II.B.3 One Step Biomass Gas Reforming-Shift Separation Membrane Reactor

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Subcontractors:
- National Energy Technology Laboratory (NETL), Pittsburgh, PA
- SCHOTT North America, Duryea, PA
- ATI Wah Chang, Albany, OR

Project Start Date: February 1, 2007
Project End Date: June 30, 2013

Objectives

GTI together with its partners, NETL, Schott North America and ATI Wah Chang are working to determine the technical and economic feasibility of using the membrane gasifier to produce hydrogen from biomass. Specifically, the team plans to:

- Reduce the cost of hydrogen from biomass to \$1.60/kg H_2 (excluding delivery).[1]
- Develop an efficient membrane reactor that combines biomass gasification, reforming, shift reaction and H_2 separation in one step.
- Develop hydrogen–selective membrane materials compatible with the biomass gasification conditions.
- Demonstrate the feasibility of the concept in a bench-scale biomass gasifier.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(L) Impurities
(N) Hydrogen Selectivity
(O) Operating Temperature
(P) Flux

Technical Targets

This project is directed at developing a membrane reactor that can be closely-coupled with a gasification reactor while having a sufficiently high hydrogen flux to achieve a hydrogen production cost of \$1.60/kg (without delivery) per the DOE 2012 technical target.

Accomplishments

- Project was restarted (February 2010) after 1 year hiatus. Selected team members completed contractual activities with GTI.
- Development of metallic, glass-ceramic membranes is in progress.
- Process development and economic analysis with initial candidate membrane is in progress.
- Membrane module design with initial candidate membrane is in progress.

Introduction

GTI has developed a novel concept of membrane reactor for clean, efficient, and low cost production of hydrogen from biomass-derived syngas. Our approach is presented in Figure 1 and shows a hydrogen-selective membrane closely coupled with a reforming or gasification reactor for direct extraction of hydrogen from the syngas. The specific objective of the project is to develop high temperature metallic or glass membranes that can be used closely-coupled with a biomass gasifier. The technical feasibility of using the membrane reactor to produce hydrogen from a biomass gasifier will be evaluated. GTI with its project team (SCHOTT North America, NETL, and ATI Wah Chang) has been evaluating potential membranes (metal, ceramic and glass) suitable for high temperature, high pressure, and the harsh environment of a biomass gasifier. The project team has been screening and testing each type of material, investigating its thermal and chemical stability, and conducting durability tests.

[1] From 2007 H2 Production technical plan. During the 2010 Annual Merit Review, the need to rebaseline costs was stated.

Approach

To conduct commercially successful research, GTI has developed a plan where efforts are concentrated in four major areas: membrane material development, membrane module development, membrane process development and membrane gasifier scale up. The initial focus of the project has been concentrated on membrane material development. Metallic and glass-based membranes have been identified as hydrogen selective membranes under the conditions of the biomass gasification, temperatures above 700°C and pressures up to 30 atmospheres. Membranes are synthesized by arc-rolling for metallic type membranes and incorporating Pd into a glass matrix for glass membranes. Testing for hydrogen permeability properties have been completed and the effects of hydrogen sulfide and carbon monoxide were investigated for perspective membranes. The initial candidate membrane chosen in 2008 was selected for preliminary reactor design and cost estimates. The overall economics of hydrogen production from this new process will be assessed and compared with traditional hydrogen production technologies from biomass. The final deliverable of the project will be a gasification membrane reactor system that is expected to meet or exceed the DOE's cost target for hydrogen production from biomass. This will be demonstrated by a bench scale gasification membrane reactor that can process approximately 2~10 kg/hr of woody biomass for hydrogen production.

Results

The project was restarted after a one year hiatus. The Arizona State University work on ceramic membranes was discontinued due to an inability to show sufficient promise for flux improvement to compete with the metallic or glass/ceramic membrane work during the project's timeframe.

NETL is pursuing a new approach for stabilizing Pd alloys for high temperature use. This approach is modeled on a strategy that has been used to strengthen and stabilize certain high performance alloys such as Ni-based super alloys for high temperature applications. This approach utilizes a two-phase microstructure for stabilization. Unlike previous approaches where the additive is concentrated at grain boundaries, the two phases in the system under consideration can form a uniform dispersion of grains rather than be concentrated at grain boundaries. In this scenario, the primary phase transports hydrogen while the secondary phase improves the high temperature strength. NETL has fabricated new alloy combinations and hydrogen permeability tests were subsequently conducted. A 55 wt% Ni-Pt alloy was successfully rolled. Figure 2 shows permeability of the alloy at 600, 700 and 800°C. Permeability of a Pd_7Pt_2Al alloy is also shown. A Pd_7Pt_2Al alloy was synthesized and oxidized in an attempt to convert the Al to oxide for grain boundaries stabilization. Pt was added to this alloy to possibly improve the strength and sulfur resistance of the membrane. Due to failure of the membrane at 700°C, there is no data of hydrogen permeability at higher temperatures to determine a potential Pt effect on alloy characteristics. Scanning electron microscopy shows that the Al is located along the grain boundaries. So, Al incorporation into an alloy with subsequent oxidation of Al to Al_2O_3 allows us to have Al located along the grain boundaries. The hydrogen permeability of synthesized alloys is lower than the permeability of the initial candidate membrane (Pd-Cu).

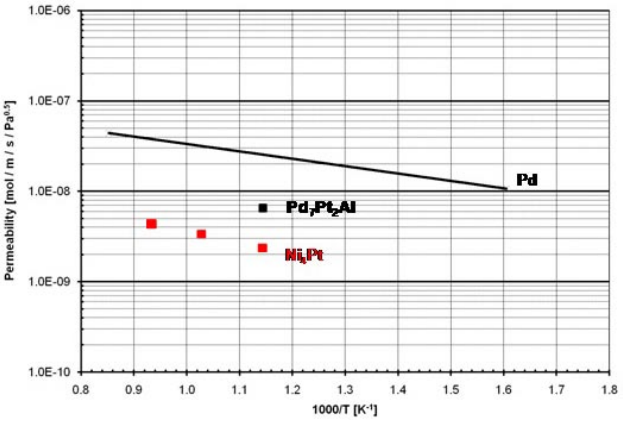

FIGURE 2. Hydrogen permeability results for Ni-Pt and Pd-Pt-Al alloys.

Glass membranes were obtained from SCHOTT and tested for hydrogen permeation. Table 1 summarizes results obtained for membranes synthesized by SCHOTT. Membranes with Pd have palladium content of about 0.05 wt%. At T=850°C, hydrogen flux was 0.02 SCFH/ft^2 at pressure difference 7.3 psi for membrane containing palladium. Pure glass synthesized at the same conditions with no palladium has no hydrogen permeation. From these results, one deduces that hydrogen transports only through the metal network in the glass.

SCHOTT has focused to synthesize metal-glass-ceramic membranes using a reducing agent. Addition of a reducing

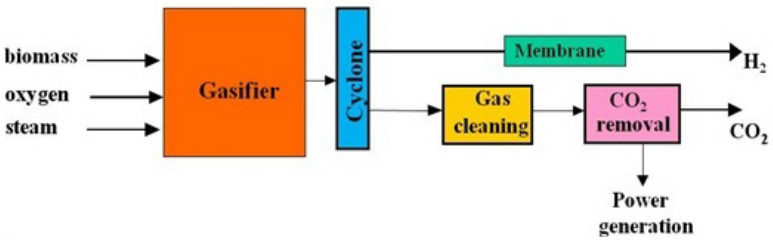

FIGURE 1. Integrated Approach to Hydrogen Production and Separation

agent (sugar) may assist hydrogen permeation by further reduction of Pd incorporated in the matrix. A few formulations with sugar additions were completed and total conductivity was measured. Also, a new melting protocol has nearly been completed this quarter that should enable SCHOTT to produce larger quantities of higher homogeneity material for permeability testing.

GTI continued to test membranes fabricated by GTI and other team members as they become available. Testing of the initial candidate membrane for 50 hours with a gas containing H_2S to try and duplicate NETL results for grain boundary failure is in progress.

GTI has resumed work on HYSYS modeling of downstream processes and variations: some modifications were implemented into three schemes for downstream processes after the biomass reactor. Different variations of process systems for producing hydrogen from biomass are being evaluated and are shown in Figure 3. Construction of HYSYS process schemes for downstream processes after biomass gasification is completed. Input data for UGAS software based on gasifier sizing, biomass types and operational conditions were selected: feedstock feed rate, temperature and pressure of gasifier, oxygen/carbon molar ratio, types of feedstock, etc. Based on gasifier design, diameters of lower and upper sections of gasifier were specified. Preliminary results were obtained to be used in HYSYS modeling. A detailed gasifier reactor drawing is in the final stage of development. A planar design for the hydrogen membrane module based on initial candidate membrane has been selected.

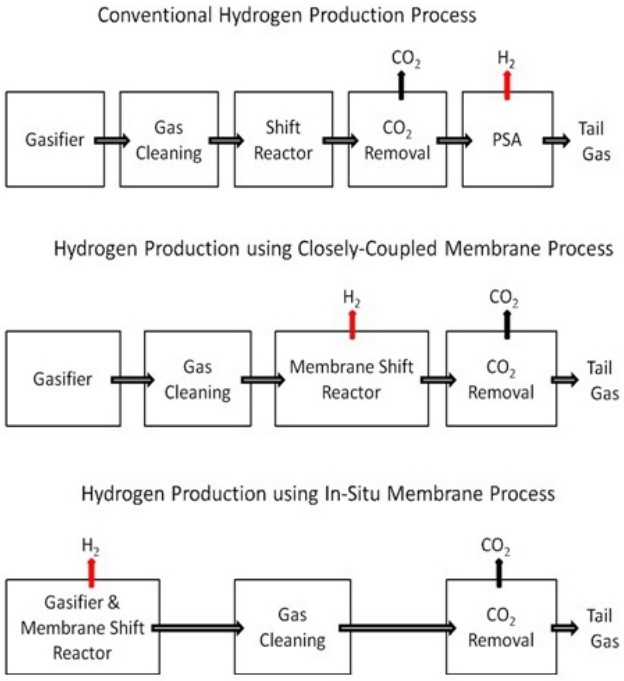

FIGURE 3. Simplified diagrams of different process variations after biomass gasification.

Conclusions and Future Directions

GTI selected $Pd_{80}Cu_{20}$ as an initial candidate membrane for integrated testing with a biomass gasifier:

- GTI and partners will continue to pursue development of membranes with greater flux and higher resistance to contaminants for the best candidate membrane.
- GTI will continue development of the membrane gasifier process and an economic analysis will be performed.
- GTI will utilize a biomass gasifier currently under construction for future membrane integration.

FY 2010 Publications/Presentations

1. Poster presentation, PD070 Roberts, 2010 Annual Merit Review, Wardman Park Marriott Hotel, Washington, D.C. June 7–11, 2010.

TABLE 1. Summary of Membranes Synthesized by SCHOTT

Date	Membrane	Ceramization Conditions: Temperature, Atmosphere	Electronic Conductivity, S/cm at 600°C	Hydrogen Permeation SCFH/ft^2	Temp, °C	Pressure Difference, psi
05/30/08	CMAS-1/2D w/Pd	1.100°C, H_2/N_2	7 x10^{-7}	0.25	850	12.0
07/21/08	CMAS-1/3 Glass-no Pd	unceramized	4 x10^{-8}	0	850	11.8
07/28/08	CMAS-1/2 w/Pd Glass	unceramized	4 x10^{-9}	0.02	850	7.4
08/05/08	CMAS-1/2C w/Pd	875°C, H_2/N_2	3 x10^{-9}	0	850	11.8
08/08/08	CMAS-1/3E	875°C, H_2/N_2	3 x10^{-6}	0	850	7.4
08/20/08	CMAS-1/2A w/Pd	875°C, Air	6 x10^{-9}	0	850	7.4
08/26/08	CMAS-1/2B w/Pd	1.100°C, Air	5 x10^{-8}	0	850	13.2