

II.B.1 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

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 \$2-4/gge (without delivery) per the DOE 2012 technical target.

FY 2012 Accomplishments

- Best candidate membrane was chosen: Pd₈₀Cu₂₀ membrane of 5 μm in thickness.
- Process development and economic analysis with best candidate membrane shows process's potential to be economically feasible.
- Fabrication of demonstration membrane module is initiated.



Fiscal Year (FY) 2012 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 \$2-4/gasoline gallon equivalent (gge) H₂ [1] (excluding delivery).
- Develop an efficient membrane reactor that combines biomass gasification, reforming, shift reaction and H₂ 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

Introduction

GTI has developed a novel concept of membrane reactor for clean, efficient, and low-cost production of hydrogen from biomass-derived syngas. GTI's 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 Glass, NETL, and 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.

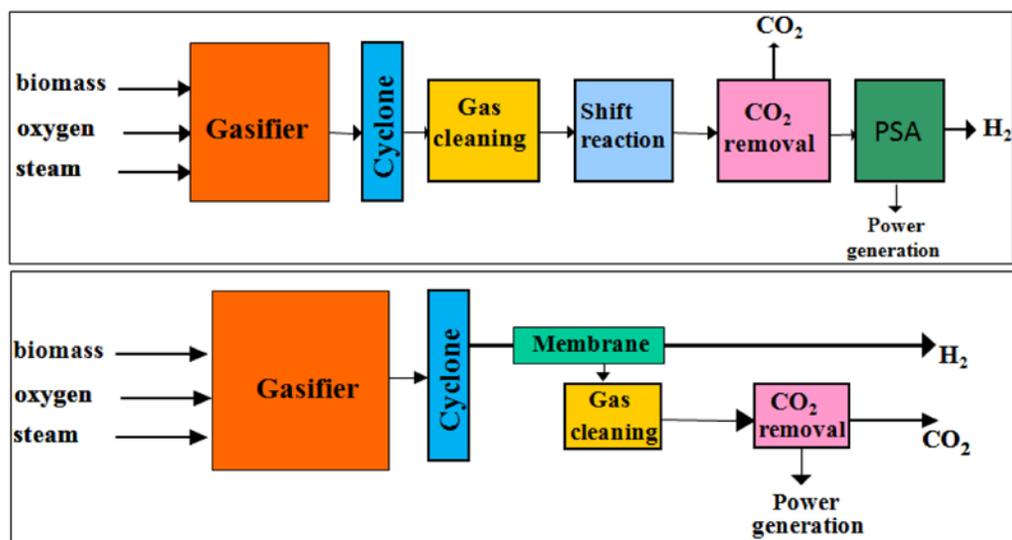


FIGURE 1. Conventional Hydrogen Production from Biomass Gasification and Biomass Gasifier with Close-Coupled Membrane

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

Based on the timeline of the project, GTI and partners from NETL and Schott researched new candidates for hydrogen-selective membranes.

NETL continued to research hydrogen-selective Pd alloys for high temperature use. Permeable alloys have desirable characteristics for hydrogen membrane applications including high permeability, high temperature strength and cost, but are very susceptible to poisoning of surface catalytic sites and surface corrosion. Therefore, methods of protecting these materials are needed. One possibility being investigated is an inorganic, nonmetallic coating that can protect these alloys at the conditions of interest. Potential inorganic coating systems are being investigated in the literature and synthesis of new tertiary alloy formulations based on Pd metal is in progress.

This year, due to relocations, membrane testing facilities at NETL continued to have a very limited availability.

A niobium-based alloy was identified that may offer high temperature stability under the conditions of interest. These alloys offer good resistance to the corrosive conditions of the post-gasifier environment, however, their hydrogen permeability is still not known. The alloy, a Pd-Cr composition was tested up to 750°C to investigate its potential application for this project. The test was conducted using 100% H₂. Over the range of 650 to 750°C, its permeability was approximately 60% of the permeability of Pd.

SCHOTT continued development of glass ceramic membranes based on results of membranes synthesized by them and tested by GTI. Five new glass melts were completed. All compositions were melted in platinum crucibles and were stable glasses. X-ray fluorescence analyses revealed excellent correspondence between input major oxide wt% and measurements on as-cast glass. Two “alloy” melts were also produced to see what the effects of introducing another metal in addition to the Pd into the base glass had on the performance of the glass. These melts

produced reasonably stable glasses, although one of them revealed evidence of small crystals in the as-cast glass as suggested by a somewhat matte-like appearance, instead of a purely glassy surface. The crystals could be either unmelted material or crystals that formed during the casting and annealing process. In any event, all samples were then ceramized under reducing conditions, ground and polished and sent to GTI for analysis. Glass membranes obtained from SCHOTT were tested for hydrogen permeation by GTI. Unfortunately, these new samples did not yield high H permeation at 800°C during testing.

GTI continued to test membranes fabricated by GTI and other team members as they became available. Pd₈₀Cu₂₀ with 5 microns thickness was tested for hydrogen permeation. Due to small thickness and frailty of metallic foil, there were problems with sealing. The results obtained before the seal failure showed high hydrogen fluxes but no stable state was achieved. These results need to be repeated. Membranes obtained from Schott were tested for hydrogen permeation: low hydrogen permeation was observed (0.04 SCFH/FT²).

Based on all results obtained during this time period, the best membrane candidate based on overall performance is Pd₈₀Cu₂₀ chosen earlier as an initial candidate, but with 5 microns in thickness. Based on inverse dependence of hydrogen permeation with thickness, we expect to increase hydrogen flux several times. For Pd₈₀Cu₂₀ membrane with 120 μm in thickness hydrogen flux at conditions (850°C, pressure difference 85 psi) is about 26 SCFH/FT². The membrane with 5 μm in thickness predicted by Sievert's law will achieved about 600 SCFH/FT² (26*120/5=624).

The fabrication of a membrane module that is compatible with the biomass gasifier is in progress. The module must be reliable, durable and cost effective. GTI fabricated the membrane module in planar design for initial candidate membrane (Pd₈₀Cu₂₀). Sealing was developed to withstand high temperatures and high pressures of operation. Figure 2 shows a section view schematic of the membrane module inside the pressure vessel.

The preliminary process design for a plant to produce hydrogen from a biomass feed using a hydrogen permeable membrane that was previously completed was subjected to a Pinch Analysis to optimize the heat integration and to minimize external heating and cooling demands. A heat exchange network (HEN) analysis then allowed individual heat exchangers to be specified and sized so that the exchanger capital cost estimation could be updated. The pressures in the various pieces of equipment in the process were then updated to make sure that pressure drop driving forces were available for these heat exchangers and all other equipment, and the sizes of the pumps and compressors in the process were updated. The updated process design was documented in a set of twelve drawings to show all the required process equipment.

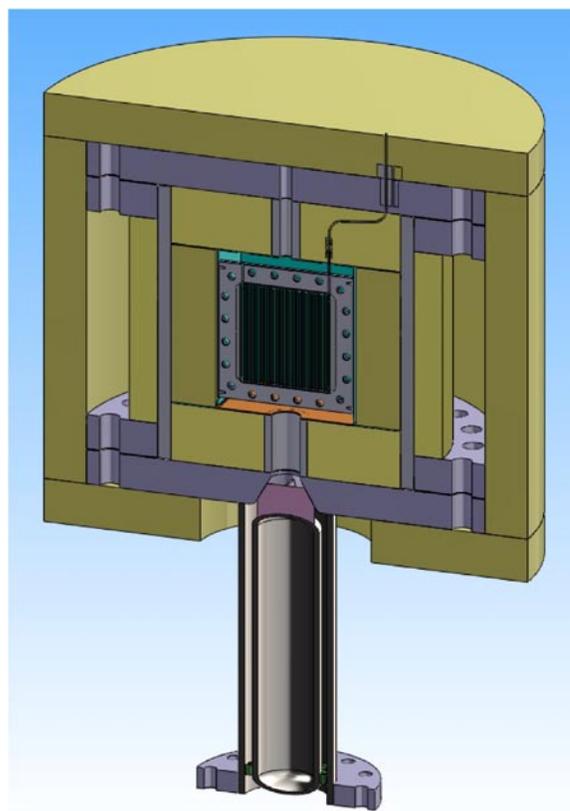


FIGURE 2. Membrane Module Unit in Pressure Vessel

Then, the focus was on engineering design and costing of the process plant that fed 2,000 tons/day of biomass and delivered high-pressure hydrogen product using a hydrogen permeable membrane. Optimum values for gasification temperature, reforming temperature and permeate pressure were used, based on optimization studies previously completed. The ASPEN model of the process was then used to determine the stream flow rates and/or process heat duties for all the process steps so that equipment sizes could be estimated. A Pinch Analysis and HEN analysis was completed so that individual heat exchangers could be sized. The sizes of pumps, vessels, conveyors, compressors, reactors, etc. were based on the flow rates and heat balance from the ASPEN model. This analysis resulted in a listing of the sizes for all major pieces of equipment in the process plant. This compares with a total of 121.5 MM\$ previously estimated from a less complete process design basis, with hydrogen delivered at 1,000 psi.

The more accurate costing increased the capital cost somewhat. If hydrogen is produced at 300 psi, the new capital cost is 129.2 MM\$, compared with the old estimate of 118.0 MM\$. The new capital and operating costs for the membrane process were input into version 3 of the H2A program [2]. This version updates the base year of the

analysis from 2005 to 2007. A revised cost of hydrogen production of \$1.82/kg was obtained, as detailed in Table 1.

TABLE 1. Hydrogen Cost of Production Estimate

Cost Component	H2 Cost, \$2007/kg
Capital Cost	0.68
Decommissioning	0.00
Fixed O& M	0.20
Feedstock Cost	0.51
Other Raw Material	0.11
By-Product Credits	0.00
Other Variable Costs	0.32
Total	1.82

A tornado diagram was prepared to show the sensitivity to several key process variables as shown in Figure 3.

The main conclusions for Task 2 “Process Development and Techno-Economic Analysis” are:

- Economic optimization was conducted for the variables of reforming (membrane) temperature, permeate pressure, and hydrogen recovery level for membranes 5 microns in thickness. Optimum permeate pressure is about 0.2 bar. Optimum membrane/water-gas shift temperature is at 1,382°F (750°C) or less.
- 2012 Membrane Model Case has recovery of 115% of original H₂. Pressure swing adsorption (PSA) Future Case [3] had about 80% recovery. Over 115% of the hydrogen produced in the gasifier can be recovered due to water-gas shift for membrane.
- Projected using H2A version 3 Cost of hydrogen production with membrane (\$1.82/kg) is less than the cost with PSA (\$2.00/kg).

Conclusions and Future Directions

- GTI and partners will continue to fabricate membrane module for hydrogen separation.
- GTI will test feasibility of membrane module closely-coupled with biomass gasifier.

FY 2012 Publications/Presentations

1. Oral presentation, PD070 Roberts, 2012 Annual Merit Review, Washington, D.C., May 13–17, 2012.

References

1. Presentation on 2011 Annual Merit Review by DOE.
2. https://apps1.hydrogen.energy.gov/cfm/register.cfm?model=02D_Future_Central_Hydrogen_Production_via_Biomass_Gasification_version_3.0.xls.
3. P. Spath, A. Aden, T. Eggeman, M. Ringer, B. Wallace, and J. Jechura, “Biomass to Hydrogen Production Detailed Design and Economics Utilizing the Battelle Columbus Laboratory Indirectly-Heated Gasifier,” NREL/TP-510-37408, May 2005.

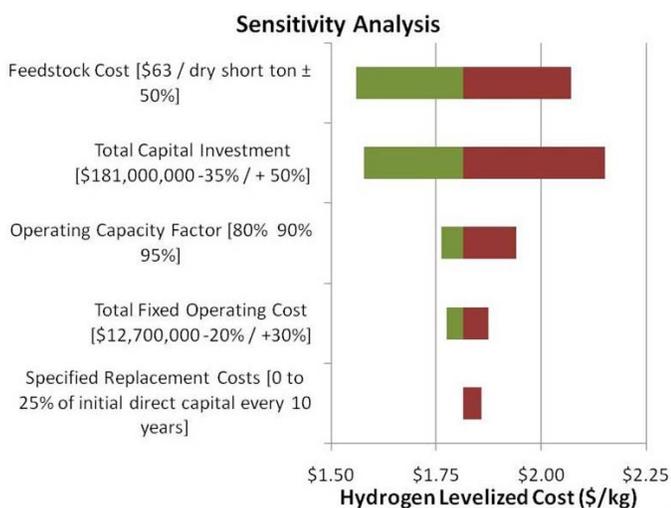


FIGURE 3. Sensitivity Analysis