

II.D.2 Water-Gas Shift Reaction via a Single-Stage Low-Temperature Membrane Reactor

Paul KT Liu

Media and Process Technology Inc. (M&P)
1155 William Pitt Way
Pittsburgh, PA 15238
Phone: (412) 826-3711; Fax: (412) 826-3720
E-mail: pliu@mediaandprocess.com

DOE Technology Development Manager:
Arlene Anderson

Phone: (202) 586-3818; Fax: (202) 586-9811
E-mail: Arlene.Anderson@ee.doe.gov

DOE Project Officer: Jill Gruber
Phone: (303) 275-4961; Fax: (303) 275-4753
E-mail: Jill.Gruber@go.doe.gov

Contract Number: DE-FG36-05GO15092

Project Start Date: July 1, 2005

Project End Date: June 30, 2008

- Flux Rate - 100 to 200 scfh/sq foot for 10 to 20 bar pressure, respectively
- Membrane Material and All Module Costs - \$60-80/ft² of membrane
- Durability - >1,100 hours
- Operating Capability - 500 psi
- Hydrogen Recovery - 80% of total gas
- Hydrogen Quality - >95% of total dry gas

Accomplishments

- We have completed the bench top experimental study and mathematical simulation to demonstrate our HiCON process to deliver 99+⁰% CO conversion with 97-99% purity and 98-75% H₂ recovery via a simple membrane reactor (MR) process, uniquely suitable for distributed hydrogen production.
- Although membranes are not ideal to deliver 99.999% purity with trace CO contamination, our study indicates that a cost acceptable post treatment unique to our proposed process can achieve this target. This, in conjunction with our HiCON process, offers a practical and economically viable process to meet the stringent feed quality requirement for a proton exchange membrane (PEM) fuel cell.
- We have established a pilot-scale testing facility for performing a pilot-scale test to verify the optimized HiCON process using a full-scale membrane tube with synthetic feed, which is expected to be completed by the end of FY 2007.

In short, with the budget available, we anticipate to complete the minimum tasks required to take this HiCON process to the next step for field demonstration.



Approach

Our overall technical approach includes three steps as follows:

1. Bench-Scale Verification (1st to 15th month)
 - 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.

Objective

The water-gas shift (WGS) reaction has been considered one of the less efficient unit operations for hydrogen production via steam reforming. A highly efficient and low temperature membrane-based WGS reaction process will be developed in a bench-scale first, then tested in a pilot-scale and finally demonstrated in a field test unit. Our existing membranes will be screened and then tailored specifically for the proposed process and reactor. In parallel, hydrogen production cost will be determined and the system integration requirement will be defined for commercialization.

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
- (M) Membrane Defects
- (Q) Testing and Analysis

Technical Targets

Technical targets for microporous membranes are listed as follows:

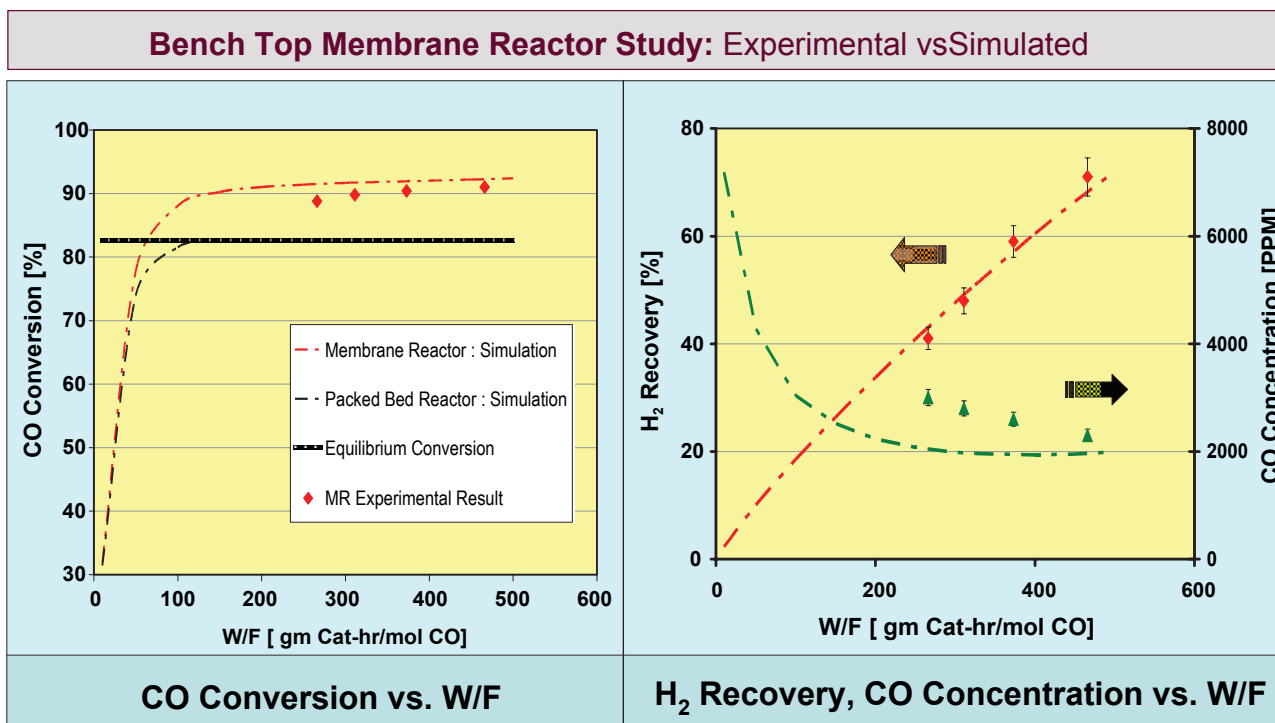
2. Pilot-Scale Testing (16th to 24th month)
 - Prepare membranes, module, and housing for pilot testing.
 - Perform pilot-scale testing.
 - Perform economic analysis and technical evaluation.
 - Prepare field testing.
3. Field Demonstration (25th to 36th month)
 - Fabricate membranes and membrane reactors and prepare catalysts.
 - Prepare site and install reactor.
 - Perform field test.
 - Conduct system integration study.
 - Finalize economic analysis and refine performance simulation.

Results

In the Year 1 report, we have presented the experimental data of CO conversion in a membrane reactor to verify the performance prediction from the mathematical simulation. During this second year, we have concentrated in the evaluation of the CO impurity level, and hydrogen recovery potential. Similar to the FY 2006 result, about 8-10% enhancement of the CO conversion was accomplished by the MR over the conventional packed bed for the ratio of catalyst dosage

to feed flow rate (W/F) between the range of 300-500 g-cat-hr/mol CO as shown in Figure 1. With the bench-top facility, we have a 10" long Compact Membrane Systems, Inc. (CMS) membrane; hydrogen recovery from 40-70% can be achieved experimentally as shown in Figure 2. The simulation predicts the hydrogen recovery very well. On the other hand, CO concentration at ~2,000 to 3,000 ppm is obtained under the experimental condition employed here. In comparison, ~2,000 ppm CO is predicted for this range of W/F. The simulation underestimates the CO concentration at the low range of W/F, i.e., 200-300 g-cat-hr/mol CO. This range of discrepancy in CO is considered acceptable for our purpose of obtaining an order of magnitude level of CO for the post-treatment.

Since an extremely high purity of hydrogen (i.e., 99.999%) is required for the PEM-type fuel cell application, it is not practical for our CMS membrane based upon its micro-porous structure to deliver hydrogen purity to meet the specification. We believe that a membrane reactor-based process can be developed, called HiCON, with the total hydrogen yield of near 90% through our process as described in Figure 3. Since hydrogen product requires post compression for storage at the distributed production site, the post treatment can be implemented at a pressure that is economically feasible. Presently three different levels of hydrogen purity are targeted from our HiCON process as described in Figure 3. In addition, the



W/F: Ratio of Catalyst Dosage to Feed FlowRate

FIGURE 1. Performance of Membrane Reactor: CO Conversion, Hydrogen Recovery and CO Contaminant vs. W/F

Bench Top Membrane Reactor Study

Experimental vs Simulated & Verification of Mathematical Model

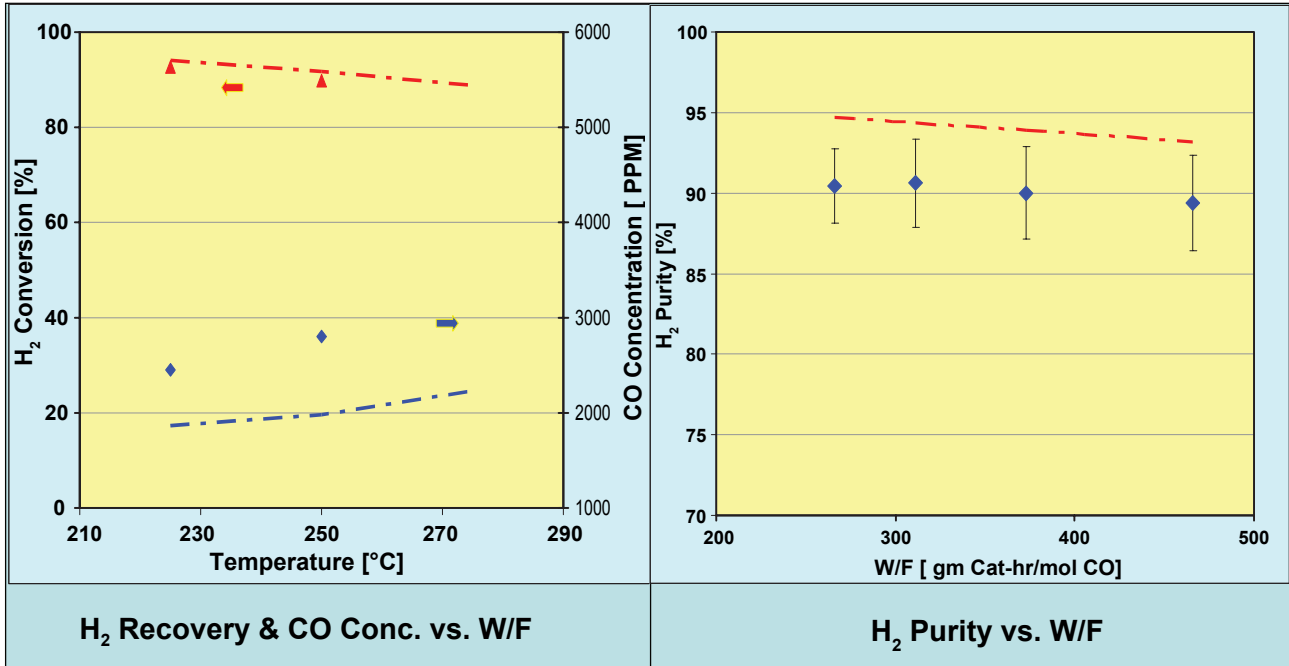


FIGURE 2. Performance of Membrane Reactor: Effect of Temperature on CO Conversion and CO Contaminant Level and Effect of W/F on Hydrogen Purity

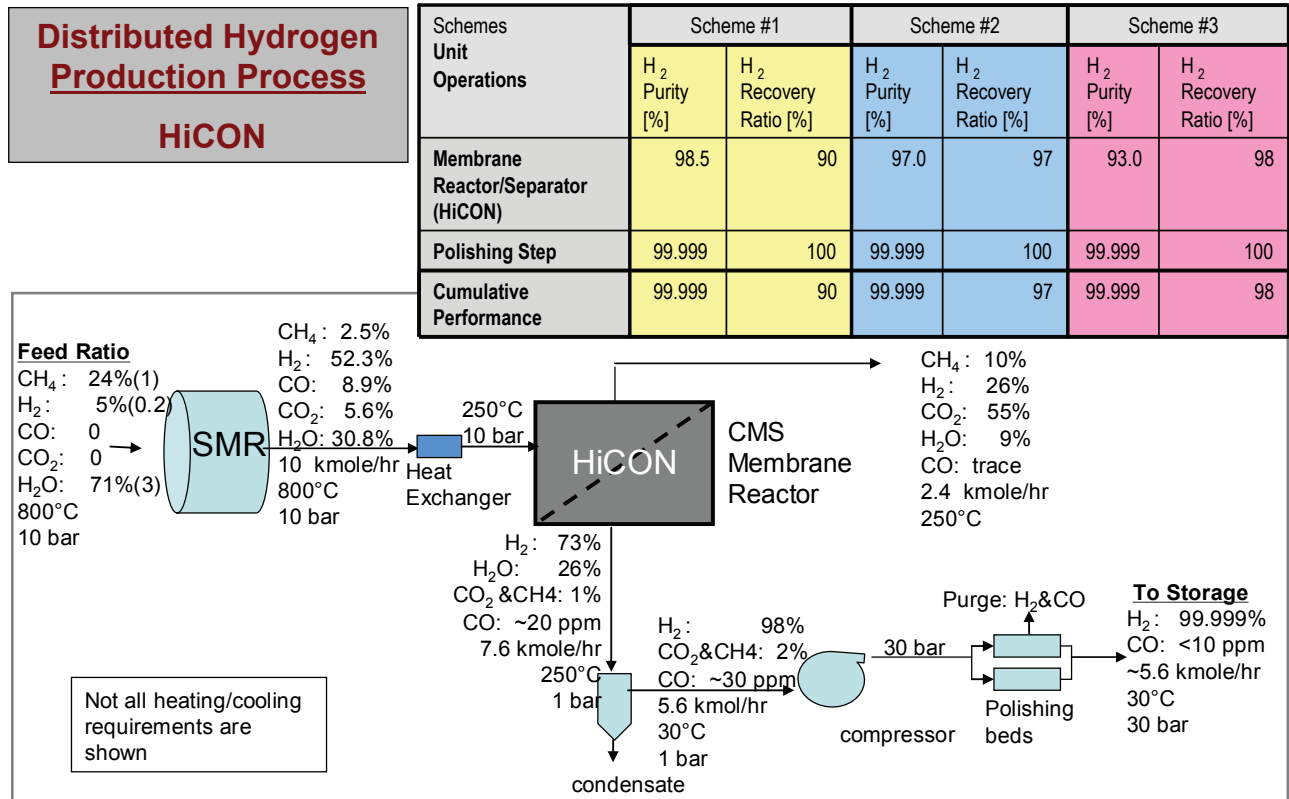


FIGURE 3. Process Diagram with Stream Composition for Steam Reforming with Our HiCON Process in Conjunction with Post Treatment

concentrations of the CO, N₂ and other contaminants in the hydrogen produced from our HiCON are much lower than that of CO₂; these trace contaminants are expected to be removed within the same absorber of our post treatment process. No separate post treatment is necessary for each contaminant.

The pressure swing adsorption (PSA) operation is conventionally practiced for hydrogen recovery from the steam reformer with a typical 70-85% hydrogen recovery. If a product stream with 99.999% purity is required, the hydrogen recovery is believed to be close to the low end of the recovery ratio. As indicated in Figure 3, the hydrogen recovery ratio is much higher if temperature swing adsorption (TSA) is employed. However, the use of our proposed TSA may require a longer bed due to the much longer cycle time, which results in the absorber bed length increase and consequent capital cost increase. A preliminary economic analysis has been performed as presented in Figure 4. Our cost analysis shows that about 5 cents/kg hydrogen produced as the capital recovery cost detailed in Figure 4. No operating cost is included. This range of cost is very insignificant in consideration of the current bulk hydrogen production

cost of \$1.00-2.40 per kg hydrogen. The distributed hydrogen production cost approximates toward the high end of this range. Thus, we believe that even with 100% safety factor, our post-treatment cost remains to be very acceptable. More importantly, this post-treatment offers an insurance policy for the upstream membrane reactor; the hydrogen product purity can be flexible within the range of 97-99%.

Conclusion and Future Directions

Our FY 2007 work indicates that our experimental results are very consistent with the mathematical prediction with regard to the important aspects of the membrane reactor performance, including hydrogen purity, CO contaminant level, CO conversion and effect of temperature. This model along with the reaction kinetic equation obtained here has been used to perform the process development and optimization study. Hydrogen purity of 99.999+% with the hydrogen recovery ratio of 90% can be delivered from our HiCON process based upon the simulation. For the remainder of the project, we will concentrate on the experimental

Preliminary Economic Analysis: Post Treatment Capital and Operating Cost
 Target: 99.999% purity H₂ Basis: 1500 kg/day H₂ production

Case A: Temperature Swing Adsorption (TSA) Integrated with Membrane Reactor			
Adsorption temperature [C]	50		
Pressurization cycle [min]	5		
Adsorption Cycle [min]	175		
Temperature Swing Regeneration [min]	180		
Feed Purity [%]	99	97	93
Adsorber ID [in]	12.6	15.7	19.8
Adsorber Height [ft]	11.8	19.9	29
Capital Cost* [\$]	134,598	214,249	333,304
Capital Recovery Cost [¢/Kg H ₂]	4.1	6.5	10.1
Hydrogen Yield [%]	~100	~100	~100

Bulk Hydrogen Cost at Production Point via Methane Steam Reforming
 \$1 – 2.4/Kg H₂ for 22-600 tons/day with \$3.5-7/GJ NG

* Example of Capital Cost Estimate: for 99% purity case
 For Quantity of 4 Adsorbers

Purchase Price of Pres Vessels, fob	\$42,032
Purchase Price of Zeolite, fob	\$2,162
Purchase Price of Support, fob	\$39
Delivery	\$2,212
Installation	\$51,090
Purchased, Deliverd & Installed	\$97,535
Piping, Valving & Instrumentation	\$19,507
Total Fixed Capital Investment	\$117,042
Other One-Time Costs	\$17,556
Other One-Time Costs	\$134,598
Not including heating equipment for TSA.	

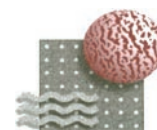


FIGURE 4. Economic Analysis of Our Proposed Post Treatment Based Upon Temperature Swing Adsorption Process

verification of the above performance using a pilot-scale unit. A barricade facility has been established to perform this test. Once the test is complete, our economic analysis will be refined and finalized to incorporate the post-treatment cost performed by an outside vendor. Depending upon the budget availability, the field demonstration with a pilot-scale unit as originally planned will be pursued.

Publications and Presentations

1. Tsotsis, T.T., Sahimi, M., Fayyaz-Najafi, B., Harale, A., Park, B.G., Liu, P.K.T., "Hybrid Adsorptive Membrane Reactor," U.S. Patent Application, February 2006.
2. Harale, A., Hwang, H., Liu, P.K.T., Sahimi, M., and Tsotsis, T.T., Experimental Studies of a Hybrid Adsorbent-Membrane Reactor (HAMR) System for Hydrogen Production," In Press *Chem. Eng. Sci.*
3. Ciora, Rich J. Jr, Paul KT Liu, and Tho T. Tsotsis, "Hydrogen Separation using Carbon Molecular Sieve Membranes", Pittsburgh Coal Conference, Pittsburgh, PA, 2006.
4. Harale, A., H. Hwang, M. Sahimi, T.T. Tsotsis, "A Hybrid Adsorbent-Membrane Reactor (HAMR) for Hydrogen Production", *AIChE Annual 2006 Meeting*, San Francisco, CA, Abstract Reviewed Paper 2006-11-14.
5. Harale, A., H. Hwang, P.K.T. Liu, M. Sahimi, T. T. Tsotsis, "Experimental Studies of a Hybrid Adsorbent-Membrane Reactor (HAMR) System for Hydrogen Production", *9th International Conference on Inorganic Membranes (ICIM 9)*, Lillehammer, Norway, Abstract Reviewed Paper 2006-06-25.