II.G.4 The Integration of a Structural Water-Gas Shift Catalyst with a Vanadium Alloy Hydrogen Transport Device

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Objective

The 2008 project objective is to build a modular water-gas shift (WGS)/membrane integrated device capable of producing 10,000 l/day hydrogen from coal-derived syngas. Two alternate designs are being fabricated for testing to compare the technical manufacturability and economics of hydrogen production.

Technical Barriers

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

(K) Durability

(P) Flux

(Q) Testing and Analysis

Technical Targets

TABLE 1. Progress Towards Meeting Technical Targets for Hydrogen Separation Membranes

Goal	2010 DOE Target	Project 2008 Estimates
Membrane flux	250 scfh/ft^2	100 scfh/ft^2
Selectivity	99.99	99.999
Pressure	400 psi	400 psi
Recovery	80%	60%
Cost	$1,000/sq ft	$600/sq ft

The project is not strictly a membrane development project, but contains three separate and important investigations to aid membrane scale–up and integration. Our goal is to meet the DOE goals for hydrogen separation membranes while completing these technical objectives.

- Development of ceramic-based WGS catalysts appropriate for inclusion in pressurized systems undergoing pressure and thermal cycling.
- Bonding practices for sealing vanadium alloy membranes to structural alloy components for manufacturability.
- Design of integrated systems suitable for scaling to large structures containing monolithic WGS catalysts and metallic vanadium membranes.

Accomplishments

- The ceramic catalysts developed are superior to commercially available WGS materials with respect to survival in a pressurized device.
- Two different viable integrated WGS/vanadium membrane device designs are under fabrication that should meet scalability issues and performance criteria.

Introduction

This project is in response to a requirement for a system that combines WGS technology with separation technology for coal-derived synthesis gas. The justification of such a system would be improved efficiency for hydrogen production. By removing hydrogen from the synthesis gas stream, the WGS

equilibrium would force more carbon monoxide to carbon dioxide and maximize the total hydrogen produced. Additional benefit would derive from the reduction in capital cost of the plant by the removal of one step in the process by integrating WGS with the membrane separation device.

Approach

The primary goal of this project is to design and fabricate a modular component that integrates the WGS catalyst and the vanadium hydrogen transport membrane capable of producing 10,000 liters of hydrogen per day. Some additional work continues on catalyst development to optimize the structural WGS catalyst and incorporate the catalyst into a monolith appropriate for inclusion in the integrated devices. Testing of the integrated devices to produce hydrogen is a substantial portion of the total work.

Testing of the scale-up device is to ensure long-term stability of the membrane separation assembly. This portion of the work is expected to occupy up to 50% of the entire project effort. Short- and long-term performance tests will be conducted in the WRI fluidized bed gasifier. This 35 lbs/hr steam/oxygen blown gasifier operates with western coals to produce 175 scfh of hydrogen in a synthesis gas mixture. Additional tests will be conducted in a second gasifier producing an alternate range of gas composition and conditions. Some work will be required to modify the existing equipment to allow operation of the additional tests.

Some economic analysis will be conducted. Data will be collected based on predicted cost of manufacturing the scaled membrane unit and the performance data recording hydrogen shift and hydrogen separation. This data will be used to calculate predicted capital cost of installation and operation of the integrated unit in a commercial facility on a per unit of hydrogen basis.

Results

Significant progress has been made with two different integrated devices under design and construction. The first device being fabricated with the assistance of Chart Energy and Chemicals Inc. uses flat circular membranes of vanadium palladium alloy supported by porous stainless steel structures (see Figure 1). Each module contains a section of monolithic WGS catalyst and two 4.5-inch diameter membranes. Four modules are required to provide sufficient surface area to supply 10,000 l/day of hydrogen from a coal gasification source. With the multiple modules, we will have some flexibility in operation of the device to arrange individual pairs of membranes in series or in parallel. Scale-up to larger devices would include both larger diameter membranes and more modules. The

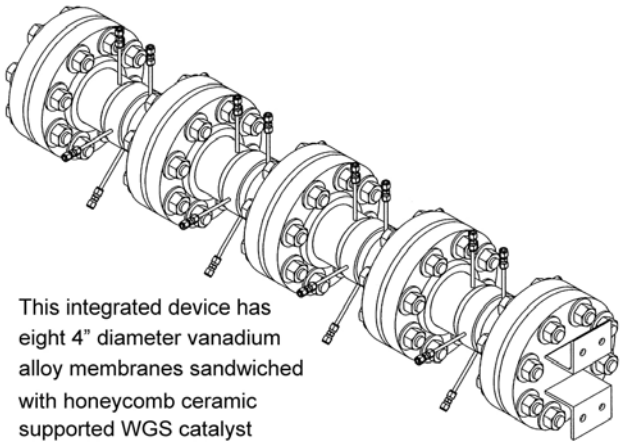

FIGURE 1. Design Drawing of a Modular Integrated WGS/Membrane Device

largest part of each module is the high-pressure flanges due to the ultimate 600-psig application. Permanent fittings using welding would eliminate these flanges and reduce total volume of each module. The elements of the design should be completed soon and fabrication is still expected during July-August, 2008.

The second scale-up unit is based on a "disc and doughnut" design produced by R. Buxbaum of REB Research and Consulting (see Figures 2 and 3). In this design, the vanadium alloy membranes are joined in pairs into a structural component capable of withstanding differential pressure. Under a subcontract from WRI, Dr. Buxbaum has prepared an integrated two-membrane unit to contain the monolithic catalyst component. Scale-up of this stackable unit appears straight-forward up to a certain number of membranes per module. In this design, all membranes would

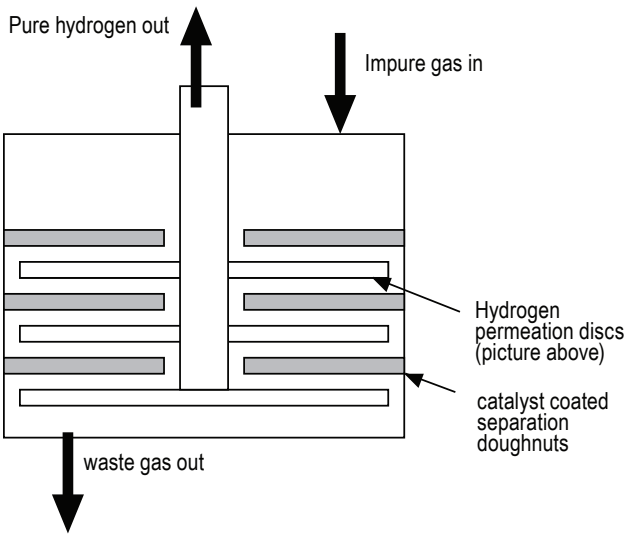

FIGURE 2. Schematic of the Disc/Donut Integrated Device Design

FIGURE 3. Photograph of the Disc/Donut Integrated Device

operate in series. The two-membrane unit has been completed and is undergoing testing. Initial pressure tests with helium indicate that the membrane system is leak-free. The first separation tests will be conducted in pure hydrogen at 100 psi before moving to the coal gasifier.

The preliminary paper design of a third type of integrated system is underway. The first two designs have certain conventional approaches to pressurized reactors in that active components such as membranes and catalyst monoliths are placed inside a structural steel vessel with appropriate inlet and outlets for gas transport. This third design is a radical departure from those conventional designs in that the active components serve as gas boundaries. Using a stacked shim process, each shim has gas pathways etched into the metal, and alternate shims act as membranes or catalyst containing syngas pathways. This approach would maximize separation area versus device volume and better control heat transport. No physical device using this technology will be built at this phase of the project, but critical issues of the shim device will be examined for further study.

WGS catalyst development continued with the addition of ceria to the conventional iron-chromium-copper oxide catalysts. Since the series of catalysts with small amounts of ceria (2 to 8 wt%) were not as effective as the initial ~4 wt% ceria catalyst, apparently due to slight differences in the preparation technique, we made adjustments to the synthesis procedure to attempt to duplicate the original ceria-containing catalyst and to determine if more active and stable catalysts can be produced. WGS catalysts prepared with low levels of ceria are comparable to the improved 15% alumina containing catalysts developed earlier in the project (Figure 4). Efforts have begun to make ceramic monoliths containing the 15% alumina WGS catalyst for incorporation into the two integrated devices described above. These experiments use a honeycomb mullite structure with multiple coast of the alumina containing WGS catalyst.

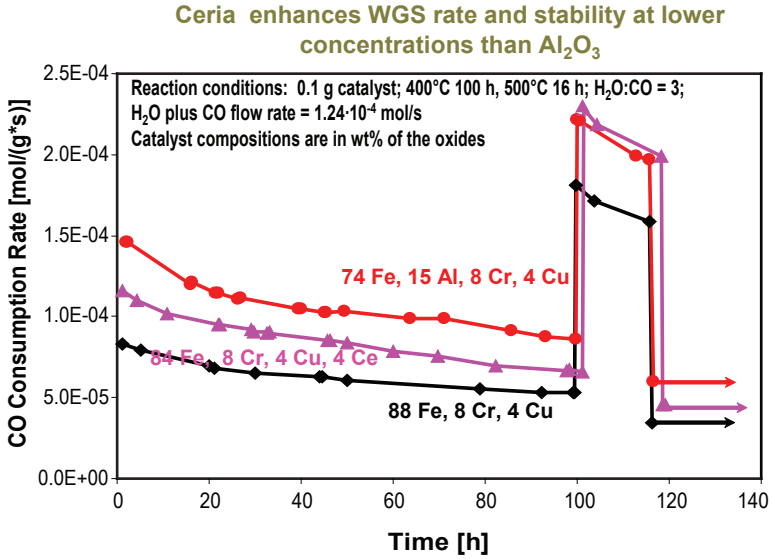

FIGURE 4. WGS Performance of the Alumina and Ceria-Based Catalysts

Conclusions and Future Directions

- Catalysts have been tested by impregnation into porous mullite substrates.
- Highest WGS activity and stability has been shown for 75Fe-15Al-8Cr-2Cu.
- Small additions of CeO_2 up to 4% look promising.
- Best catalysts are being prepared on mullite monoliths for incorporation into integrated devices.
- One integrated WGS/membrane device capable of 10,000 l/day hydrogen separation has been fabricated and is under testing for hydrogen production. A second integrated device of alternative design is in fabrication and due soon.
- After preliminary testing under pure hydrogen, both integrated devices will be tested on the WRI fluidized bed coal gasifier.
- A third design based on shim technology is being examined as paper study.
- Future work will involve the next 10x scale-up of an integrated device.

FY 2008 Publications/Presentations

1. 2007 DOE Hydrogen Program Review, May 2007, T. Barton.

2. Structural Water Gas Shift Catalysts-Tiberiu Popa, Guoqing Xu, Thomas L. Barton, and Morris D. Argyle* 20th ROCKY MOUNTAIN REGIONAL MEETING Joint ACS/AIChE, AUGUST 29 – September 1, 2007, DENVER, COLORADO.

3. Structural Water Gas Shift Catalysts-Tiberiu Popa, Guoqing Xu, Thomas L. Barton, and Morris D. Argyle AIChE- The 2007 Annual Meeting, 3–9 Nov. 2007, Salt Lake City, UT.

4. Structural Water Gas Shift Catalysts-Tiberiu Popa, Guoqing Xu, Thomas L. Barton, and Morris D. Argyle WSCC 22nd Annual Symposium, March 14, 2008, Albuquerque, NM.

5. NETL Hydrogen Review Meeting, Morgantown, WV, April, 2008.

6. DOE Annual Hydrogen Review meeting, Washington, D.C., June, 2008.