the Energy to Lead

One Step Biomass Gas Reforming-Shift Separation Membrane Reactor

2010 DOE Hydrogen Program Review
June 7, 2010

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Project ID PD070

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Overview

Timeline

> Start: 02/01/2007

> End: 06/30/2013

> Percent complete: 35%

Budget

> Total project funding:	$3,396,186
—DOE share:	$2,716,949
—Contractors share:	$679,237
> Funding received in FY09:	$0
> Funding for FY10:	$350,000

Overview (con't)

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
  - $2-3/kg H_2 from biomass delivered target
  - $1.60/kg H_2 from biomass without delivery

Partners

- Arizona State University
- National Energy Technology Laboratory
- Schott North America
- Wah Chang, an Allegheny Technology Company

Relevance: Technical Targets: Dense Metallic Membranes for Hydrogen Separation and Purification[a]

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

[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.

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Relevance: Project Objectives

Long-term goal:

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

Short-term goal:

Evaluation of synthesized metallic and glass ceramic membranes to fabricate a module for testing with the 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 design and construction

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Approach: Scope of Work (Continued)

- 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
- Task 6. Project Management and Reporting

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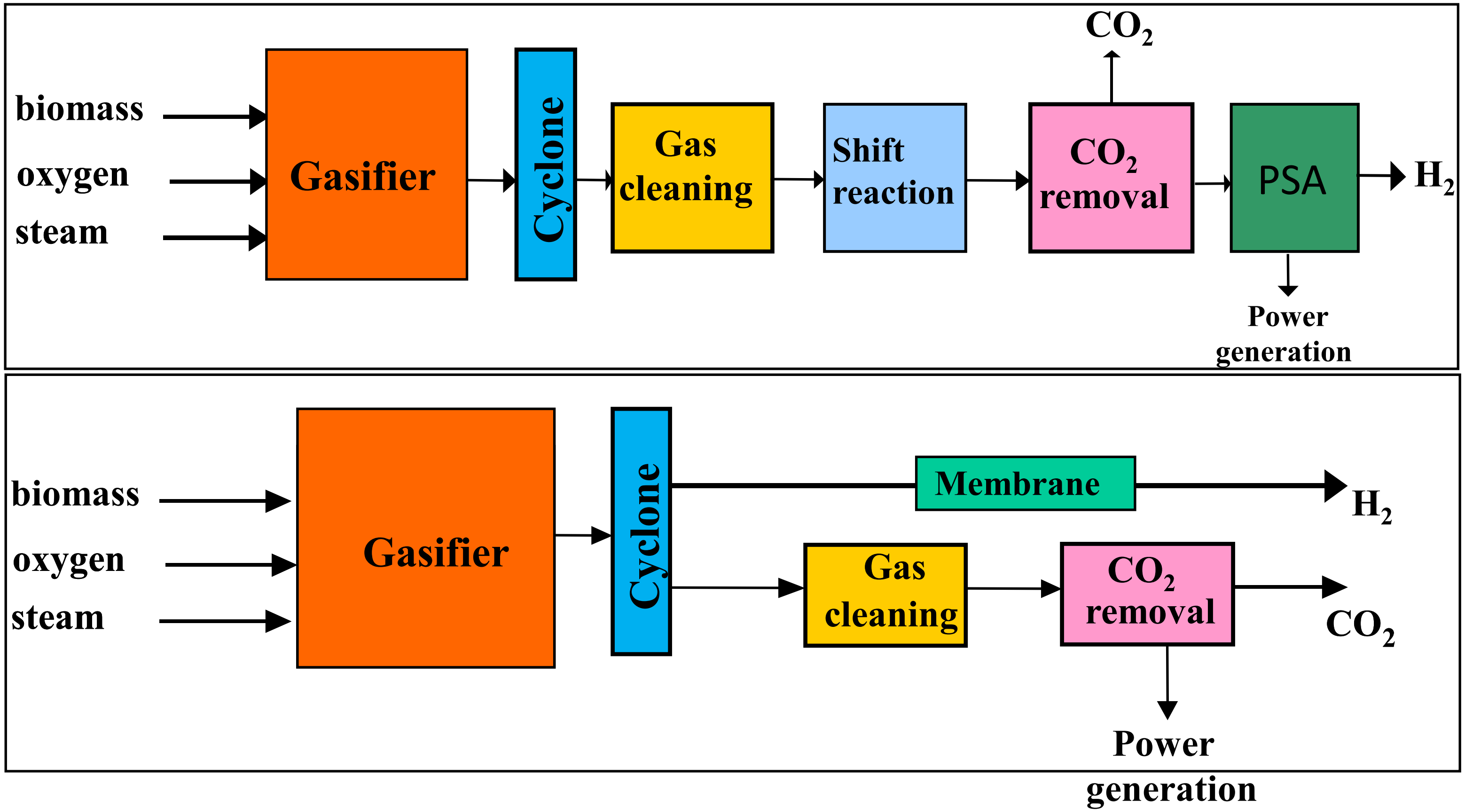
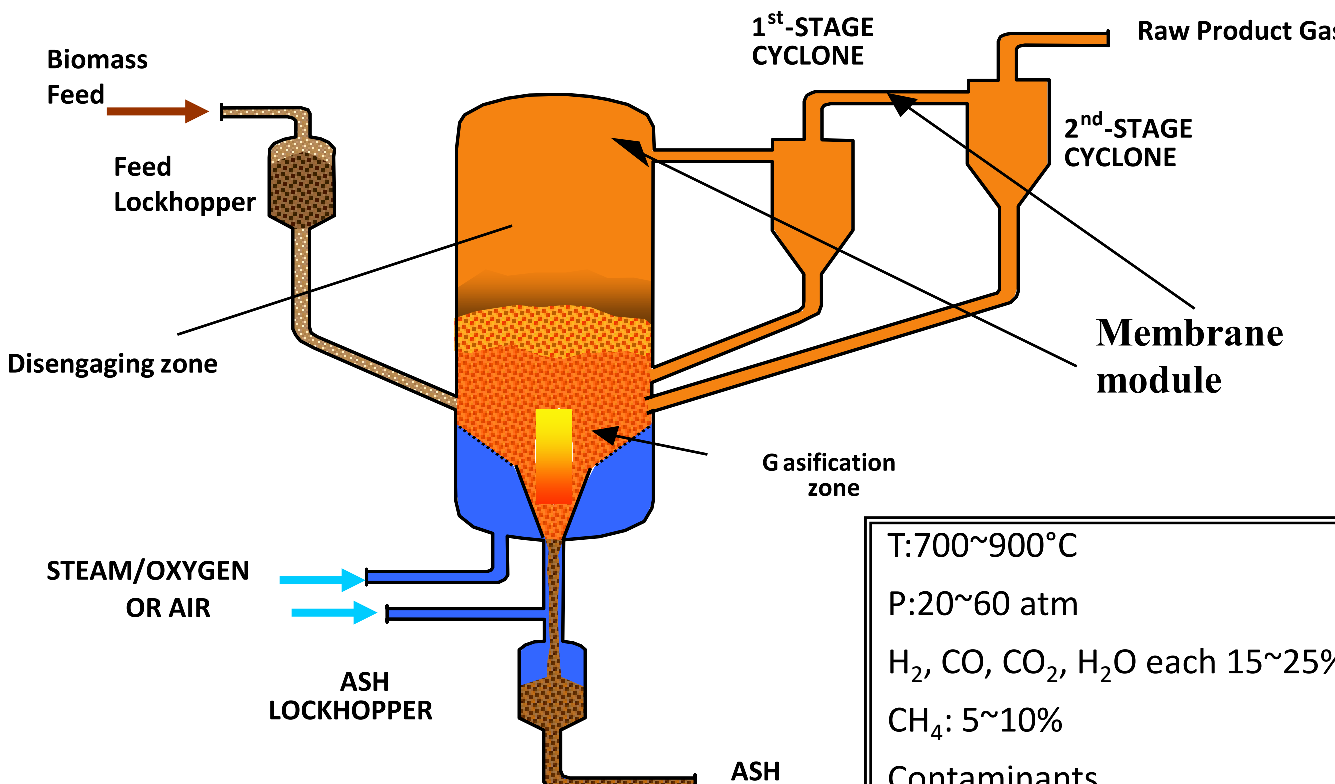
Approach Milestones

Task	Revised/ Planned
1.4 Select Initial Candidate Membrane	6/30/08
1.5 Select Best Candidate Membrane	12/30/11
2.0 Process Development & Econ Analysis	9/30/10
	6/30/12
4.1 Membrane Module Design	6/30/10
2.0 Integrated Testing with bench gasifier	6/30/12

Approach: Conventional Hydrogen Production from Biomass Gasification and Biomass Gasifier with Close Coupled Membrane



Approach: GTI's Fluidized Bed Gasifier RENUGAS® Ideal for Membrane Gasification Reactor



T:700~900°C

P:20~60 atm

H_2, CO, CO_2, H_2O each 15~25%

CH_4: 5~10%

Contaminants

Approach: Potential Benefits of Membrane Reactor for Hydrogen Production from Biomass

- **High H_2 production efficiency:**
  Thermodynamic analysis indicates potentially over 40% improvement in H_2 production efficiency over the current gasification technologies

Eliminate loss in PSA tail gas	
More CO shift	$H_2O+CO = CO_2+H_2$
Reform CH_4	$CH_4+H_2O = CO+3H_2$

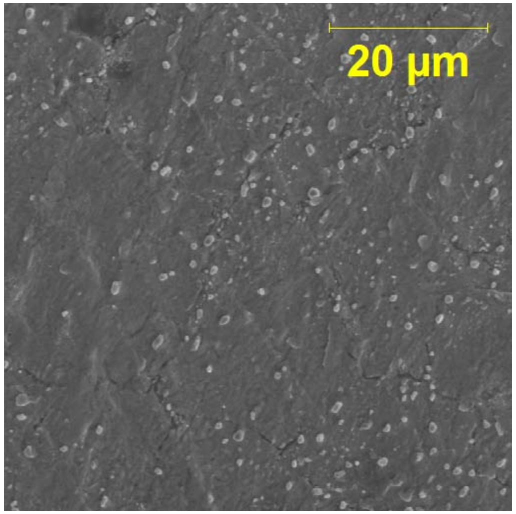
- **Low cost:**
  reduce/eliminate downstream processing steps
- **Clean product:**
  no further conditioning needed, pure hydrogen
- **CO_2 sequestration ready**:
  simplify CO_2 capture process
- **Power co-generation**:
  utilization of non-permeable syngas

Technical Accomplishments and Progress: Metallic Membranes-DOE NETL

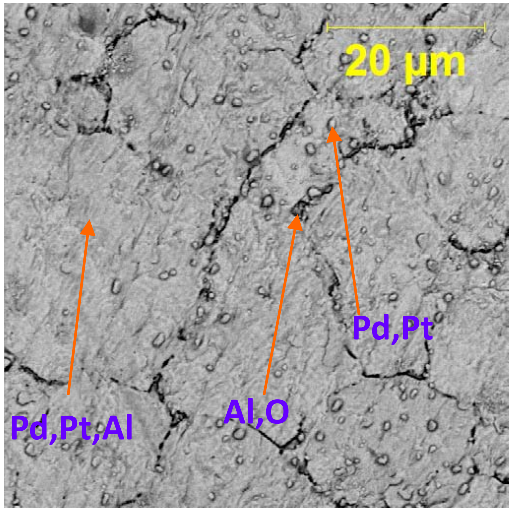
Addition of Stabilizing Elements

Select elements have shown promise in enhancing corrosion resistance, mechanical strength and stabilization of grain boundaries.

PdPtAl



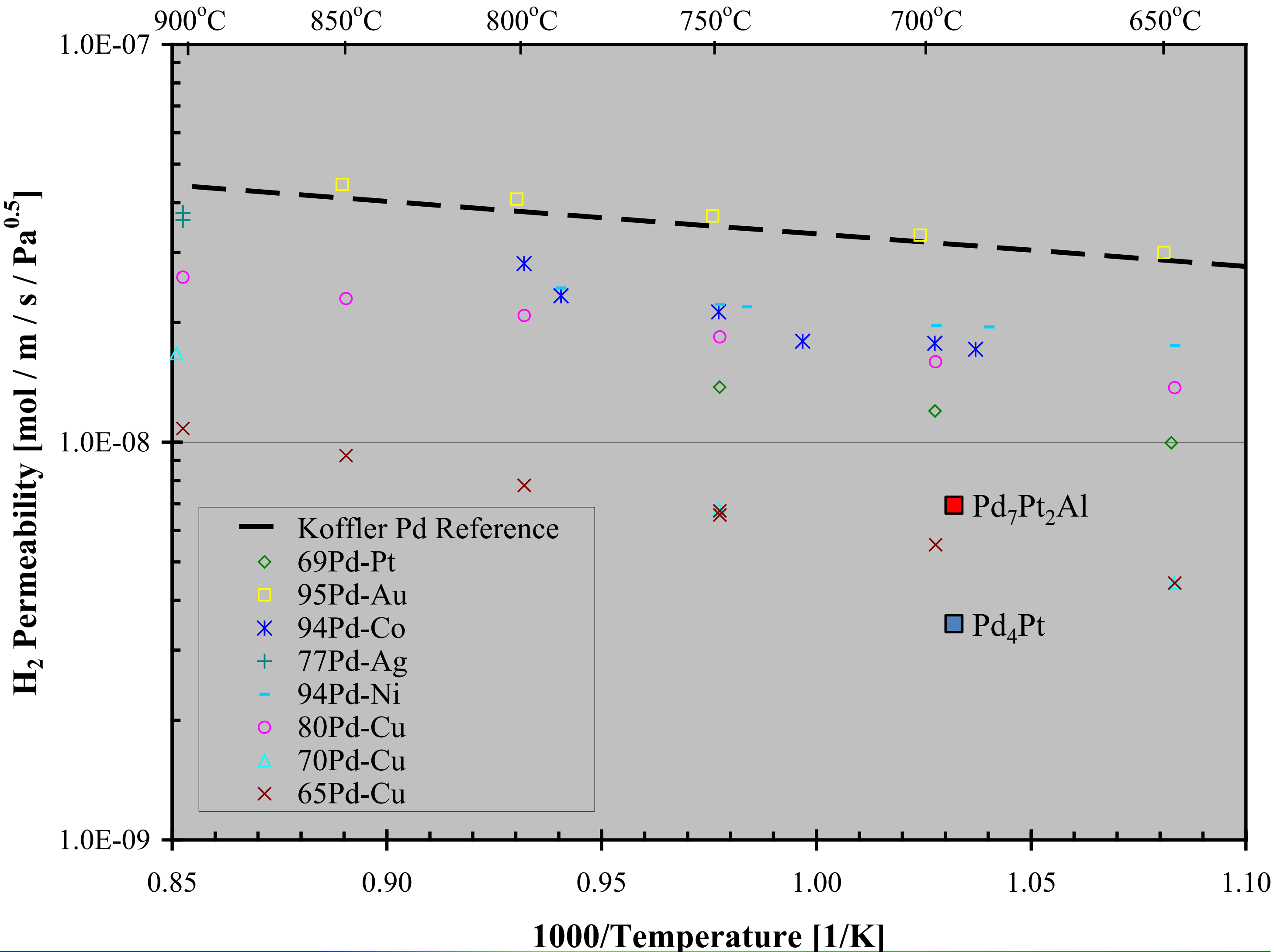
Secondary



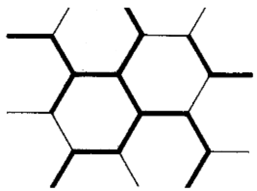
Backscattered

"ODS" (oxide dispersion stabilized) alloy
BH9-147 = Pd_7Pt_2Al annealed 800 C in air 1 hour to "force" oxide growth

Technical Accomplishments and Progress: Membrane Performance in H_2 - DOE-NETL



Technical Accomplishments and Progress: Metal-Glass-Ceramic Membranes- Schott

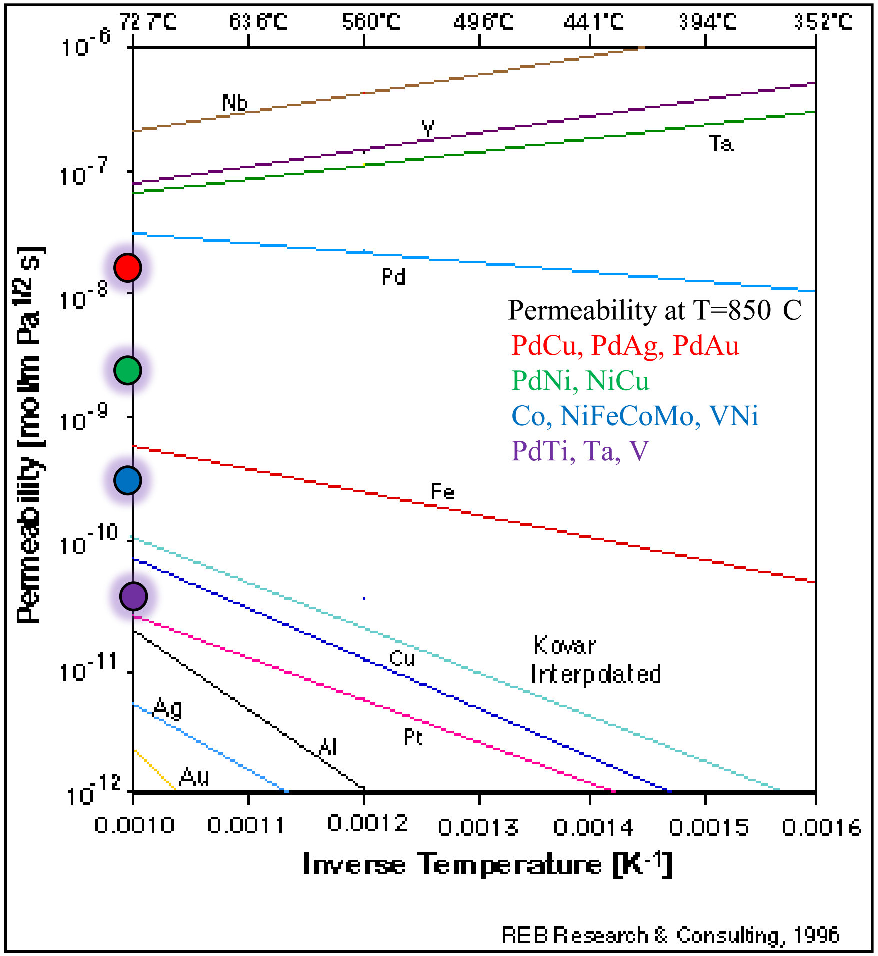


Desired microstructure

- 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

Membrane	Ceramization conditions: temperature, atmosphere	Hydrogen permeation, SCFH/FT^2	Temperature, °C	Pressure difference, psi	Electronic conductivity, S/cm at 600°C
CMAS-1/3 Glass-no Pd	unceramized	0	850	11.8	4×10^{-8}
CMAS-1/2 w/Pd Glass	unceramized	0.02	850	7.4	4×10^{-9}
CMAS-1/2D w/Pd	1100°C, H_2/N_2	0.15	350	35.7	7×10^{-7}
CMAS-1/2D w/Pd	1100°C, H_2/N_2	0.25	850	12.0	7×10^{-7}

Technical Accomplishments and Progress: Metallic Membranes- GTI



Surface oxide layer:
chemical etching, electrochemistry

Catalytic protective layer:
electrochemistry

Hydrogen embrittlement:
use alloy instead of pure metals

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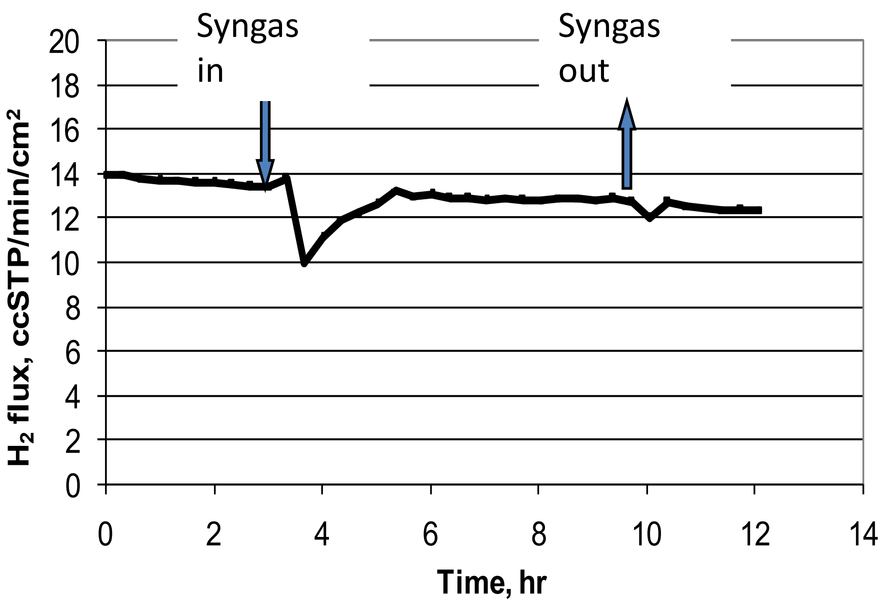
Technical Accomplishments and Progress: Selection of Initial Candidate Membrane

Pd-Cu foil was identified as an initial membrane candidate and screened using the following sequence of experiments:

- **H_2/He permeation testing at about 850ºC and ambient pressure**
- **H_2/He permeation testing at about 850ºC and higher pressures to 30 atmospheres**
- **H_2/He permeation testing with H_2/He and certain contaminants as H_2S at about 850ºC and higher pressures to 30 atmospheres**
- **Permeation testing with simulated biomass-derived syngas at about 850ºC**
- **Longer term durability testing with simulated biomass-derived syngas at about 850ºC**

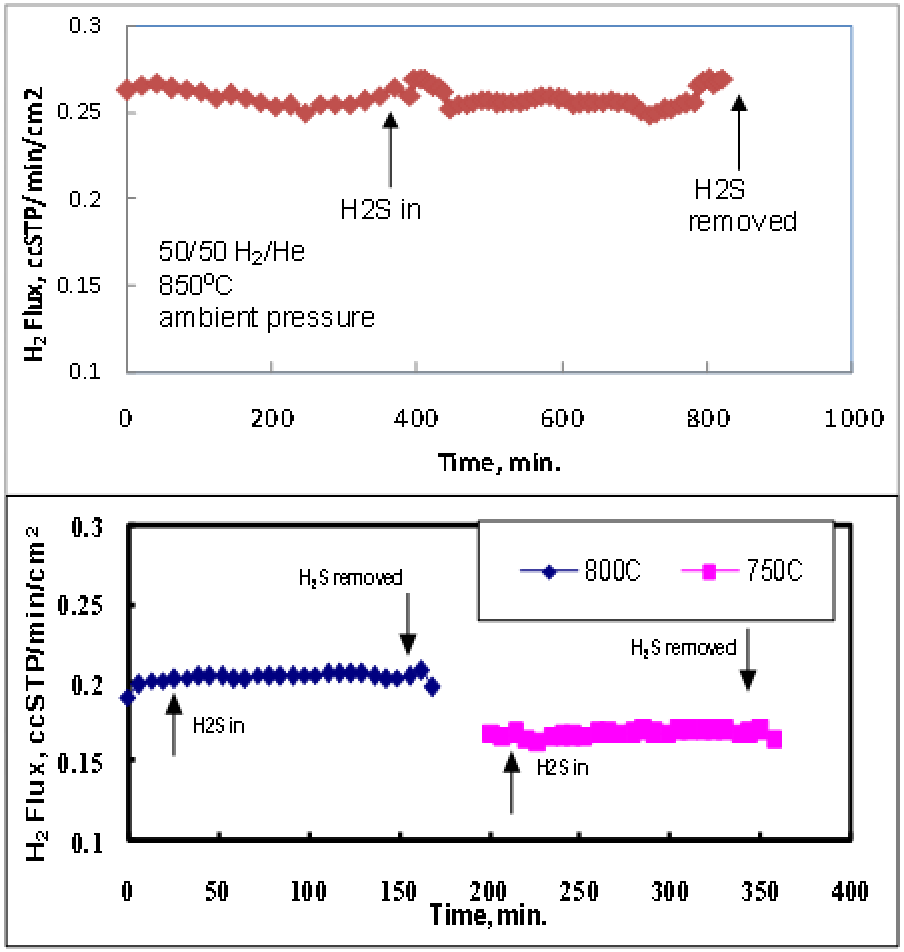
Technical Accomplishments and Progress: Permeation Testing with Simulated Biomass-Derived Syngas



- Thickness-100 microns
- Feed: 20%H_2/80%He
- Syngas mixture composition: 20%H_2, 20% CO,10% CO_2, 10% H_2O balance of He
- Feed pressure-30 atm
- Temperature – 850ºC
- Sweep gas- N_2

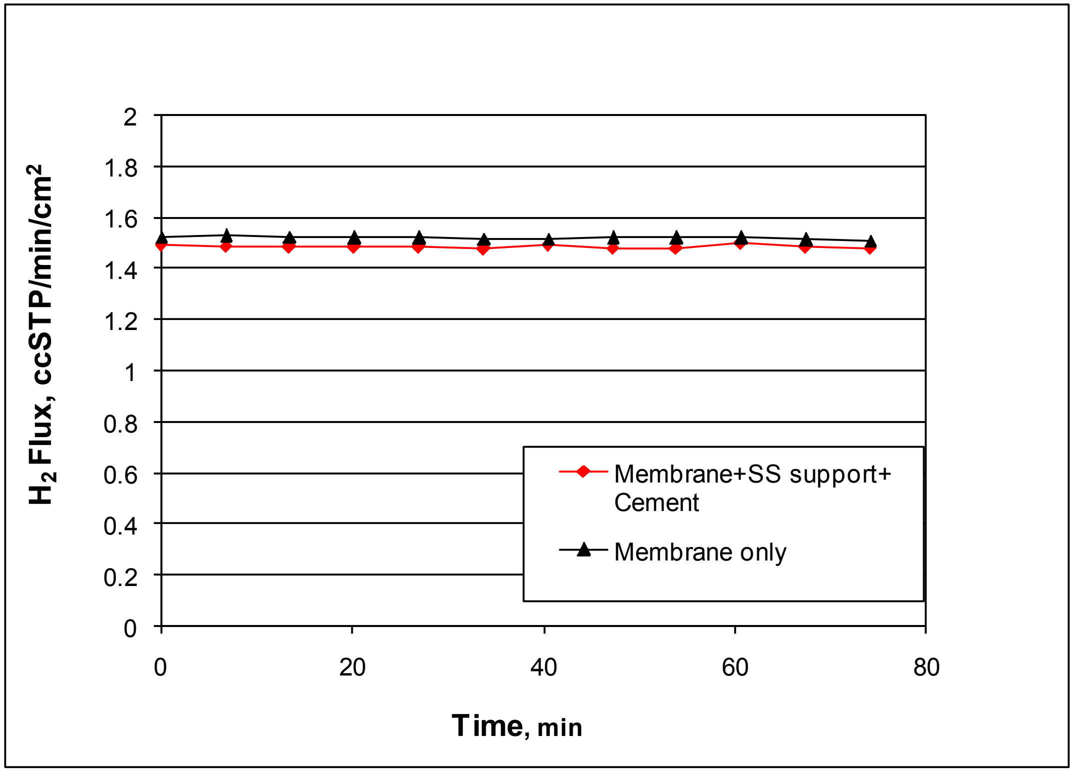
Almost no effect on hydrogen permeation

Technical Accomplishments and Progress: Effect of H_2S on $Pd_{80}Cu_{20}$ alloy Membrane



Sulfur tolerance at 750-850°C

Technical Accomplishments and Progress: Testing of Porous Support for Mechanical Stability and Transport Resistance



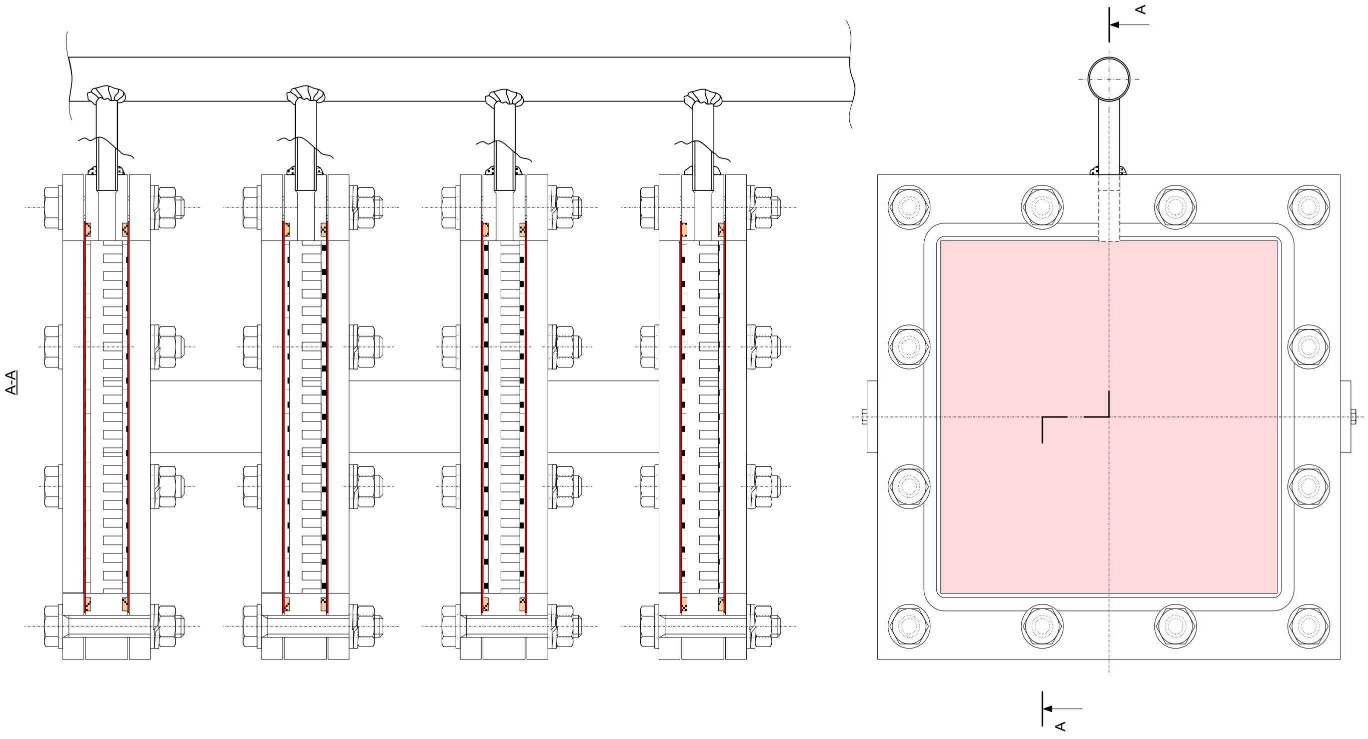
Ceramic, stainless steel and titanium porous substrates were tested for support structure.

SS porous support

- (20 μm in pore size)
- Coated by cement
- High mechanical stability
- No mass transfer resistance.

Technical Accomplishments and Progress: Design of Membrane Module

Draft version of membrane module designed by GTI and reviewed by Wah Chang



Technical Accomplishments and Progress: Catalysts for Tar Cracking, Reforming and Shift Reactions

$C_nH_m + nH_2O \rightarrow nCO + (m/2+n)H_2$	Tar Decomposition
$CH_4 + H_2O \rightarrow CO_2 + 3H_2$	Methane reforming
$CO + H_2O \rightarrow CO_2 + H_2$	Water-Gas Shift

Ni-based catalysts: deactivation, sintering, volatilization of nickel, carbon formation.

Solutions: use as "secondary", steam addition, lower temperature, removal of hydrogen.

Conclusion: Tar cracking, reforming and water-gas shift reactions can be catalyzed by Ni-based catalyst. H_2-selective membrane promotes reactions to higher degree of completion

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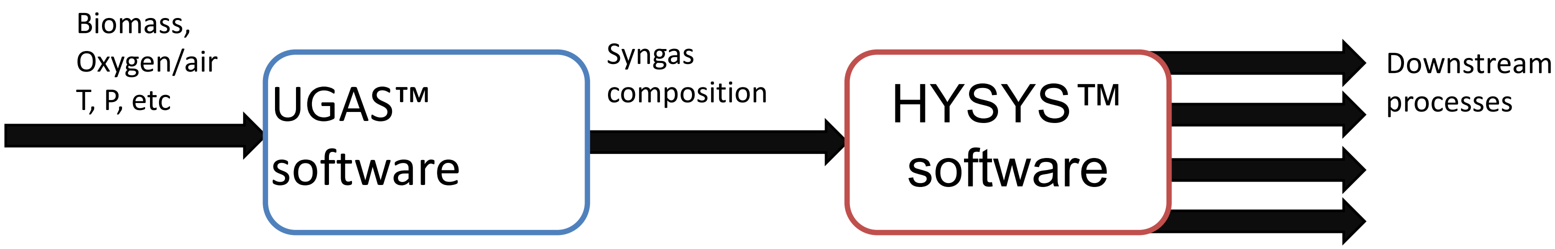
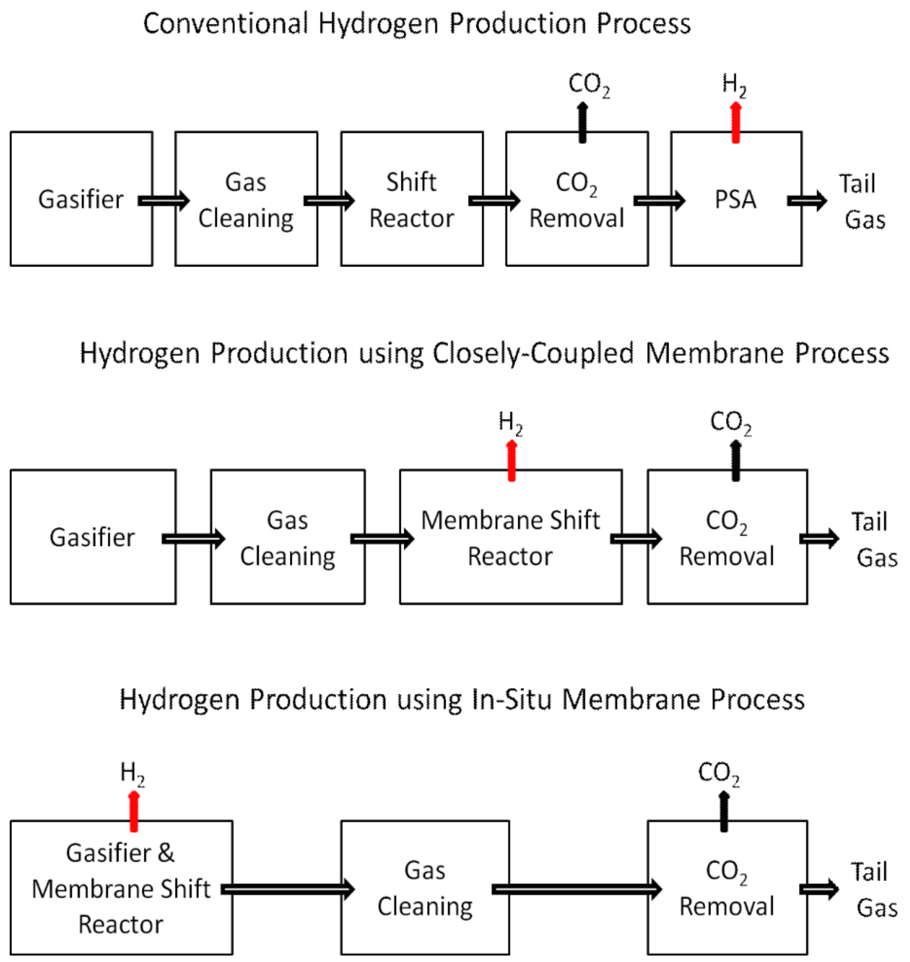
Technical Accomplishments and Progress: Gasification Membrane Reactor Process Development and Economic Analysis



- **UGAS ™software is used to predict product composition from biomass gasifier.**
- **Downstream processes variations**

Target: Biomass gasification membrane reactor technology will meet the DOE's cost target of \$2.5/Kg H_2.

Technical Accomplishments and Progress: Simplified Diagrams of Different Process Variations after Biomass Gasification



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Proposed Future Work

- Continue to identify metal additives to enhance the catalytic activity of Pd-based alloys in the presence of sour gas-H_2S and chemical and mechanical stability of highly-permeable Pd-based alloys-NETL and GTI
- Synthesis of Pd-containing glass-ceramic membranes-Schott
- Process Development and Economic Analysis for different downstream processes after biomass gasification ("go/no-go" point)
- Fabrication of membrane module integrated with biomass reactor

Summary

> Project was initiated again (February 2010) after 1 year hiatus. Selected team members began contractual activities with GTI

> Initial candidate membrane was chosen and “go” decision was made

> Development of metallic, glass-ceramic membranes are in progress

> Process development and Economic analysis is in progress- go/no go point

> Membrane module design is in progress

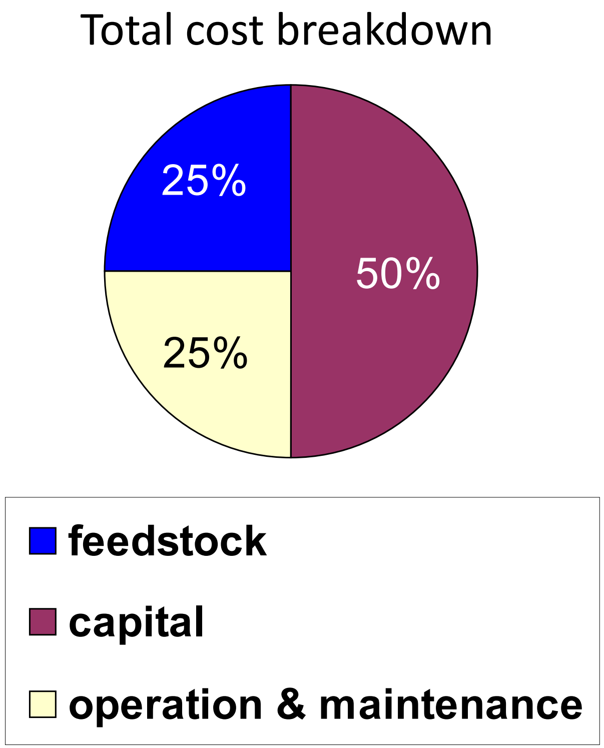
Summary

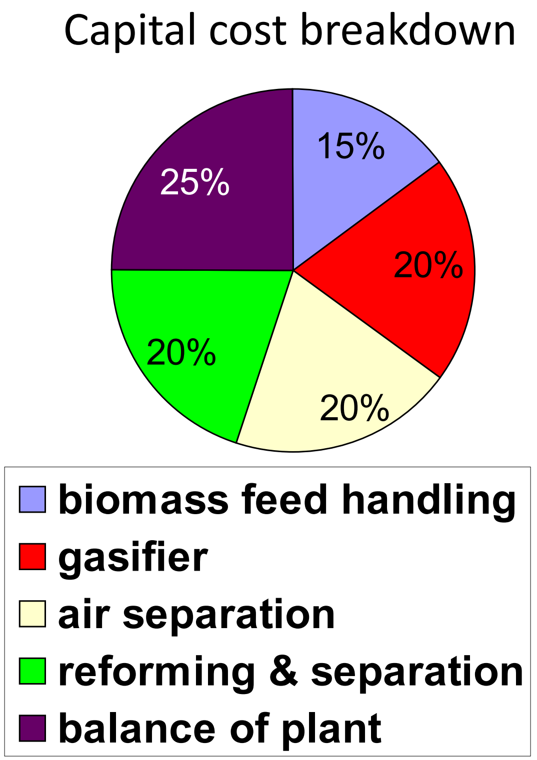
Hydrogen Permeation Fluxes for Different Types of Membranes

Membrane Composition	Hydrogen Flux SCFH/FT^2	Temperature (^oC)	ΔP H_2 psi	Effect of H_2S	Effect of Syngas
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
<1%Pd-glass	0.15	350	35.7	n/a	n/a
<1%Pd-glass	0.25	850	12.0	n/a	n/a

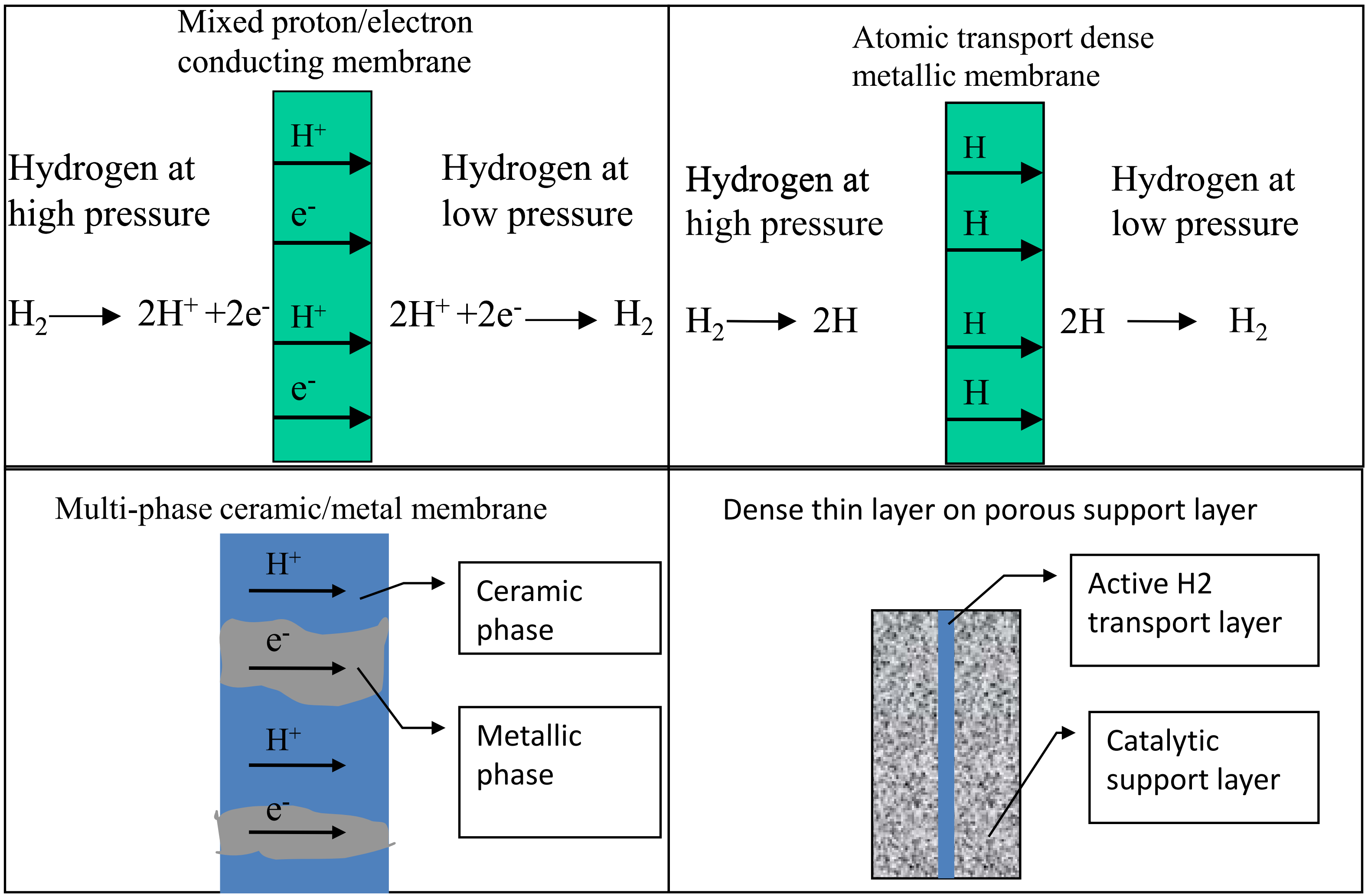
Supplemental Slides

Hydrogen Production Cost from Biomass Gasification





Advanced Inorganic Membranes for Biomass Gasification Application



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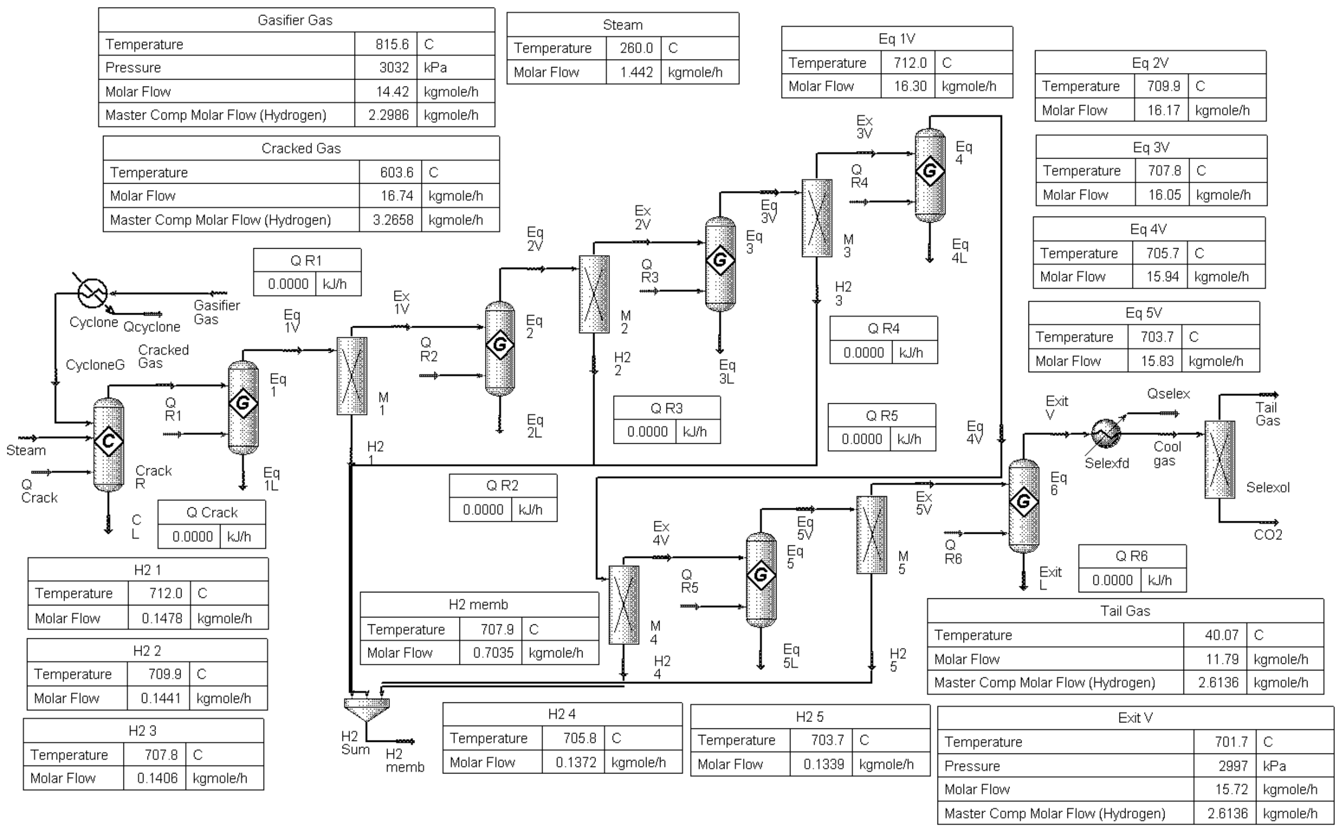
Technical Accomplishments and Progress: HYSYS^{TM} Scheme of Downstream Processes for Membrane Closely-coupled to Gasifier



Project Time Schedule