

High-Performance, Durable, Palladium Alloy Membrane for Hydrogen Separation and Purification

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Project ID #PD005

Overview

Timeline

- July, 2005 start date
- Sept., 2011 end date
- 65% complete

Barriers

- Operational durability
- Compatibility to impurities
- Manufacturing cost

Budget

- \$4 Million Project Total
 - \$2.4M DOE share
 - \$1.6M Contractor share
- FY09 Funding \$0
- FY10 Funding \$500K

Partners

- Colorado School of Mines
- ORNL – High Temperature Materials Lab
- End user – to be determined

Relevance- Objectives

The project objective is development, demonstration and economic analysis of a **Pd-alloy membrane** that enables the production of **99.99% pure H₂** from reformed ethanol at a cost **< \$3/gge**.

The objectives from April 09 - March 10 were to:

- ✓ Continue **optimization** and characterization of the membrane formation process
- ✓ Conduct **extensive testing** of Pd-alloy membranes in pure gas streams and in **syngas/WGS** reaction environments for parametric evaluation of their performance
- ✓ Demonstrate membrane performance **meeting the goals** of several **milestones** set for the **Phase III go/no go decision**
- ✓ Complete the **techno-economic modeling** in collaboration with Directed Technologies Inc. to determine influence of membrane parameters on cost of Hydrogen production

Relevance - Addressing Barriers

- **Operational Durability**

- Addressed through alloy and composite membrane structure
- Demonstrated long-term (500 hr) **stable performance in syngas** environment
- Demonstrated stability against rapid **thermal cycling**

- **Compatibility to Impurities**

- Evaluated effect of **CO and H₂O** on membrane performance
- Determined acceptable **H₂O:CO ratio** for stable performance
- Conducted limited tests with low concentration **H₂S** exposure
 - Observed reversible H₂ flux decline with H₂S exposure

- **Manufacturing Cost**

- Target cost is estimated based on sales price to end user for membrane in a module
- Manufacturing scale-up increases yield and reduces cost

DOE HFI Membrane Performance Targets*

Performance Criteria	2006 Status	2010 Target	2015 Target
Flux SCFH/ft ² @20 psi ΔP H ₂ partial pressure, 400°C (Pure H ₂ gas)	>200	250	300
Membrane Cost, \$/ft ² (including all module costs)	1500	1000	<500
ΔP Operating Capability, system pressure, psi	200	400	400 - 600
Hydrogen Recovery (% of total gas)	60	>80	>90
Hydrogen Permeate Quality	99.98%	99.99%	>99.99%
Stability/Durability	<1 year	2 years	>5 years

* 2007 Technical Plan. Technical Targets: Dense Metallic Membranes for Hydrogen Separation and Purification www1.eere.energy.gov/hydrogenandfuelcells/mypp

Approach - Overall Technical Approach

- **Develop a commercially viable Pd alloy membrane to enable the design of economical processes for hydrogen production**
 - Pd alloy composite membrane is shown to have both high flux rate and high separation factor for separating H₂ from ethanol/NG reformat gas
 - Commercial scale-up of high quality porous metal substrate along with alloy development, deposition methods and module design pursued
- **Increase the overall energy efficiency of a H₂ reforming system through use of membrane technology for process intensification**
 - Membranes with high operating temperatures can be heat integrated to reduce thermal loss within the system
 - Membranes with high separation factor can reduce system complexity, size and operating cost
 - Membrane reactors can reduce the cost of pressure vessels, reduce catalyst volumes and overall capital and operating cost

Approach – Progress FY09/10

- **Membrane Development**

- Continue optimization of the substrate materials in terms of consistency, homogeneity and surface roughness. Scale up substrate synthesis to 12” elements – ready for manufacturing.
- Improve deposition methods and post treatment during fabrication of Pd-alloy membrane inventory

- **Parametric Membrane Testing in Syngas Environment**

- Experimentally determine effect of syngas components on the membrane performance to identify optimized operating conditions
- Evaluate membrane durability in long term syngas exposure and aggressive thermal cycling operation
- Devise approaches for reducing concentration polarization effects

- **Economic Evaluation**

- Update costs based on membrane scale-up and module design
- Estimate influence of operating parameters on the cost of hydrogen production guiding overall approach to minimize H₂ cost

Technical Accomplishments & Progress

Summary of Previous Accomplishments

- **Develop substrate process:** Porous metal media substrate tubes made from 310SC alloy stainless steel and rated for use at 550°C and 20 bar that can be made in longer lengths and ZrO₂ diffusion barrier fabrication process was scaled up to 12-inch lengths
- **Improve membrane deposition process:** Modified deposition methods to repeatedly produce thin Pd alloy membranes (≤ 2 microns) with high separation factors (greater than 20,000). Incorporated air oxidation and layering sequence to improve membrane performance
- **Fabricate test samples:** Produced various Pd-Au alloy tubular membranes 5-30% Au and thickness 1.0-3.5 microns and established inventory for parametric testing
- **Membrane performance** Analyzed the effect of alloy composition, process conditions and operational procedures on membrane performance
- **Design membrane for high ΔP :** Carried out tensile strength and strain at failure for Pd-alloy foils over the composition range of 0-38 mass % Au to determine high pressure operating capability for the functional membrane layer
- **Performed preliminary testing in mixed gas streams:** A limited amount of testing was carried out in mixed gas test streams to determine effect of other gas components
- **Estimated cost:** Module design, fabrication techniques and materials for a stand alone membrane separator device show that \$1,000 per ft² of area cost to end user is achievable
- **Initiated techno-economic analysis:** Conducted preliminary H₂ production cost analysis using DTI's H₂A based model and Pall provided costs. Initial results showed the cost of the separation device (PSA or membrane) is a small percent (<10%) of capital cost and is not the dominating factor. Greater membrane recovery however significantly reduces the cost of H₂,

Technical Accomplishments & Progress

Summary of Accomplishments for April 09 - March 10

- Continued optimization and characterization of the membrane formation process. Developed a technique with multiple thin layer sequence for increasing hydrogen selectivity
- Conducted extensive testing of Pd-alloy membranes in pure gas streams and in syngas/WGS reaction environments for parametric evaluation of their performance
- Demonstrated membrane performance meeting the goals of several milestones set for the Phase II completion and secured go decision to move to Phase III
- Completed the techno-economic modeling in collaboration with Directed Technologies Inc. to determine influence of membrane parameters on cost of Hydrogen production
- ORNL determined maximum pressure capability of the Pd-alloy membrane at room temperature. The membrane tube didn't collapse even with external pressure of up to 4000 psia.

Significant progress towards establishing viability

Technical Accomplishments and Progress— Meeting Phase II Milestones

1. Test Pd-Au alloy membranes to determine parametric performance in WGS reaction environments for at least 100 hrs

Time. H_2 flux was stable with time

Thermal Cycling. H_2 flux was reproducible for over 50 cycles tested.

High Pressure. Tests at 170 psig over 100 hours – high flux (285 SCFH/ft²)

Feed flow rate. Increase in flow rate reduces concentration polarization effect.

CO content. H_2 flux reduced by 5% with CO increase from 2% to 5%

Steam/CO ratio. Stable performance at steam/CO ratios above 1.5

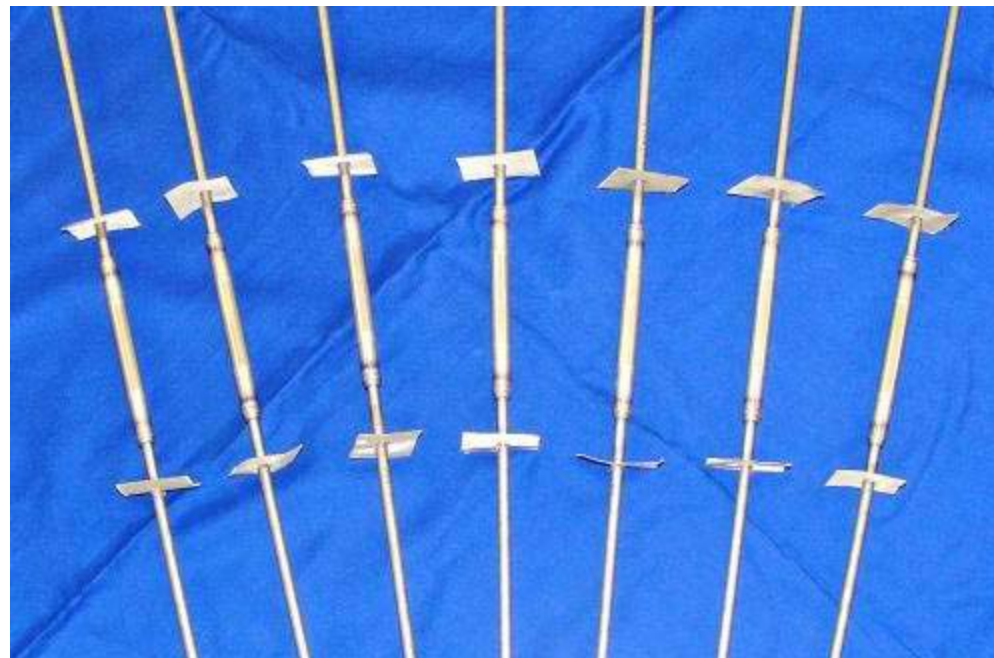
H_2S content. Strong effect of H_2S content (5-25 ppm) but reversible. Pd/Au alloy more resistant than pure Pd.

Notable performance. With syngas feed at 170 psig the H_2 flux was 285 SCFH/ft² and the H_2 purity was 99.997% with a H_2 recovery of 78%.

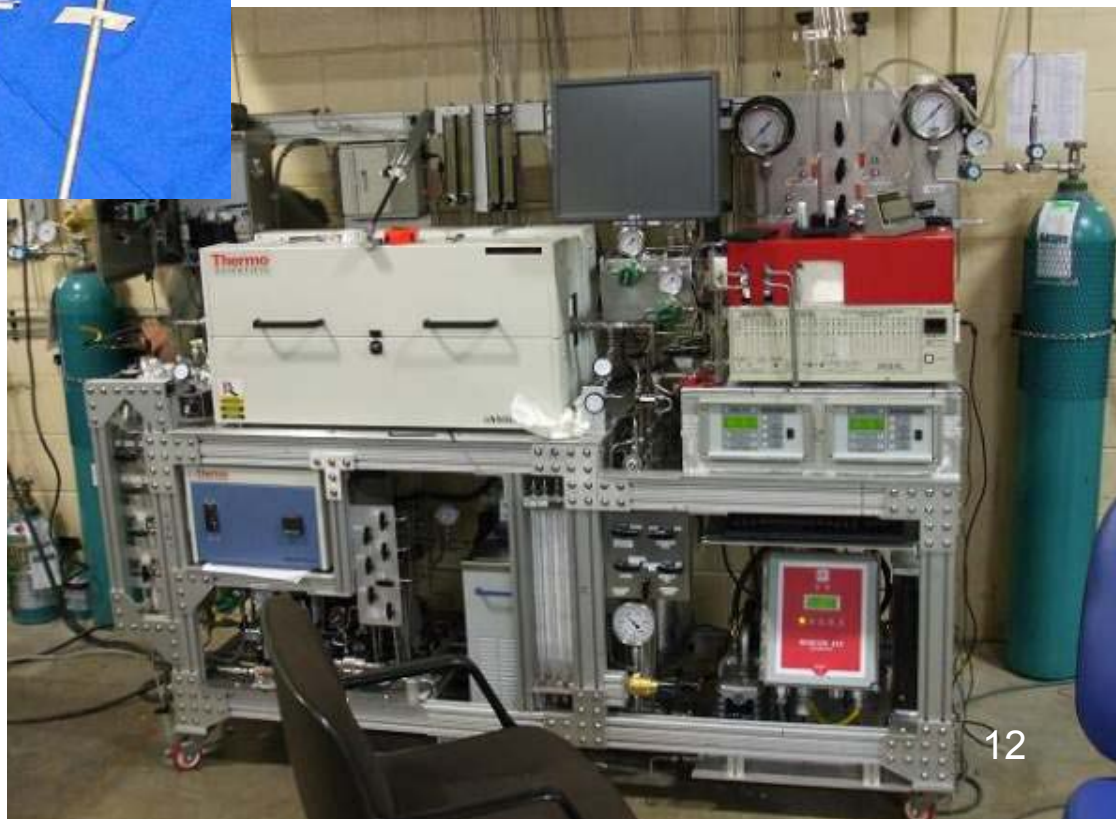
Technical Accomplishments and Progress – Meeting Phase II Milestones (cont.)

2. Test a Pd-Au alloy membrane in WGS for 500 hrs. to determine performance H_2 flux remained constant at 65 SCFH/ft² for last 460 hours
3. Determine performance trends as a function of Au level and membrane thickness Better performance with Pd-Au alloy in syngas – continuing work
4. Based on average performance data, calculate the surface area to produce 1500 kg/day H_2 With H_2 flux of 105 SCFH/ft²(@20 psid, 400 C), 90% H_2 recovery, ~ 50 ft² for a NG process and ~ 70 ft² for an ethanol process.
5. Design a membrane module based on this surface area to produce 1500 kg/day H_2 A conceptual multi-tube module design was prepared with consideration to minimize concentration polarization effects.
6. Estimate the cost of this membrane module in high volume production The estimated high volume cost of a membrane module < \$1000/ft². The WGS membrane reactor module cost for ethanol-based process < \$70,000.
7. Submit the surface area and production cost to DTI for cost of H_2 production analysis Analysis indicated that H_2 cost of \$2.99/kg, achievable with an integrated Pd-alloy membrane reactor/separator system.

Technical Accomplishments Membrane Fabrication and Testing

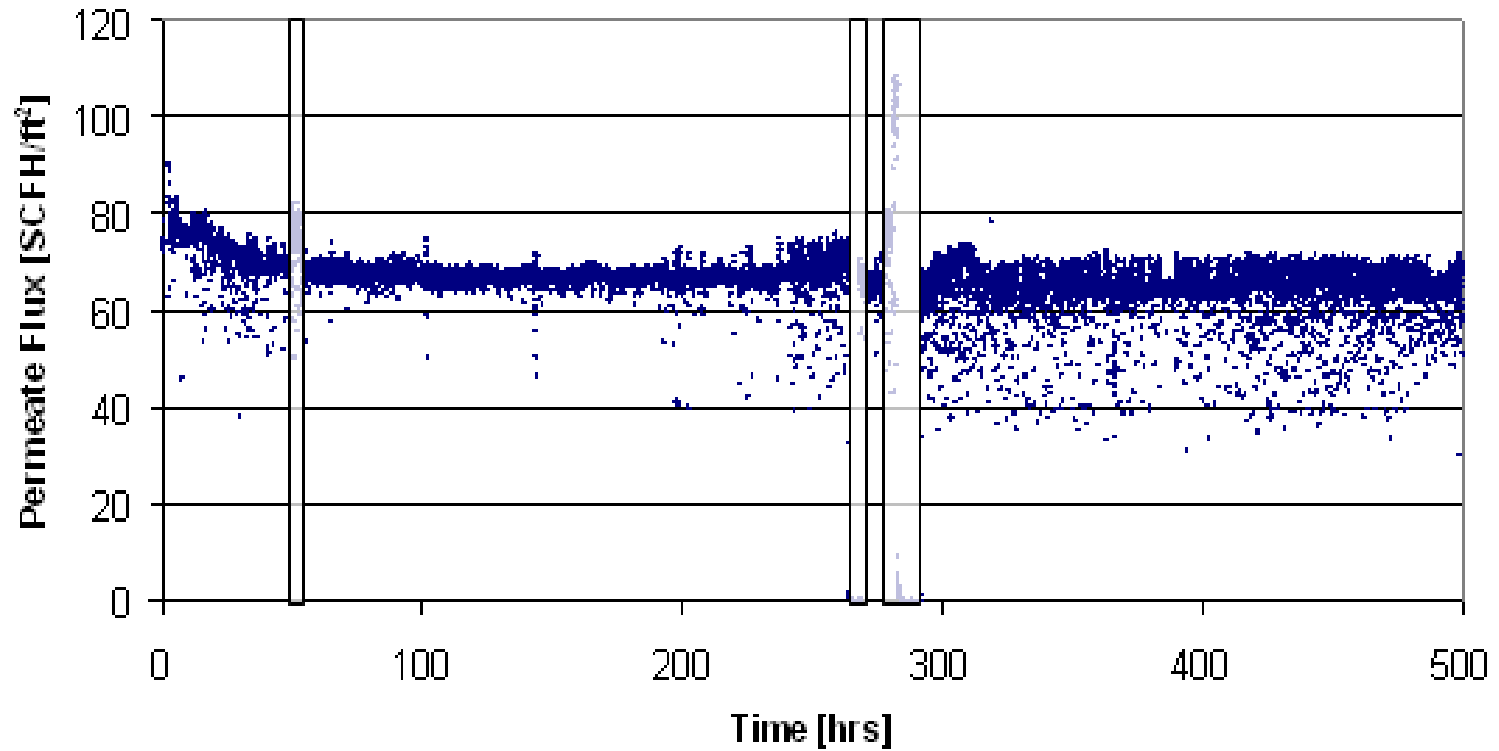


Selection of tubes of varying Pd-Au alloys ready for testing on the automated water gas shift test stand



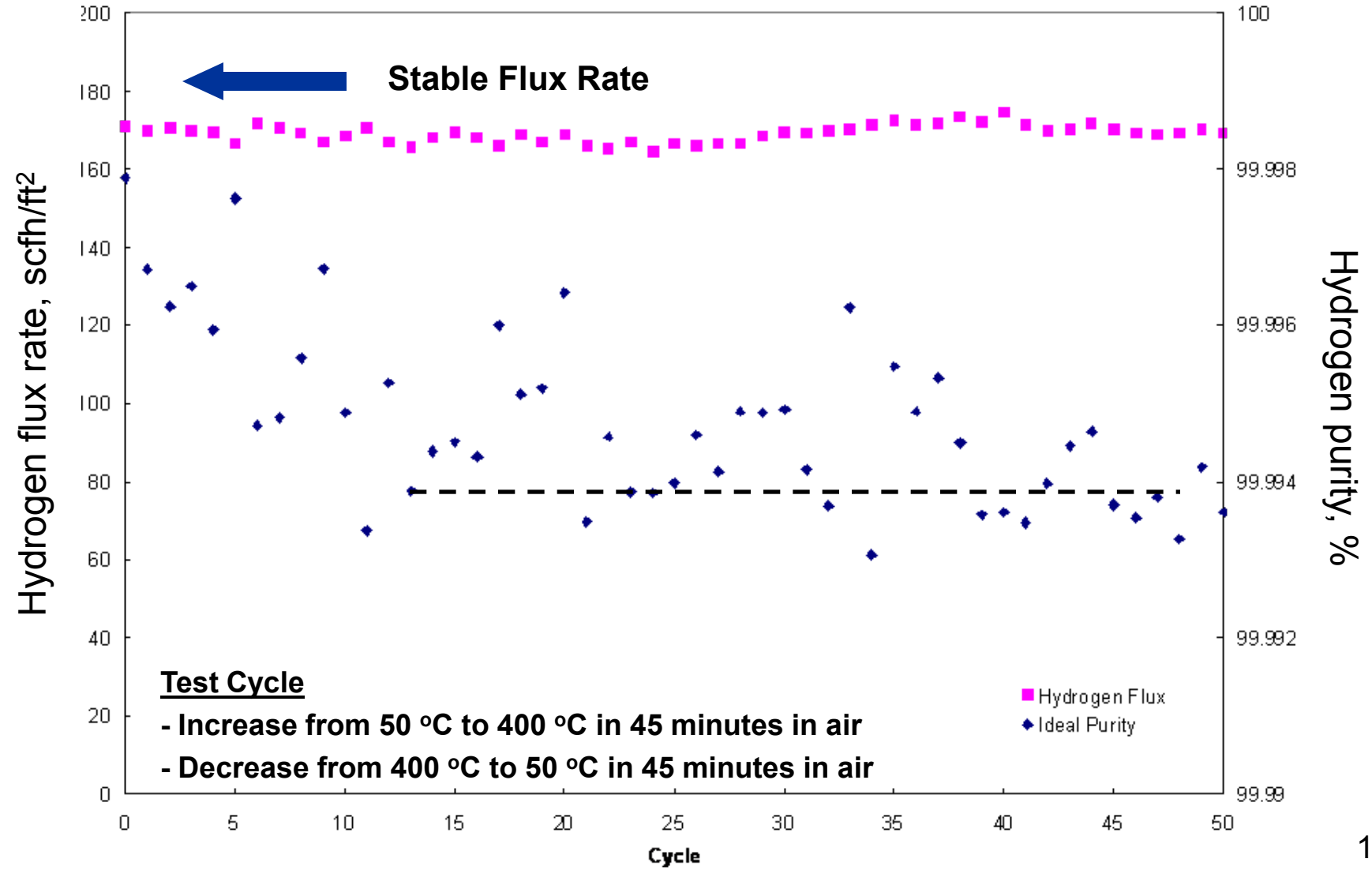
Technical Accomplishments & Progress

Long term testing in syngas environment

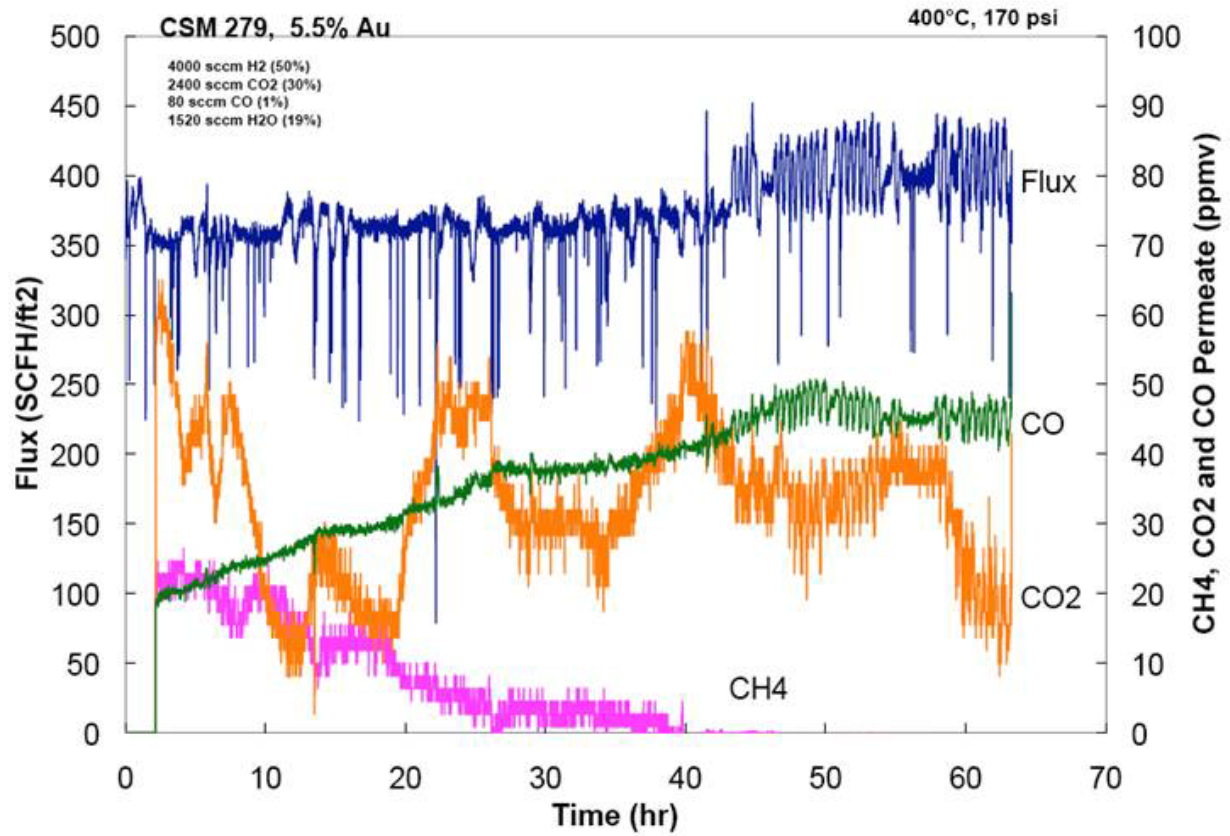


Post-WGS composition: 50% H₂, 30% CO₂, 1% CO, 19% H₂O
Feed 85 psig, permeate 5 psig, 400°C, 2 SLPM
H₂ flux remained constant at 65 SCFH/ft² through 500 hrs
- H₂ recovery 56%, H₂ purity 99.8%

Technical Accomplishment – Thermal Cycle Durability



Technical Accomplishments & Progress



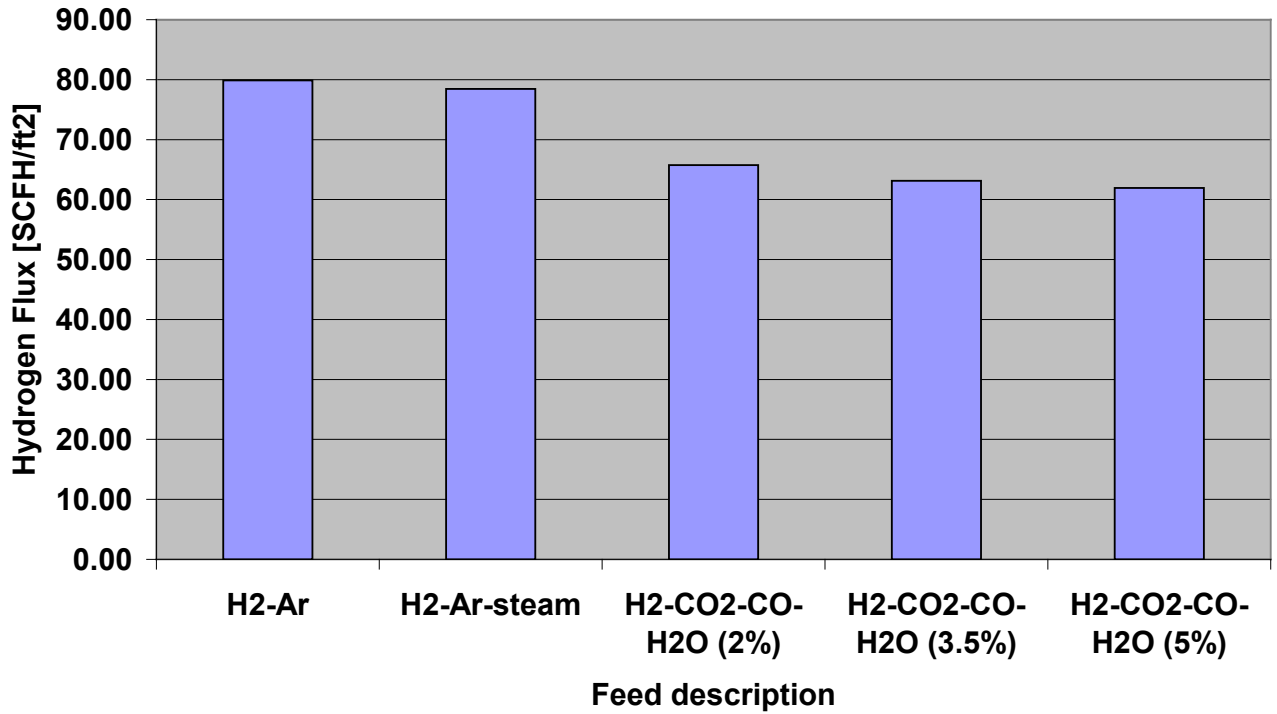
Membrane performance results under high pressure (170 psig) and 400 °C
H₂ flux 400 SCFH/ft² H₂ purity 99.99% and H₂ recovery 78%
(Tests conducted by TDA Research)

High purity and high flux by membrane demonstrated

Technical Accomplishments & Progress

Determination of effect of CO and H₂O on Membrane Flux

CSM247, Pd_Au, 2wt%, ~ 2.74 microns, T=400 C
Pf=120 psig and Pp=5 psig, H₂ in feed ~49 vol%, CO₂ =25 to 28%, H₂O = 21%

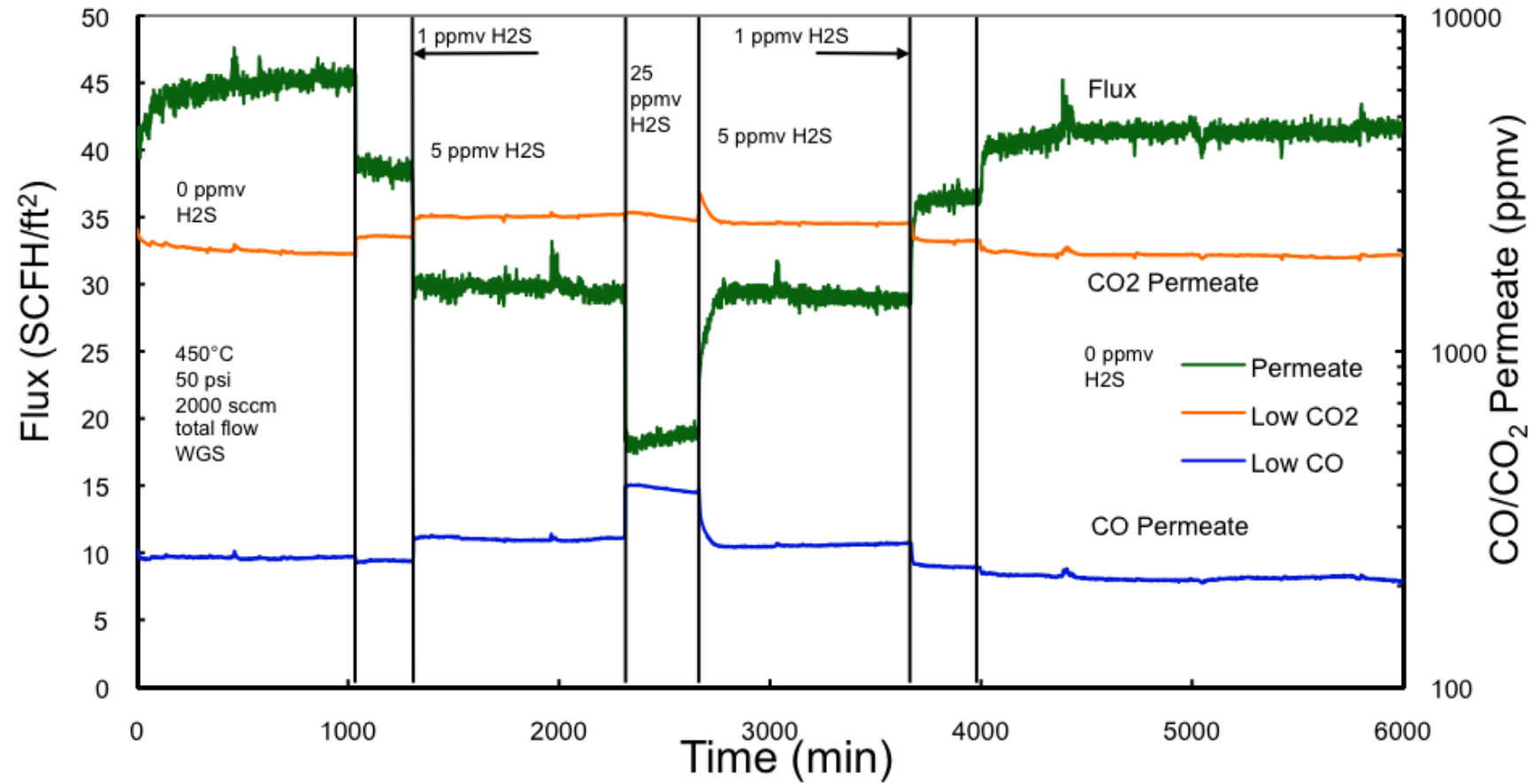


Hydrogen flux decreased slightly (5%) with an increase in CO in the WGS mixture from 2% to 5%.

H₂ flux 64 SCFH/ft² , H₂ purity 99.99% H₂ recovery 60%

Technical Accomplishments & Progress

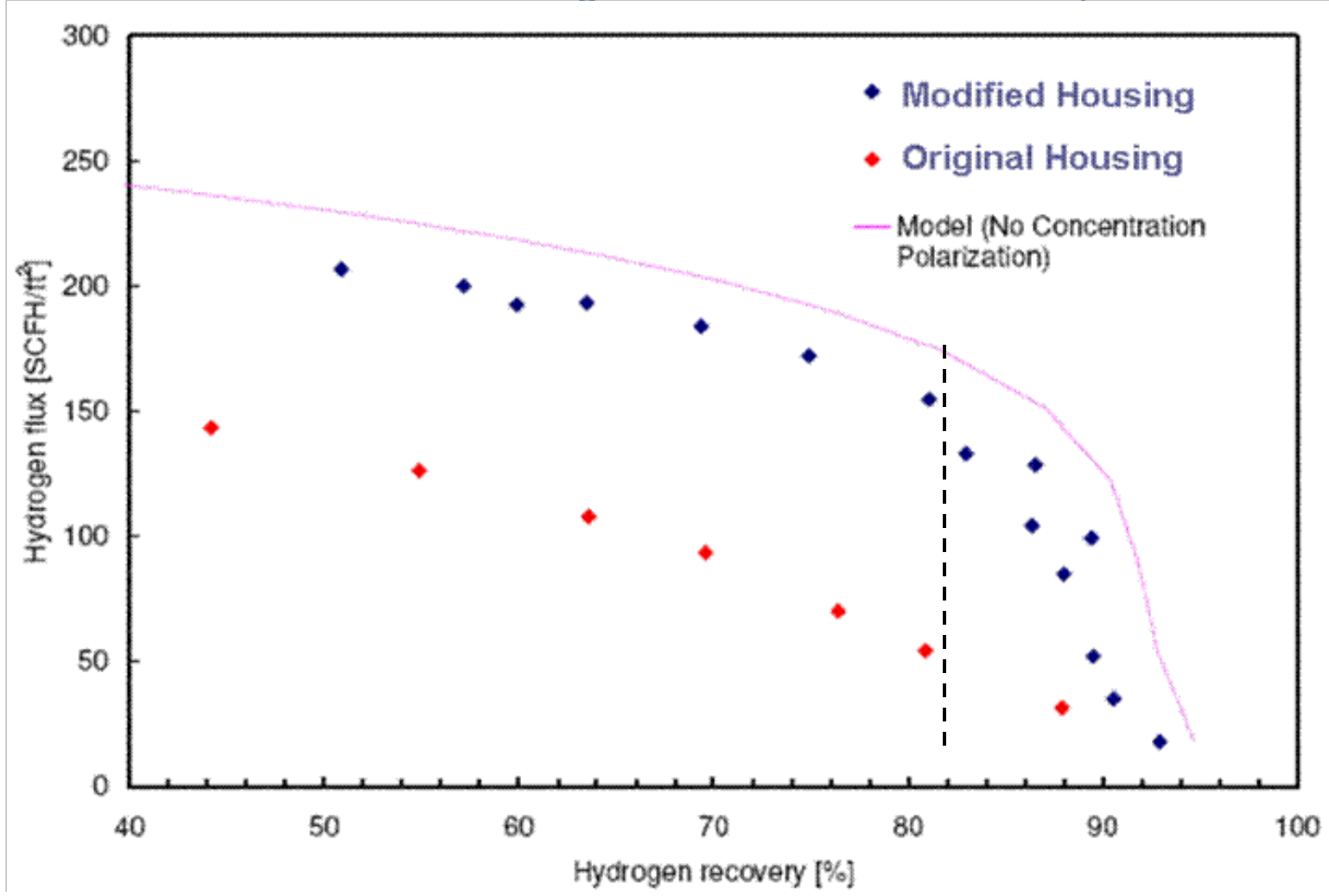
Effect of H₂S concentration in the feed gas



The H₂ flux decreased with increasing H₂S content, however, the flux was almost fully recovered when the H₂S was removed from the feed stream.

Technical Accomplishments & Progress

Membrane module design to reduce concentration polarization



H₂ flux 160 SCFH/ft²

H₂ purity 99.995%

H₂ recovery 82%

Technical Accomplishments & Progress

Techno-Economic Modeling Background

- Membrane cost analysis done by Pall Corp. included - scale-up to 1m length, pressure vessels and multi-tube modules, manufacturing and volume production and economies of scale estimates
- H₂ production model (H2A) by Directed Technologies Inc. was used for cost analysis of medium temperature ethanol integrated reformer/ WGS/membrane separator system coupled with a forecourt model
- H₂ production cost for 1 kg or “gallon of gas equivalent” (GGE) is determined for given process, operating conditions and capital costs
- Preliminary sensitivity analysis was conducted by DTI for determining the influence of membrane permeability, overall H₂ recovery, and cost of membrane tubes on the cost of H₂ for 1500 kg/d H₂ production rate
- Hydrogen recovery and overall ethanol conversion efficiency were found to be most influential for cost of hydrogen compared to cost of membranes themselves

Technical Accomplishments & Progress

Techno-Economic Modeling Preliminary Results

Flow Rate (scfh/ft ²)	H ₂ Recovery (%)	Cost of Hydrogen – Integrated Ethanol membrane Reactor \$/kg (GGE) of Hydrogen								
		150			200			250		
Membrane Tube Cost (\$/ft ²)		\$300/ft ²	\$500/ft ²	\$700/ft ²	\$300/ft ²	\$500/ft ²	\$700/ft ²	\$300/ft ²	\$500/ft ²	\$700/ft ²
	90%	\$2.98	\$3.00	\$3.01	\$2.97	\$2.98	\$3.00	\$2.96	\$2.98	\$2.99
	80%	\$3.06	\$3.07	\$3.08	\$3.05	\$3.06	\$3.07	\$3.05	\$3.05	\$3.06
	70%	\$3.17	\$3.18	\$3.19	\$3.17	\$3.17	\$3.18	\$3.16	\$3.17	\$3.18

- Membrane flux rate (area) and cost have minor impact on cost of H₂
 - Cost of membranes <10% of total capital cost
- Increasing hydrogen recovery decreased cost of H₂ in this range
- Ethanol efficiency – 68.87% at 90% H₂ recovery,
- Increasing ethanol conversion efficiency to 79.4% was shown to reduce the cost of hydrogen to \$2.67/kg by DTI in an earlier study

Preliminary results approach DOE target of <\$3 per GGE

Collaborations

- **Pall Corporation:** Prime contractor responsible for porous substrate development, membrane testing, membrane scale-up, design/fabrication of modules and development of production technology, technical and feasibility analysis and technology commercialization
- **Colorado School of Mines:** Sub-contractor focused on the material science. Responsibility includes selection of Pd-alloy compositions, fabrication of membranes and testing for compatibility.
- **ORNL-HTML:** Sub-contractor focused on the evaluation of material properties using unique test equipment and techniques. Includes mechanical properties and alloy structure at operating temperature.
- **Directed Technologies Inc.** Independent contractor to the DOE. Used module costs/performance to estimate H₂ cost by H₂A model for an integrated membrane reformer/water gas shift reactor configuration.
- **H₂ producer – End User:** Active discussions are in progress for participation by a commercial hydrogen producer as an End User in the Phase III program for critical techno-economic analysis.

Future Work (Phase III)

- Complete optimization of membrane synthesis steps, composition, and thickness for high flux, selectivity, and durability
- Conduct long term durability testing to develop a comprehensive data base to convince potential end users. Evaluate the effect of process conditions on membrane performance
- Scale up membrane synthesis to 12" elements with testing to verify the membranes meet all performance goals
- Design/fabrication of a multi-tube membrane module
- In collaboration with an end-user, design a full scale membrane module and develop membrane-based process for 1500 kg/d H₂ production and compare costs with a conventional system
- Expand the techno-economic analysis to different configurations with integrated membrane reactor/separator for optimizing cost of H₂ (e.g. high pressure membrane reformer)

Establish overall economic viability for H₂ production via membrane based reforming

Summary

Technical Accomplishments Achieved This Year

- Improved membrane synthesis & conditioning process
- Scaled up the ceramic coated AccuSep[®] substrate to 12” length
- Scale-up to **Pd-alloy membranes to 12”** length is in process
- Conducted extensive testing of Pd-alloy membranes in pure gas streams and in syngas/WGS reaction environments for performance and durability data on high pressure WGS test stands
- Demonstrated membrane performance meeting the goals of several milestones set for the Phase II completion and secured GO decision to move to Phase III
- Completed the preliminary techno-economic modeling in collaboration with Directed Technologies Inc. to determine influence of membrane parameters (flux, recovery, cost) on cost of Hydrogen

Summary - Performance Progress Against Targets

4-inch membrane module at 400°C

Performance Criteria	2010 Target	2015 Target	Pall Status 2009
Flux SCFH/ft ² @20 psi ΔP H ₂ partial pressure & 15 psig permeate side pressure	250	300	270*
Membrane Cost, \$/ft ² (including all module costs)	\$1,000	<\$500	<\$1,000
ΔP Operating Capability, system pressure (psi)	400	400 - 600	400
Hydrogen Recovery (% of total gas)	>80	>90	>60**
Hydrogen Permeate Quality	99.99%	>99.99%	99.99% ***
Stability/Durability	2 years	>5 years	TBD

*Maximum observed flux in pure H₂/N₂. Average flux over more than 20 samples ~ 190 SCFH/ft². Economic analysis indicates separation factor rather than flux to be stronger determinant of cost of hydrogen production

** Measured on a 50%H₂/21%H₂O/up to 3.5% CO/balance CO₂ mixed gas WGS stream. The experimentally observed recovery is determined by chosen operating conditions and is not necessarily a limit of the membrane performance.

*** Projected purity based on H₂/N₂ ideal selectivity.

Backup/Additional Data Slides

Technical Accomplishments and Progress— Meeting Phase II Milestones

1. Test Pd-Au alloy membranes to determine parametric performance in WGS reaction environments for at least 100 hrs

Time. H₂ flux was stable with time after an initial decline from 73 to 65 SCFH/ft² in first 40 hours.

Thermal Cycling. H₂ flux was reproducible with thermal cycling in H₂/Ar for 50 cycles tested.

High Pressure. H₂ flux was high (285 SCFH/ft²) and the membrane withstood high pressure (170 psig) for more than 100 hours tested.

Feed flow rate. H₂ flux increased by 55% as the feed flow rate was increased from 2 to 6 L/min due to a reduction in the concentration polarization effect. Hydrogen purity remained high.

CO content. H₂ flux decreased by 5% with an increase in CO in the WGS mixture from 2% to 5%

Technical Accomplishments and Progress – Meeting Phase II Milestones (cont.)

Steam/CO ratio. The membrane performed well at steam/CO ratios above 1.5

H₂S content. H₂ flux decreased with increasing H₂S content (5-25 ppm). The flux was almost fully recovered when the H₂S was removed from the feed.

H₂ flux decreased 87% under WGS conditions with 5 ppm H₂S for the pure Pd sample @ 400°C. Under the same test conditions, the flux decreased 65% for a 5% Au alloy membrane. At 450°C, the flux decrease for the Au alloy membrane was only 33%. These results are encouraging for the potential application of Pd-alloy in severe environments.

Notable performance in WGS. At 170 psig feed pressure and 6 LPM WGS feed flow rate in a 2” single membrane tube module, the H₂ flux was 285 SCFH/ft² and the H₂ purity was 99.997% with a H₂ recovery of 78%.

Notable performance in 70H₂/30Ar. At 75 psig in a 2” single membrane tube module H₂ flux was 160 SCFH/ft² and H₂ purity was 99.995% with a H₂ recovery of 82%.

Technical Accomplishments and Progress – Meeting Phase II Milestones (cont.)

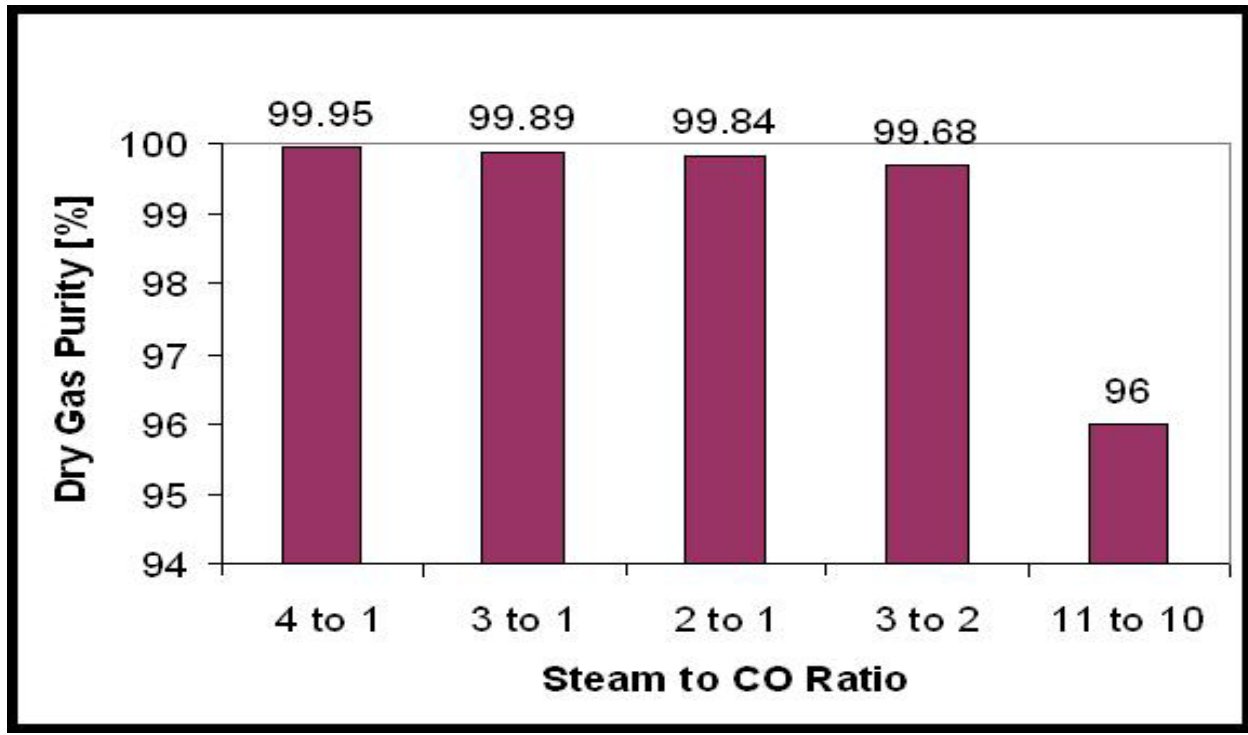
2. Test a Pd-Au alloy membrane in WGS for 500 hrs. to determine performance H_2 flux was stable with time for 500 hours. Flux remained constant at 65 SCFH/ft² for 460 hours after an initial decline from 73 SCFH/ft² in the first 40 hours.
3. Determine performance trends as a function of Au level and membrane thickness Completed one series. Pd-Au alloy membrane exhibited a 10% flux reduction, whereas pure Pd membrane exhibited a 30% flux reduction in a WGS atmosphere. Additional work is recommended.
4. Based on average performance data, calculate the surface area to produce 1500 kg/day H_2 From the performance data obtained and taking an average flux of 105 SCFH/ft², an average recovery of 90%, the WGS membrane reactor area estimated by model simulations to produce 1500 kg/day H_2 was 50 ft² for a NG reformer-based process and was 70 ft² for an ethanol reformer-based process.

Technical Accomplishments – Meeting Phase II Milestones (cont.)

5. Design a membrane module based on this surface area to produce 1500 kg/day H₂. A generic conceptual multi-tube module design was prepared with consideration to minimize gas phase mass transfer (concentration polarization) effects.
6. Estimate the cost of this membrane module in high volume production. The estimated high volume cost of a membrane module is < \$1000/ft². The cost of WGS membrane reactor modules with 70 ft² total membrane area for 1500 kg/day ethanol-based hydrogen production plant is < \$70,000.
7. Submit the surface area and production cost to DTI for cost of H₂ production analysis. Based on the flux of 150 SCFH/ft², an average recovery of 90% and the calculated membrane area required to produce 1500 kg H₂ per day of 96.7 ft², a DTI cost analysis resulted in a H₂ cost of \$2.99/kg, achievable with an integrated Pd-alloy membrane reformer/separator system.

Technical Accomplishments & Progress

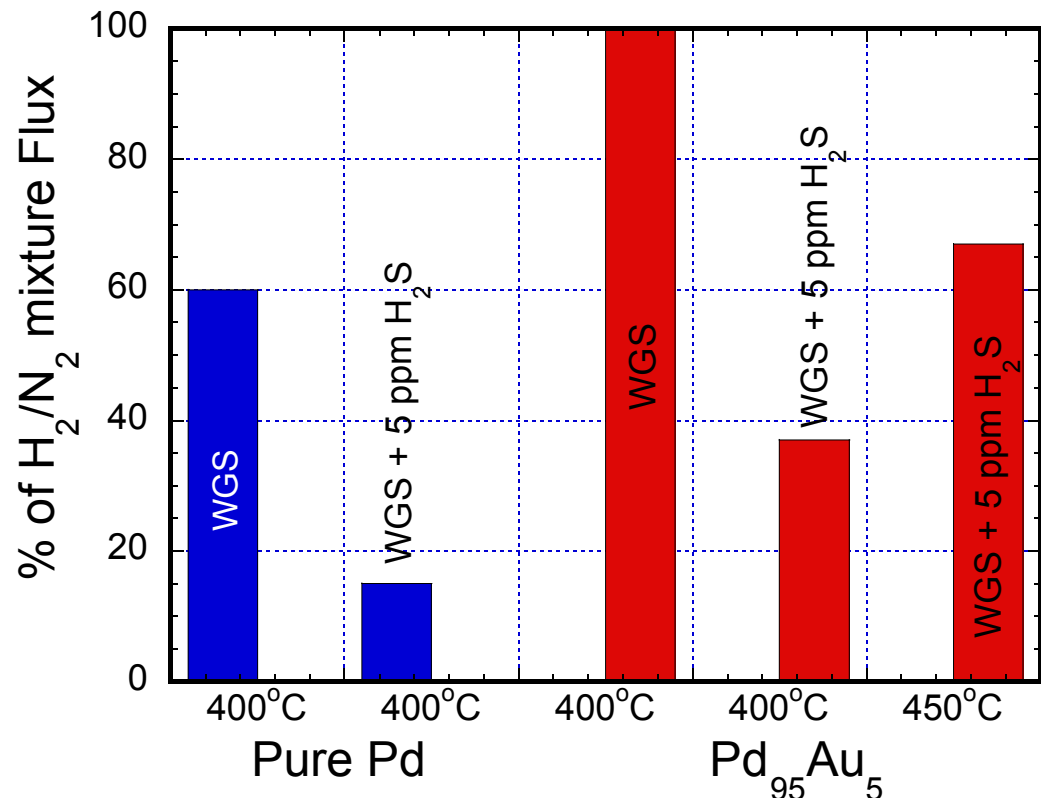
Effect of Steam/CO ratio in the feed gas



- H₂ flux did not significantly change with varying steam to CO ratios
- The membrane performed well at steam to CO ratios above 1.5
- At a steam to CO ratio of 1.1 to 1 significant increase in the impurities in the permeate was observed

Technical Accomplishments & Progress

Effect of H₂S in the feed gas



- The H₂ flux for the pure Pd sample decreased by 40% in WGS environment. No decrease for the Pd-Au alloy when exposed to the same WGS environment.
- With 5 ppm H₂S in the feed, the pure Pd flux decreased by 83%, and the Pd-Au flux decreased by 65% reduction at 400 °C.
- The flux reduction was only 33% at 450 °C.

Technical Accomplishment - Module Design/Cost Estimate

