# II.C.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:
Sara Dillich
Phone: (202) 586-7925; Fax: (202) 586-2373
E-mail: sara.dillich@ee.doe.gov

DOE Project Officer: Jill Sims
Phone: (303) 275-4961; Fax: (303) 275-4788
E-mail: Jill.Sims@go.doe.gov



Contract Number: DE-FG36-05GO15092

Project Start Date: July 1, 2005
Projected Ended Date: June 30, 2009


## Project Objective

The water-gas shift (WGS) reaction is less efficient when high carbon monoxide (CO) conversion is required, such as for the distributed hydrogen production applications. A highly efficient and low temperature membrane-based WGS reaction process will be developed on 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, the hydrogen production cost will be determined and the system integration requirement will be defined for commercialization. Finally, high hydrogen purity at high hydrogen conversion/recovery efficiency will be our overall strategy to 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
(M) Membrane Defects
(N) Hydrogen Selectivity
(R) Cost

## Technical Targets

Technical targets for microporous membranes are listed below:

- Flux Rate - 200 scfh/ft$^2$ for 20 psi pressure drop
- Membrane Material and All Module Costs - \$200/ft$^2$ of membrane
- Durability - >26,280 hours of testing has been completed
- Operating Capability - 400 psi pressure drop across the membrane
- Hydrogen Recovery - >80% (of total gas)
- Hydrogen Quality - greater than 99.5 percent of total (dry) gas

## Accomplishments

- **Process Synthesis for Distributed $H_2$ Production based upon WGS/Membrane Reactor (MR)** A distributed hydrogen production process has been synthesized based upon our WGS/MR + polishing system to produce hydrogen with high overall methane conversion (85%) and 99.999% hydrogen purity.
- **High $H_2$ Recovery vs High $H_2$ Purity is no longer a Choice** Our lab experimental results indicate 90% hydrogen recovery at 99% purity is achievable with our HiCON (High CO Conversion) process. A process development unit (PDU) unit has been assembled to experimentally verify this simulation by the end of the project period.
- **Production of 99.999% with Operating Cost-Free Polishing Step** Our experimental result demonstrated that 99.999% purity $H_2$ was produced with an adsorption-based polishing step. Through integration with the HiCON process, this polishing step can be operated with negligible operating cost.
- **Process Flow Diagram and Heat Integration with PRO/II** PRO/II design package was used for the development of the process flow diagram based upon our HiCON process and heat integration. The finalized design with optimized heat integration was used as input for H2A analysis.
- **Performing H2A Analysis** A preliminary H2A analysis has been performed based upon our simulation result. Once the experimental results from the PDU unit become available, we will finalize the process flow diagram and the H2A analysis by the end of the project period.

- **Assembly of Pilot Testing Unit** A stand-alone pilot testing unit is under construction, which will be used for in-house pilot testing (under Phase I) and field demonstration (under Phase II if the budget is available).

✧ ✧ ✧ ✧ ✧

## Approach

Our overall technical approach includes three steps as follows:

1. Bench-Scale Verification (1st to 15th month)
   - Evaluate membrane reactor: use mathematical simulations to evaluate the existing membrane and catalyst
   - Experimental verification: use upgraded membrane and existing catalyst via bench unit
   - Validate membrane and membrane reactor performance and economics
2. Pilot-Scale Testing (16-24th 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 (25 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

During this year we have focused on the experimental study to demonstrate the ability of our proposed process, HiCON, to deliver hydrogen product with 99.999% purity at a high hydrogen recovery ratio. In the previous year, we identified the possible effect of $CO_2$ on hydrogen permeance in a $H_2/CO_2$ mixture, particularly for applications where high purity hydrogen is required. On the other hand, no adverse effects were observed in the presence of CO and $H_2O$. While we are continuing the investigation of this specific issue, we have spent some effort to evaluate a different type of membrane specifically designed for the purpose of delivering hydrogen product with 99+% purity as input to our polishing step. Using 75-95% $H_2$/25-5%$CO_2$ as mixtures, we have investigated $H_2$ purity vs. hydrogen recovery at 350°C and 140 psig. The results are presented in Figure 1. In addition, our simulation result is consistent with the experimental data. Using this experimentally verified mathematical model, we have performed the mixture separation using the feed similar to our application. The result shows that at 90-95% hydrogen recovery ratio, we can achieve 98.8 to >99.9% purity hydrogen with a surface area requirement of up to 25 $m^2$ for a 100 kg/day system. This purity and recovery ratio meets the specification we set for the polishing step.

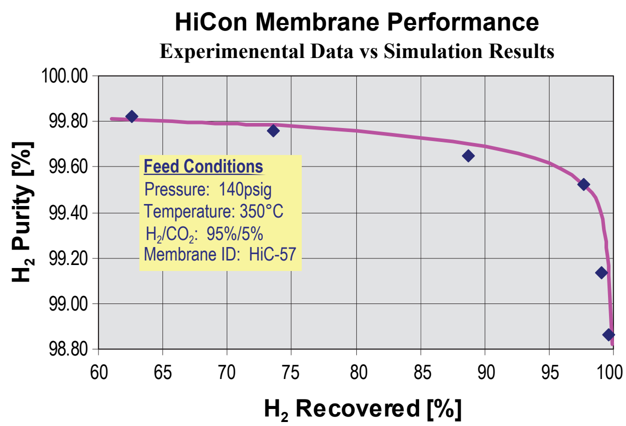


**FIGURE 1.** Performance of Membrane with Improved Hydrogen Selectivity Targeting Production of >99% Purity as Feed for Polishing Step

We had performed some engineering analysis previously to demonstrate the feasibility of using an adsorption-based polishing step to meet the hydrogen purity requirement, i.e., 99.999%. Our HiCON process has been streamlined and refined this year; its updated process schematic is presented in Figure 2. During this year, we have performed an experimental study to verify (i) the effluent from the adsorber we designed meets the purity spec, (ii) the adsorption capacity reaches the steady state after the 2nd cycle, and (iii) the bed sized required for 100 and 1,500 kg/day of hydrogen are acceptable. The adsorption capacities determined from the three cycle adsorption/regeneration study appears to be stable as presented in Figure 3. However, the capacity obtained here is about 50% of the capacity published in the literature. The experimentally obtained result by us will be used for our cost analysis. In addition, we have performed the experimental study to determine concentration vs. time for the initial breakthrough period to demonstrate the ability to deliver >99.999% purity as shown in Figure 3. Adsorber sizing and design has been completed, showing that an acceptable footprint of adsorbers can be developed to achieve our purity objective.

We have also focused on the optimization of the process flow diagram and heat integration for our proposed process. We have completed the first go-around of the process flow diagram development using PRO/II design package for both our proposed and the

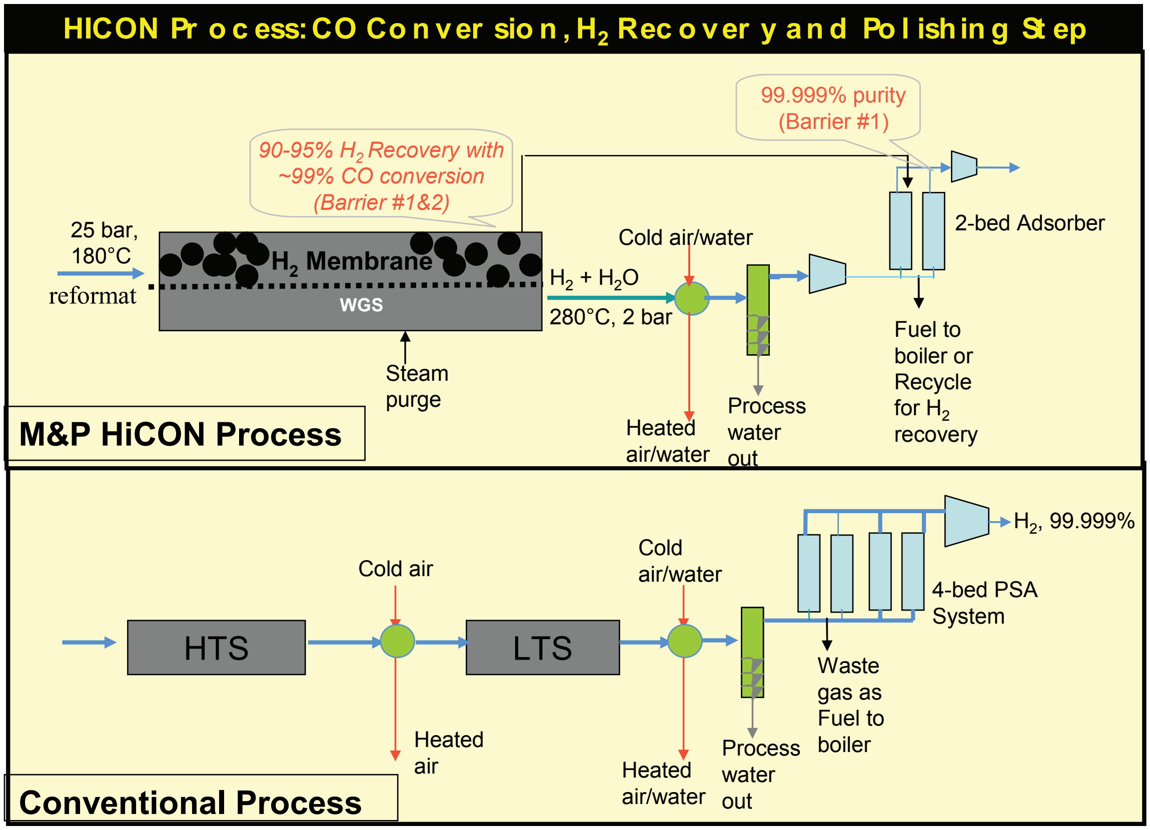


**FIGURE 2.** Comparison of M&P HiCON Process vs. Conventional Process. Also Shown are the Barriers Overcome by Our Proposed Process.

**Experimental study: production of 99.999% $H_2$ via Polishing Step**

| Experimental Results | | Projected for Actual Operating Condition | |
|---|---|---|---|
| Adsorbent Dosage | 38 gm | | |
| Adsorer | 3/4"ID x 10"L | | |
| Flow rate | 3 cc/sec | | |
| Pressure | 80 PSI | Feed Pressure | 308.7 psig (20 bar) |
| Composition | 95.41% H2 | equi. Comp [% | 98.592 |
| | 4.59% CO2 | | 1.408 |

| Effluent | | | | Influent | Effluent | | |
|---|---|---|---|---|---|---|---|
| time (min) | H2 Purity (% | CO2 % in gas | % Error ** | % H2 Purity | P, CO2, psia | %CO2 Impurity | % H2 Purity |
| 2 | 100 | No $CO_2$ Detected | | 98.592 | 0.000 | 0.000 | 100.000 |
| 5 | 100 | No $CO_2$ Detected | | 98.592 | 0.000 | 0.000 | 100.000 |
| 10 | 99.992 | 0.008 | 0.080 | 98.592 | 0.008 | 0.002 | 99.998 |
| 15 | 99.913 | 0.087 | 0.058 | 98.592 | 0.082 | 0.027 | 99.973 |
| 25 | 99.934 | 0.066 | 0.028 | 98.592 | 0.063 | 0.020 | 99.980 |
| 35 | 99.956 | 0.044 | 0.049 | 98.592 | 0.042 | 0.013 | 99.987 |
| 75 | 99.906 | 0.094 | 0.107 | 98.592 | 0.089 | 0.029 | 99.971 |

**% error is calculated from the GC calibration data

| Adsortpion cycle | 1st | 2nd | 3rd | Adsorption | Regeneration |
|---|---|---|---|---|---|
| Capacity (mole/kg) | 1.98 | 1.88 | 1.88 | 44°C | 160°C |

**FIGURE 3.** Effluent Purity and Capacity of Adsorber as Polishing Step for Our HiCON Process Targeting 99.999% Hydrogen Purity

base case, i.e., the steam methane reformer (SMR) + the conventional pressure swing adsorption (PSA) system. Both cases have been evaluated in terms of the fuel consumption and productivity. Although the methane conversions are the same for both cases, the hydrogen conversion/recovery from the M&P case is about 93% vs. the conventional 75% as summarized in Figure 4. Thus, the net gain of our proposed process is about 25% hydrogen productivity over the base case.

A pilot testing unit is being assembled and tested. This unit will be used for the demonstration of the entire HiCON process. The results generated from this test will be used for the H2A analysis by the end of the project.

| *Energy efficiencies for individual steps* | Our Proposed SMR+HiCON | Conventional SMR+PSA |
|---|---|---|
| Production System Feedstock Consumption (kJ Feedstock (LHV)/kg of H2) | 164,872 | 224,234 |
| Production Unit Hydrogen Efficiency (%) | 85.6% | 69.0% |
| Production Electricity Consumption (kWhe/kg of H2) | 0.000 | 0.000 |
| Production Step Efficiency (%) | 73.1% | 53.8% |
| Compression, Storage and Dispensing Electricity Consumption (kWhe/kg of H2) | 2.7 | 1.9 |
| Compression, Storage and Dispensing Step Efficiency (%) | 92.1% | 94.4% |
| Total System Efficiency (%) | 67.3% | 50.8% |
| Process water consumption (L/kg of H2) | 9.7 | 9.7 |

**FIGURE 4.** Comparison of Our HiCON vs Conventional Processes in Terms of Key Performance Parameters

## Conclusions and Future Direction

The choice between high purity and high yield is no longer a problem under our proposed HiCON process. Our experimental study and engineering analysis performed in 2008 conclude that a 99.999% purity hydrogen product can be produced based upon our proposed HiCON in conjunction with a polishing step. The polishing step has been developed and experimentally verified. Its unique features include negligible operating cost, simplicity and acceptable footprint size. In addition, the hydrogen recovery from our HiCON is about 93% based upon PRO/II analysis vs. the conventional 75%. Thus, the net gain of our proposed process is about 25% hydrogen productivity over the base case. For the remainder of Fiscal Years 2008-2009, we will (i) complete the PDU testing using a single, full-scale hydrogen selective membrane and synthetic feed to generate performance database for H2A analysis; (ii) complete pilot-scale testing to demonstrate the optimized HiCON process; and (iii) complete the H2A economic analysis for hydrogen production via the developed HiCON process.

## FY 2008 Publications and Presentations

**1.** 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," *Chem. Eng. Sci., 62, 4126, 2007.*

**2.** Chen, F., Mourhatch, R., Tsotsis, T.T., and Sahimi, M., "Pore Network Model of Transport and Separation of Binary Gas Mixtures in Nanoporous Membranes," *J. Membrane Sci*., 315, 48, 2008.

**3.** 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," Submitted for Publication, *Chem. Eng. Sci.*