

## **IV.C.6 Hydrogen Production via Commercially Ready Inorganic Membrane Reactor**

*Paul Liu*

*Media & Process Technology, Inc.*

*1155 William Pitt Way*

*Pittsburgh, PA 15238*

*Phone: (412) 826-3721; E-mail: mandpmain@aol.com*

*DOE Technology Development Manager: John Winslow*

*Phone: (412) 386-6072; Fax: (412) 386-4822; E-mail: John.Winslow@netl.doe.gov*

*DOE Project Officer: Udaya Rao*

*Phone: (412) 386-4743; E-mail: Udaya.Rao@netl.doe.gov*

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*Subcontractors:*

*University of Southern California*

*Pall Corporation*

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### **Objectives**

- Construct a commercially ready membrane reactor for hydrogen production that can achieve CO<sub>2</sub> capture with minimum or no parasitic energy consumption, and demonstrate the improvement in the efficiency of hydrogen production using this reactor.
- Data collected during the bench-scale demonstration will be used to further refine an existing mathematical model and to design and build a pilot-scale testing unit using this commercially ready membrane reactor (MR) to demonstrate the concept.

### **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:

- L. Durability
- M. Impurities
- O. Selectivity
- P. Operating Temperature
- Q. Flux
- S. Cost

The project also addresses one or more of the barriers described in Section 5.1.5.1., Technical Barriers – Central Production Pathway in the Hydrogen from Coal – Research, Development, and Demonstration Plan of the DOE Office of Fossil Energy.

## Technical Targets

Table 1 lists the targets that the project will attempt to meet during its implementation.

**Table 1.** Technical Targets: Micro Porous Membranes for Hydrogen Separation and Purification

Performance Criteria	Units	2003 Status	2005 Target	2010 <sup>a</sup> Target	2015 <sup>a</sup> Target
Flux Rate	scfh/ft <sup>2</sup>	100	100	200	300
Membrane Material and All Module Costs	\$/ft <sup>2</sup> of Membrane	\$450-\$600	\$400	\$200	<\$100
Durability	Hours	<8,760	8,760	26,280	>43,800
ΔP Operating Capability	psi	100	200	400	400-1000
Hydrogen Recovery	% of total gas	60	>70	>80	>90
Hydrogen Purity	% of total (dry) gas	>90%	95%	99.5%	99.99%

<sup>a</sup> Assumes a two-stage membrane system or a membrane + pressure swing adsorption

## Approach

- Complete conversion of CO in a single-stage water-gas-shift membrane reactor (WGS-MR) under mild conditions, i.e., existing low-temperature-shift (LTS) reaction temperature, 200 to 250°C, and catalysis with a stoichiometric steam/CO ratio.
- Concentrate CO<sub>2</sub> on the reject side of the MR for CO<sub>2</sub> capture with minimum or no parasitic energy consumption.
- Reduce gas clean-up burden via (i) pre-treatment at a manageable temperature, e.g., 250°C vs >450°C for existing hot gas clean-up; (ii) reduced contaminant removal requirement in the pre-treatment; and (iii) combining contaminant (such as sulfur and others) removal with the CO<sub>2</sub> capture in the same step.
- Incorporate thermal management into the WGS reactor to streamline the WGS operation.
- Finally, conduct a pilot-scale demonstration of this commercially ready MR to replace existing two-stage packed bed WGS reactors.

## Accomplishments

- Set up apparatus to fabricate carbon molecular sieve (CMS) membrane.
- Measured hydrogen permeance of CMS membrane.
- Investigated hydrothermal stability of CMS membrane.
- Completed the mathematical model development and experimental verification.
- Demonstrated enhanced CO conversion and efficient hydrogen recovery using the proposed MR.
- Incorporated thermal management into the membrane reactor.
- Deposited hydrogen selective membrane on existing porous ceramic membrane from Media and Process Tech Inc. and stainless steel metallic substrate from Pall Corporation, and measured hydrogen flux and selectivity of the composite structure.

## Future Directions

- Establish a database for the composition and range of impurities in coal gasifier off-gas which may impair the membrane and catalyst materials under normal operating conditions.

- Complete mathematical simulation and experimental evaluation of the WGS reaction using a membrane reactor under the recommended operating conditions, and further demonstrate the potential thermal management approach.
- Establish a WGS process scheme comprising the CMS/AccuSep membrane reactor, plus required pre- and post-treatment, and evaluate its economics.
- Perform an experimental study to quantify the effect of the impurities and estimate the economics of any required pretreatment.

## **Introduction**

There is a need to develop technologies to improve the efficiency (reducing both capital and operating cost) of hydrogen production via a commercially ready membrane reactor. The proposed technology can achieve enhanced hydrogen conversion and streamline thermal management as well as provide CO<sub>2</sub> capture with minimum or no parasitic energy consumption. The technology resulted from the teaming of two industrial companies, combining the hydrogen-selective membrane from Media and Process Technology Inc. with stainless steel porous substrates/modules provided by Pall Corp. Further feasibility of the proposed technology has been demonstrated via mathematical simulation by the University of Southern California (USC), a subcontractor to this project.

A bench-top reactor will be constructed and operated to demonstrate the above benefits. Then, a pilot-scale demonstration of this commercially ready membrane reactor to replace existing two-stage packed bed reactors will be conducted. Hydrogen separation, CO<sub>2</sub> capture, and contaminant removal can be integrated into the power generation system with the proposed hardware and process.

## **Approach**

Complete conversion of CO in a single-stage WGS-MR under mild conditions, i.e., existing low-temperature-shift (LTS) reaction temperature, 200 to 250°C, and catalysis with a stoichiometric steam/CO ratio, will be examined and tested. The membrane reactor will then be designed based on a low-cost option or a large-scale option. Finally, a pilot-scale demonstration of the commercially ready membrane reactor will be conducted to replace existing two-stage packed bed WGS reactors.

## **Summary**

The project team has been able to produce several accomplishments, including the set-up of an apparatus to fabricate a CMS membrane. Measurement of hydrogen permeance of the CMS membrane was conducted as well as an investigation of the hydrothermal stability of the CMS membrane. Finally, the hydrogen-selective membrane was deposited on a porous stainless steel metallic substrate from Pall Corporation, and the hydrogen flux and selectivity of the composite structure were measured.

## **FY 2005 Publications/Presentations**

1. Ciora, R.J., Fayyaz, B., Liu, P.K.T., Suwanmethanond, V., Mallada, R., Sahimi, M., and Tsotsis, T.T., "Preparation and Reactive Applications of SiC Membranes", *Chem. Eng. Sci.*, **59**, 4957 (2004).
2. Ciora, R.J. Jr. and Liu, P.K.T., "Nanoporous Hydrogen Selective Membranes for Water-Gas-Shift Reaction", 20<sup>th</sup> Annual Intl. Pgh. Coal Conference, Pittsburgh, PA (2003).
3. Ciora, R.J. Jr. and Liu, P.K.T., "Carbon Molecular Sieve Membranes for Hydrogen Separations and Production", 21<sup>st</sup> Annual Intl. Pgh. Coal Conference, Osaka, Japan (2004).
4. Ciora, R.J. Jr. and Liu, P.K.T., "Carbon Molecular Sieve Membranes for Gas Separations", AIChE Spring National Meeting, Atlanta, GA (2005).
5. Ciora, R.J. Jr. and Liu, P.K.T., "Results from Bench and Pilot Scale Testing that Demonstrate the Superior Performance and Material Stability of Inorganic Membranes over Polymeric Membranes and Competing Inorganic Membranes: Applications in Hydrogen Recovery", to be presented at 22<sup>nd</sup> Annual Intl. Pgh. Coal Conference, Pittsburgh, PA (2005).
6. Fayyaz, B., Harale, A., Park, B.G., Liu, P.K.T., Sahimi, M., and Tsotsis, T.T., "Design Aspects of Hybrid Adsorbent-Membrane Reactors (HAMR) for Hydrogen Production", *In Press Ind. Eng. Chem. Res.*