

## II.1.4 Integration of a Structural Water-Gas Shift Catalyst with a Vanadium Alloy Hydrogen Transport Device

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Contract Number: DE-FC26-05NT42454

Subcontractor:

University of Wyoming, Laramie, WY

Start Date: July 2006

Projected End Date: December 31, 2007

### Objectives

The objective of this work is to produce a device, scalable in nature, which performs both the water-gas shift (WGS) and hydrogen separation functions for a stream of synthesis gas derived from gasification of coal. WRI proposes to develop a device that would improve a hydrogen production system that consists of three steps that would realize: 1) an improved monolithic WGS catalyst that provides efficient conversion of carbon monoxide and structural support for a stacked assembly of membranes; 2) an improved vanadium alloy hydrogen transport membrane suitable for the chemical and physical environment of the coal-derived synthesis gas stream; and 3) an integrated stacked catalyst and membrane assembly scalable for commercial devices and economically designed for mass production. By using this approach, total hydrogen will be maximized and an additional benefit would also be derived 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.

- Develop a structural WGS catalyst capable of withstanding compressive forces.

- Develop vanadium alloy hydrogen separation membranes for fabrication of devices by brazing.
- Integrate the WGS catalyst and metallic membranes into a device and test under gasifier conditions.



### Introduction

The research topic for this project requires 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 the overall 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 plant by the removal of one step in the process by integrating WGS with the membrane separation device.

### Approach

This work will focus on the development of three key components of an integrated system to produce high purity hydrogen: 1) an improved monolithic WGS catalyst that provides efficient conversion of carbon monoxide and structural support for a stacked assembly of membranes, 2) an improved vanadium alloy hydrogen transport membrane suitable for the chemical and physical environment of the coal-derived synthesis gas stream, and 3) an integrated stacked catalyst and membrane assembly scalable for commercial devices and economically designed for mass production. The structural WGS catalyst will have a formulation that will eliminate the friable nature of current iron oxide-based pellets. The shape of the catalyst will be important in the structure. Standard ceramic processing techniques will be used to formulate, mix, extrude and sinter porous corrugated sheets of catalyst. Testing of the ceramic for catalytic activity and compression strength will be conducted.

A series of ternary vanadium alloys will be obtained. These alloys will be based on previous research on vanadium alloys as hydrogen transport materials and enhanced for improved brazing performance. The alloys will be fabricated into foils and tested for hydrogen sulfide, steam and chlorine stability, hydrogen flux, braze strength, and hydrogen embrittlement resistance versus temperature and hydrogen concentration.

A device will be designed and fabricated in which the WGS catalyst acts as a structural part of the stacked components. The device will be tested for pressure integrity, hydrogen transport, catalyst activity, and performance improvements over current technology. The tests will be conducted in a syngas stream from a fluidized bed coal gasifier located at WRI. For the project, WRI will be partnered with the Department of Chemical and Petroleum Engineering at the University of Wyoming.

### Accomplishments

- Catalysts have been tested by impregnation into porous mullite substrates.
- Highest activity and stability have been shown for 75Fe-15Al-8Cr-2Cu.
- Producing high surface area monoliths of this catalyst series may be problematic due to sintering at higher operational temperatures.
- Multiple vanadium alloys were obtained and tested for brazing performance with copper.
- Based on the brazing tests and analysis of the literature, guidelines were developed to anticipate performance of vanadium alloys with respect to hydrogen transport and fabricability based on alloying elements.
- Elements that are potentially positive to both hydrogen transport performance and brazing performance are in alphabetical order: cerium, copper, iron, manganese, molybdenum, nickel, and zinc.
- Additional alloying elements may be sufficiently advantageous to transport characteristics to overcome their detrimental effect on brazing.
- Brazing results for vanadium and structural alloys including mild steel, 304 stainless steel and 9Cr 1Mo steel were generally excellent.
- A physical model was produced with three layers of vanadium foil (2.25" diameter) and 304 SS, capable of being used as an integrated device (Figure 1).

- Assembled a slipstream system that can be cleaned for particulates condensate, sulfur and mercury. A secondary vessel is heated and compressed for testing catalysts, membranes or the integrated system.
- Produced ceramic components that have high WGS activity and have sufficient compressive strength to resist differential pressures up to 450 psig.
- Fabricated and tested vanadium hydrogen transport membranes and several sulfide-based catalysts under operational conditions for 100 hours.
- Tested the integrated WGS/membrane device under true coal gasification conditions in an environment including some levels of steam, sulfur, and particulates.

### Future Work

- Complete CeO<sub>2</sub> effect investigation on WGS performance.
- Investigate WGS monolith catalyst further
- Conduct mechanical testing of Cu braze strengths to compare to literature results for Au and Ag-based on brazes.
- Fabricate and braze two additional devices of alternate geometry to adjust for thermal expansion and scale-up issues.
- Complete 80 hours of testing on integrated devices in coal-derived syngas to examine sulfur and other contamination issues.

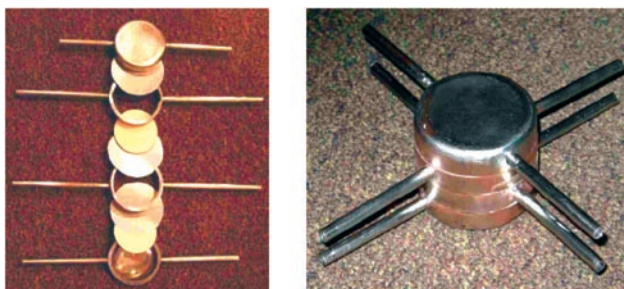


FIGURE 1. Brazed Integrated Device Model with Three Membranes