II.D.2 One Step Biomass Gas Reforming-Shift Separation Membrane Reactor

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Subcontractors:
- Arizona State University, Tempe, AZ
- National Energy Technology Laboratory (NETL), Pittsburgh, PA
- Schott North America, Duryea, PA
- ATI Wah Chang, Albany, OR

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Objectives

- Reduce the cost of hydrogen from biomass to \$1.60/kg H_2 (without 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 survive the rigors of gasification reactor conditions 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

- Permeation configuration for hydrogen permeation experiments at high temperature (up to 900°C) and pressures (up to 30 atmospheres) was designed and constructed.
- Sealing (copper O-ring and glass) for membranes operating at high temperature and pressure was developed for all types of membranes.
- Different types of membranes (metallic, ceramic and glass) were synthesized and tested for hydrogen permeation.
- An initial candidate membrane was selected and a sequence of experiments was conducted to test the effect of carbon monoxide and hydrogen sulfide on the membrane's durability and flux.

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Introduction

GTI and the project team have developed a novel concept of membrane reactor for clean, efficient, and low-cost production of hydrogen from biomass-derived syngas. The approach is shown in Figure 1 and shows a membrane inside the fluidized-bed gasifier to extract hydrogen directly from the gasifier using a high temperature H_2-selective membrane. The concept incorporates a hydrogen-selective membrane within the reactor or outside the reactor but 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 ceramic, metallic or glass membranes that can be used within a biomass gasifier or closely-coupled. The technical feasibility of using the membrane reactor to produce hydrogen from a biomass gasifier will be evaluated. GTI with its project team (Arizona State University, Schott Glass, NETL, and Wah Chang) has

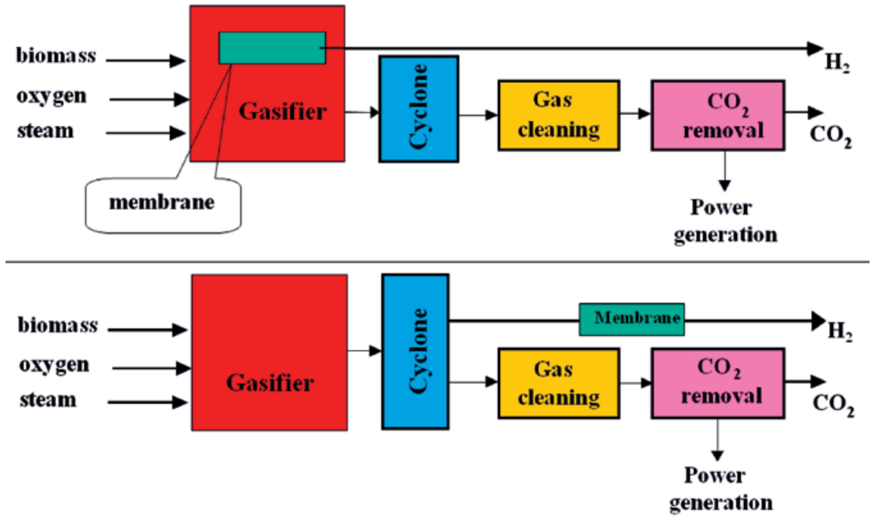

FIGURE 1. Integrated Approach to Hydrogen Production and Separation

been evaluating potential membranes (metal, ceramic and glass) suitable for high temperature, high pressure, and harsh environment of a biomass gasification. The project team has been screening and testing each type of material, investigating its thermal and chemical stability, and conducting durability tests. The best performing membranes will be selected for preliminary reactor design and cost estimates.

Approach

To conduct a commercially successful research project GTI has developed a plan where efforts are concentrated in four big areas: membrane material development, membrane module development, membrane process development and membrane gasifier scale-up. Initial focus of the project is concentrated on membrane material development. Metallic, ceramic 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. At the beginning, membranes are synthesized by using the liquid citrate method for ceramic types, electroplating for metallic membranes and incorporation of Pd into a glass network for glass membranes. Testing for hydrogen permeability properties is done and the effect of hydrogen sulfide and carbon monoxide was investigated for perspective membranes.

Results

GTI identified the procedure used to down-select the metals to be evaluated for an initial candidate membrane. As shown in Figure 2, four series of metals were identified and tested based on a literature review. Each metal series is shown in a different color: red, green, blue, and purple. The red series (PdCu, PdAg, and PdAu) showed the highest permeability. Each of the color series in sequence showed a decreased permeability (order of magnitude) for the green, blue, and the lowest permeability for the purple series.

After the metallic series screening, the sequence then used for evaluation of initial candidate membranes

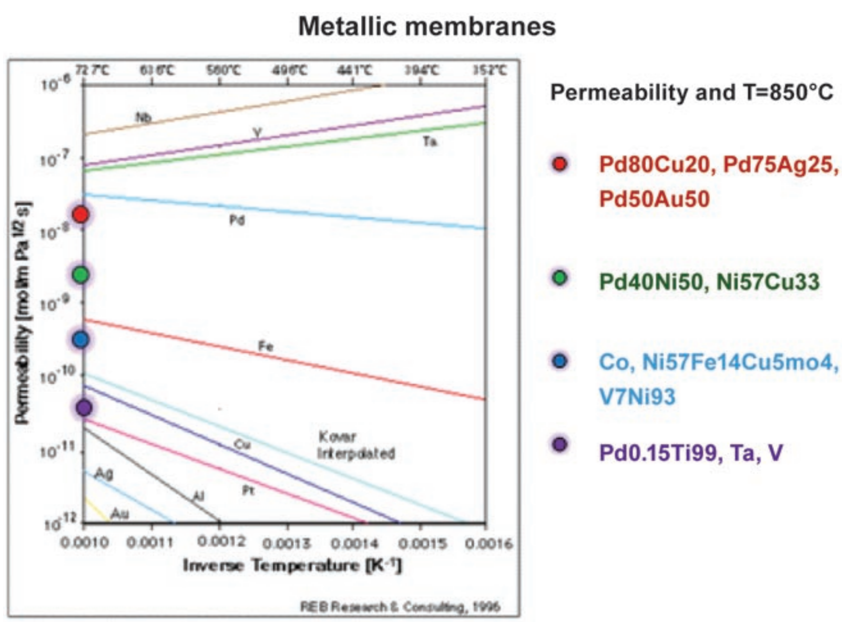

FIGURE 2. Permeability of Metallic Membranes along with Literature Data

for metallic as well as ceramic and composite (glass ceramic) membranes is shown below.

Sequence for Evaluation of Initial Candidate Membranes at GTI:

- H_2/He permeation testing at 850°C and ambient pressure.
- H_2/He permeation testing at 850°C and higher pressures to 30 atmospheres.
- H_2/He permeation testing with H_2/He and specific contaminants as H_2S at 850°C and higher pressures to 30 atmospheres.
- Permeation testing with simulated biomass-derived syngas at 850°C.
- Long-term durability testing with simulated biomass-derived syngas at 850°C.

Table 1 shows permeability test results for metallic, ceramic and glass ceramic membranes. Based on the tabulated results, the metallic membranes clearly show much higher fluxes than the ceramic or glass ceramic membranes. Initial tests on the ceramic and glass ceramic membranes show promise but clearly need additional development work as proposed in the original work plan to DOE.

TABLE 1. Hydrogen Permeation Fluxes for Different Types of Membranes

Membrane Composition	Hydrogen Flux	Temperature	ÄP H_2	Effect of H_2S	Effect of Syngas
	SCFH/FT^2	(°C)	psi		
50Pd50Au	12.8	850	86.7	15% decrease	n/a
80Pd20Cu	47.2	850	216.2	7% decrease	n/a
80Pd20Cu	25.6	850	85.1	n/a	7% decrease
75Pd25Ag	36.8	850	52.9	15% decrease	5% decrease
69Pd31Pt	24.5	750	79.3	18% decrease	n/a
95Pd5Au	81.9	750	79.8	35% decrease	n/a
77Pd23Ag	36.0	700	78.0	n/a	n/a
94Pd6Ni	40.5	750	79.6	n/a	n/a
80Pd20Cu	27.7	900	80.5	n/a	n/a
SrCe0.95Tm0.05O3	0.03	850	1.47	n/a	n/a
<1%Pd-glass	0.15	350	35.7	n/a	n/a
<1%Pd-glass	0.25	850	12.0	n/a	n/a

n/a - not applicable

Conclusions and Future Directions

Based on these results, GTI have selected Pd80Cu20 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 complete the membrane gasifier process development and economic analysis.
- GTI will design and build a biomass gasifier.