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

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Project ID: pd_44_ma

Overview

Timeline

- Start : 5/7/2007
- Finish : 5/6/2010
- 61% 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
- DOE Award #: DE-FC26-07NT43058
- DOE Project Manager:
  Dr. Daniel Driscoll

Subcontractor

- Adsorption Research Inc. (ARI)

Barriers

- **Barriers Addressed:**
  - Long-term selectivity stability
  - H_2 flux targets
  - Mixed gas & WGS reaction studies
  - CMR modeling simulations
  - Process intensification
  - Absorbent selection 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					

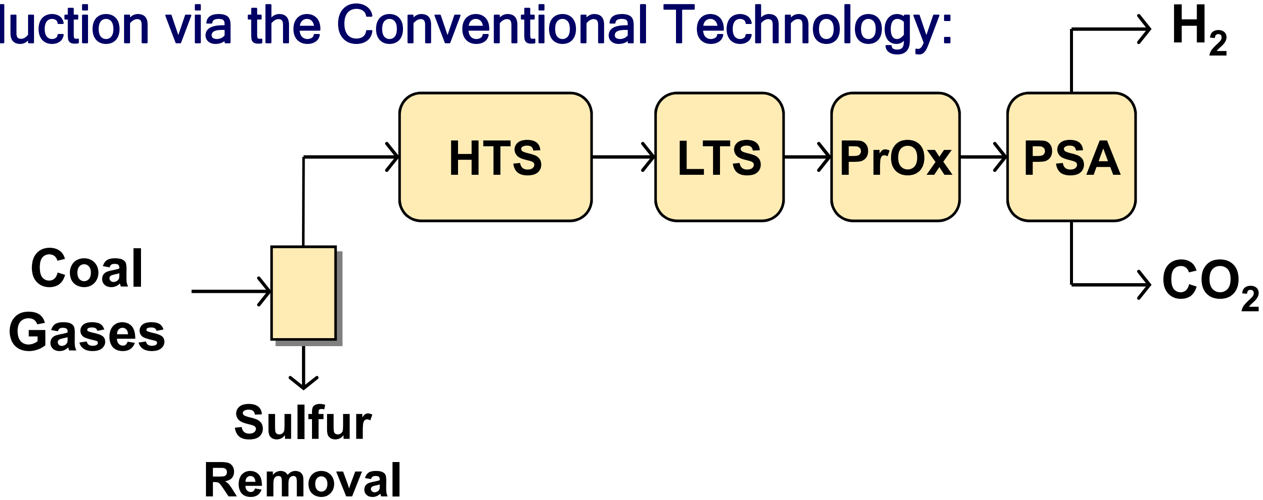
** DOE-NETL Test Protocol v7 – 05/10/2008

Project Objectives & Relevance

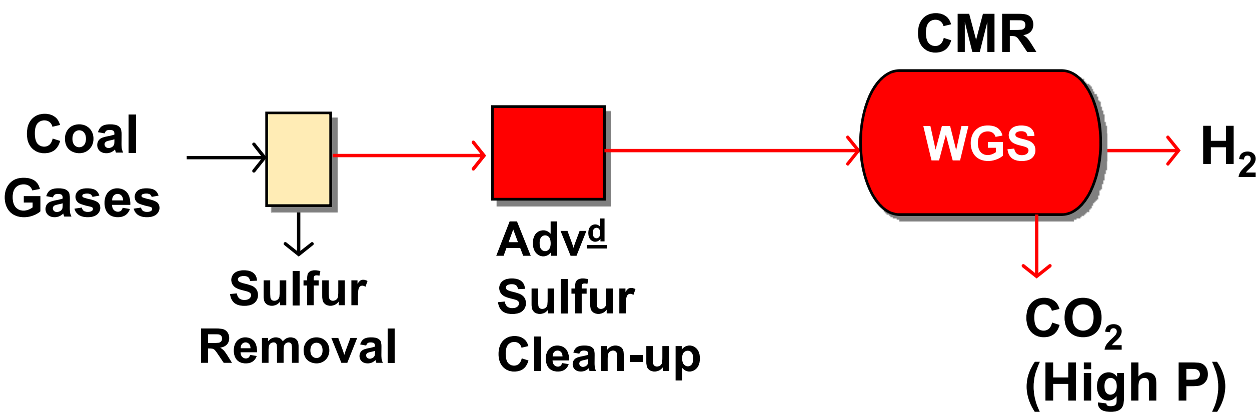
- Synthesis of composite Pd and Pd/alloy porous Inconel membranes for WGS shift reactors with long-term thermal, chemical and mechanical stability with special emphasis on the stability of hydrogen flux and selectivity
- Demonstration of the effectiveness and long-term stability of the WGS membrane shift 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												

WPI

Membrane Properties & Permeation Test Set-up

- **Membrane:**

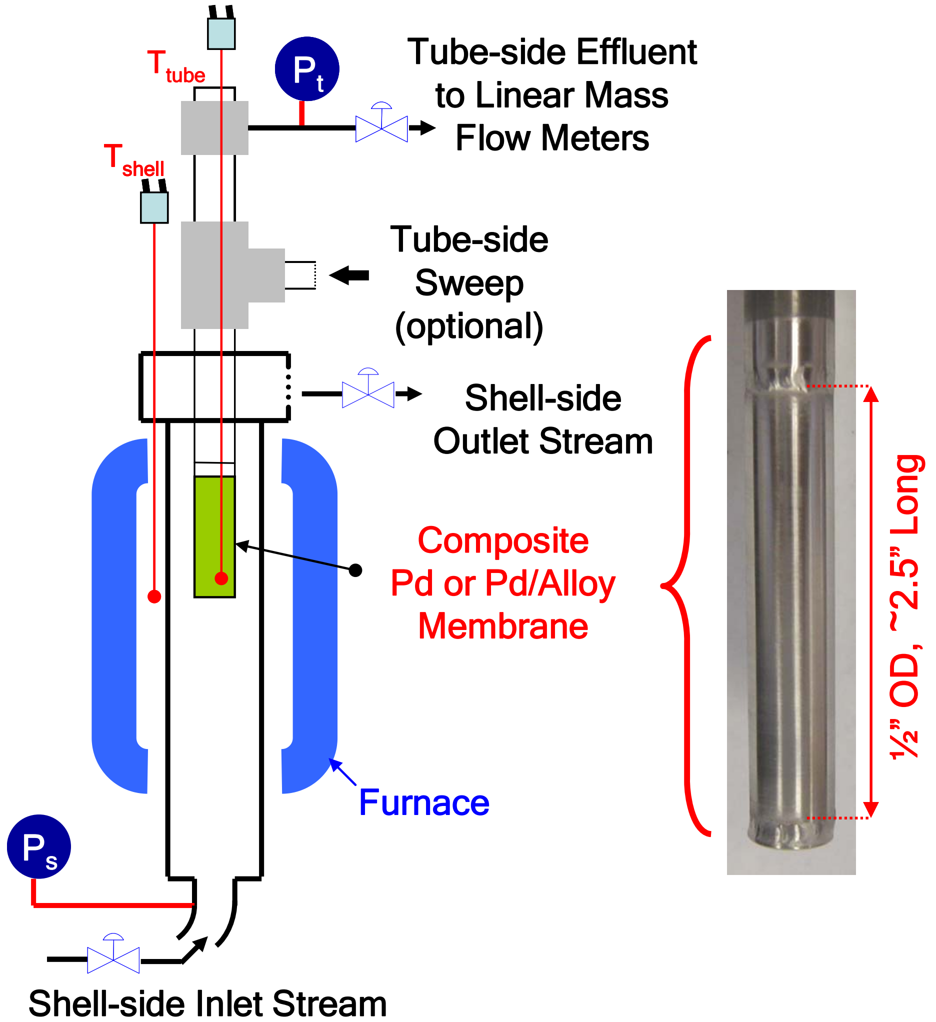
  Pd supported on porous Inconel (media grade 0.1 μm)

- **Method of Preparation:**
  Electroless Plating

- **Geometry:**

  Tubular (Plated on the outside of a tube)

- **Membrane Area** ≈ 25 cm^2



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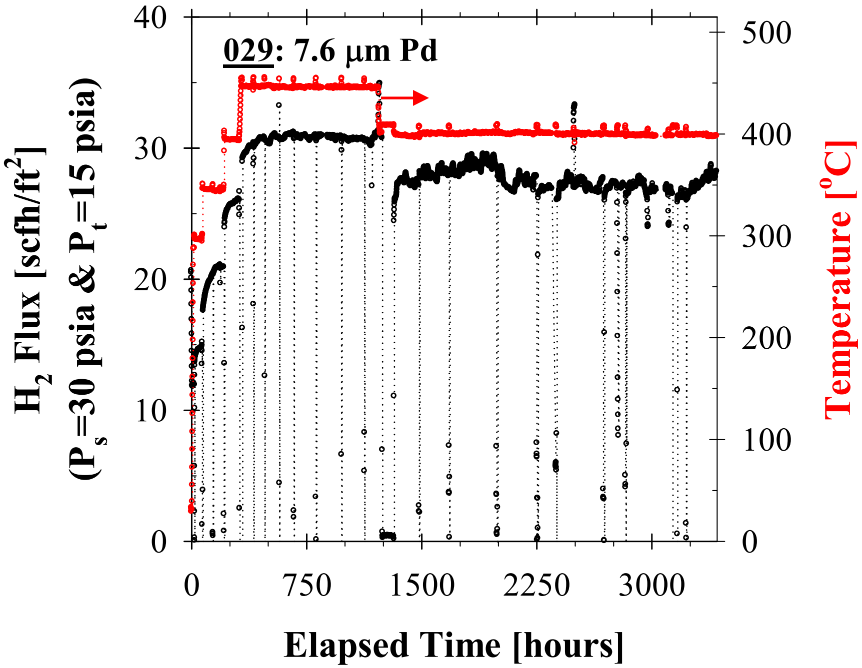
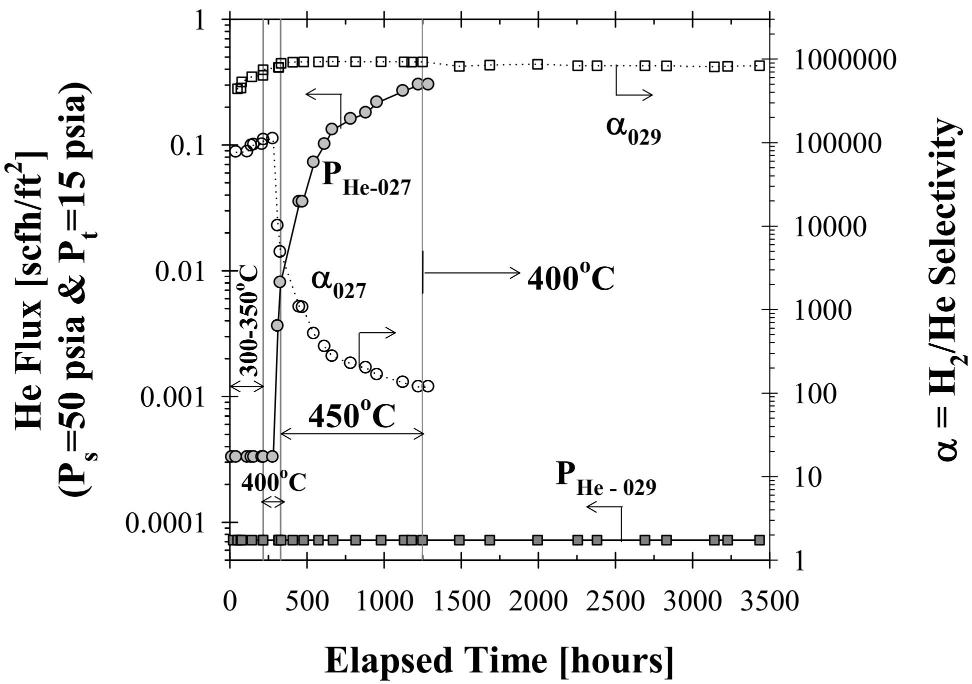
Long-Term Selectivity Stability





- Excellent long-term H_2/He selectivity stability was achieved over a total testing period of ~3550 hours (>147 days).
- High pressure flux measurements of the membrane 029 (7.6 μm thick pure-Pd/Inconel) at ~400 & 450°C and at a ΔP of ~100 psi (P_{High}=115 psia & P_{Low}=15 psia), led to a H_2 flux of ~150 & 166 scfh/ft^2, respectively, with essentially infinite ideal H_2/He selectivity.

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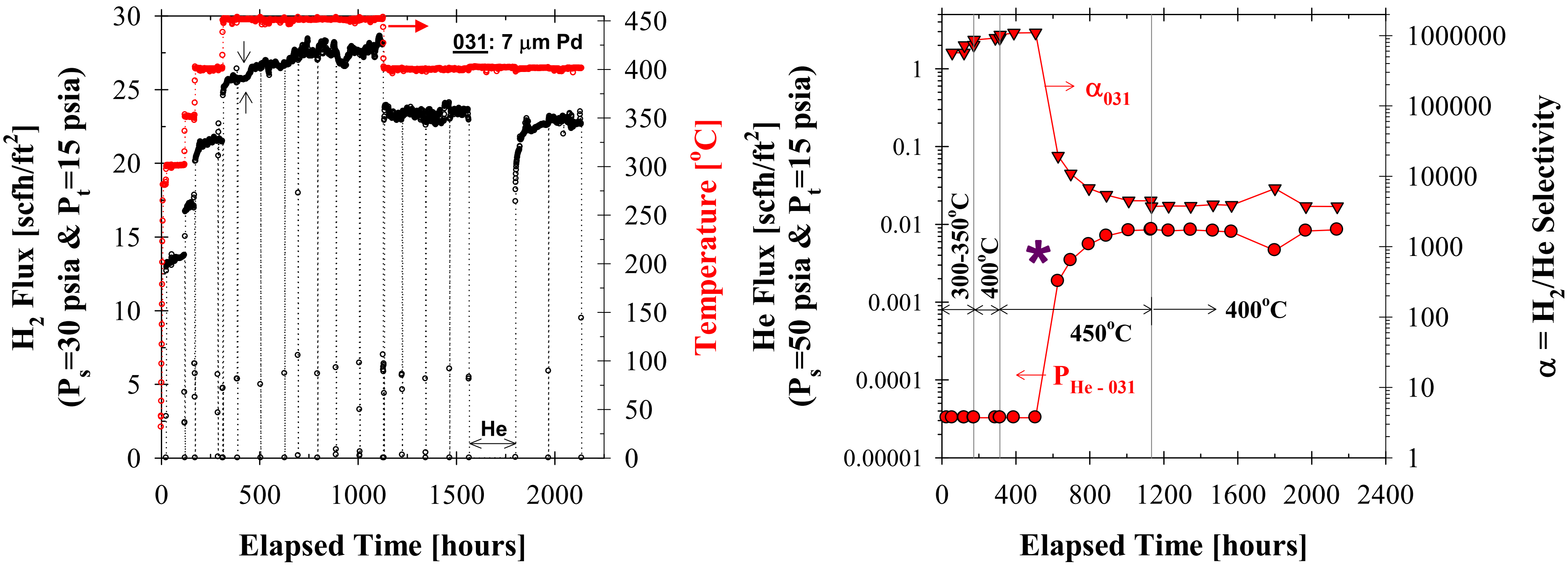
Reproducibility of the Long-Term Selectivity Stability



➢ The excellent H_2/He selectivity stability of the membrane 029 over the temperature range of 300-450°C, was successfully re-produced with the membrane 031 (7 µm thick pure-Pd/Inconel).

➢ At ~450°C and at a ΔP of 15 psi (P_{High}=30 psia & P_{Low}=15 psia), the H_2 flux and the final H_2/He selectivity were ~26.6 scfh/ft^2 & ~4500, respectively, after a total testing period of ~2200 hours (>90 days).

* At ~500 hours (450 °C) the sudden change in the leak profile was due to a defect formed and/or present during the synthesis, which was not cured completely and did not contribute to any further leak growth.

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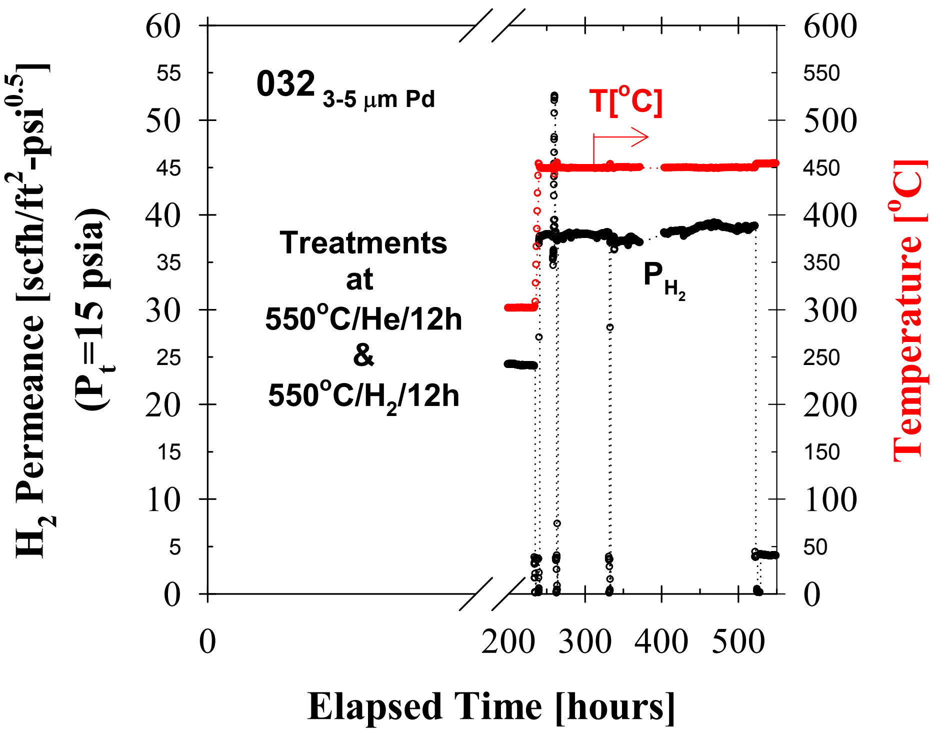
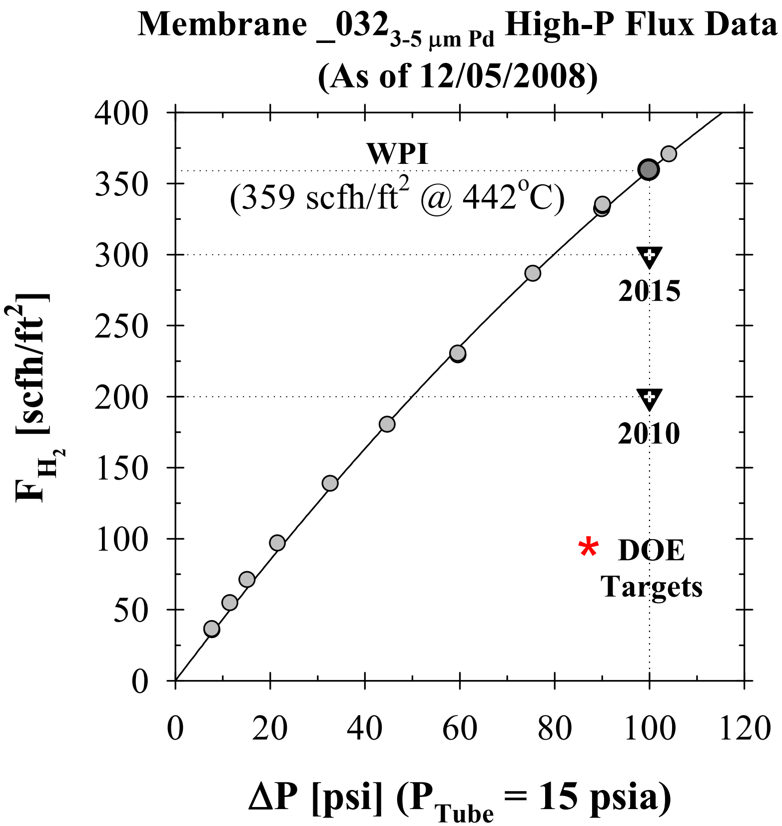
Progress Towards DOE H_2 Flux Targets

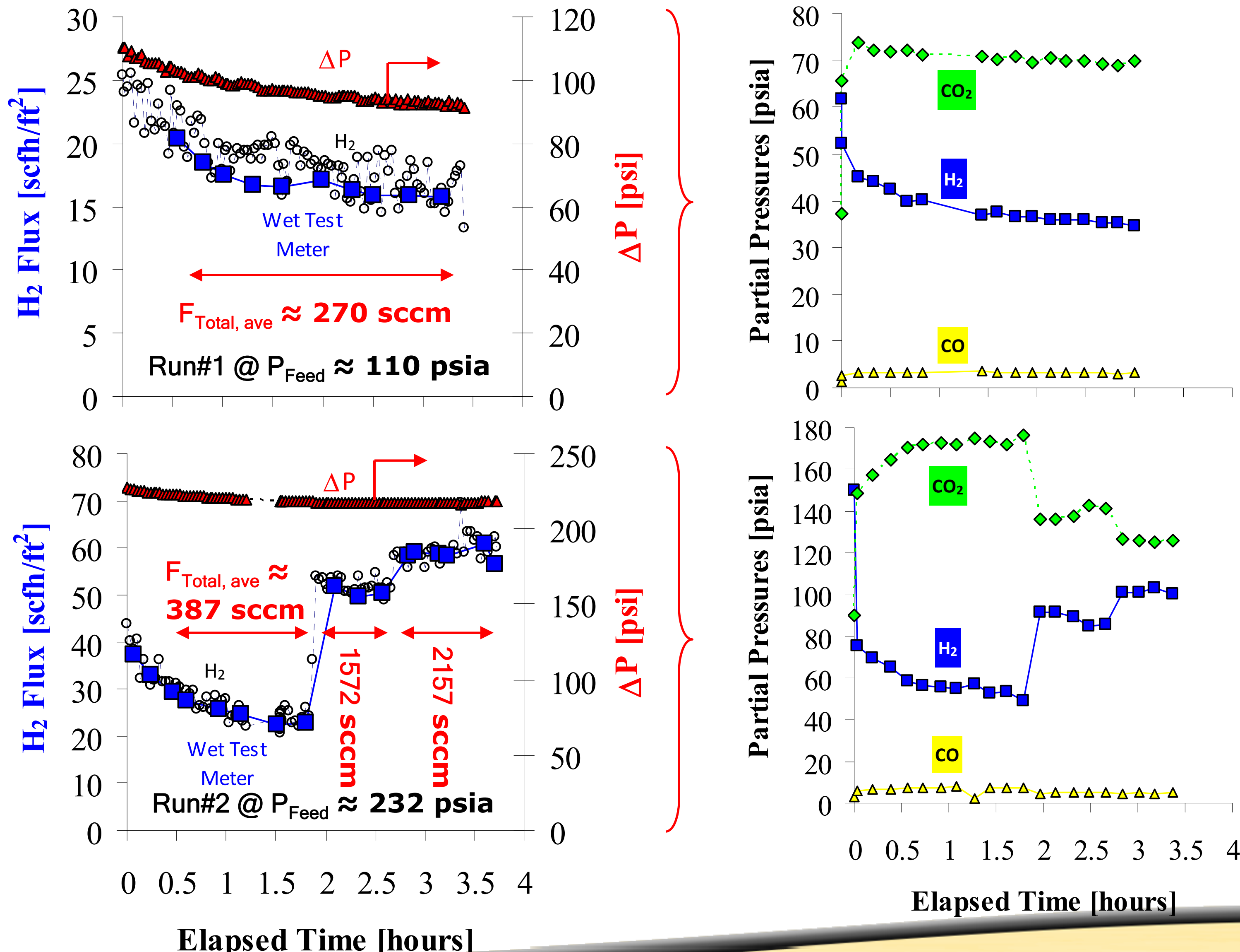




- At 442°C & at a ΔP of 100 psi (P_{High}=115 psia & P_{Low}=15 psia), the H_2 flux of the 3-5 μm thick Pd/Inconel membrane 032 was as high as ~359 scfh/ft² at the end of ~285 hours of testing with H_2/He selectivity of ~450, which exceeded the DOE's 2010 and 2015 H_2 flux targets.

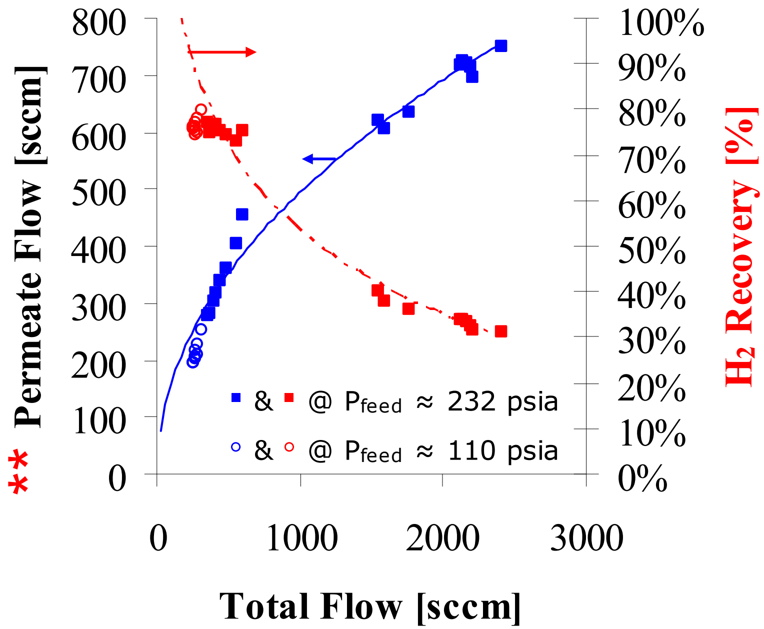
* DOE-NETL Test Protocol v7 – 05/10/2008

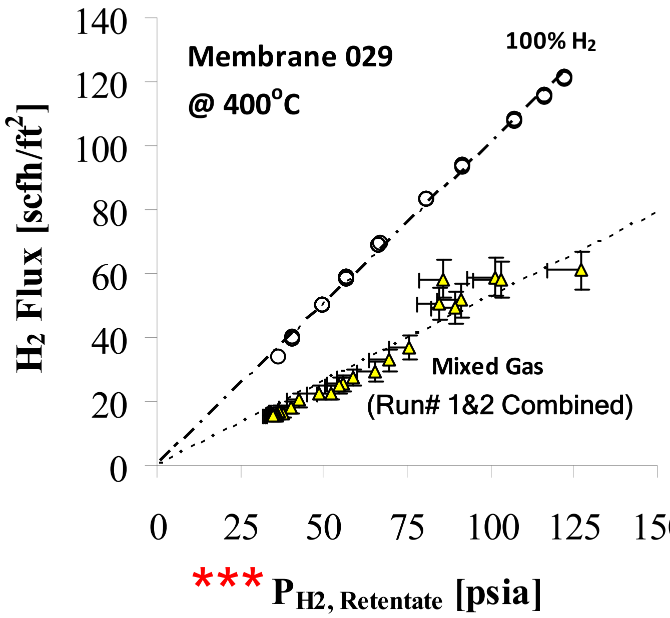
Mixed Gas Testing* of Membrane $029_{7.6\ \mu m\ Pd}$

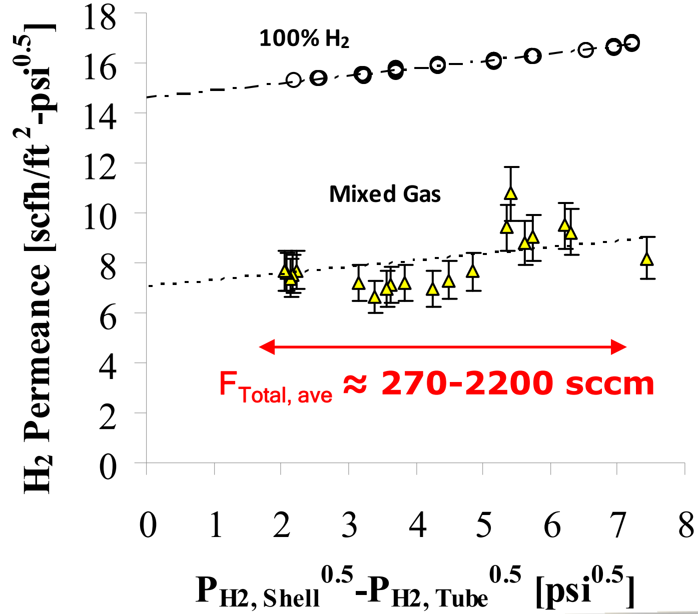


* 61.7% H_2, 37.1% CO_2 & 1.2% CO

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







- Compared to the pure H_2 flux, the lowering of the H_2 flux for the mixed gas testing was primarily due to the changes in the H_2 partial pressure along the length of the reactor caused by the removal of H_2 at a high permeation rate.

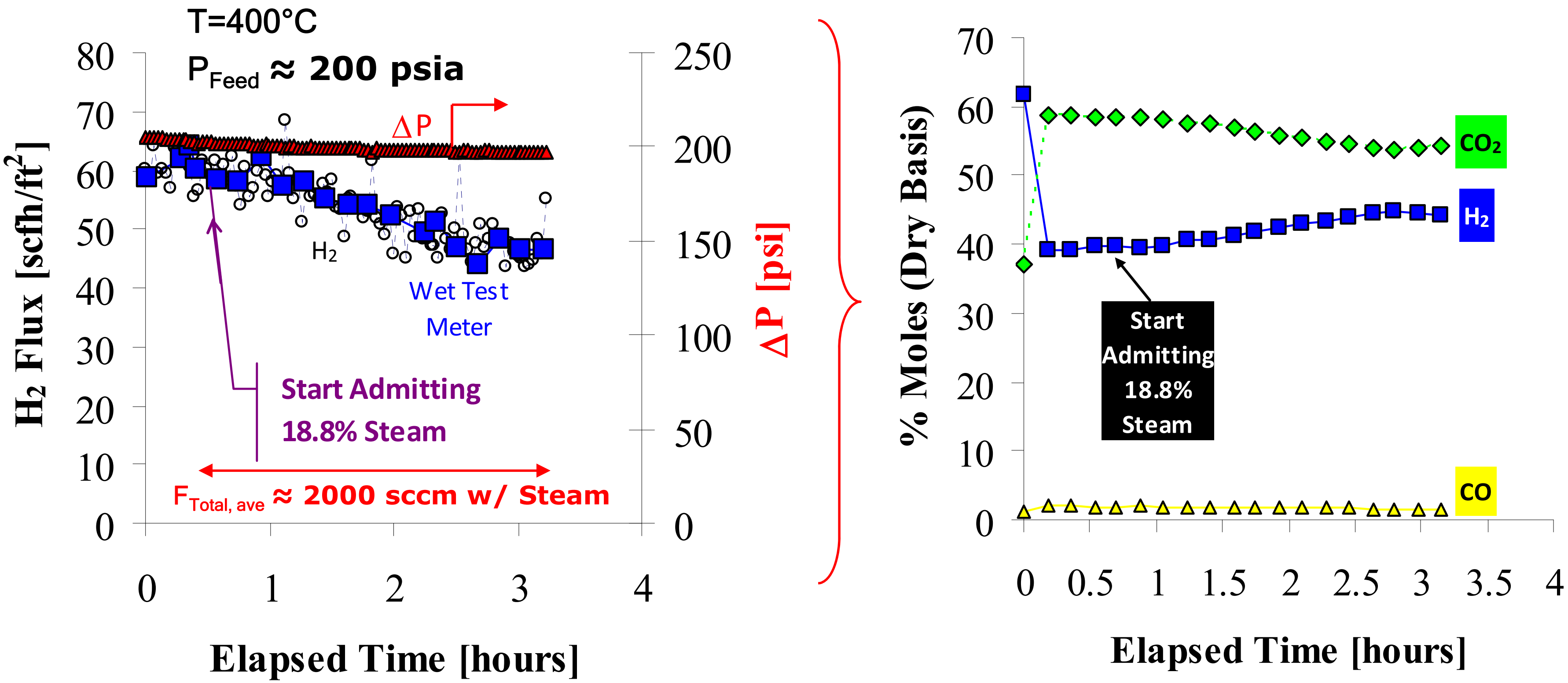
* 61.7% H_2, 37.1% CO_2 & 1.2% CO

** H_2 only, no other gases detected in the permeate

*** H_2 partial pressure at the retentate exit is based on the GC analysis

WPI

Mixed Gas Testing** of Membrane 029$_{7.6\ \mu m\ Pd}$ with Steam

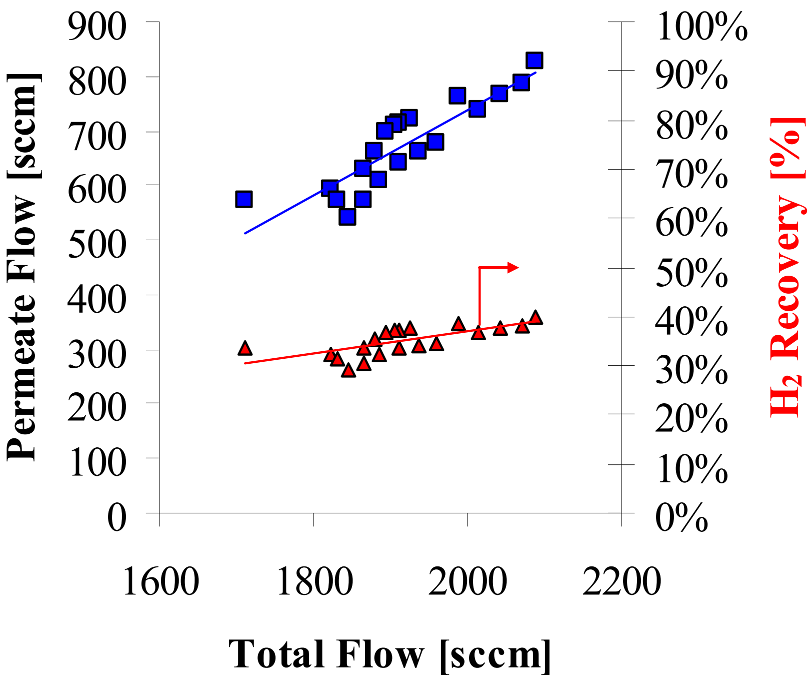


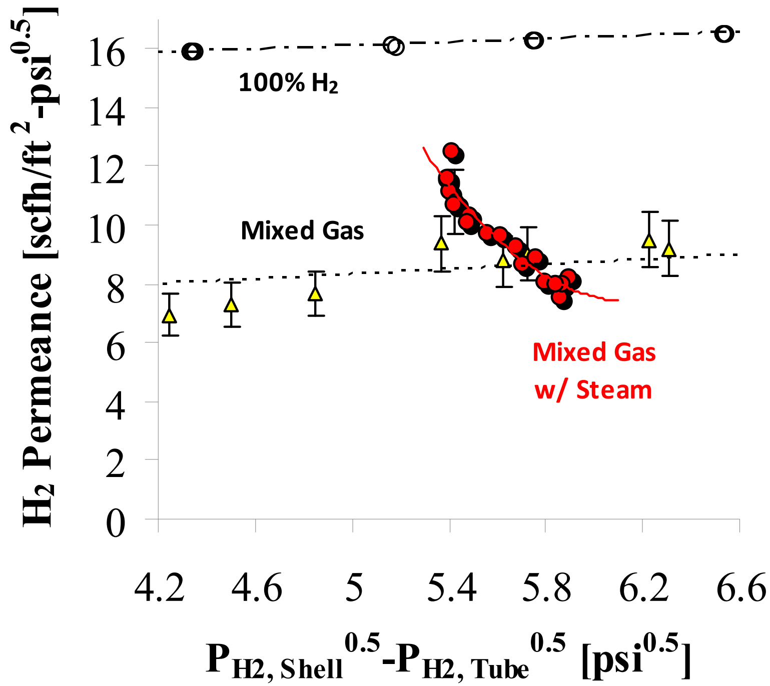
 Technical Accomplishments

** 50.1% H_2, 30.1% CO_2, 18.8% H_2O & 1.0% CO

WPI

Mixed Gas Testing** of Membrane 029 $_{7.6\ \mu m\ Pd}$ with Steam



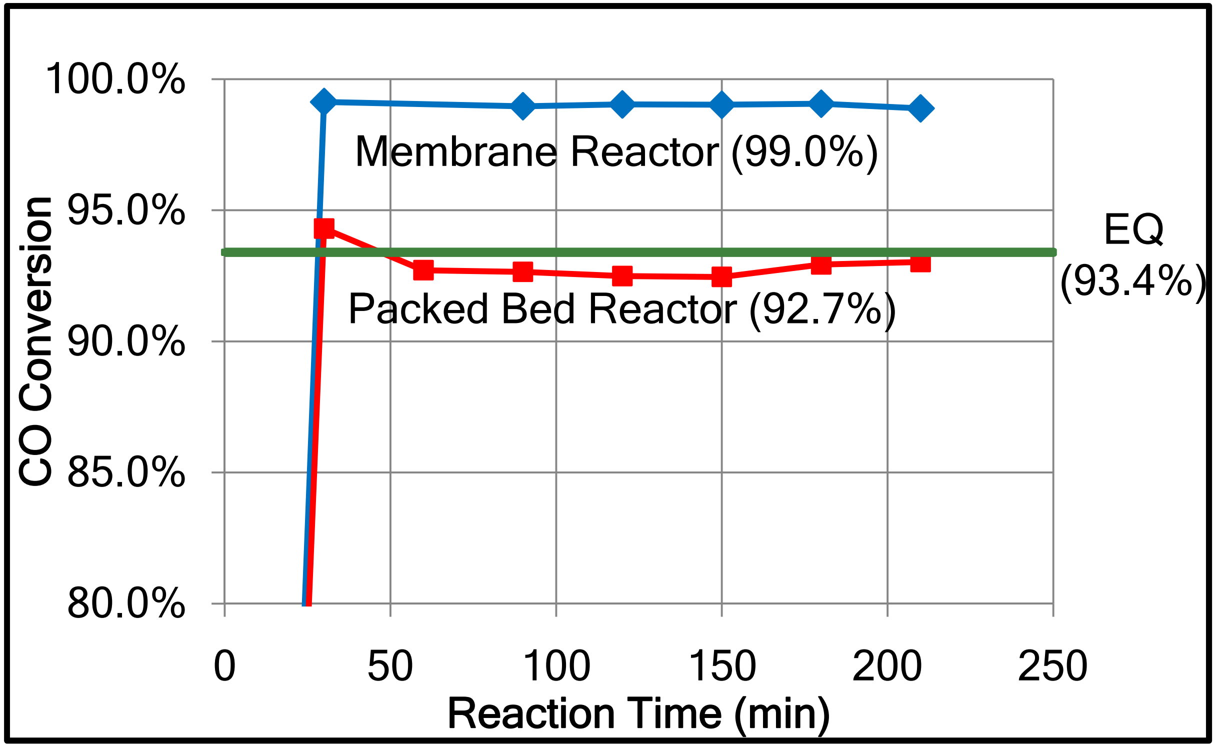


Factors affecting hydrogen flux under mixed-gas testing conditions:

- Dilution of H_2 concentration on the feed side due to the presence of other gases
- The change of H_2 partial pressure due to the in-situ removal of H_2 along the length of the membrane module
- Gas phase mass transfer limitations due to the formation of a concentration boundary layer (Concentration polarization)
- Competitive adsorption of other gas components on the membrane surface

** 50.1% H_2, 30.1% CO_2, 18.8% H_2O & 1.0% CO

WGS Reaction in a Pd-based* CMR

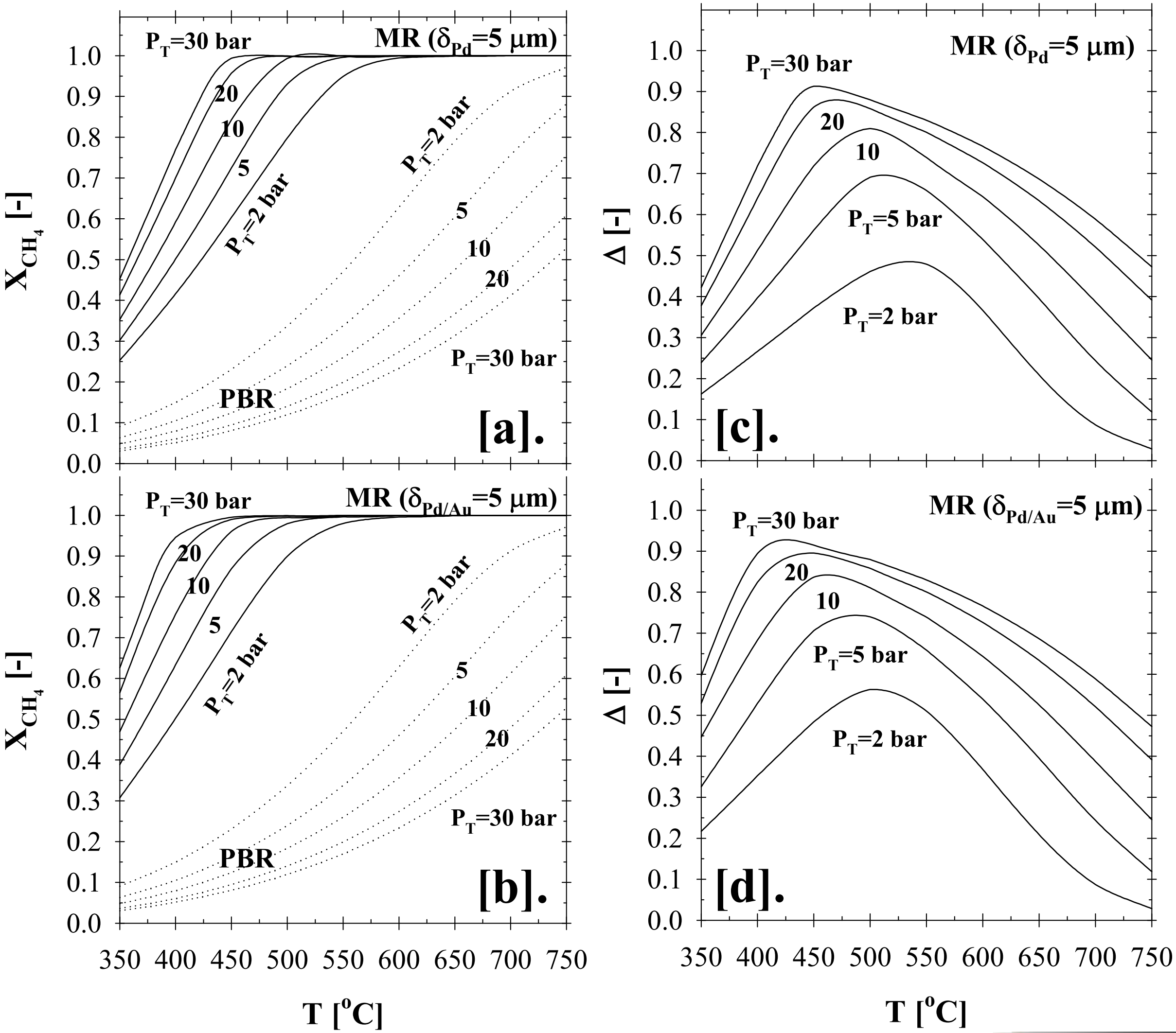


	Packed Bed Reactor	Membrane Reactor
T (°C)	346	349
H_2O/CO	1.55	1.44
P (psig)	200	200
GHSV**$_{STP}$ (hr^{-1})	151	149

- CO conversion vs. time is shown for both a membrane reactor (red) (*Membrane 0.1-AA-2: 12.5 m Pd) and a packed bed reactor (blue) fed with the conditions listed in the table
- Estimated equilibrium conversion for the conditions listed is shown in green
- The feed consisted of CO and H_2O
- The membrane reactor had a tube-side pressure of 14.5 psia, H_2 recovery was 89.9%
- The packed bed reactor contained a stainless steal tube with the same dimensions as the membrane

** GHSV=Total Feed Flowrate/Volume of the Reactor

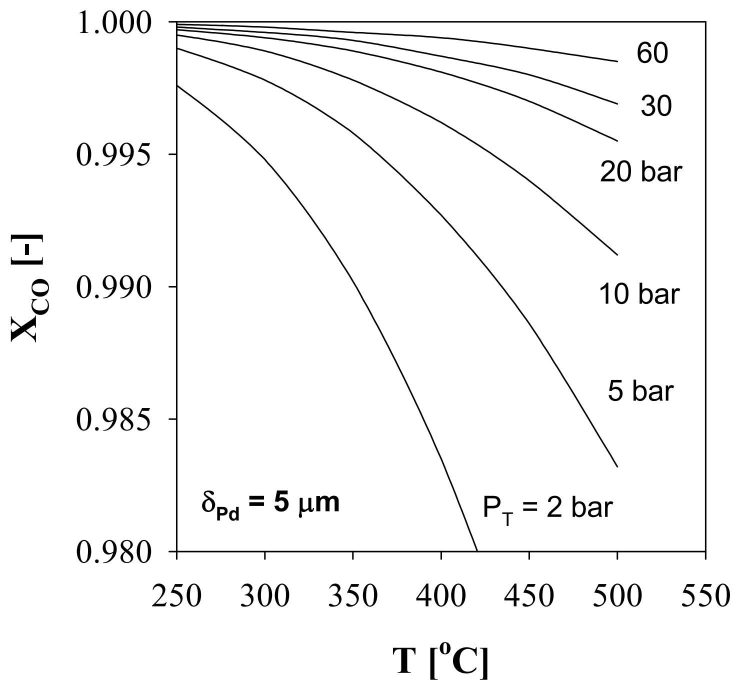
CMR Modeling of the MSR* Reaction w/ Process Intensification Analysis

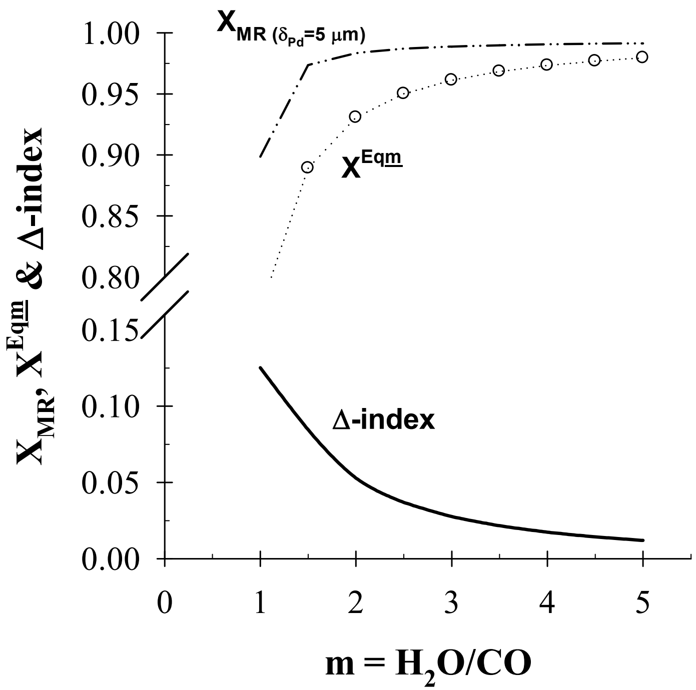


- The superior performance of the CMRs over that of conventional PBRs was amply demonstrated over a wide range of operating conditions.
- Impact of operating conditions on the CMR performance was successfully simulated & targeting analysis was utilized to optimize and evaluate the best performance range via the proposed process intensification indicator Δ-index. $\left(\Delta = X_{CH_4,MR} - X_{CH_4,PBR}\right)$

* MSR: Methane Steam Reforming

CMR Modeling of the WGS* Reaction w/ Process Intensification Analysis





- At 400°C and 60 bar the total CO conversion, X_{CO}, simulated for the CMR and the PBR were 99.9 and 88.9%, respectively. As the driving force for the H_2 permeation increased with the higher pressure on the reaction side, the in-situ removal of the high partial pressure H_2 resulted in an enhancement of the X_{CO} in the case of Pd-based CMR over the entire temperature range.
- In contrast to conventional reactors operated under excess steam-to-CO ratios, the Δ-index analysis showed that the CMR operation below m<2, can further improve the CO conversion of the WGS reaction by ~13%, provided that the coke formation was avoided by utilizing a highly active & selective catalyst for WGS reaction.

$\left(\Delta = X_{CO,MR} - X_{CO,PBR}\right)$

* WGS: Water-Gas Shift

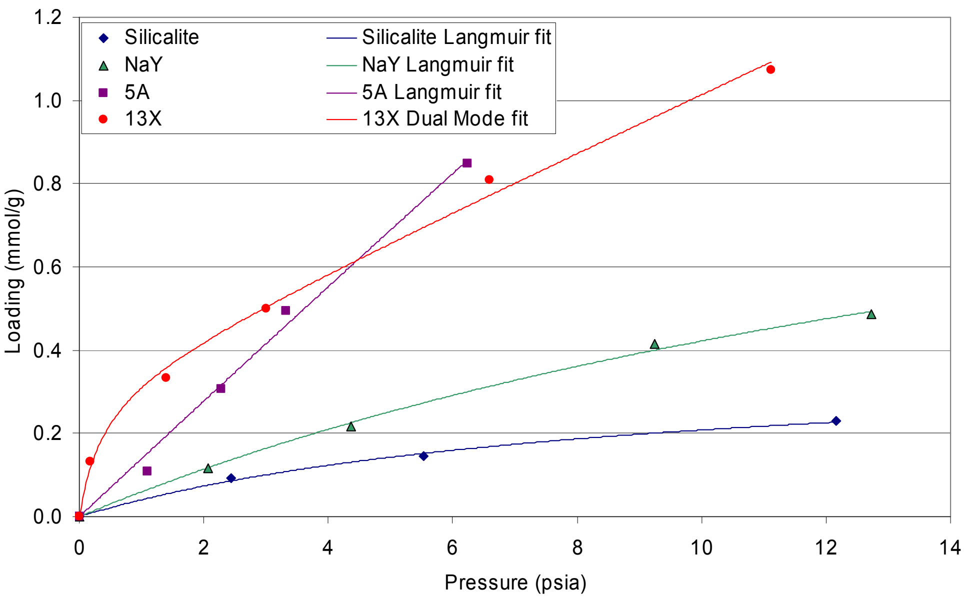
Collaborations
Adsorption Research Inc. (ARI); sub

(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 of the adsorbents 5A, 13X, NaY and Hisiv3000 were measured at 200 and 230°C for CO_2, COS and H_2S and the equilibrium data were fitted using the Langmuir equation. The eq$^{\underline{m}}$ isotherms at 200 and 230°C were also measured for the water vapor.
- To evaluate both short-time and long-time diffusion behavior of the adsorbents 5A, 13X, NaY and Hisiv 3000, transient uptake tests for CO_2, COS and H_2S were conducted at 200 & 230°C.

Adsorption Results @ 200°C

H_2S Isotherms



- The development of the pressure swing adsorption (PSA) system and the demonstration of a suitable adsorbent in cyclic operation at 200°C & 200 psia is underway.

Proposed Future Work (FY09 & FY10)

- 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 (i.e., 2-D non-isothermal finite element modeling via the Comsol Multiphysics)
- Continue process intensification & performance assessment analyses coupled with process control strategies
- Initiate economical analysis for the proposed process intensification framework
- Complete building & testing of a Pressure Swing Adsorption (PSA) system (sub: ARI)

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

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), with membrane $029_{7.6\ \mu m\ Pd/Inconel}$
- Achieved re-producible long-term H_2/He selectivity stability (~2200 hours, >90 days) with membrane $031_{7\ \mu m\ Pd/Inconel}$ at T = 300-450°C.
- Flux of ~359 scfh/ft^2, which exceeded the DOE's 2010 and 2015 H_2 flux targets [Membrane $032_{3\text{-}5\ \mu m\ Pd/Inconel}$ @ T=442°C & ΔP of 100 psi (with P_{Low}=15 psia)].
- Initiated mixed gas experiments (61.7% H_2, 37.1% CO_2 & 1.2% CO w/ or w/o 19% Steam) using membrane $029_{7.6\ \mu m\ Pd}$ at 400°C & ΔP=100-200 psi (with P_{Low}=15 psia).
- Achieved 99% total CO conversion and 89.9% H_2 recovery in a 12.5 µm thick Pd-based CMR operated at ~350°C, ΔP=200 psi (P_{Low}=15 psia) H_2O/CO=1.44 and $GHSV_{stp}$=150 h^{-1}. Under similar conditions, $X_{CO,PBR}$ & $X_{CO,Eqm}$ were 92.7% & 93.4%, respectively.
- Successfully completed MSR & WGS reaction modeling studies and initiated process intensification analysis.
- Completed property & isotherm measurements for the selected adsorbents and initiated PSA system construction.

Project Summary Table

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