II.B.2 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

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Project End Date: June 30, 2013

Fiscal Year (FY) 2011 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) H_2[1] (excluding delivery).
- 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 Hydrogen, Fuel Cells and Infrastructure 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 2011 Accomplishments

- Development of metallic, glass-ceramic membranes is in progress.
- Preliminary process development and economic analysis with initial candidate membrane proves economic feasibility of the process.
- Membrane module design with initial candidate membrane is finished.
- Fabrication of membrane module is in progress.

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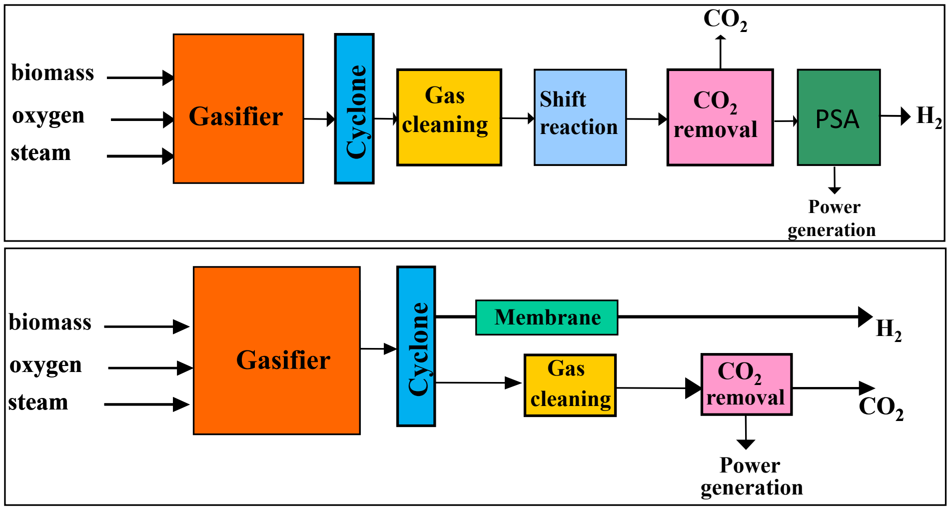
Introduction

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 conventional hydrogen production from biomass gasification and 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.

[1] From presentation on 2011 Annual Merit Review by DOE.



PSA - pressure swing adsorption

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 has 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

GTI and partners from NETL and Schott continued researching new candidates for hydrogen-selective membranes.

NETL is pursuing a new approach for hydrogen permselective Pd alloys for high temperature use. Superpermeable 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. A good method to counter these effects is by coating the alloy with a second alloy such as one containing Pd to provide catalytic activity and corrosion protection. Unfortunately, such coatings are likely to be unstable at the temperatures of interest. Therefore, alternative 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.

Two new Pd-based ternary alloys are being fabricated. The alloying components were selected to attempt to improve high temperature strength and alter surface chemistry to improve impurity resistance. A new niobium/tantalum alloy has been 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 not known. More information on the characteristics of these alloys is currently being sought. If they continue to look promising, samples will be acquired or synthesized for testing. Also, 55 wt% Ni-Pt and PdPtAl synthesized earlier in the presence of H_2S is being tested. Due to membrane testing relocations, very restricted membrane testing facilities have been available for several months.

Schott continued development of glass ceramic membranes based on results of membranes synthesized by them and tested by GTI. A new melting protocol was completed to produce larger quantities of material with greater homogeneous properties for permeability testing. Total conductivity was measured. Electrical conductivity results indicated Schott has fabricated highly-conducting samples; however, this is likely a necessary condition, though not sufficient, to ensure H permeation. Only direct permeation measurements can address this point.

Glass membranes were obtained from Schott and tested for hydrogen permeation. Unfortunately, these new samples, processed using similar means as in 2008, did not yield measurable H permeation at 800°C during testing at GTI. Schott plans to focus on other Pd-containing glass-ceramics, including Pd-Cu and Pd-Ag alloys, and subsequent submittal of these materials for testing by GTI.

GTI continued to test membranes fabricated by GTI and other team members as they become available. The initial candidate membrane Pd-Cu was tested for long-term stability at 800°C in syngas (20% hydrogen, 20% carbon monoxide, 10% carbon dioxide, 10% water and 0.03 % of hydrogen sulfide with balance of helium) atmosphere. The membrane has 83% of initial hydrogen permeation flux after 22 hours. The test was stopped due to a sealing failure. New sealing techniques that can withstand a sour atmosphere were researched.

$Pd_{90}Ta_{10}$ and $Pd_{60}Cu_{20}Ni_{20}$ foils were tested for hydrogen permeation. The results show lower hydrogen permeability as compared with initial candidate membrane ($Pd_{80}Cu_{20}$). Also, $Pd_{80}Cu_{20}$ with thickness 5 microns was purchased. Based on reverse dependence of hydrogen permeation with thickness, we expect to increase hydrogen flux four times. GTI continues to search for a new more promising alloy.

The design of a membrane module that is compatible with the biomass gasifier was completed. The module must be reliable, durable and cost-effective. The membrane module is of planar design for the initial candidate membrane ($Pd_{80}Cu_{20}$). Calculations were made to ensure no diffusion limitation for hydrogen permeation process and uniform gas distribution. Sealing was developed to withstand high temperatures and high pressures of operation. A support was designed to ensure high mechanical stability. Wah Chang assisted in review of membrane module design and their suggestions were incorporated to the membrane module design. Figure 2 shows membrane module inside the pressure vessel.

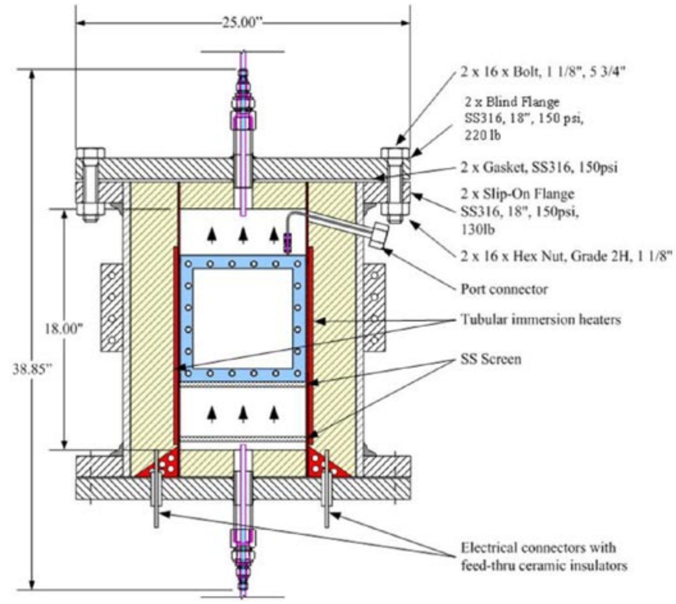
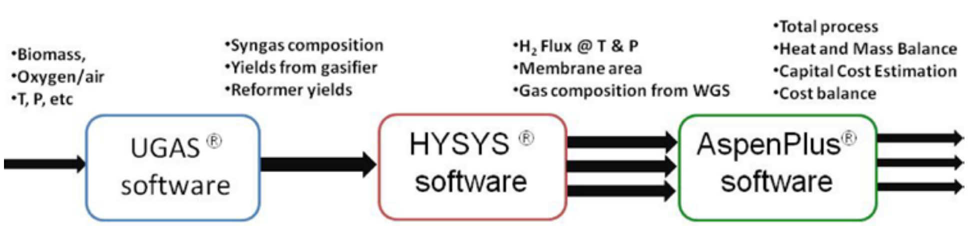


FIGURE 2. Membrane Module Unit in Pressure Vessel

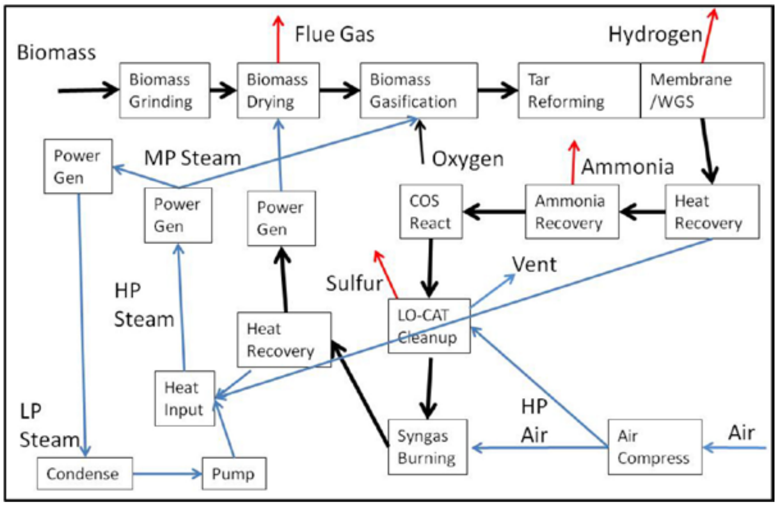
A preliminary techno-economic analysis was performed to determine the potential economic viability of hydrogen production from biomass gasification using an initial candidate membrane-$Pd_{80}Cu_{20}$ foil. Estimating the costs of the process compared to the conventional technology can determine the economic feasibility of a project. Also the analysis is useful in directing research toward areas in which improvements will result in the greatest cost reductions. As the economics of a process are evaluated throughout the life of the project, advancement toward the final goal of commercialization can be measured.

Figure 3 shows the modeling software sequence for process development and costing. RENUGAS® modeling software output such as syngas composition, temperature, pressure, etc was used as input data for the HYSYS® software. The HYSYS model of the process was used to determine the membrane area needed at the specified process conditions for a given level of hydrogen recovery. 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.



T - temperature; P - pressure; WGS - water-gas shift

FIGURE 3. Process Modeling Scheme



HP - high pressure; LP - low pressure

FIGURE 4. Process Steps in Gasification with Hydrogen Selective Membrane

The capital cost basis was taken from the pressure swing adsorption (PSA) advanced case [1], and capital cost requirements were scaled from that for the membrane cases. In all the cases, hydrogen compressors were included to raise the pressure of the permeate hydrogen to 300 psi for consistency with the PSA cases. Figure 4 shows that the scope of the membrane process includes feed drying, gasification, reforming with hydrogen recovery, heat recovery, gas clean-up, combustion, and power generation. The main conclusions for Task 2 "Process Development and Techno-Economic Analysis" are:

- Identified process variables affecting process economics.
- 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. Optimum hydrogen recovery is at 100% of reformer product H_2.
- Economic cost of hydrogen production is comparable with PSA.

Conclusions and Future Directions

- 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 full economic analysis will be conducted.
- Membrane module design was completed. The module demonstrated a flux rate of 80+ SCFH/ft^2 and is capable of 125 SCFH/ft^2.
- Fabrication of membrane module with initial candidate membrane is in progress.
- GTI will test feasibility of membrane module closely-coupled with a biomass gasifier.

FY 2011 Publications/Presentations

1. Oral presentation (PD070) Roberts, 2011 Annual Merit Review, Washington, D.C., May 9-13, 2011.

References

1. 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.