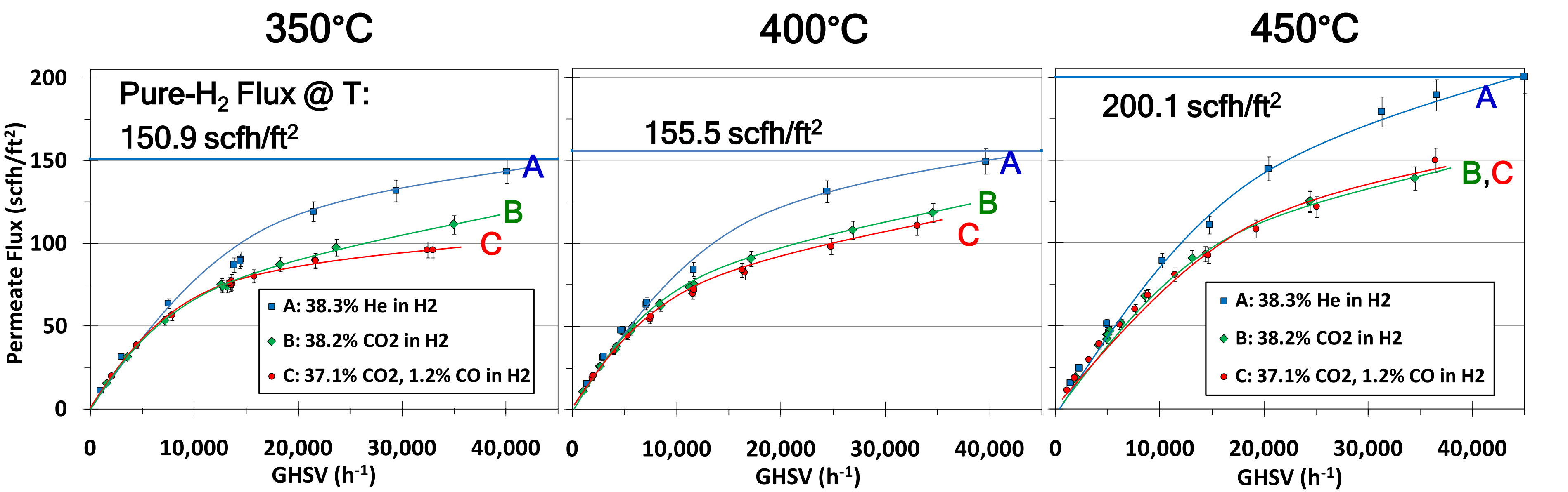


➢ At 442°C & at a ΔP of 100 psi (P_{High}=115 psia & P_{Low}=15 psia), the H_2 flux of the 3-5 μm thick Pd/Inconel membrane #032 was as high as ~359 scfh/ft² at the end of ~285 hours of testing with H_2/He selectivity of ~450 (H_2 purity ≥99.8%), which exceeded the DOE's 2010 and 2015 H_2 flux targets.

* DOE-NETL Test Protocol v7 – 05/10/2008

DOE $Target_{2015}$:300 scfh/ft² @ ΔP (H_2) =100 psi, T = 300-600°C

Mixed Gas Testing of AA-6 18.1 μm Pd

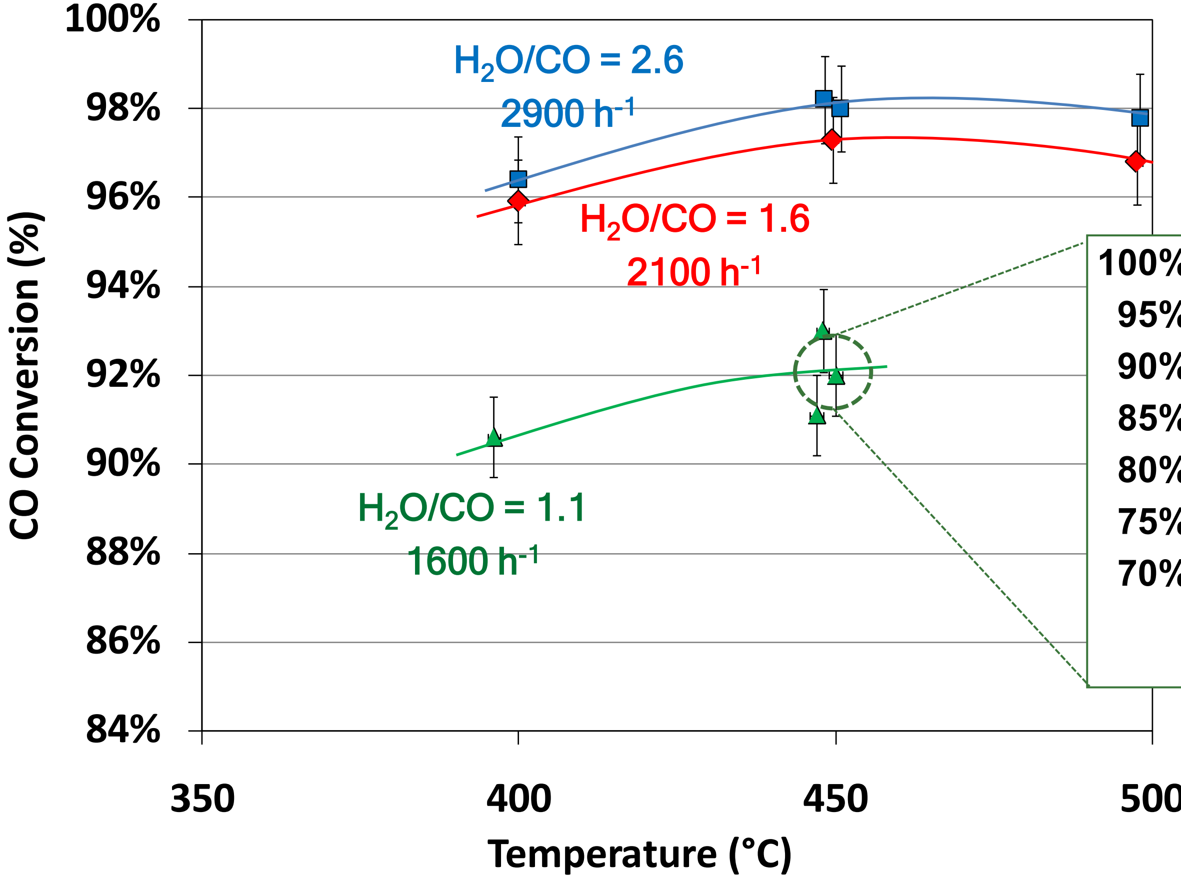


P_{Total} = 212 psia
P_{H2} = 116 psia

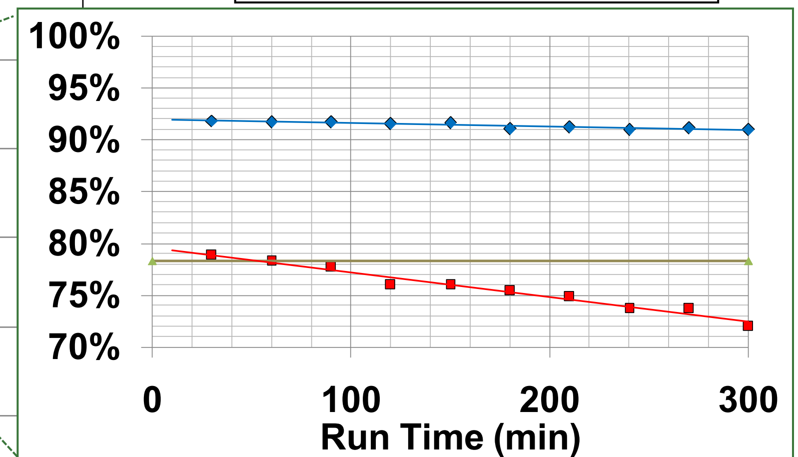
(Membrane: AA-6)
Area = 0.025 ft²
Selectivity > 2200

- Temperature dependant permeance inhibition due to CO observed at 350 and 400°C, insignificant above 400°C
- Gas boundary layer resistance observed by comparison of Mixture A (high diffusivity H_2/He) and Mixture B (low diffusivity H_2/CO_2)
- H_2 recovery of up to 92% achieved at low GHSV

WGS CMR$_{18.1\ \mu m\ Pd}$: CO & H_2O Feed



P_{Total} = 212 psia
(Membrane: AA-5)
Selectivity > 1700

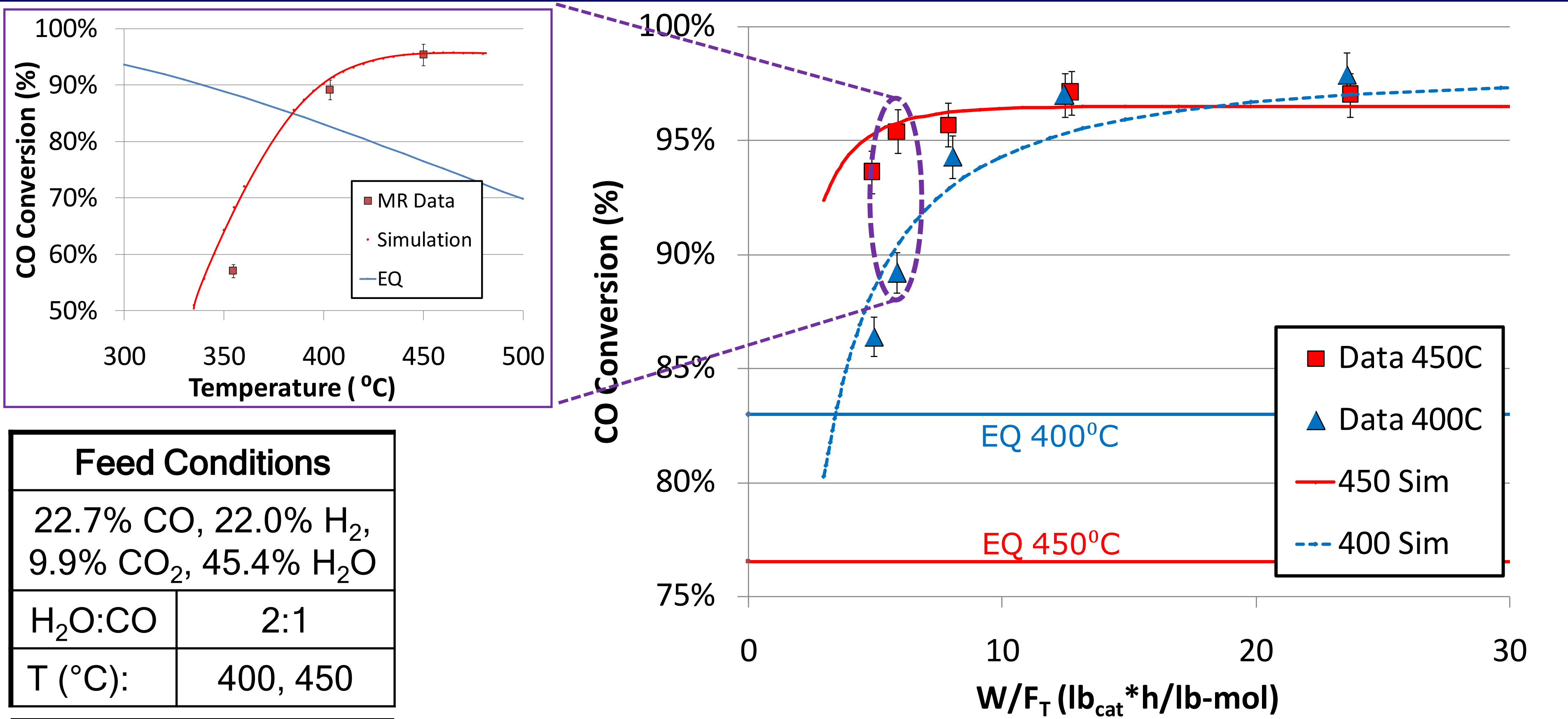


Coking on membrane surface

- High CO conversion, in significant excess of EQ, was achieved for all experiments
- Evidence of coke formation was only observed in experiments with low H_2O/CO = 1.1

Flux @ 450°C = 35.7 scfh/ft^2 (ΔP of 14.7 psi)

WGS $CMR_{11.6\ \mu m\ Pd}$: Syngas Feed



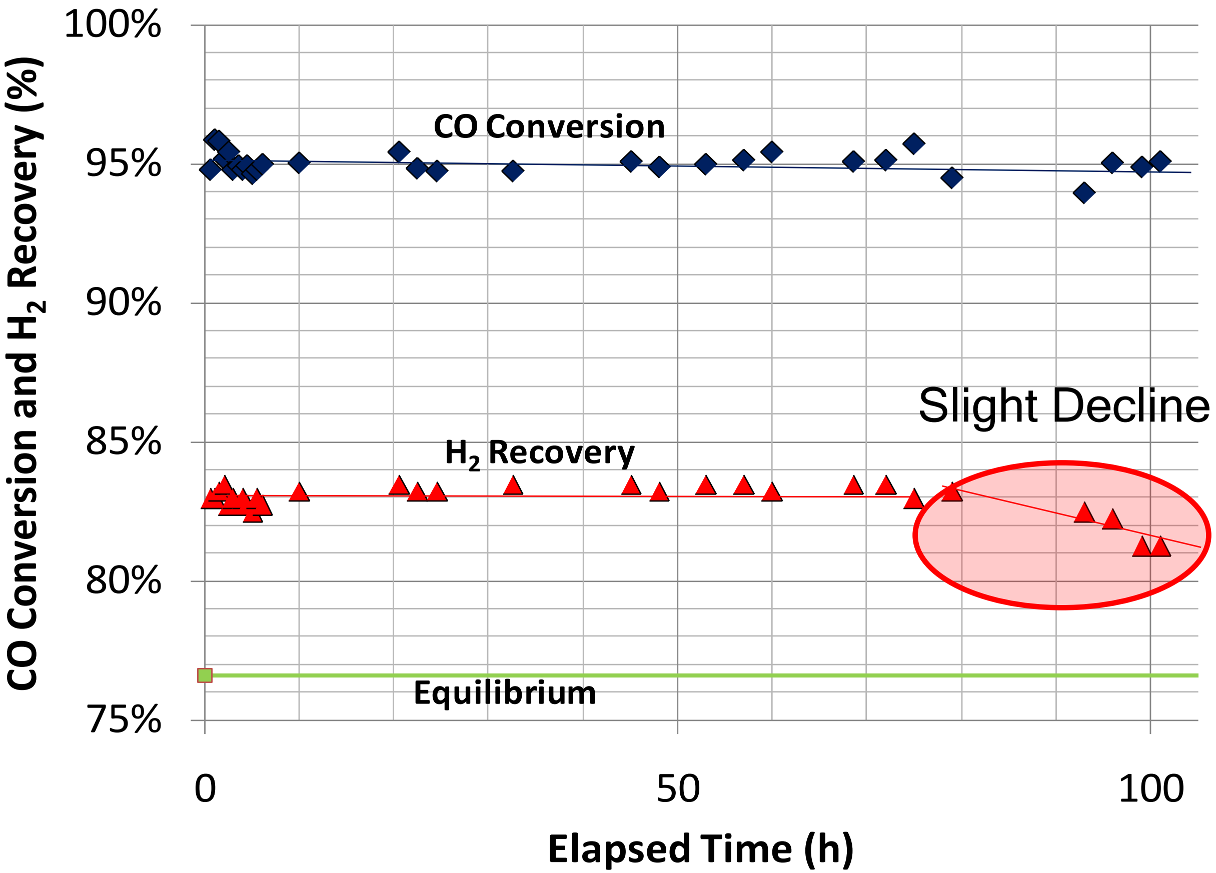
Feed Conditions	
22.7% CO, 22.0% H_2, 9.9% CO_2, 45.4% H_2O	
H_2O:CO	2:1
T (°C):	400, 450

P_{Total} = 206 psia
(Membrane: AA-8)
Selectivity > 1500

- **CO conversion approached 'dynamic equilibrium' as time factor increased above ~12 lb_{cat}*h/lb-mol**
- **At low time factor, H_2 recovery and CO conversion were limited by the H_2 permeance of the membrane**

Flux @ 450°C = 44.0 scfh/ft^2 (ΔP of 14.7 psi)

Long-term WGS $CMR_{13.1\ \mu m\ Pd}$



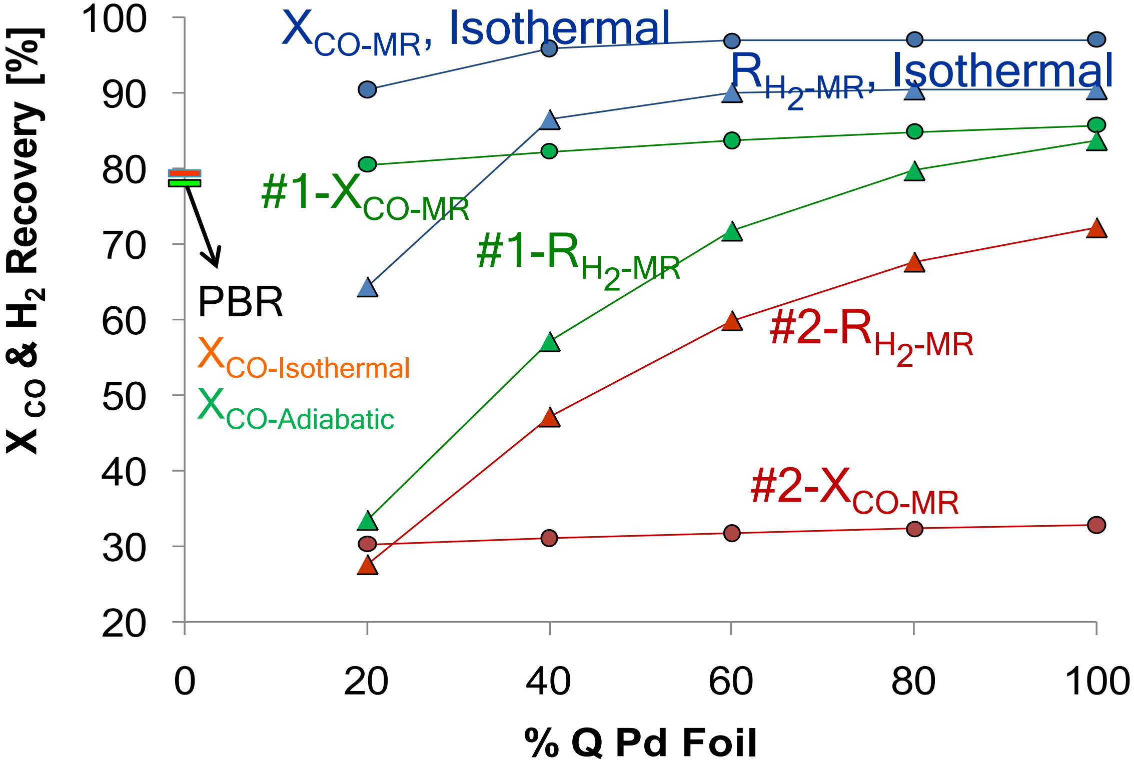
Feed Conditions	
22.7% CO, 22.0% H_2, 9.9% CO_2, 45.4% H_2O	
H2O/CO	2.0
GHSV (h^{-1}):	4500
T (°C):	450

Membrane: AA-8R	
Selectivity (F_{H2}/F_{He})	
Initial	4000
After WGS Experiment	400 (-90%)
Permeance ($scfh/ft^2psi^{0.5}$)	
Initial	27.9
After WGS Experiment	26.6 (-4.6%)

- Stable CO conversion and H_2 recovery were observed for up to 80 hours
- Stable H_2 permeance after WGS test
- Significant selectivity decline after test

Flux @ 450°C = 44.3 $scfh/ft^2$ (ΔP of 14.7 psi)

Process Intensification - Effect of Permeability



Feed: Slurry-feed coal-derived syngas*

Adiabatic:
#1 T_{feed}=300°C
#2 T_{feed}=260°C

P_{Rxn}= 220 psia
P_{Tube} 14.7 psia
$T_{Iso-Rxn}$ = 450°C
$\alpha_{H_2/He}$ = ∞
GHSV = 8081h^{-1}

- The permeability had a more prevalent effect on the adiabatic reactor H_2 recovery.
- The adiabatic reactor could achieve high X_{CO} and R_{H_2} only at low inlet flow rates due to admitting the feed at low temperature to protect the membrane.

  (X_{CO} = 85% and R_{H_2} = 90% at GHSV = 1600h^{-1}).
- Isothermal MR performance surpasses the adiabatic MR for the current reaction conditions.

*Hla et al., Chem. Eng. J.146,(2009) 148-154

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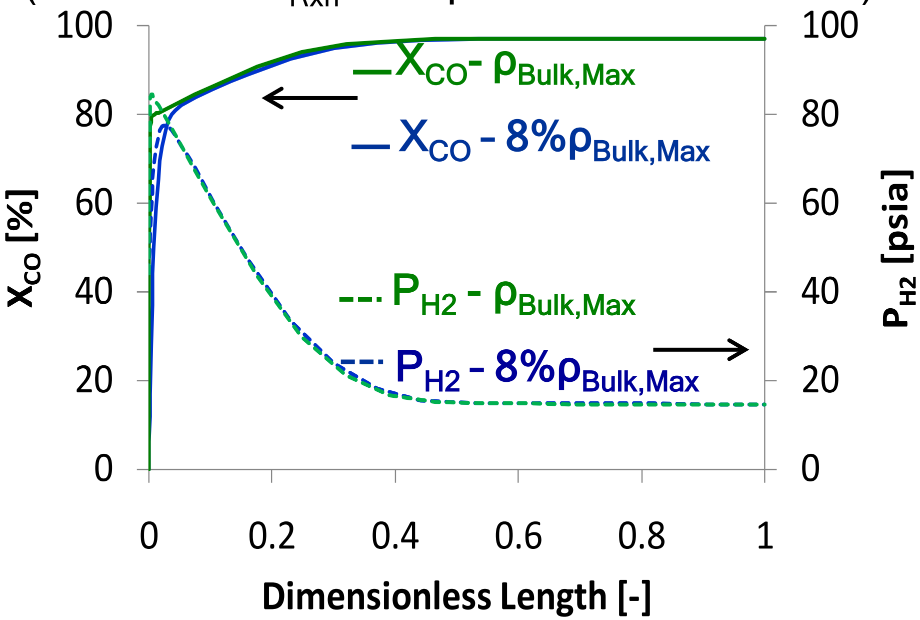
Process Intensification - Effect of Bulk Catalyst Density

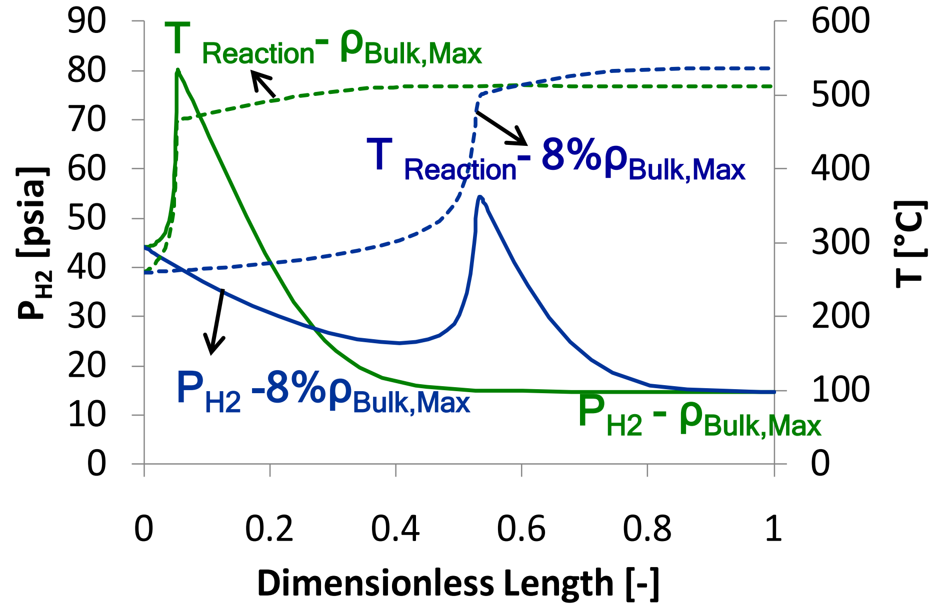
Isothermal MR

(T = 450°C / P_{Rxn}= 220psia / GHSV =1600h^{-1})



Adiabatic MR

(T_{feed} = 260°C / P_{Rxn}= 220psia / GHSV =1600h^{-1})



- Packing the reactor with less catalyst would not affect the production specifications and would reduce the cost.
- ↓ρ_{Bulk} ➡ Controlled T_{Rxn} rise ➡ $V_{effective}$ increased from 40% to 80% of the V_{total}

$$\rho_{Bulk,max} = \frac{W_{Cat,Max}}{V_{Reactor}}$$

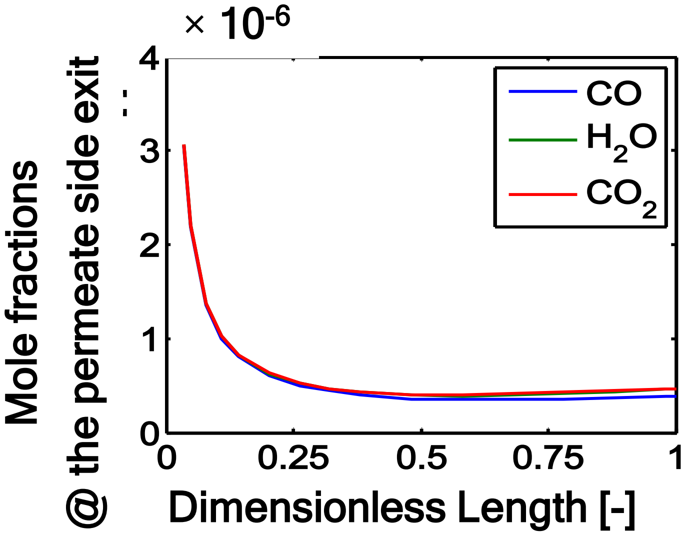
GHSV =3200h^{-1}	Isothermal				Adiabatic			
%$\rho_{Bulk,Max}$	8		100		8%		100%	
	PBR	MR	PBR	MR	PBR	MR	PBR	MR
X_{CO}[%]	79.5	97	79.5	97	17.2	34	78.2	95.2
F_{H2} [scfh]	0.89	1.1	0.89	1.1	0.47	0.5	0.87	1.1

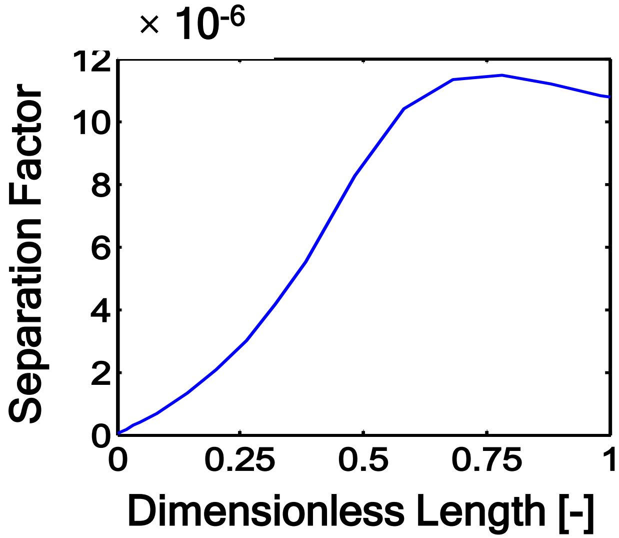
Process Intensification - Model for the membranes with $\alpha_{H_2/He} \neq \infty$

Dusty Gas Model (DGM) for the multi-component gas diffusion

- $H_2 + CO + H_2O + CO_2$

$$S_F = \frac{\left[x_{H_2}/\left(x_{CO} + x_{H_2O} + x_{CO_2}\right)\right]^{Permeate\ Side}}{\left[x_{H_2}/\left(x_{CO} + x_{H_2O} + x_{CO_2}\right)\right]^{Reaction\ Side}}$$





X_{CO} [%]	H_2 Purity [%]
97	99.999869

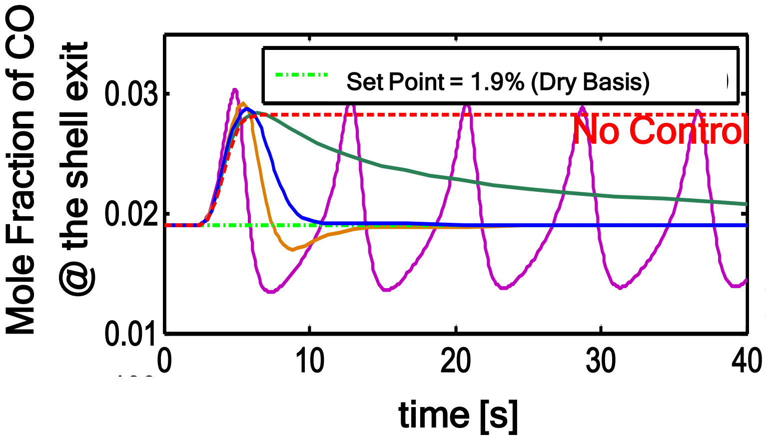
- $\alpha_{H_2/He}$ does not affect X_{CO} within the range of 50 – 50×10^3.
- Experimental $\alpha_{H_2/He} \geq 1000$ (Data obtained under this project)
- No detectable CO in the permeate side of the Pd-based membrane with $\alpha_{H_2/He} = 1000$

Process Control
Regulator and Servo Mechanism Problems

The main objective of the proportional integral controller was to reduce the CO fractions at the reactor exit by manipulating the inlet steam flow rate to enhance the MR performance by increasing the CO conversion. (Assume $\alpha_{H_2/He} = \infty$)

Regulator Problem [Disturbance rejection]

P_T = 220 → 147 psia



Controller tuning for K_c-RP

Optimum K_c = 0.006 and τ_I = 1.25 s

X_{CO} = 97.1% & $H_2O:CO$ = 3.3

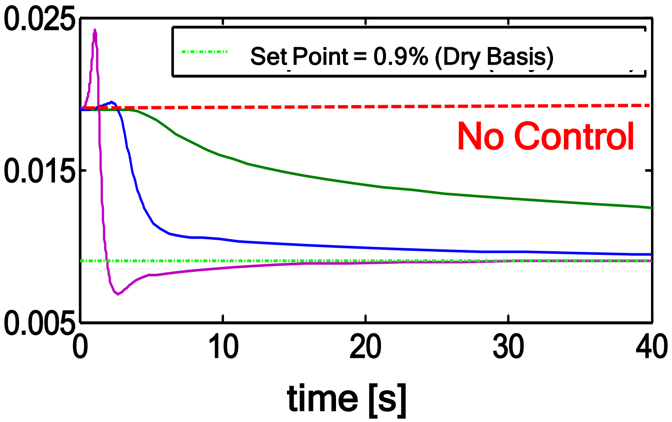
Tuning Targets

- Smooth transition
- Energy efficient
- (Less steam)
- Fast & stable response
- No oscillation

Servo Mechanism Problem [Set-point tracking]

Set point = 1.9 → 0.9 % CO^{Dry} @ Rxn side exit

PBR f_{CO}=7% (Dry basis)



Controller tuning for K_c - SP

Optimum K_c =0.009 and τ_I = 1 s

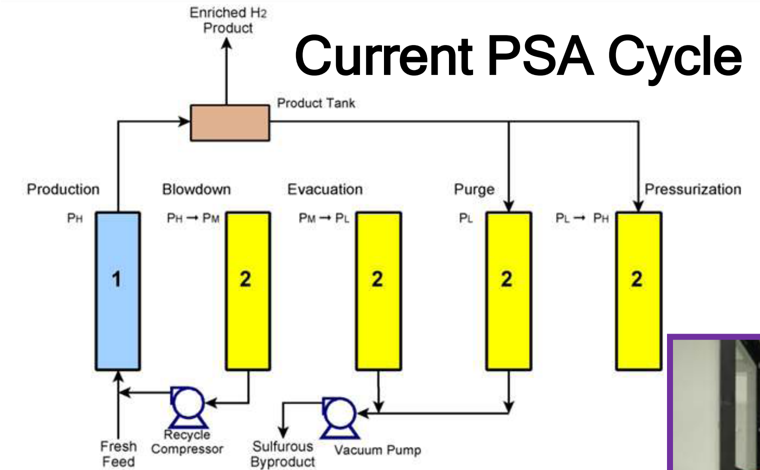
X_{CO} = 97.3% & $H_2O:CO$ = 6.8

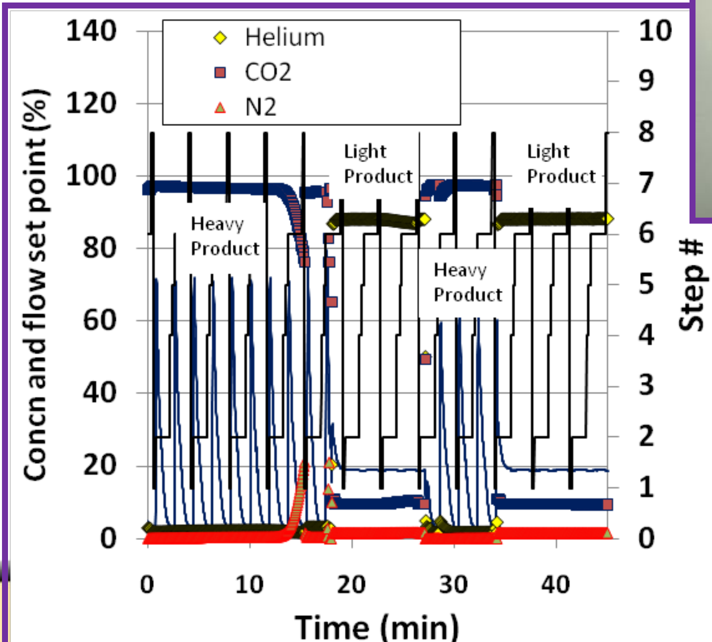
Collaborations

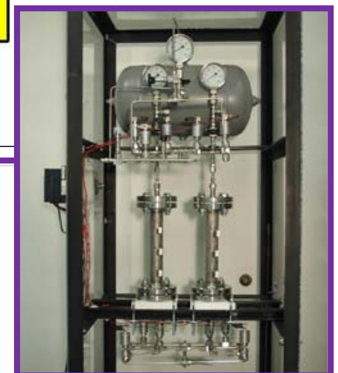
Adsorption Research Inc. (ARI); sub

(Through telephone conversations and quarterly report to the prime)

- ARI completed adsorption selection & property measurement for Zeolite 5A, Zeolite 13X, NaY and Hisiv3000
- The equilibrium isotherms measurements & the transient uptake tests to evaluate both short-time and long-time diffusion behavior of the adsorbents 5A, 13X, NaY and Hisiv3000 were conducted at 200 and 230°C for CO_2, COS, H_2S and the water vapor.
- Completed the pressure swing adsorption (PSA) system and demonstrated the cyclic operation at 200°C & 200 psia with 5A to ensure the accuracy of the simulations.
- For a three-component mixture, showed a recovery of 99+% of helium when a recycle of the blow-down gas was used







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Proposed Future Work (FY10 & FY11)

- Scaling-up to 1" & 2" OD Membranes
- Continue WGS reaction and mixed gas testing studies
- Complete 2010 technical target screening and qualification tests* phase 1 and phase 2
- Synthesis of thin separation layers to achieve higher H_2 flux using support with minimum mass transfer resistance
- Continue Pd/Au alloying studies to improve H_2 flux
- Conduct long-term sulfur poisoning & recovery experiments
- Further refinement & improvement of the CMR model
- Continue process intensification & performance assessment analyses coupled with process control strategies
- Initiate economical analysis for the proposed process intensification framework
- Complete testing of a Pressure Swing Adsorption (PSA) system (sub: ARI)

* Table 4 in DOE-NETL Test Protocol v7 – 05/10/2008

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Project Summary

- Achieved excellent long-term H_2/He selectivity stability of essentially infinite over a total testing period of ~3550 hours (>147 days) at 300-450°C & at a ΔP of 15-100 psi (P_{Low}=15 psia).
  - Conducted an additional ~3000 hours of mixed gas permeation testing (61.7% H_2, 37.1% CO_2 & 1.2% CO w/ and w/o 19% Steam) at 400°C & ΔP of 1-14 atm (P_{Low}=1 atm) that resulted in stable H_2 flux and minimal inhibition effects of steam, CO_2 and CO at T > 400°C & low total flow rates (≤ 5000 sccm).
- At 450°C, the long-term H_2/He selectivity stability was successfully re-produced with several membranes with H_2 purity ≥99.99% over a testing period of 30-90 days.
- Flux of ~359 scfh/ft^2, which exceeded the DOE's 2010 and 2015 H_2 flux targets [T=442°C & ΔP of 100 psi (with P_{Low}=15 psia)].
- Reduced the number of synthesis steps for the large scale preparation for potential commercialization of WPI's composite Pd-based membrane production technologies.
- Completed mixed gas & WGS testing of composite Pd/Inconel membranes:
  - Effects of temperature dependent CO inhibition and gas boundary layer mass transfer resistance were isolated in mixed gas experiments.
  - 98% CO conversion and 81% H_2 recovery were achieved in a 18.1 µm thick Pd-based CMR operated at 450°C, ΔP=200 psi (P_{Low}=15 psia) and $GHSV_{stp}$ = 2900 h^{-1}, with a CO and steam feed, exceeding the equilibrium conversion of 93%.
  - 95% CO conversion and 83% H_2 recovery were achieved for over 80 hours of WGS testing in a 13.1 µm thick Pd-based CMR operated at 450°C, ΔP=200 psi (P_{Low}=15 psia) and $GHSV_{stp}$ = 4500 h^{-1}, with syngas feed, exceeding the equilibrium conversion of 76%.

Project Summary

- Successfully completed steady-state MSR & WGS reaction modeling studies & process intensification analysis:
  - Studied the effect of permeability in Adiabatic & Isothermal membrane reactor, Adiabatic feed temperature, catalyst loading and changes in CO conversion, and the effect of selectivity on H_2 purity and CO conversion by utilizing the Dusty Gas Model.
- Successfully completed unsteady-state WGS reaction modeling studies and implemented process control strategies:
  - Characterized the reactor's dynamic behavior via detailed simulation studies based on the lumped reactor model approximation & showed that the transient state ended in 10 seconds with $X_{CO,Iso}$ = 97% when the coal-derived syngas feed was used.
  - Model-based analysis of the automatically controlled MR was able to recover the disturbed system due to pressure drop from 220 to 147 psia in 20 seconds and kept $X_{CO,Iso}$ at 97%. The CO fraction of 2% was reduced to 1% with the application of the servo mechanism controller.
  - The retentate stream consisted of mostly CO_2 and H_2 would be ready to be sequestered at high pressure after the energy value of the remaining H_2 is used.
- Completed property & isotherm measurements for the selected adsorbents (Sub, ARI).
- Completed the PSA system construction and initiated PSA testing at 200°C and a feed pressure of 200 psia (with P_{low}=1 atm) (Sub, ARI).

Project Summary Table: Permeation Results

	DOE Targets§		Current WPI Membranes (1/2" OD, 2.5" Length, ~24 cm^2)					
	2010	2015	#025R	#027	#029	#030	#031	#032
Flux [scfh/ft^2]	200	300	65.9	36.1	166	178	26.6	359
ΔP (psi) H_2 partial pressure (P_{Low}=15 psia)	100*	100*	15	15	100	102	15	100
Temperature [°C]	300-600	250-500	400	400	450	442	450	442
H_2/He Selectivity	n/a	n/a	~220	~120	∞	10000	~4500	~450
Total Test Duration [hours]	n/a	n/a	1015	~1250	~4500	~1400	~2200	~523
Thickness [μm]	n/a	n/a	4.2 Pd	6.2 Pd/$Au_{5\ wt\%}$	7.6 Pd	7.9 Pd	7.0 Pd	3-5 Pd
WGS Activity	Yes	Yes	Not tested	Not tested	Not tested	Not tested	Not tested	Not tested
CO Tolerance	Yes	Yes	Not tested	Not tested	Yes	Not tested	Not tested	Not tested
S Tolerance [ppm]	20	>100	Not tested	Not tested	Not tested	Not tested	Not tested	Not tested
H_2 Purity	99.5%	99.99%	99.0%	99.5%	≥99.999%	≥99.99%	99.98%	99.8%
ΔP Operating Capability (Max. Sys. Pressure, psi)	400	800-1000	15**	15**	225**	102**	15**	100**

§ DOE-NETL Test Protocol v7 - 05/10/2008, * Standard conditions are 150 psia hydrogen feed pressure and 50 psia hydrogen sweep pressure

** Maximum pressure tested, however, the ΔP can be higher since previous WPI membranes were tested up to 600 psi under MSR reaction conditions

Project Summary Table: Mixed Gas & WGS Reaction Results

	DOE Targets§		Current WPI Membranes (1/2" OD, 2.5" Length, ~24 cm^2)				
	2010	2015	AA-4R*	AA-5R*	AA-6R*	AA-7R*	AA-8R*
Flux [scfh/ft^2]	200	300	262.3	108.6	427.0	98.1	96.4
ΔP (psi) H_2 partial pressure (P_{Low}=15 psia)	100**	100**	245.1	71.0	222.7	45.4	37.1
Temperature [°C]	300-600	250-500	400	450	450	450	450
H_2/He Selectivity	n/a	n/a	71,000	2,800	1,100	25	670
Total Test Duration [hours]	n/a	n/a	1,030	1,080	860	350	970
Thickness [μm]	n/a	n/a	14.4	18.1	18.1	14.3	13.4
WGS Activity	Yes	Yes	Not tested	w/ packed catalyst	Not tested	w/ packed catalyst	w/ packed catalyst
CO Tolerance	Yes	Yes	Yes	Yes	Yes	Yes	Yes
S Tolerance [ppm]	20	>100	Not tested	Not tested	Not tested	Not tested	Not tested
H_2 Purity	99.5%	99.99%	99.99%	99.96%	99.91%	96.2%	99.85%
ΔP Operating Capability (Max. System Pressure, psi)	400	800-1000	250	250	250	250	250

§ DOE-NETL Test Protocol v7 - 05/10/2008

* R - repaired by mechanical treatment and Pd plating

** Standard conditions are 150 psia hydrogen feed pressure and 50 psia hydrogen sweep pressure

WPI