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the Energy to Lead

One Step Biomass Gas Reforming-Shift Separation Membrane Reactor

2011 DOE Hydrogen Program Review
May 10, 2011

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Mark Davis	Schott North America
Brett Krueger	Wah Chang (an Allegheny Company)

Project ID PD070

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Overview

Timeline

- Start: 02/01/2007
- End: 06/30/2013
- Percent complete: 50%

Budget

- Total project funding: $3,076,186 DOE share: $2,396,949
  Contractors share: $679,237
- Funding received in FY10: $350,000
- Funding for FY11: $350,000 planned

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

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

Wah Chang Company (Industry) - Membrane module design

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 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

Task 6. Project Management and Reporting

Approach: Milestones

Task	Revised/ Planned	Completed
1.4 Select Initial Candidate Membrane	3/15/08	6/30/08
1.5 Select Best Candidate Membrane	12/30/11	
1.5 Develop Membrane with Flux of 125 SCFH/ft2	6/15/11	
2.0 Process Development & Econ Analysis	9/30/10	10/07/10*
	6/30/12	
4.1 Membrane Module Design	6/30/10	9/17/10
2.0 Integrated Testing with Bench Gasifier	6/30/12	

* Preliminary economic calculations indicate DOE Target can be met.

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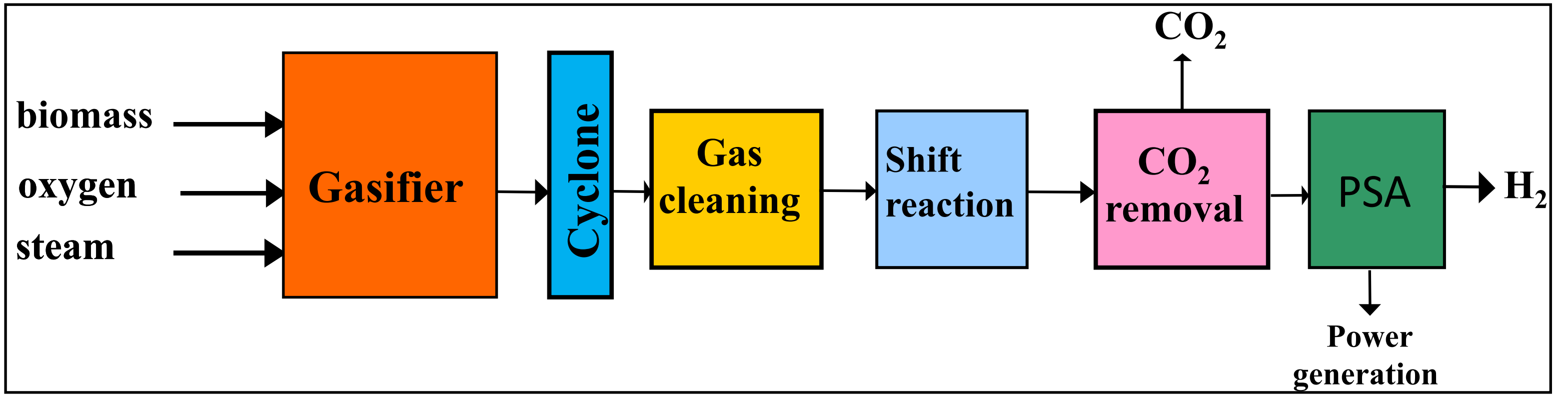
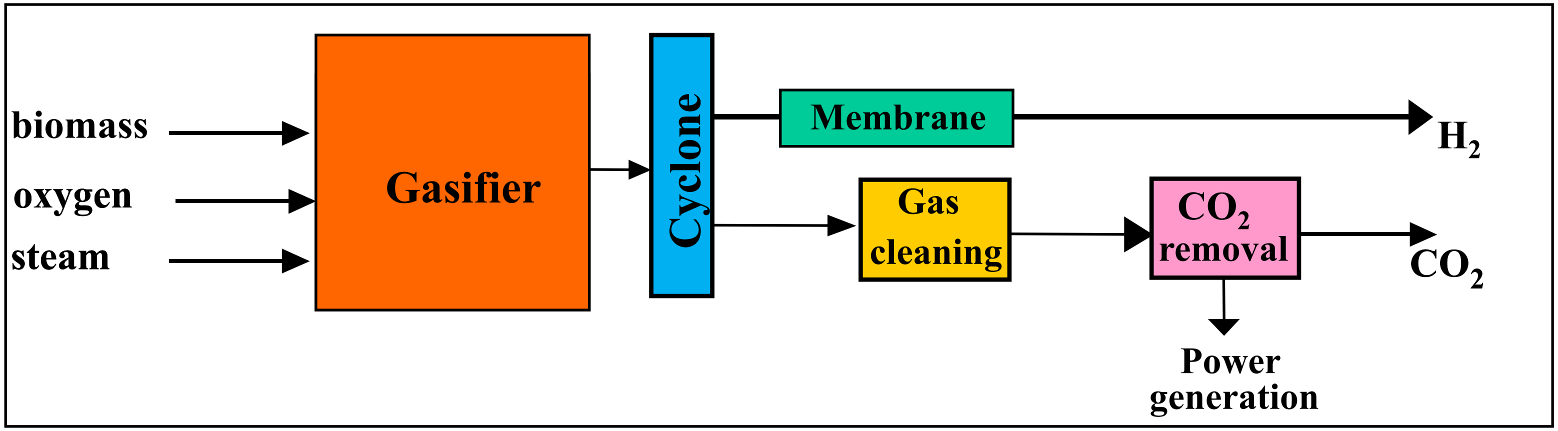
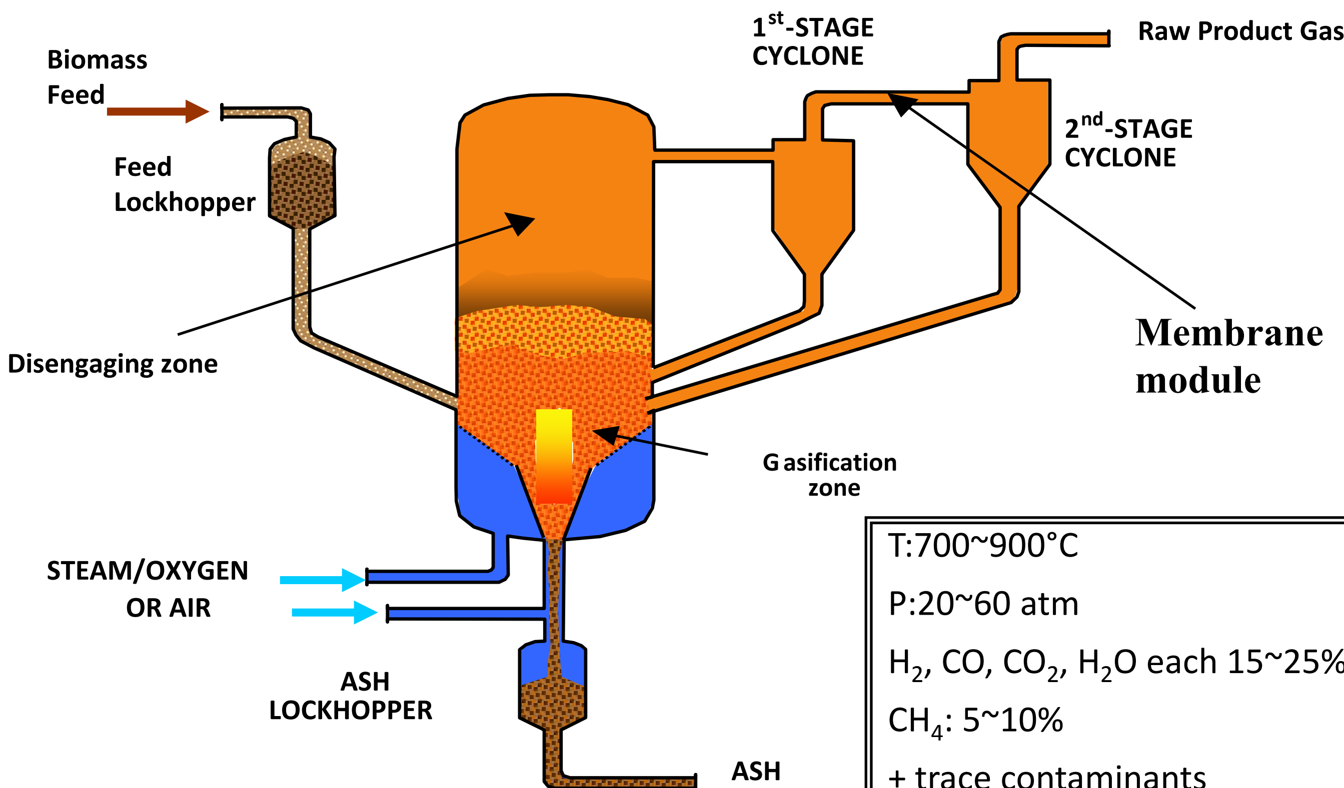
Approach: Conventional Hydrogen Production from Biomass Gasification and Biomass Gasifier with Close Coupled Membrane





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%

+ trace contaminants

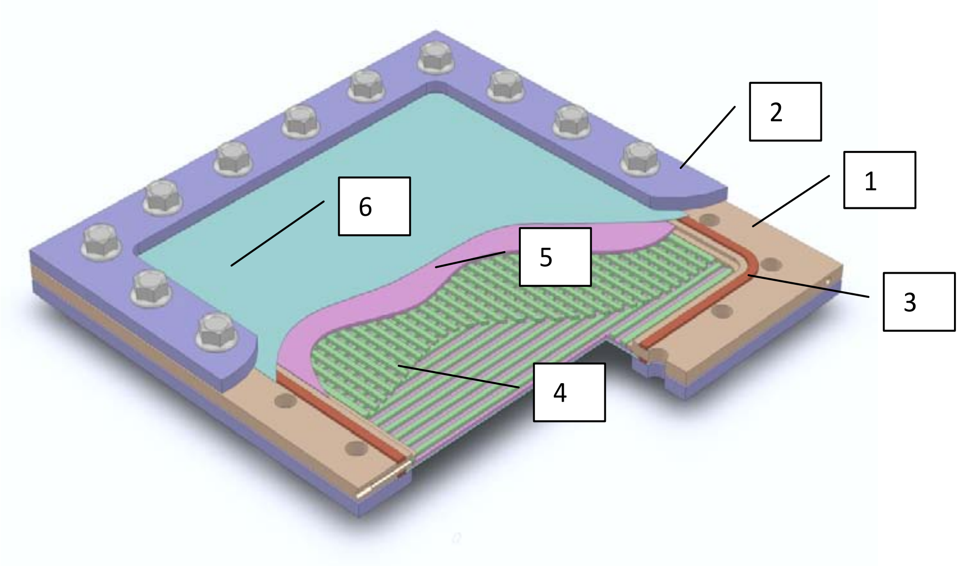
Approach: Potential Benefits of Membrane Reactor for Hydrogen Production from Biomass

- **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

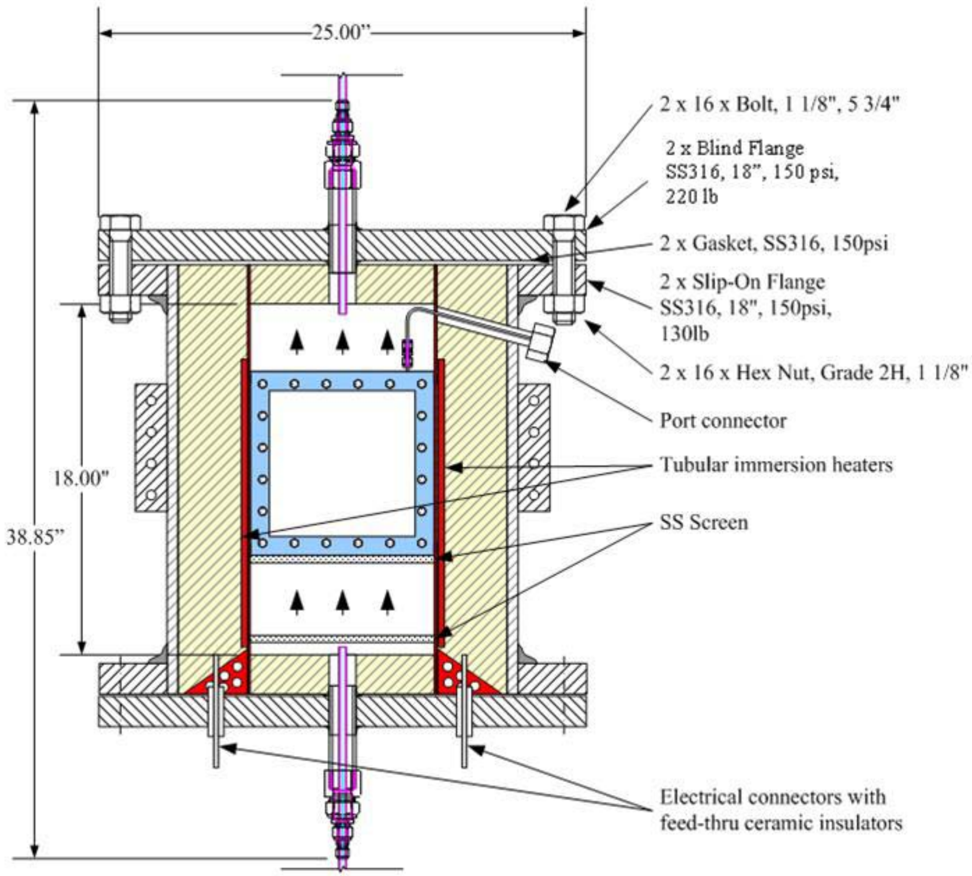
Technical Accomplishments and Progress: Membrane Module Design

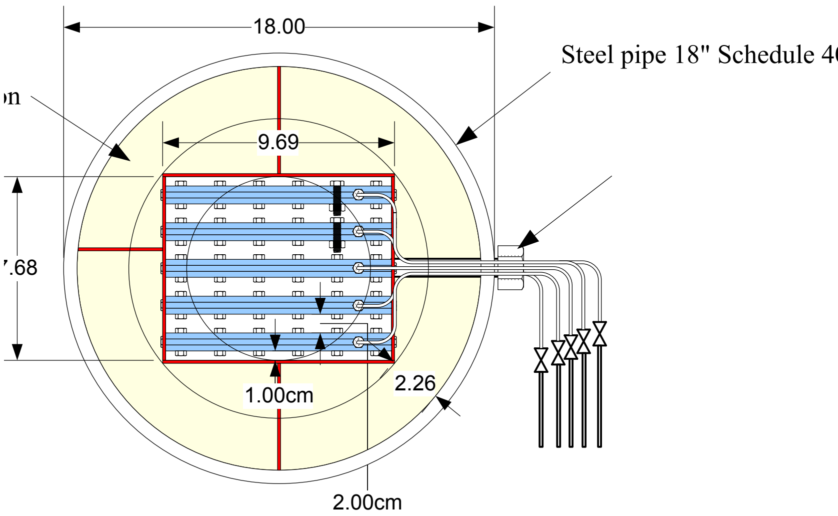


1-base plate
2-clamping frame
3-copper gasket
4-slotted metal support
5-porous support
6-membrane

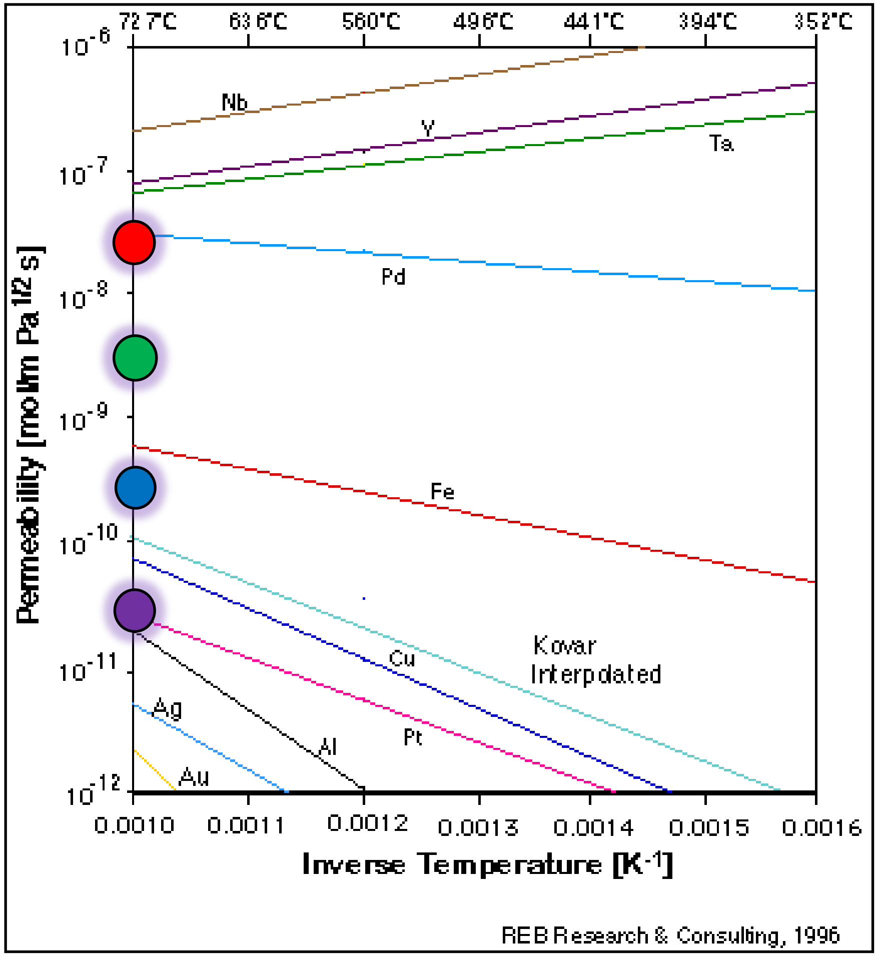
- Planar design
- Copper gaskets coated by silicon
- Hastelloy C-276 body, porous supports and additional mechanical support
- Cement as intermetallic layer
- Distance between channels-turbulent regime
- An initial candidate- $Pd_{80}Cu_{20}$ foil
- Review of membrane module design by Wah Chang
- Potential Sites for Membrane Module: Auburn University and GTI's FFTF

Technical Accomplishments and Progress: Membrane Module Design- GTI and Wah Chang review





Technical Accomplishments and Progress: Metallic Membranes- GTI



	Advantages	Disadvantages
Pd-based membranes	Relatively high flux Catalytic activity for H_2 dissociation	Cost Resistance to impurities issue
Non-Pd membrane	High potential for H_2 flux Inexpensive	Poorly catalytic surface H_2embrittlement

Potential remedies
Engineered surface coatings
Alloying

Permeability at T=800-850°C

PdCu PdTa PdAg (Pd:60-100%)
PdNi PdAu Pd-NiCu-Pd (Pd:0-55%)
Pd-Co-Pd Pd-NiFeCuMo-Pd
Pd-VNi-Pd
Pd-PdTi-Pd Pd-Ta-Pd Pd-V-Pd

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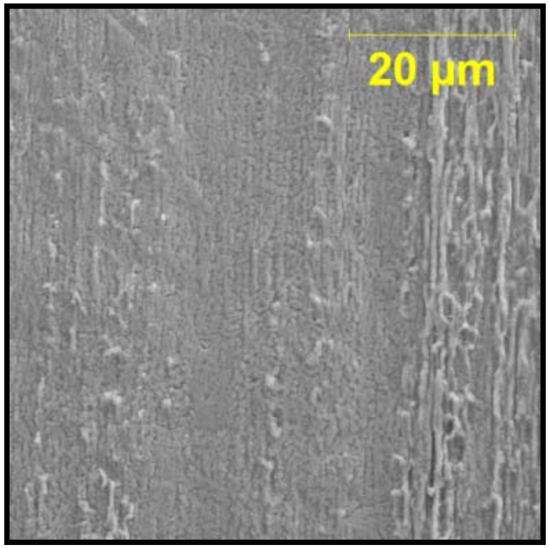
Technical Accomplishments and Progress: Membrane Performance in H_2 - NETL

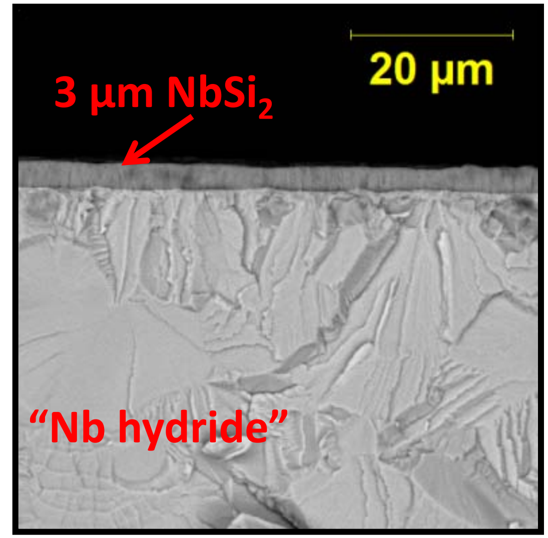
Test of concept

$NbSi_2$ on Nb



Membrane Test

700°C
100% H_2
2 psi

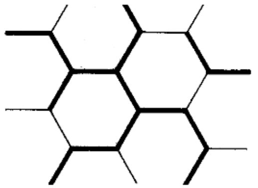


Result: **Failed quickly due to formation of brittle Nb hydride, but silicide coating appears permeable to H_2**

- **Five new Pd-Cu ternary alloys have been fabricated**
- **Alloying elements selected for potential structural stabilizing effect and/or effect on surface characteristics**

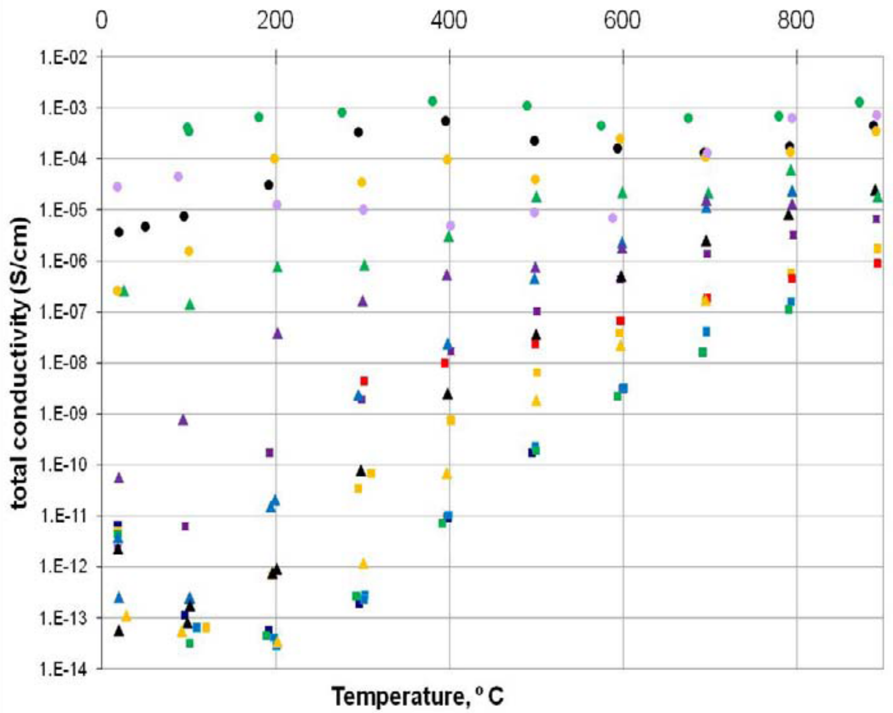
Note: Membrane testing has been on hold due to relocation of testing facilities to a new facility. Membrane testing is expected to restart by May 2011.

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


Desired microstructure

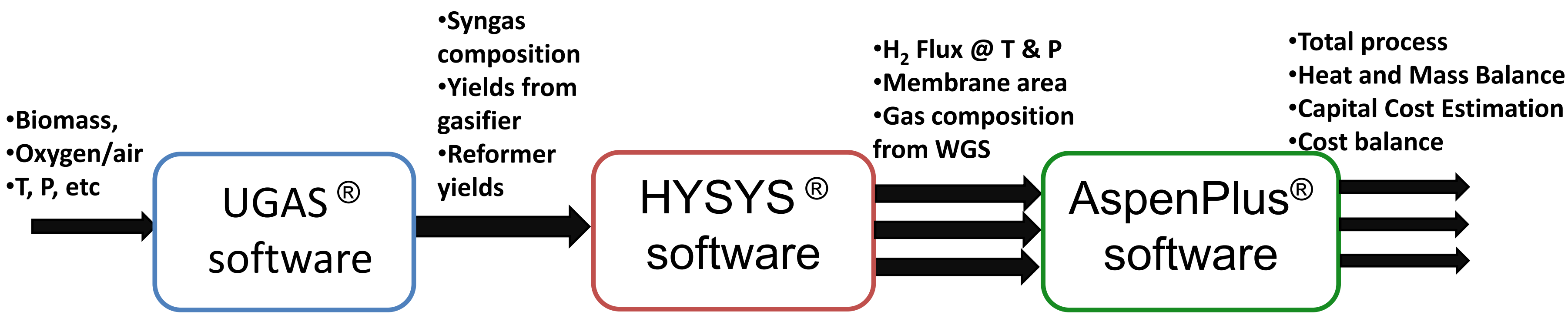
- Segregation of appropriate metals (e.g., Ag-Pd) along grain boundaries during high degrees of crystallization for selected compositions
- Combined ion-exchange (e.g., Ag-Pd) and heat treatment under a reducing atmosphere
- Co-sintering of glassy powder + metal (e.g., Ag-Pd) to produce a high metal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

Membrane	Hydrogen permeation at 850°C, SCFH/FT^2	Electronic conductivity, S/cm at 600°C
Base1-1/3 Glass-no Pd	0	4×10^{-8}
Base1-1/2 w/Pd Glass	0.02	4×10^{-9}
Base1-1/2D w/Pd	0.25	7×10^{-7}



- **One Base Composition**
- **Different Dopants**
- **Different Processing Conditions**

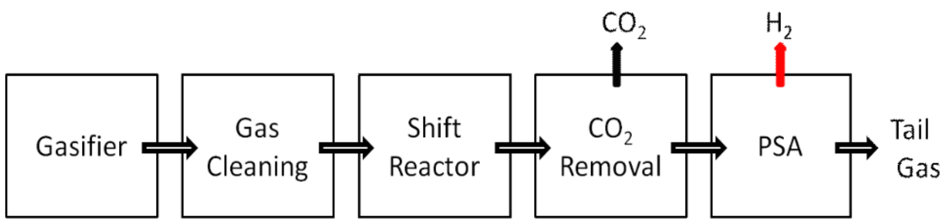
Technical Accomplishments and Progress: Process Optimization Strategy



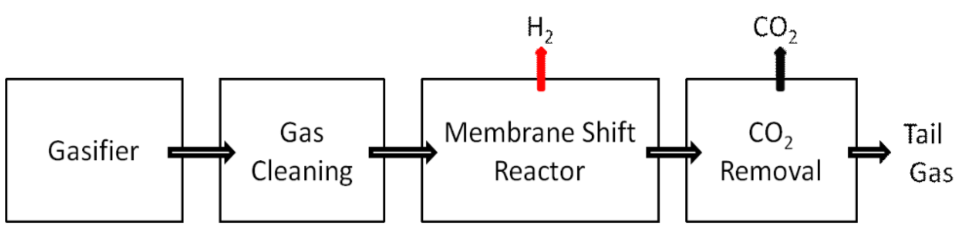
- UGAS® Process Model
  - Yields from gasifier @ T & P
  - Reformer yields (removes heavy (tar) components and increases H_2 concentration.)
- Hysys ® Model with Excel Spreadsheet
  - Determines flux @ T & P (5 equal-area zones)
  - Sizes membrane area for a fixed amount of H_2 recovery
  - Determines 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: Simplified Diagrams of Different Process Variations after Biomass Gasification

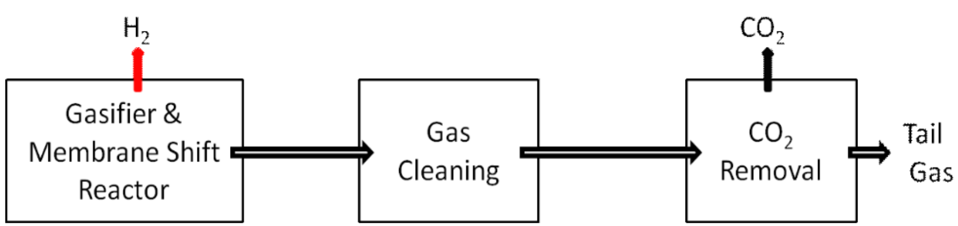
Conventional Hydrogen Production Process



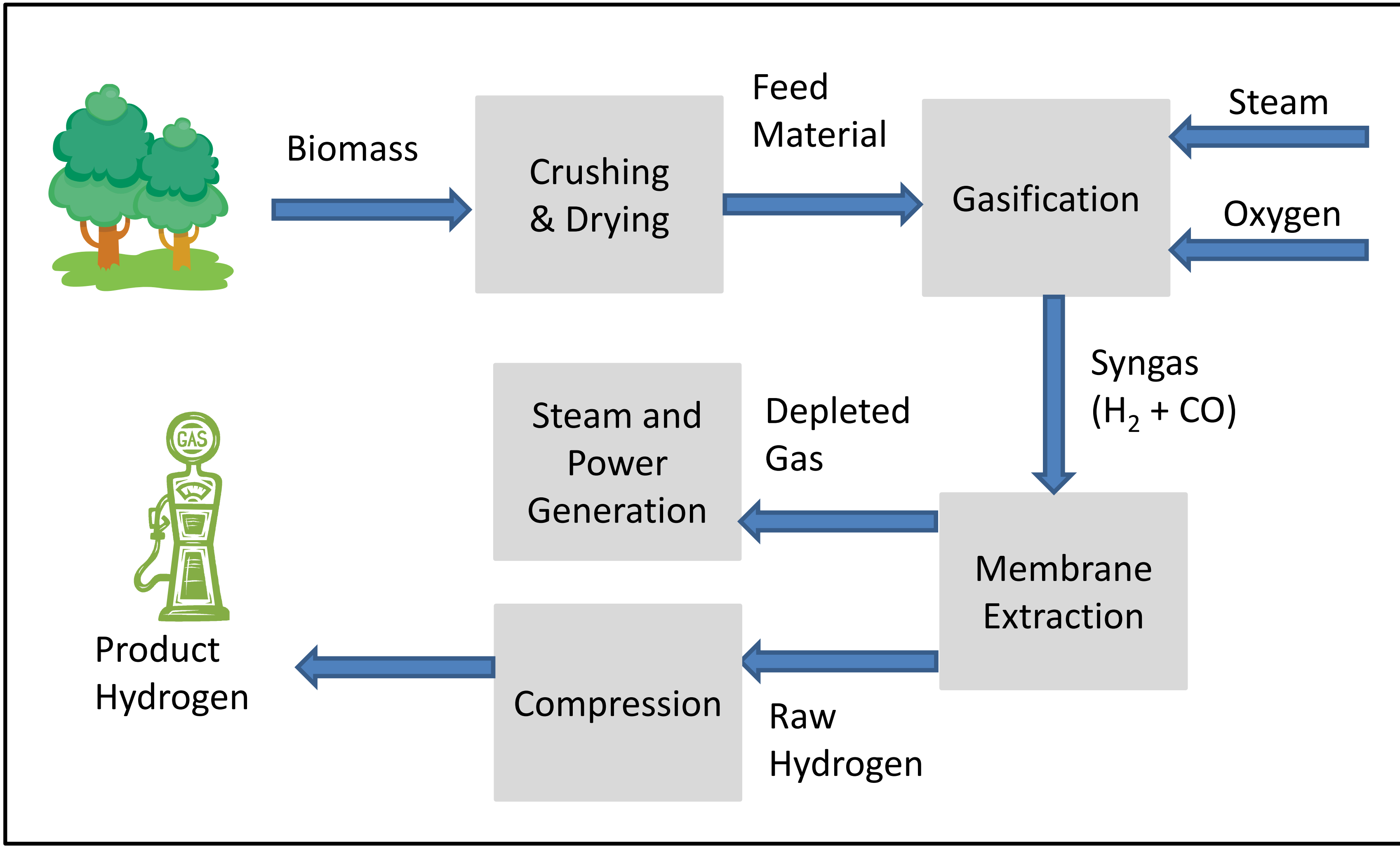
Hydrogen Production using Closely-Coupled Membrane Process



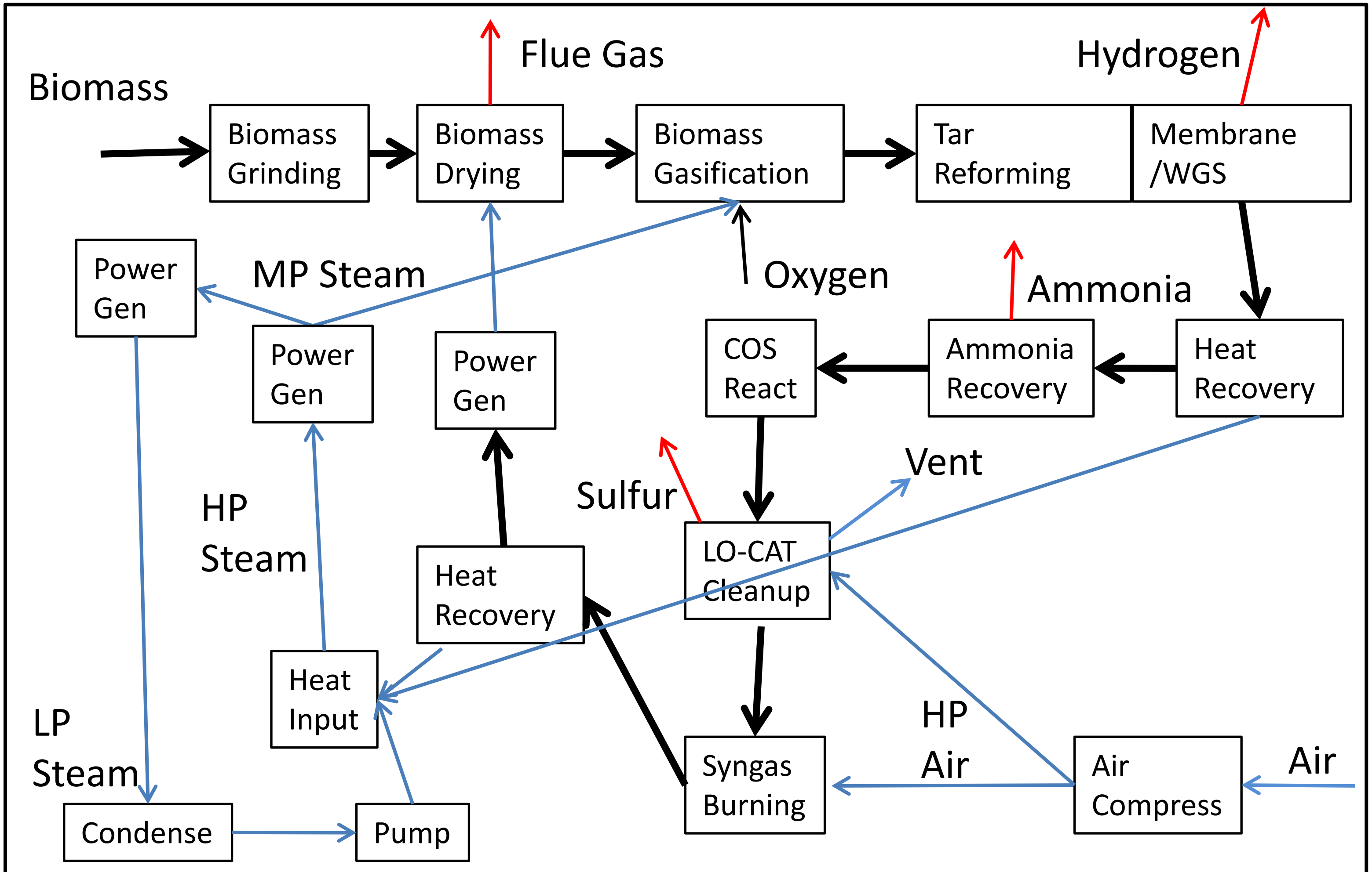
Hydrogen Production using In-Situ Membrane Process



Technical Accomplishments and Progress: Process Simulation Basis



Technical Accomplishments and Progress: Process Flow Diagram



Technical Accomplishments and Progress: PSA and Closely-Coupled Membrane Cases

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

Closely-Coupled Membrane case:

Scaled from the Aspen model using economic bases from the PSA case:

The size bases for flow rates and heat duties for these calculations - Goal Design process flow diagrams (Appendix D)

The capital cost bases for the scaling calculations - Goal Design Summary of Individual Equipment Costs (Appendix I)

Technical Accomplishments and Progress: Preliminary Economic Analysis

	$/kg		
	PSA	Membrane	
Case		6F	7F
Gasify T		1472	1472
WGS T		1472	1382
Membrane thickness		5	5
Permeate p, bar		0.2	0.2
H2 Recovery	81%	100%	100%
Area M	Adv	2442	2826
Wood	0.40	0.41	0.40
Oxygen	0.00	0.13	0.13
Power	0.05	-0.06	-0.04
Fuel	0.03	0.03	0.04
MTIO	0.10	0.10	0.10
Capital	0.38	0.39	0.38
Salaries+OH	0.07	0.08	0.08
Cat & Chem	0.10	0.06	0.06
Water	0.03	0.03	0.03
Total ex H2 compr.	1.169	1.184	1.172
Incl. H2 Compression			
Power	0.09	-0.02	-0.01
MTIO	0.11	0.11	0.10
Capital	0.40	0.40	0.39
Total	1.218	1.233	1.221

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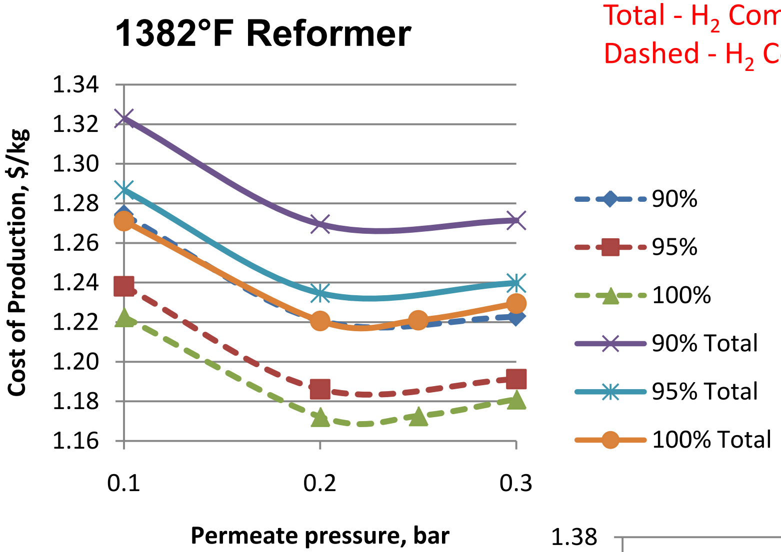
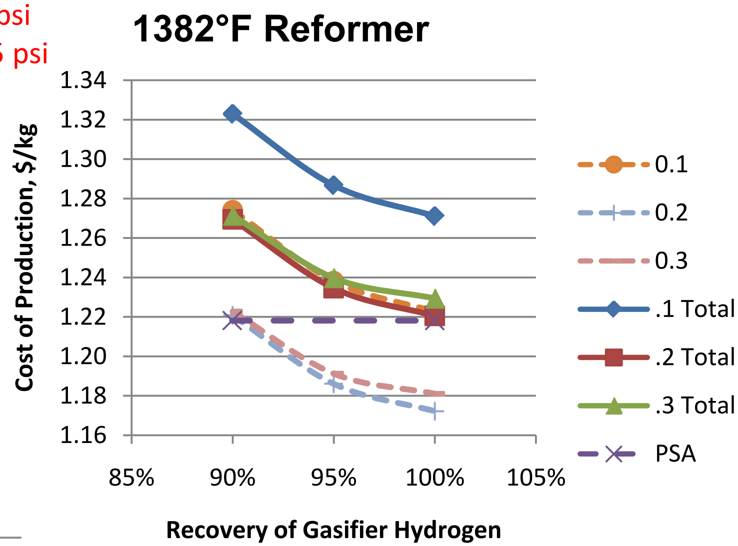
Technical Accomplishments and Progress: Membrane Economic Process Parameters

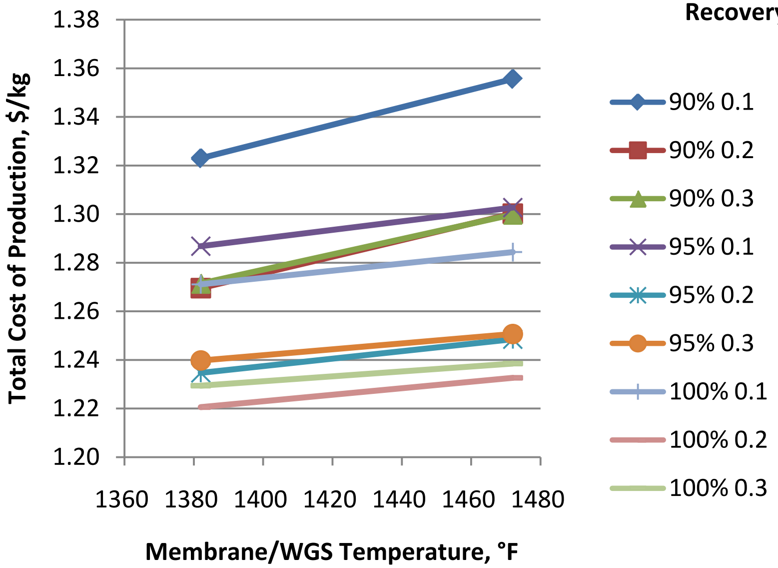
- Temperature Increase
  - + Increases flux
  - - Decreases H_2 partial pressure with WGS
- Membrane Area Increase
  - + Increases hydrogen recovery
  - - Increases capital cost
- Permeate Pressure Increase
  - - Decreases flux
  - + Decreases compression cost

Technical Accomplishments and Progress: Effect of Permeate Pressure, H_2 Recovery (Area)

Total - H_2 Compression to 1000 psi
Dashed - H_2 Compression to 315 psi







Technical Accomplishments and Progress: Conclusions for Preliminary Economic Analysis

- Economic analysis verified the technology will meet the DOE cost target of \$1.60/kg H_2, based on a feasibility study of the membrane materials and the initial conceptual process design.
- Economic cost of hydrogen production via membrane is comparable with PSA.
- Optimum permeate pressure is about 0.2 bar.
- Optimum membrane/ WGS temperature is at 1382°F (750°C) or less.
- Optimum hydrogen recovery is at 100% of reformer product H_2

Proposed Future Work

- Continue to identify metal additives to enhance the catalytic activity, chemical and mechanical stability of Pd-based alloys in the presence of sour-H_2 and investigate coatings for non-Pd 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) - GTI
- Fabrication of membrane module integrated with biomass reactor - GTI

Summary

- Project was initiated again (February 2010) after 1 year hiatus.
- Continued development of metallic, glass-ceramic membranes
- Continued process development and economic analysis - Go/No Go decision point
- Membrane module design was completed. Module capable of a flux rate of 80+ SCFH/ft^2

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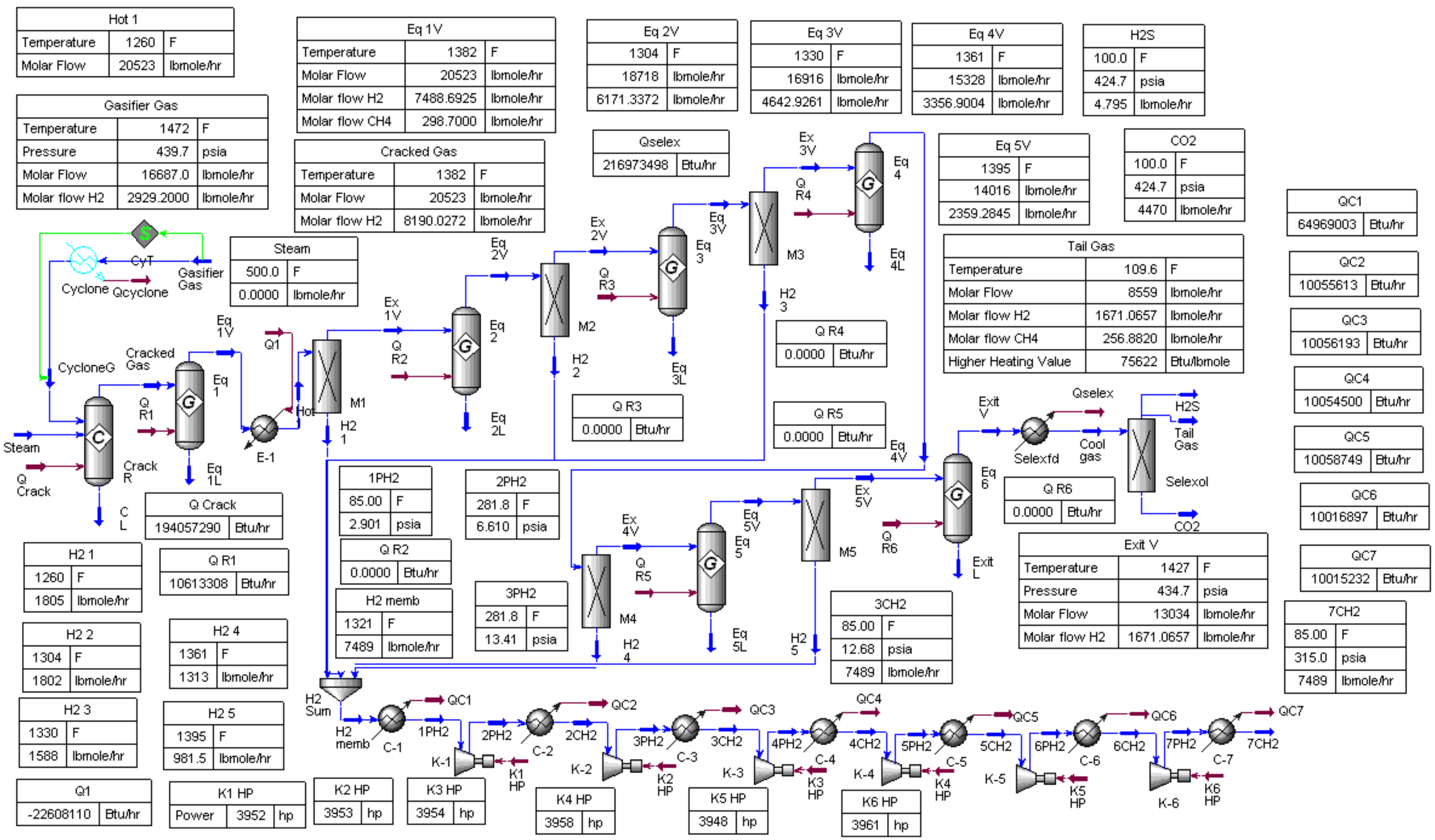
Technical Back-Up Slide

Technical Accomplishments and Progress: Potential Sites for Membrane Module

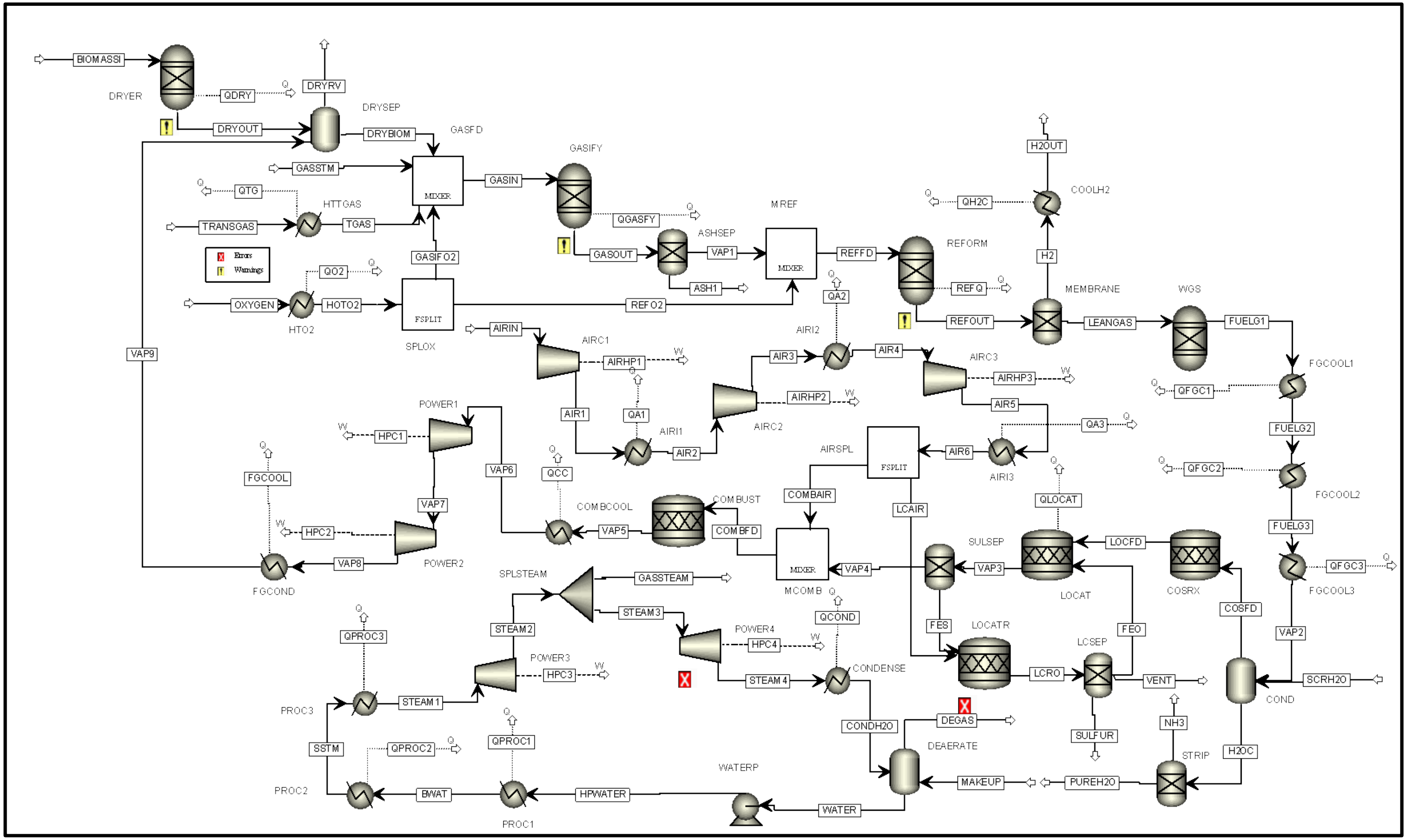
Auburn University

Gas Technology Institute-FFTF

Technical Accomplishments and Progress: Hysys ® Model



Technical Accomplishments and Progress: Aspen Plus® Model



Technical Accomplishments and Progress: Pinch Analysis

Technical Accomplishments and Progress: Utilities estimation

	Power, kw		
	PSA	6F	7F
Feed handling & drying	742	742	742
Gasification, reforming	3636	1949	1883
Compression, S removal	26058	0	0
Shift, PSA	159	0	0
Membrane	0	0	0
H2 Compression final	4190	3827	3939
H2 Comp to 315 psi		18528	19066
Steam system	662	371	273
Power generation	-29974	-31883	-30896
Cooling water	1152	368	198
Miscellaneous	3660	3660	3660
Total	10285	-2438	-1135
Total ex H2 comp	6095	-6265	-5074

Technical Accomplishments and Progress:

Capital Cost Estimation by Scaling

	1382 F, Case 7J (100% recovery at 300 psi), 0 .25 bar permeate		
	MMBtu/hr	lb/hr	2005$
Flue Exch	0.80		49622
Dryer		367437	19992961
S100			20042584
Reform exch 1	2.70		36652
Reform exch 2	168.20		2372426
Gasifier & blower	0.00		0
Renugas			24407784
Reform/ regen		100000	3636944
S200			30453806
Water cooler	0.90		32530
LOCAT heater		317507	7304
ZnO heater	51.59	0	194574
Syngas compr		0	0
Reformer blower		385441	96649
Sludge pump		997	20503
LOCAT vessel		0	0
Zno beds		0	0
Precomp KO		0	0
Postcomp KO		0	0
Sludge tank		21718	30608
S300			382168

	MMBtu/hr	lb/hr	2005$
Shift and PSA			0
Membrane		3297	23079000
HT Shift		383018	1275459
Comp intercool	125.40	15096	143567
Comp air cool		15096	154334
Comp H2O cool		15096	50822
H2 comp		15096	2508133
H2 Comp (300psi)	23726hp		11024574
Precomp KO		15096	36283
Post KO		15096	37910
S500			13955624
Blowdown cool		144121	4690
Water cooler		60000	15075
Boiler & pumps		144121	8810331
S600			8830096
S700			3621184
Bldg & structure			6368000
Plant			**108 million**
Plant ex H2 comp			**105 million**

Advanced Inorganic Membranes for Biomass Gasification Application