One Step Biomass Gas Reforming-Shift Separation Membrane Reactor

2011 DOE Hydrogen Program Review
May 17, 2012

Michael Roberts  Co-PI-presenter  GTI
Razima Souleimanova  Co-PI  GTI
Bryan Morreale  National Energy Technology Laboratory
Mark Davis  Schott North America
Brett Krueger  ATI Wah Chang

Project ID PD070
Overview

Timeline
- Start: 02/01/2007
- End: 06/30/2013
- Percent complete: 75%

Budget
- Total project funding: $3,396,186
  - DOE share: $2,396,949
  - Contractors share: $999,237
- Funding received in FY11: $350,000
- Planned Funding for FY12: $556,452

Barriers
- Hydrogen Production from Biomass Barriers
  - G. Efficiency of Gasification, Pyrolysis, and Reforming Technology
  - I. Impurities
  - N. Hydrogen Selectivity
  - O. Operating Temperature
  - P. Flux

DOE Technical Targets
- $2-4/gge H₂ from biomass delivered target
Collaborations:

Partners

Arizona State University (Academic)- Ceramic membranes (completed their efforts 2008)

National Energy Technology Laboratory (Federal)- Metallic membranes

Schott North America Corporation (Industry)- Glass-ceramic membranes

ATI Wah Chang (Industry) - Membrane module design review
### Relevance: Technical Targets: Dense Metallic Membranes for Hydrogen Separation and Purification

<table>
<thead>
<tr>
<th>Performance Criteria</th>
<th>Units</th>
<th>2006 Status</th>
<th>2010 Target</th>
<th>2015 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux Rate(^b)</td>
<td>scfh/ft(^2)</td>
<td>&gt;200</td>
<td>250</td>
<td>300</td>
</tr>
<tr>
<td>Module Cost (+ membrane material)(^c)</td>
<td>$/ft(^2) of membrane</td>
<td>1,500</td>
<td>1,000</td>
<td>&lt;500</td>
</tr>
<tr>
<td>Durability(^d)</td>
<td>hr</td>
<td>&lt;8,760</td>
<td>26,280</td>
<td>&gt;43,800</td>
</tr>
<tr>
<td>Operating Capability(^e)</td>
<td>psi</td>
<td>200</td>
<td>400</td>
<td>400-600</td>
</tr>
<tr>
<td>Hydrogen Recovery</td>
<td>%</td>
<td>60</td>
<td>&gt;80</td>
<td>&gt;90</td>
</tr>
<tr>
<td>Hydrogen Quality(^f)</td>
<td>% of total (dry) gas</td>
<td>99.98</td>
<td>99.99</td>
<td>&gt;99.99</td>
</tr>
</tbody>
</table>

\(^a\) Based on membrane water-gas shift reactor with syngas.

\(^b\) Flux at 20 psi hydrogen partial pressure differential with a minimum permeate side total pressure of 15 psig, preferably >50 psi and 400°C.

\(^c\) Although the cost of Pd does not present a significant cost barrier due to the small amount used, the equipment and labor associated with depositing the material (Pd), welding the Pd support, rolling foils or drawing tubes account for the majority of membrane module costs.

The $1,500 cost status is based on emerging membrane manufacturing techniques achieved by our partners and is approximately $500 below commercially available units used in the microelectronics industry.

\(^d\) Intervals between membrane replacements.

\(^e\) Delta P operating capability is application dependent. There are many applications that may only require 400 psi or less. For coal gasification 1000 psi is the target.

\(^f\) It is understood that the resultant hydrogen quality must meet the rigorous hydrogen quality requirements as described in Appendix C. These membranes are under development to achieve that quality. Membranes must also be tolerant to impurities. This will be application specific. Common impurities include sulfur and carbon monoxide.
Relevance: Project Objectives

Long-term goal:

Determine the technical and economic feasibility of using the gasification membrane reactor to produce hydrogen from biomass

- flux 270 SCFH/ft²
- purity 99%
- cost $2.00/kg

Short-term goal:

Evaluation of synthesized metallic and glass ceramic membranes to fabricate a module for testing with a bench scale gasifier
Approach: Scope of Work

Task 1. Membrane material development
- 1.1 Ceramic material synthesis & testing
- 1.2 Metallic material synthesis & testing
- 1.3 Composite membrane synthesis & testing
- 1.6 Optimization of selected candidate membranes

Task 2. Gasification membrane reactor process development and economic analysis

Task 3. Bench-scale biomass gasifier modification

Task 4. Integrated testing of initial membrane with gasifier
- 4.1 Design of membrane module configuration
- 4.2 Membrane module fabrication
- 4.3 Testing of bench-scale membrane reactor

Task 5. Integrated testing of best candidate membrane with gasifier
## Approach: Milestones

<table>
<thead>
<tr>
<th>Task</th>
<th>Revised/Planned</th>
<th>Completed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4 Select Initial Candidate Membrane (Pd$<em>{80}$Cu$</em>{20}$)</td>
<td>3/15/08</td>
<td>6/30/08</td>
</tr>
<tr>
<td>1.5 Select Best Candidate Membrane (Pd$<em>{80}$Cu$</em>{20}$)</td>
<td>12/30/11</td>
<td>2/15/12</td>
</tr>
<tr>
<td>1.5 Develop Membrane with Flux of 125 SCFH/ft²</td>
<td>6/15/11</td>
<td>6/15/11</td>
</tr>
<tr>
<td>2.0 Process Development &amp; Econ Analysis</td>
<td>9/30/10</td>
<td>10/07/10*</td>
</tr>
<tr>
<td>Go/ No Go</td>
<td>6/30/12</td>
<td></td>
</tr>
<tr>
<td>4.1 Design Membrane Module</td>
<td>6/30/10</td>
<td>9/17/10</td>
</tr>
<tr>
<td>2.0 Testing Membrane Module Integrated with Bench Gasifier</td>
<td>6/30/13</td>
<td></td>
</tr>
</tbody>
</table>

* Preliminary economic calculations indicate DOE Target can be met.
Approach: Conventional Hydrogen Production from Biomass Gasification and Biomass Gasifier with Close Coupled Membrane
Technical Accomplishments and Progress: Membrane Module Fabrication

Membrane Module is in fabrication process - 50% complete in FY2011:

- Base plates, clamping frames, slotted metal supports are fabricated
- Membranes, porous supports, copper gaskets are cut and ready for use
- Heaters, insulation are purchased and ready to install
- Reactor shell fabrication is in progress

Expected date of completion: August, 2012

Membrane Module Design used in manufacturing

1-base plate (SS316)
2-clamping frame (SS316)
3-copper gasket
4-slotted metal support (SS316)
5-porous support (SS316)
6-membrane (Pd$_{80}$Cu$_{20}$)
Technical Accomplishments and Progress: Membrane Module Fabrication-General View

5 stacked Membrane Module
5 stacks are needed to have enough membrane area to produce 2 lb/day of H₂
Based on overall performance, 80Pd-Cu has demonstrated the best potential. Pd80-Cu results were presented at AMR2011.
Technical Accomplishments and Progress:
Metal-Glass-Ceramic Membranes- Schott

- Segregation of appropriate metals (e.g., Ag-Pd) along grain boundaries during high degrees of crystallization for selected compositions
- Combined ion-exchange (e.g., Ag-Pd) and heat treatment under a reducing atmosphere
- Co-sintering of glassy powder + metal (e.g., Ag-Pd) to produce a high metal content-containing glass-ceramic

Results:
- No flux detected through the glass alone
- All flux occurs at grain boundaries when Pd is present

Conclusions:
- Disappointing flux results
- Low $H_2$ permeability as compared with metallic Membranes- More research is needed.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Hydrogen permeation at 800°C, SCFH/FT²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base1-1/3 Glass-no Pd</td>
<td>0</td>
</tr>
<tr>
<td>Base1-1/2 w/Pd Glass (Work done this FY)</td>
<td>0.04</td>
</tr>
<tr>
<td>Base1-1/2D w/Pd BEST-presented on AMR2011</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Technical Accomplishments and Progress: Process Optimization Strategy

- **UGAS® Process Model**
  - Yields from gasifier @ T & P
  - Reformer yields (removes heavy (tar) components and increases H₂ concentration.)

- **Hysys® Model with Excel Spreadsheet**
  - Determines flux @ T & P (5 equal-area zones)
  - Sizes membrane area for a fixed amount of H₂ recovery
  - Determines gas composition from WGS (partial pressure driving force)

- **Aspen Plus® Model**
  - Determines total process heat and material balance
  - Allows capital cost estimation from scaling
  - Allows operating cost balance – steam and power generation from pinch analysis
Technical Accomplishments and Progress: Process Simulation Basis

- Biomass
- Crushing & Drying
- Gasification
  - Steam
  - Oxygen
  - Syngas $(H_2 + CO)$
- Steam and Power Generation
- Compression
- Membrane Extraction
  - Raw Hydrogen
  - Depleted Gas
- Product Hydrogen

- Raw Hydrogen
Technical Accomplishments and Progress: Membrane Economic Process Parameters

- **Temperature Increase**
  - + Increases flux
  - - Decreases $H_2$ partial pressure with WGS

- **Membrane Area Increase**
  - + Increases hydrogen recovery
  - - Increases capital cost

- **Permeate Pressure Increase**
  - - Decreases flux
  - + Decreases compression cost

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasifier Temperature, F</td>
<td>1292</td>
<td>1800</td>
</tr>
<tr>
<td>Reformer Temperature, F</td>
<td>1292</td>
<td>1800</td>
</tr>
<tr>
<td>Permeate Pressure, bar</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Hydrogen Recovery (of gasifier output)</td>
<td>80%</td>
<td>115%*</td>
</tr>
</tbody>
</table>

Flux rate was calculated using empirical formulas from temperature and hydrogen partial pressure driving force. Membrane area was calculated to achieve the target hydrogen recovery.

* Includes $H_2$ generated by WGS reaction and methane reforming
Technical Accomplishments and Progress: Approach to Membrane Case

Process was modeled as 5 stages (with the same membrane area) – each with a Hydrogen Membrane followed by WaterGas Shift: $\text{H}_2\text{O} + \text{CO} \leftrightarrow \text{H}_2 + \text{CO}_2$

As gas flows over the membrane, $\text{H}_2$ is removed from the composition (originally at WGS equilibrium). Outlet from membrane stage 1 (M 1) has lower $\text{H}_2$ content than the feed (outlet from Reform), but the same amounts of the other gas components.

As the gas flows over the WGS catalyst (WGS 1 outlet), $\text{H}_2$ and $\text{CO}_2$ contents are increased while $\text{CO}$ and $\text{H}_2\text{O}$ contents are decreased due to the WGS stoichiometry.

As the process is repeated, the $\text{H}_2\text{O}$ and $\text{CO}$ contents decrease, while the $\text{CO}_2$ content increases. The $\text{H}_2$ content decreases as the removal by the membranes exceed the amount created by WGS.
Technical Accomplishments and Progress: Approach to Membrane Case

The feed gas composition from the reformer was not formed with WGS catalyst and is at a slightly lower WGS equilibrium temperature. As the gas passes through the stages, the \( \text{H}_2 \) partial pressure driving force for the membrane decreases, but always stays above the 2 psia pressure on the permeate side of the membrane.

The total recovery amounts to 115% of the 8110 mol/hr of \( \text{H}_2 \) originally present in the reformer product gas.
Technical Accomplishments and Progress: Latest Economic Evaluation Case (8J) Basis

Input:  
1292 °F (700°C) gasifier
1292 °F (700°C) membrane and reformer
7410 m² membrane needed
0.2 bar permeate pressure

Results:  
115% of molecular H₂ recovered from gasifier outlet
7410 m² membrane needed
Cost $1.82/kg

PSA Case:  
80% of molecular H₂ recovered from gasifier outlet
Cost $2.00/kg
## Technical Accomplishments and Progress:
### Detailed Capital Cost (ASPEN Results) Estimation

<table>
<thead>
<tr>
<th>Item</th>
<th>Preliminary, 2005 MM$</th>
<th>Updated in FY12, 2005 MM$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>18.8</td>
<td>20.3</td>
</tr>
<tr>
<td>Gasifier</td>
<td>12.0</td>
<td>12.9</td>
</tr>
<tr>
<td>Gas Processing</td>
<td>14.7</td>
<td>18.9</td>
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<tr>
<td>Membrane</td>
<td>30.3</td>
<td>29.6</td>
</tr>
<tr>
<td>Air Compression</td>
<td>21.9</td>
<td>23.6</td>
</tr>
<tr>
<td>H₂ Compression</td>
<td>3.3</td>
<td>3.5</td>
</tr>
<tr>
<td>Steam System</td>
<td>4.9</td>
<td>5.3</td>
</tr>
<tr>
<td>Utilities</td>
<td>11.4</td>
<td>12.2</td>
</tr>
<tr>
<td>Buildings</td>
<td>6.4</td>
<td>6.4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>123.7</strong></td>
<td><strong>132.7</strong></td>
</tr>
</tbody>
</table>
| Total, excluding H₂   | **118.0**              | **129.2**                 | compression to 1000 psi
## Technical Accomplishments and Progress: 
Utilities estimation

<table>
<thead>
<tr>
<th></th>
<th>PSA</th>
<th>8J</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed handling &amp; drying</td>
<td>742</td>
<td>742</td>
</tr>
<tr>
<td>Gasification, reforming</td>
<td>3636</td>
<td>980</td>
</tr>
<tr>
<td>Compression, S removal</td>
<td>26058</td>
<td>26856</td>
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<tr>
<td>Shift, PSA</td>
<td>159</td>
<td>0</td>
</tr>
<tr>
<td>Membrane</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H$_2$ Compression final</td>
<td>4190</td>
<td>5543</td>
</tr>
<tr>
<td>H$_2$ Compression to 315 psi</td>
<td>25688</td>
<td></td>
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<tr>
<td>Steam system</td>
<td>662</td>
<td>156</td>
</tr>
<tr>
<td>Power generation</td>
<td>-29974</td>
<td>-52484</td>
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<tr>
<td>Cooling water</td>
<td>1152</td>
<td>539</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>3660</td>
<td>3660</td>
</tr>
<tr>
<td>Total</td>
<td>10285</td>
<td>11680</td>
</tr>
<tr>
<td>Total ex H$_2$ comp to 1000 psi</td>
<td>6095</td>
<td>6137</td>
</tr>
</tbody>
</table>

**PSA case:** 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
**Technical Accomplishments and Progress: Detailed Capital Cost Estimation**

<table>
<thead>
<tr>
<th>Cost Component</th>
<th>H2 Cost, $ 2007 /kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital Cost</td>
<td>0.68</td>
</tr>
<tr>
<td>Decommissioning</td>
<td>0.00</td>
</tr>
<tr>
<td>Fixed O&amp; M</td>
<td>0.20</td>
</tr>
<tr>
<td>Feedstock Cost</td>
<td>0.51</td>
</tr>
<tr>
<td>Other Raw Material</td>
<td>0.11</td>
</tr>
<tr>
<td>By-Product Credits</td>
<td>0.00</td>
</tr>
<tr>
<td>Other Variable Costs</td>
<td>0.32</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1.82</strong></td>
</tr>
</tbody>
</table>
Technical Accomplishments and Progress: Sensitivity Analysis

- **Feedstock Cost** [$63 / dry short ton ± 50%]
- **Total Capital Investment** [$181,000,000 - 35% / +50%]
- **Operating Capacity Factor** [80%  90%  95%]
- **Total Fixed Operating Cost** [$12,700,000 - 20% / +30%]
- **Specified Replacement Costs** [0 to 25% of initial direct capital every 10 years]

Cost dominated by feedstock and capital equipment
Technical Accomplishments and Progress:  
Conclusions for Economic Analysis

- 2012 Membrane Case (8J) has recovery of 115% of H₂ from gasifier. Previous Membrane case (7F) had 100% recovery. PSA Future Case had about 80% recovery.

- Cost of hydrogen production with membrane ($1.82/kg) is less than the cost with PSA ($2.00/kg).

- Over 115% of the hydrogen produced in the gasifier can be recovered due to Water Gas Shift for membrane.

- Further optimization of process conditions and cost reduction is possible:
  - Temperature decrease (<700°C)
  - Increase of H₂ recovery (>115%)
  - Reduce membrane cost by purchasing volume discount
Proposed Future Work

- Complete Process Development and Economic Analysis for different downstream processes after biomass gasification: more optimization on process temperatures, \( H_2 \) recovery and permeate pressure

- Complete fabrication of membrane module integrated with biomass reactor: finish fabrication of all parts

- Laboratory testing of individual module and stacked modules (5): leak checking and testing using simulated syngas

- Integrated testing of membrane module with gasifier: \( H_2 \) production during biomass gasification using fabricated membrane module
Summary

- Membrane Pd$_{80}$Cu$_{20}$ Best Performance Results
- Membrane module design was completed. Module capable of a flux rate of 80+ SCFH/ft$^2$
- Fabrication of Initial Membrane Module for Bench Gasifier 50% completed
- Economic Analysis showed

<table>
<thead>
<tr>
<th>PSA</th>
<th>Preliminary</th>
<th>V2.2</th>
<th>v3</th>
<th>Preliminary (7F)</th>
<th>V2.2 (8J)</th>
<th>v.3 (8J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2, $/kg</td>
<td>1.17</td>
<td>1.47</td>
<td>2.00</td>
<td>1.17</td>
<td>1.28</td>
<td>1.82</td>
</tr>
</tbody>
</table>
Technical Back-Up Slide
**Advanced Inorganic Membranes for Biomass Gasification Application**

<table>
<thead>
<tr>
<th>Mixed proton/electron conducting membrane</th>
<th>Atomic transport dense metallic membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrogen at high pressure</strong></td>
<td><strong>Hydrogen at high pressure</strong></td>
</tr>
<tr>
<td>$H_2 \rightarrow 2H^+ + 2e^-$</td>
<td>$H_2 \rightarrow 2H$</td>
</tr>
<tr>
<td><strong>Hydrogen at low pressure</strong></td>
<td><strong>Hydrogen at low pressure</strong></td>
</tr>
<tr>
<td>$2H^+ + 2e^- \rightarrow H_2$</td>
<td>$2H \rightarrow H_2$</td>
</tr>
</tbody>
</table>

**Multi-phase ceramic/metal membrane**

- Ceramic phase
- Metallic phase

**Dense thin layer on porous support layer**

- Active H2 transport layer
- Catalytic support layer
Approach: GTI’s Fluidized Bed Gasifier RENUGAS®
Ideal for Membrane Gasification Reactor

- Biomass Feed
- Feed Lockhopper
- Disengaging zone
- Gasification zone
- 1st-STAGE CYCLONE
- 2nd-STAGE CYCLONE
- Raw Product Gas
- Membrane module
- STEAM/OXYGEN OR AIR
- ASH LOCKHOPPER
- ASH

**T**: 700~900°C
**P**: 20~60 atm
- H₂, CO, CO₂, H₂O each 15~25%
- CH₄: 5~10%
- + trace contaminants
Technical Accomplishments and Progress: Potential Sites for Membrane Module

Auburn University
Gas Technology Institute-FFTF
Technical Accomplishments and Progress: Process Flow Diagram

- Biomass
  - Biomass Grinding
  - Biomass Drying
  - Biomass Gasification
- Membrane/WGS
- Tar Reforming
- LO-CAT Cleanup
- Heat Recovery
- Syngas Burning
- Air Compress
- Air
- Heat Recovery
- Power Gen
- HP Steam
- LP Steam
- Condense
- Pump
- Flue Gas
- Hydrogen
- Oxygen
- Ammonia
- Heat Recovery
- MP Steam
Technical Accomplishments and Progress: Case 8J
Technical Accomplishments and Progress: Aspen Plus® Model
Technical Accomplishments and Progress:
Pinch Analysis

![Graph showing technical accomplishments and progress in pinch analysis with various lines representing different heat duties and temperatures. The graph includes labels for external heat, external cooling, steam, and power.]