II.C.3 Water-Gas Shift Reaction via a Single Stage Low-Temperature Membrane Reactor

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Objective

The water-gas shift (WGS) reaction becomes less efficient when the high carbon monoxide (CO) conversion is required, such as for the distributed hydrogen production applications. Our project objective includes:

- Develop a highly efficient and low temperature membrane-based WGS reaction process in a bench scale first, then tested in a pilot-scale and finally demonstrated in a field test unit.
- Screen our existing membranes and then tailor them specifically for the proposed process and reactor.
- Determine hydrogen production cost and define the system integration requirement for commercialization.
- Reduce the capital and operating cost for distributed hydrogen production applications.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(K) Durability
(N) Hydrogen Selectivity
(O) Operating Temperature
(R) Cost

Technical Targets

Technical targets for microporous membranes are listed below:

- Flux Rate - 100 to 200 scfh/ft^2 for 10 to 20 bar pressure, respectively.
- Membrane material and all module costs - \$60-80/ft^2 of membrane.
- Durability - >1,100 hours of testing has been completed.
- Operating capability - 500 psi.
- Hydrogen recovery - 80% (of total gas).
- Hydrogen quality - greater than 95 percent of total dry gas.

Accomplishments

- **Limited Economic Advantages by the Membrane-Based Process.** Our membrane reactor process (HiCON, combining WGS/H_2 separation via carbon molecular sieve [CMS] membranes) delivers minor cost benefit, in comparison with the conventional (WGS + pressure swing adsorber) process according to H2A analysis. Case studies in DOE H2A analysis show similar results. Hydrogen produced at a low pressure is the main cause.
- **Innovative Solution to Deliver H_2 at Higher Pressure.** An innovative process concept to deliver a higher pressure hydrogen product, e.g., 100 psig, from the membrane process has been developed. This innovation reduces the electricity-driven compression requirement and thus the operating cost. Degree of improvement is presented below.
- **Membrane Development/Modifications (2nd Iteration) to Implement Innovation.** Pd thin film supported on our commercial ceramic substrate/module has been developed to implement the above innovation. This Pd membrane is low-cost, steam stable, and able to sustain the high pressure, i.e., ≥300 psig, uniquely qualified for the proposed innovation. Its long term operation stability, e.g., >30 thermal cycles (room temperature to 350°C) and >2 months on-stream (H_2+H_2O), has been demonstrated.
- **Economic Analysis of the Improved Process.** The H2A analysis on the improved process demonstrates

cost savings potential for a typical membrane-based process. Our preliminary, un-optimized analysis (via PRO/II) exhibits ~5% cost reduction by our membrane-based production process. Optimization is presently underway.

- **Pilot-Scale Membrane Bundle/Module Development and Testing.** Pilot-scale membrane bundle/housing has been prepared and tested under multiple thermal/pressure cycles and is ready for field testing. Hydrogen recovery using a pilot-scale module (i.e., 0.1 m^2, 21 scfh/hr at 50 psig) has been successfully fabricated and its performance is consistent with the results obtained from the single tube bench top unit, e.g., ≥99.5% purity at 93% recovery.
- **Preparation of Hydrogen Separator for Field Testing.** A pilot-scale hydrogen selective membrane/module (150 scfh H_2, 1.5 m^2) is currently under preparation, and will be delivered to our end user in June 2009 for field testing using reformate generated from an autothermal reformer (ATR).
- **Applications for Other Reforming Processes with our CMS Membranes.** Our carbon-based hydrogen selective membrane has been upgraded. Its permeate flux is comparable or better than the Pd/Cu foil at the comparable temperature range. Its stability in the presence of contaminants, e.g., H_2S, has been field tested, and is ideally suitable for use with other reformates, where the Pd-based membrane may have a lack of material stability.

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Introduction

Membrane separation has been traditionally considered as a simple, low-cost and compact process. Thus, membrane process has been considered under this project as a WGS reactor/separator for enhancing the hydrogen production efficiency for distributed hydrogen production. In this project, we have focused on the development of the technology components required for integrating a membrane reactor process for distributed hydrogen production.

Approach

Our overall technical approach includes three steps as follows:

1. Bench-Scale Verification
   - Evaluate membrane reactor: use existing membrane and catalyst via math simulation.
   - Experimental verification: use upgraded membrane and existing catalyst via bench unit.
   - Validate membrane and membrane reactor performance and economics.
2. Pilot-Scale Testing
   - Prepare membranes, module, and housing for pilot testing.
   - Perform pilot-scale testing.
   - Perform economic analysis and technical evaluation.
   - Prepare field testing.
3. Field Demonstration
   - Fabricate membranes and membrane reactors and prepare catalysts.
   - Prepare site and install reactor.
   - Perform field test.
   - Conduct system integration study.
   - Finalize economic analysis and refine performance simulation.

Results

1. **Evaluation of M&P Hydrogen Selective Pd Membranes:** Our Pd membranes have been comprehensively evaluated under multiple temperature cycles and extended thermal/hydrothermal testing as shown in Figures 1 and 2. The membrane has shown excellent long-term performance stability under thermal cycling between 350 and 25°C and under hydrothermal conditions at 350°C with 25-85% H_2 and steam for the balance. Our cost/performance ratio meets/exceeds the DOE target. More importantly, the membrane is prepared on existing commercial ceramic membrane products; thus the membrane module preparation can be readily developed.
2. **Separation Performance Results of Pd Membranes in Pilot-Scale Modules (0.1 m^2):** The H_2 purity and the H_2 recovery ratio obtained from a pilot-scale module meet the specifications required by our end user for fuel processing via ATR and the requirement for distributed hydrogen production via a steam methane reformer (SMR) after post treatment

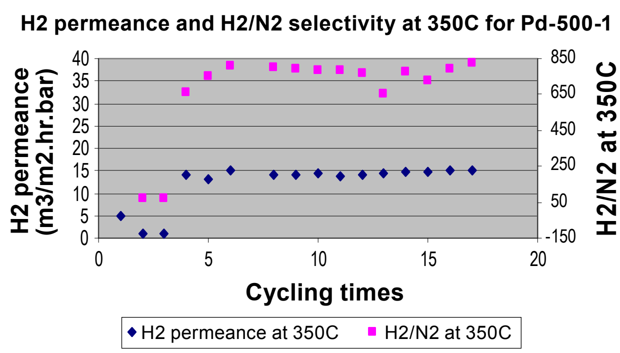

FIGURE 1. Characterization of M&P hydrogen selective membrane through thermal cycling between 25 and 350°C.

(presented in previous presentations). In addition, the selectivity and permeance obtained from the mixtures above are similar to those obtained from single components, indicating the dilution effect is negligible (Figure 3).

3. **Delivery of High Purity Hydrogen Permeate at Higher Pressure with Minimum/No Parasitic Energy Consumption:** To deliver the hydrogen product at a higher pressure with our proposed process concept, the membrane surface area requirement increases to achieve a similar recovery ratio. Thus a low-cost membrane is a must. Our innovation shows the potential to achieve further cost reductions for the membrane-based process. No optimization has been performed, which will be complete by the end of this project to finalize the ultimate cost savings potential (Table 1).
4. **Field Test Activities in Fiscal Year 2008-2009:** M&P H_2 selective membranes will be field tested for fuel reforming to produce 152 scfh hydrogen for a 5 kWh fuel cell power generation unit.

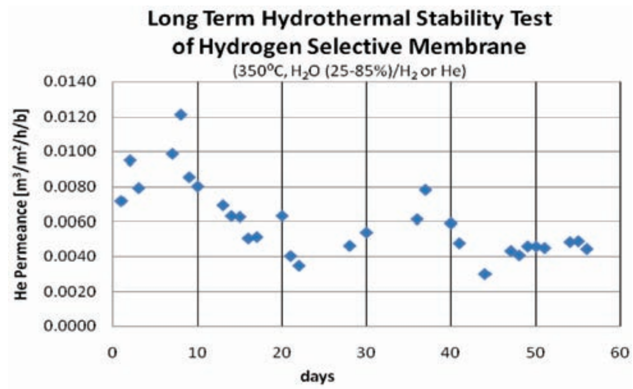

FIGURE 2. Long-term hydrothermal stability test of our hydrogen selective membrane at 350°C and in the presence of 25-85% H_2 and steam for the balance.

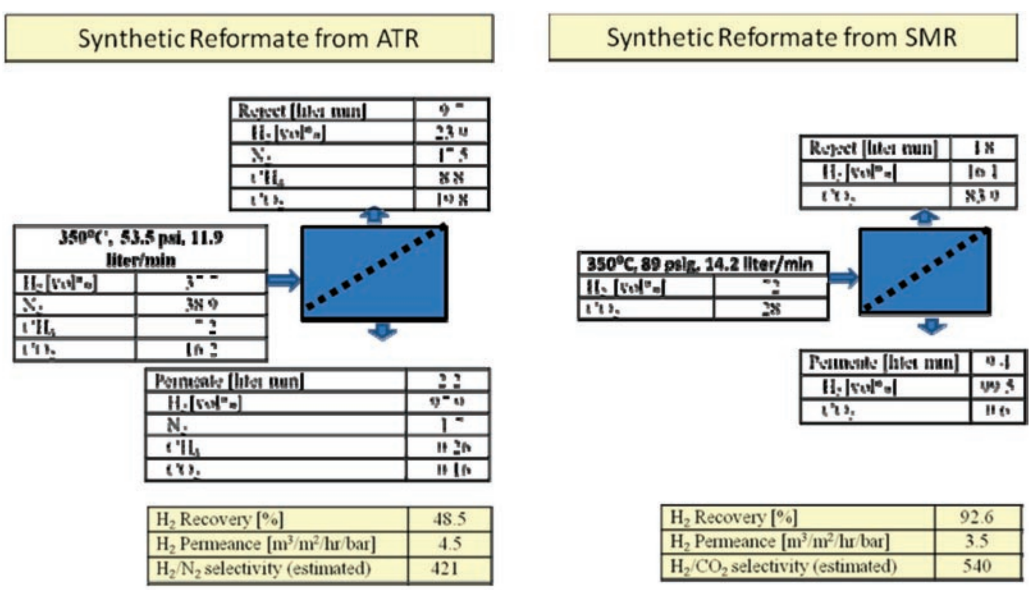

FIGURE 3. Separation performance of M&P hydrogen selective membrane for hydrogen recovery from synthetic reformates generated from ATR and SMR.

TABLE 1. Performance and economic analysis of our hydrogen selective membrane as a WGS membrane reactor with permeate delivered at a high pressure for distributed hydrogen production.

Energy Data	SMR + PSA	Ours
Methane Conversion [%]	82	82
Hydrogen Recovery [%]	75	90
NG Feedstock [NM^3/ kg H_2]	4.49	4.3
Utilities [kWh/kg/H_2]	1.11	1.54
Steam Purge Ratio [-]	NA	0.3
Deliver H_2 Pressure [psig]	300	90
Post Compression [psig]	5,280	5,280

NG - natural gas
NA - not applicable

Specific Item Cost Calculation based upon DOE H2A Studies

Cost Component	Hydrogen Production Cost Contribution ($/kg), SMR + PSA	Hydrogen Production Cost Contribuion ($/kg), Ultimate MR*	Hydrogen Production Cost Contribuion ($/kg), Ours
Capital Costs	0.45	0.32	0.40
Decommissioning Costs	0.00	0.00	0.00
Fixed O&M	0.16	0.13	0.14
Feedstock Costs	0.91	0.96	0.87
Other Raw Material Costs	0.00	0.00	0.00
Byproduct Credits	0.00	0.00	0.00
Other Variable Costs (including utilities	0.10	0.19	0.13

O&M - operation and maintenance

Parameters	1st Stage	2nd Stage	Cumulative	Single [control]
Feed Pressure [psig]	300	300	300	300
Permeate Pressure [psig]	90	90	90	0
Purge Ratio [% of feed]	18	18	36	0
H_2 Recovery [%]	74	16	90	90
H_2 Purity [%]	99.88	99.7	99.849	99.935
Membrane Surface Area [m^2]	1	0.5	1.5	0.63

Conclusions and Future Direction

During this year, we have:

- developed and comprehensively tested low-cost Pd membranes supported on our ceramic substrate,
- demonstrated successfully separation performance of our Pd membrane in pilot-scale units, and
- demonstrated potential to alleviating economic barriers by a membrane-based process with our innovation.

Presently, we are preparing H_2 selective membranes/modules for field testing. For the rest of the project period, we plan to:

- complete the field test for hydrogen separation with our existing end user to demonstrate its commercial viability in the field, and
- select an end-user to complete the field test for the membrane reactor study.

FY 2009 Publications and Presentations

1. Harale, A., Hwang, H., Liu, P.K.T., Sahimi, M., and Tsotsis, T.T., Design Aspects of a Hybrid Adsorbent-Membrane Reactor (HAMR) System for Hydrogen Production," In Press,, *Chem. Eng. Sci.*.

2. Harale, A., Hwang, H., Liu, P.K.T., Sahimi, M., and Tsotsis, T.T., Experimental Studies of a Hybrid Adsorbent-Membrane.