IV.B.8 A Novel Membrane Reactor for Hydrogen Production from Coal

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Objectives

- Develop a novel membrane reactor for high efficiency, clean, and low cost production of hydrogen from coal.
- Determine the technical and economic feasibilities of using a membrane reactor to produce hydrogen from coal.
- Evaluate potential membrane (ceramic and metal) suitable for high temperature, high pressure, and dirty coal environments.
- Select the best performing membrane for preliminary reactor design and cost estimates.
- Assess the overall economics of hydrogen production from this new process and compare with other hydrogen production technologies from coal.

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
- N. Defects
- 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, which was issued by the DOE Office of Fossil Energy.

Technical Targets

Tables 1 and 2 list the targets that the project will attempt to meet during its implementation.

Table 1. Technical Targets: Ion Transfer Membranes for Hydrogen Separation and Purification[a]

Performance Criteria	Units	2003 Status	2005 Target	2010 Target	2015 Target
Flux Rate	scfh/ft^2	60	100	200	300[b]
Cost	$/ ft^2	2,000	1,500	1,000	<$500
Durability	Hours	<8,760	8,760	26,280	>43,800
ΔP Operating Capability	psi	100	200	400	400-1000
HydrogenRecovery	% of total gas	60	>70	>80	>90
Hydrogen Purity	% of total (dry) gas	>99.9	>99.9	>99.95	99.99

[a] Targets are derived from Table 3.1.5. from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, March 2005.

[b] Flux upper limit for ion transport membranes.

Table 2. Technical Targets for the Water Gas Shift Reaction[a]

Performance Criteria	Units	Current Status	2005 Target	2010 Target	2015 Target
Reactor Type	–	Multiple Fixed beds	To be determined		
Catalyst Form	–	Pellets	To be determined		
Active Metal	–	Cu/Zn or Fe/Cr or Co/Mo	To be determined		
Temperature	°C	200-550	300-450	300-500	200-600
Pressure	psia	450-1150	450	750	>1,000
Approach to Equilibrium	°C	8-10	10	6	<4
Min Steam/Co Ratio	Molar	2.6	3.0	2.5	<2
Sulfur Tolerance	–	Varies	Low	Moderate	High
Chloride Tolerance	–	Varies	Low	Moderate	High
Water Tolerance	–	Varies	Low	Moderate	High
Stability/Durability	Years	3-7	3	7	>10
Reactor Cost Reduction	%	–	–	>15%	>30%

[a] Targets are derived from Table 6 of the Hydrogen from Coal RD&D Program, June 10, 2004.

Approach

- Identify the best membrane materials to be used for the proposed applications.
- Construct a high temperature and high pressure membrane permeation unit test facility and evaluate the candidate membranes' H_2-selective properties.
- Develop conceptual design of membrane modules and reactor configurations to ensure that the concept can be practically implemented and perform membrane reactor modeling to assist in process design and optimization.

- Integrate the concept into a flowsheet simulation to develop process options and calculate overall hydrogen production rates and thermal efficiencies.
- Estimate the cost of hydrogen production from this new technology and compare with other known technologies for hydrogen production from coal.

Accomplishments

- Completed the design work for the membrane permeation unit capable of operating at up to 1000°C and 1000 psi, procured major components and parts, and initiated screening and testing of hydrogen membranes under gasification conditions.
- Completed the construction of the high-temperature and high-pressure permeation unit.
- Developed membrane reactor models for a fluidized bed gasifier incorporating major gas phase reactions in the membrane gasifier and hydrogen permeation via mixed proton-electron conducting materials. The model will help guide material development/screening, and provide the basis for the conceptual design of the membrane gasifier.
- Selected promising membrane materials for next phase tests. Perovskite was identified as a leading membrane material for further tests.
- Completed hydrogen permeation measurement for membrane materials supplied from University of Cincinnati and University of Florida.
- Completed conceptual design of the membrane gasifier configuration for a plant of 1000 tons per day (TPD) coal. Design was based on initial hydrogen permeation data and modeling.
- Identified one concept for addressing chemical stability issues of the perovskite membrane. Completed flowsheet simulation for hydrogen production based on membrane gasifier processes.

Future Directions

- Complete technical and economic assessment of the membrane gasifier technology. Perform initial estimate for the cost of hydrogen from coal based on the selected membrane gasifier process.
- Continue improving hydrogen flux.
- Conduct permeation testing with simulated syngas.
- Develop membranes with catalytic support layer.
- Scale-up membrane.
- Test with bench-scale gasifier.

Introduction

Currently hydrogen can be produced from carbonaceous materials such as coal, biomass, and petroleum coke by reacting them with oxygen and steam in a gasification reactor under elevated temperature (800-1400°C) and pressure ranging from 1 to 100 atm. The gaseous effluent from the gasifier contains H_2, CO, CO_2, CH_4, H_2O, H_2S and other contaminants. This gas stream then goes through a water-gas-shift (WGS) reaction, where CO and H_2O are reacted to form H_2 and CO_2. Sulfur and other contaminants are removed before hydrogen is separated and purified in a pressure swing adsorption (PSA) unit or through membrane separation. This process generally has about 50-60% thermal efficiency. There is a strong need to develop a more efficient process to reduce the cost of producing hydrogen from solid fuels.

This project explores a coal-to-hydrogen conversion process with thermal efficiency of 80% or higher with significant cost reduction by process simplification. The concept incorporates a hydrogen-selective membrane within a gasification reactor for the direct extraction of hydrogen from generated coal synthesis gases. Both coal gasification reactions and hydrogen separation can be accomplished simultaneously within this membrane reactor, thus maximizing hydrogen production.

Approach

GTI will work with several membrane manufacturers and research groups to identify the best membrane materials to be used for the proposed applications. GTI will construct a high temperature and high pressure membrane permeation unit test facility and evaluate the candidate membranes' H_2-selective properties by focusing on the effects of gasification temperatures and gas contaminants on the performance of candidate membranes. GTI will develop the conceptual design of membrane modules and reactor configurations to ensure that the concept can be practically implemented and perform membrane reactor modeling to assist in process design and optimization. The results from membrane reactor modeling will be integrated into a flowsheet simulation to develop process options and calculate overall hydrogen production rates and thermal efficiencies. Finally, GTI will estimate the cost of hydrogen production from this new technology and compare with other known technologies for hydrogen production from coal.

Results

GTI has successfully completed the design work for the membrane permeation unit capable of operating at up to 1000°C and 1000 psi, the procurement of major components and parts, and has initiated screening and testing of hydrogen membranes under gasification conditions. The construction of a high-temperature and high-pressure permeation unit was completed as was development of membrane reactor models for fluidized bed gasifiers incorporating major gas phase reactions in the membrane gasifier and hydrogen permeation via mixed proton-electron conducting materials.
The model will help guide the material development/ screening process and provide the basis for the conceptual design of the membrane gasifier. Perovskite was then identified as the leading membrane material for further tests.

Conclusions

It was found that a membrane gasification reactor can improve hydrogen production over the conventional coal gasification process by 30-50% for the same amount of coal feed. The membrane reactor performance was determined by the kinetics of the reforming reaction, the equilibrium of shift reaction (high temperature), and membrane hydrogen permeability. Finally, it was found that catalysts are needed for the reforming reaction.

FY 2005 Publications/Presentations

1. Shain J. Doong, Estela Ong, Francis Lau, Arun C. Bose, and Ron Carty, "Direct Extraction of Hydrogen from Coal Using a Membrane Reactor Within a Gasifier" paper presented at 21'st International Pittsburgh Coal Conference, Osaka, Japan, September 2004
2. Shain J. Doong, Francis Lau, Mike Roberts, and Estela Ong, "GTI's Solid Fuel Gasification to Hydrogen Program" paper presented at the 3rd Natural Gas Technology Conference, Orlando, FL, February, 2005
3. Francis Lau and Shain Doong, "Coal to Hydrogen: A Novel Membrane Reactor for Direct Extraction" paper presented at GCEP (Global Climate & Energy Project) Energy Workshops, Stanford University, CA, April 2004