the Energy to Lead

One Step Biomass Gas Reforming-Shift Separation Membrane Reactor

2011 DOE Hydrogen Program Review
May 17, 2012

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Project ID PD070

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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 H_2 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

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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.

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/ft^2
- 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

Task	Revised/ Planned	Completed
1.4 Select Initial Candidate Membrane ($Pd_{80}Cu_{20}$)	3/15/08	6/30/08
1.5 Select Best Candidate Membrane ($Pd_{80}Cu_{20}$)	12/30/11	2/15/12
1.5 Develop Membrane with Flux of 125 SCFH/ft2	6/15/11	6/15/11
2.0 Process Development & Econ Analysis	9/30/10	10/07/10*
Go/ No Go	6/30/12	
4.1 Design Membrane Module	6/30/10	9/17/10
2.0 Testing Membrane Module Integrated with Bench Gasifier	6/30/13	

* Preliminary economic calculations indicate DOE Target can be met.

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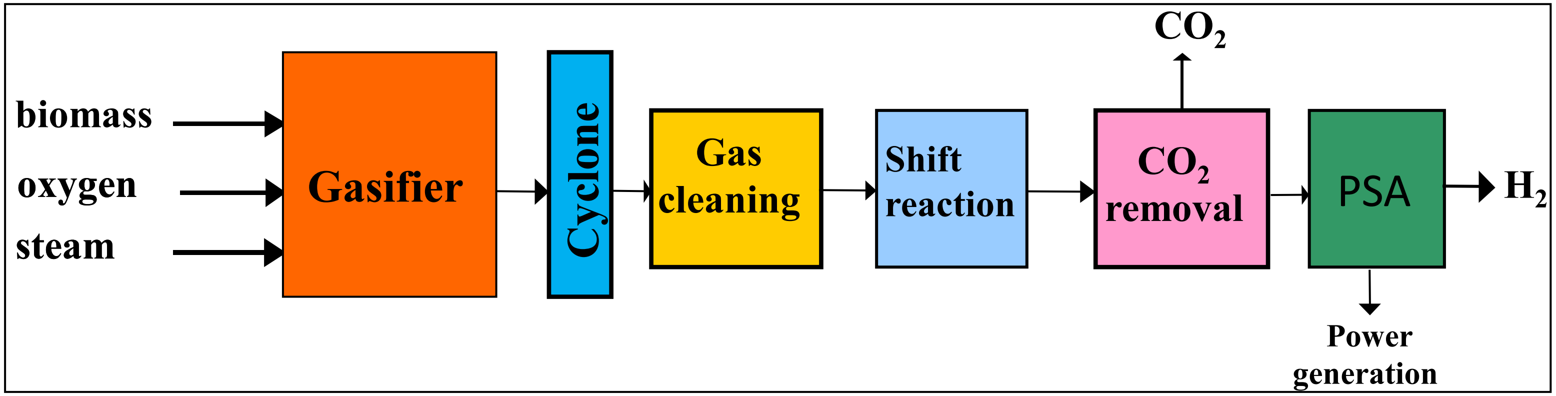
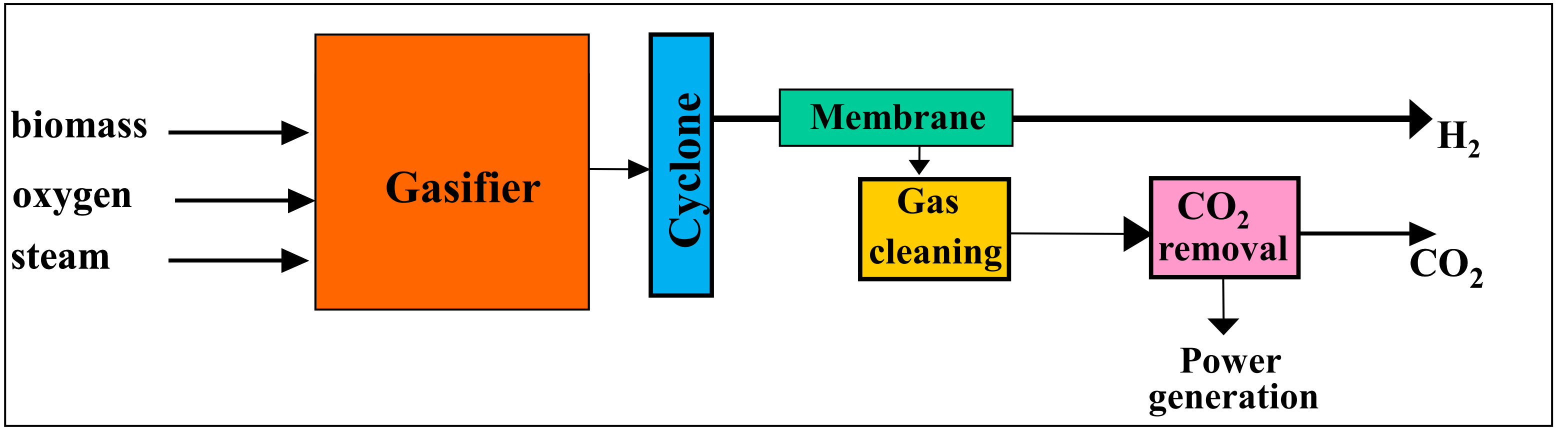
Approach: Conventional Hydrogen Production from Biomass Gasification and Biomass Gasifier with Close Coupled Membrane





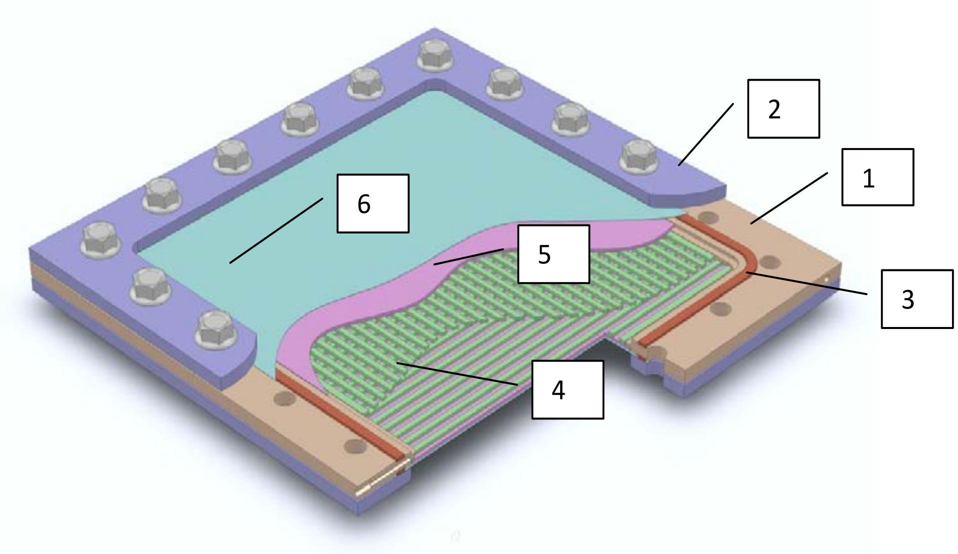
Technical Accomplishments and Progress: Membrane Module Fabrication

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

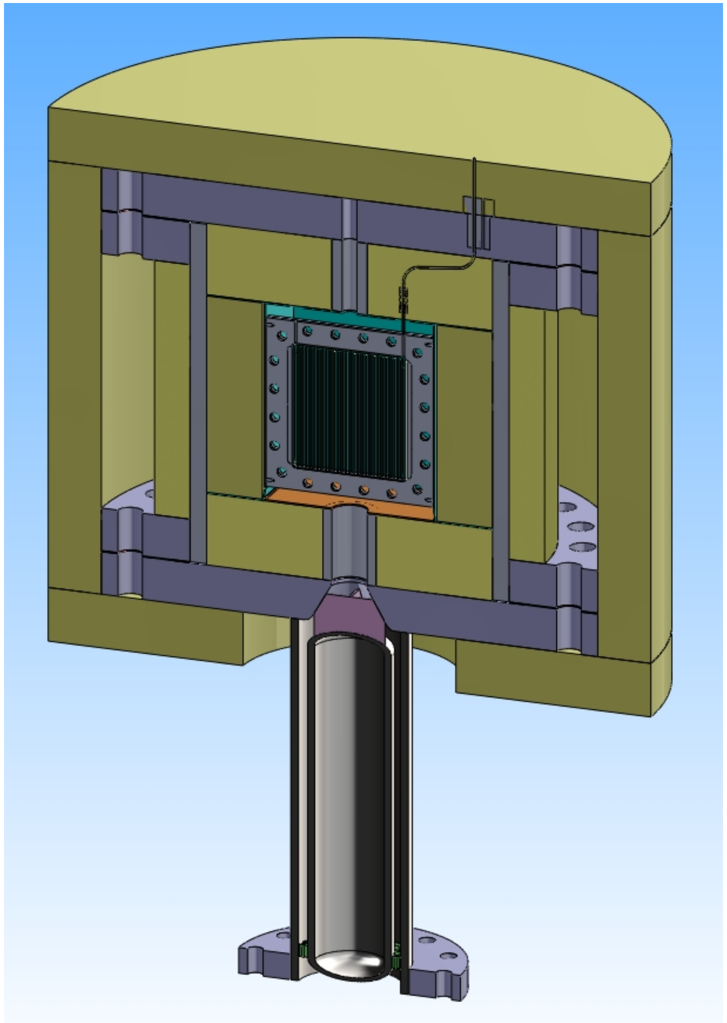
  Expected date of completion: August, 2012

Membrane Module Design used in manufacturing

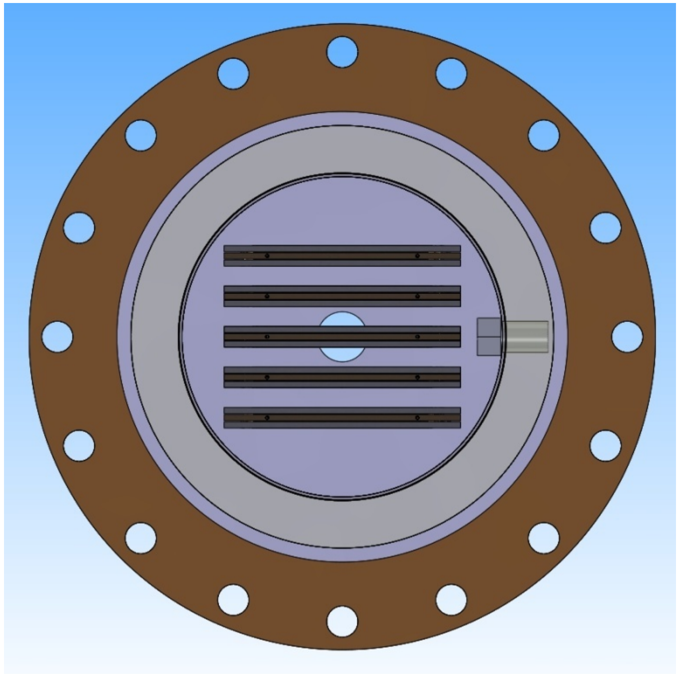


1-base plate (SS316)
2-clamping frame (SS316)
3-copper gasket
4-slotted metal support (SS316)
5-porous support (SS316)
6-membrane ($Pd_{80}Cu_{20}$)

Technical Accomplishments and Progress: Membrane Module Fabrication-General View



3-D View of Membrane Module



5 stacked Membrane Module
5 stacks are needed to have enough membrane area to produce 2 lb/day of H_2

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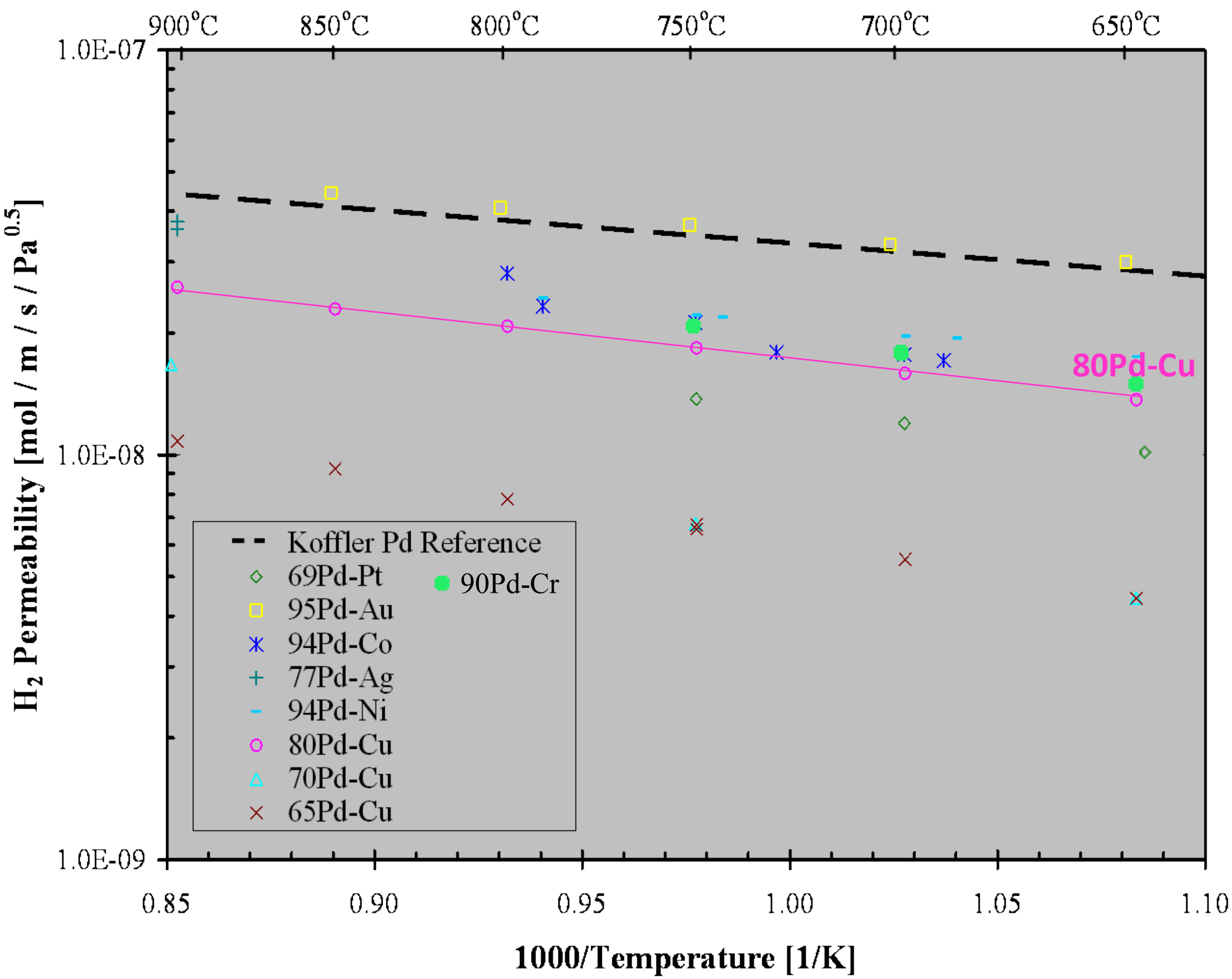
Technical Accomplishments and Progress: Membrane Performance in H_2 - NETL



Based on overall performance, 80Pd-Cu has demonstrated the best potential.
Pd80-Cu results were presented at AMR2011

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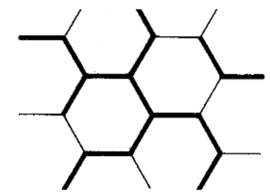
Technical Accomplishments and Progress: Metal-Glass-Ceramic Membranes- Schott

- 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



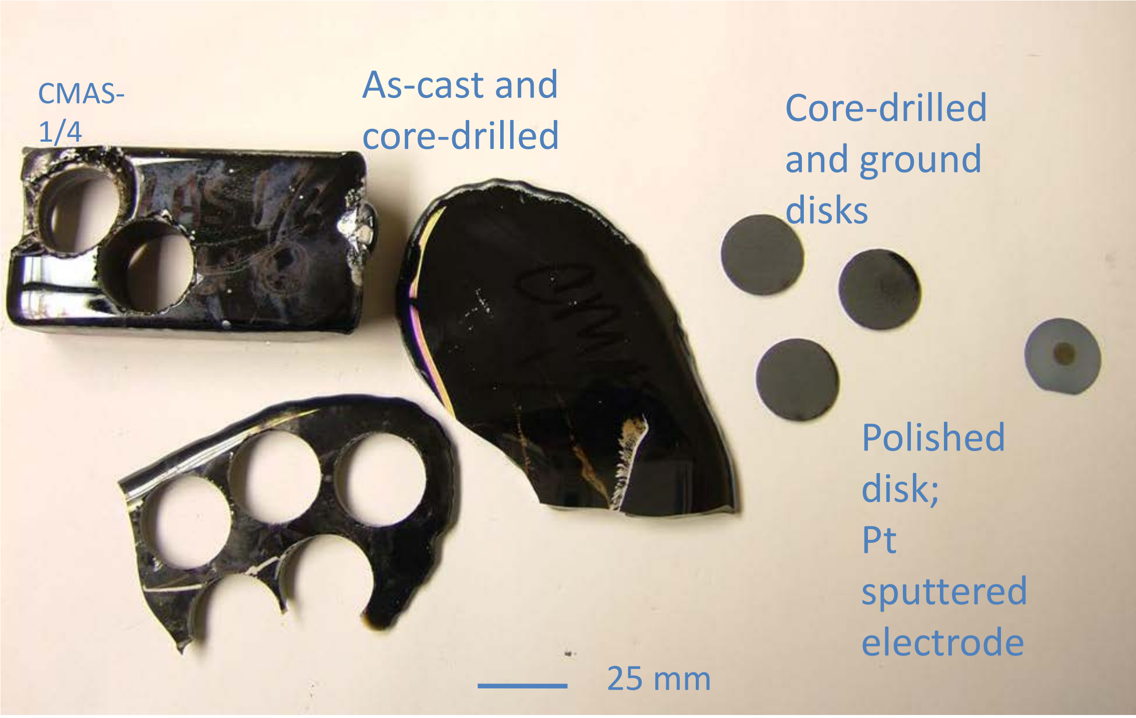
Results:

- 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.

Membrane	Hydrogen permeation at 800°C, SCFH/FT^2
Base1-1/3 Glass-no Pd	0
Base1-1/2 w/Pd Glass (Work done this FY)	0.04
Base1-1/2D w/Pd BEST-presented on AMR2011	0.25



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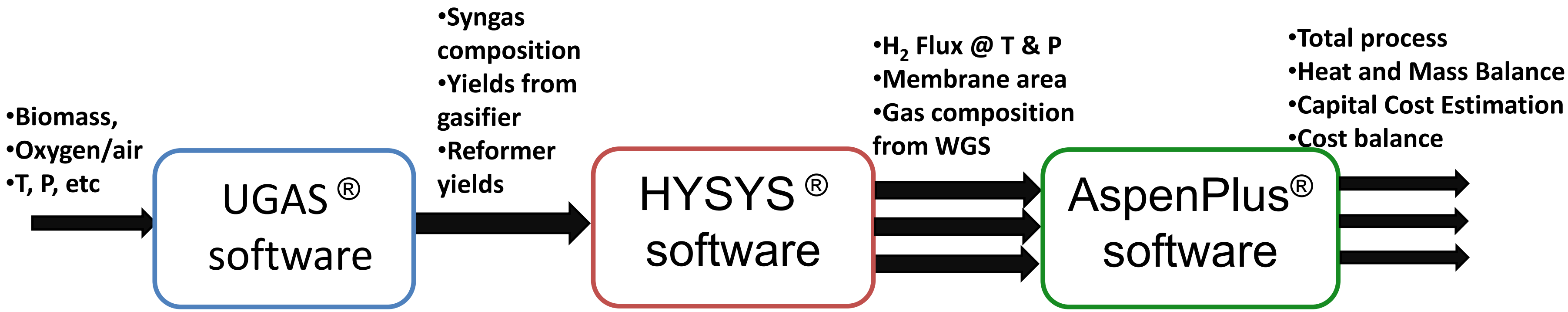
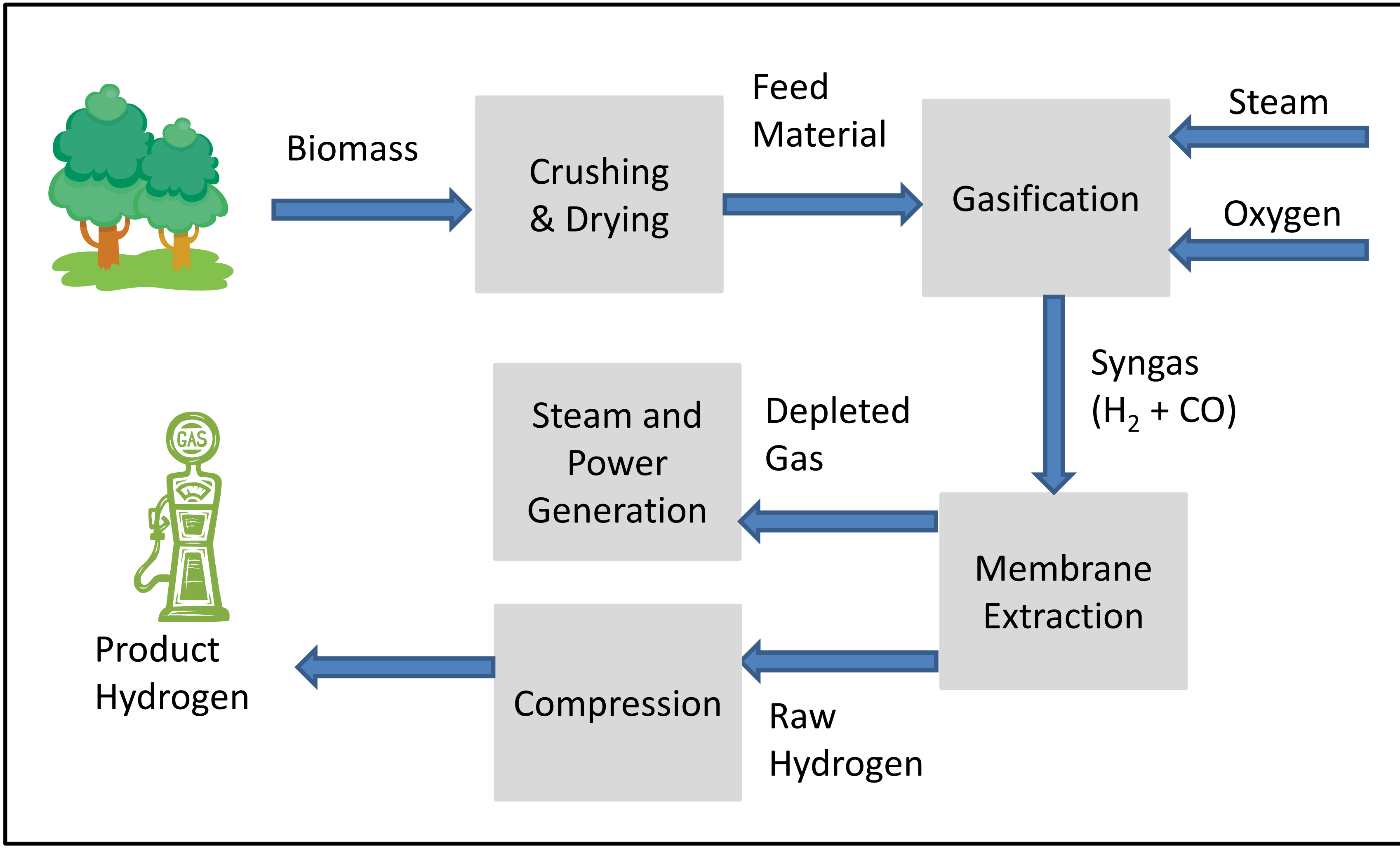
Technical Accomplishments and Progress: Process Optimization Strategy



- 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: Process Simulation Basis



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

Parameter	Minimum	Maximum
Gasifier Temperature, F	1292	1800
Reformer Temperature, F	1292	1800
Permeate Pressure, bar	0.1	0.3
Hydrogen Recovery (of gasifier output)	80%	115%*

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

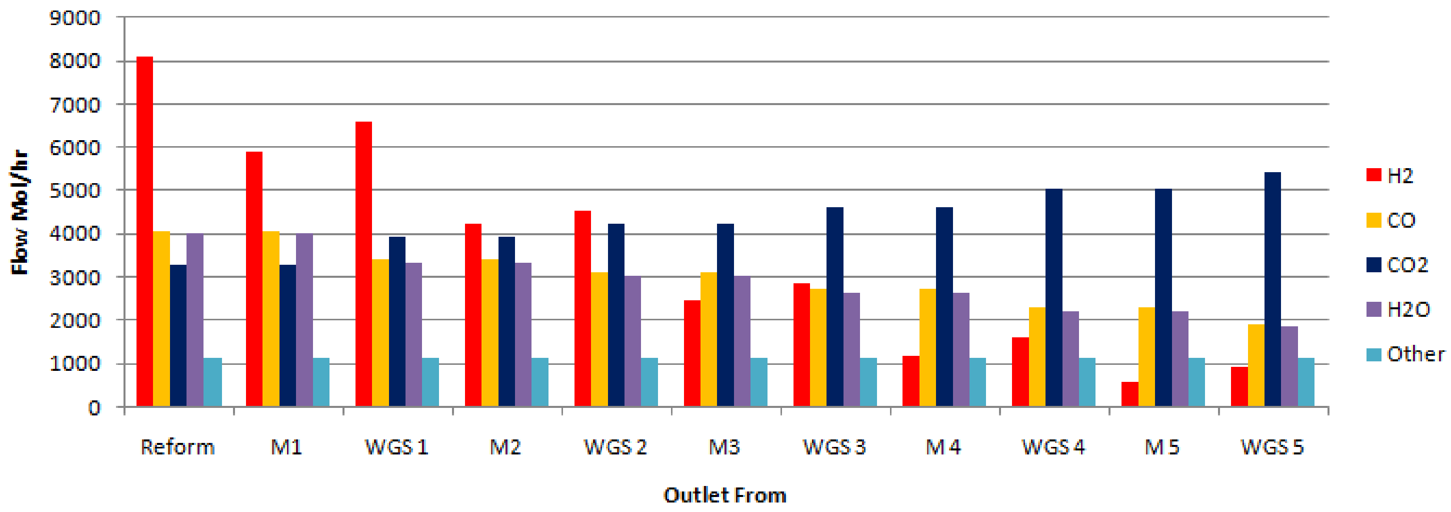
Technical Accomplishments and Progress: Approach to Membrane Case

Process was modeled as 5 stages (with the same membrane area) – each with a Hydrogen Membrane followed by Water Gas Shift: $H_2O + CO \leftrightarrow H_2 + CO_2$

As gas flows over the membrane, H_2 is removed from the composition (originally at WGS equilibrium). Outlet from membrane stage 1 (M 1) has lower 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), H_2 and CO_2 contents are increased while CO and H_2O contents are decreased due to the WGS stoichiometry.

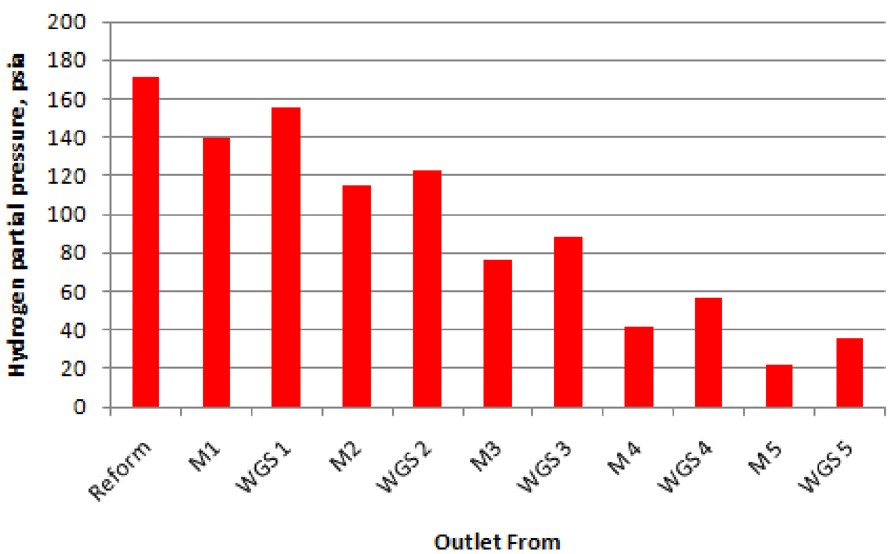
As the process is repeated, the H_2O and CO contents decrease, while the CO_2 content increases. The H_2 content decreases as the removal by the membranes exceed the amount created by WGS.

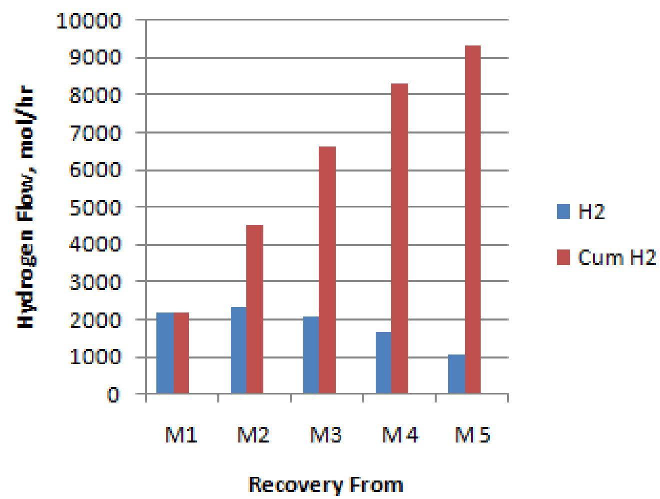


Technical Accomplishments and Progress: Approach to Membrane Case

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 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 H_2 originally present in the reformer product gas

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Technical Accomplishments and Progress: Latest Economic Evaluation Case (8J) Basis

Input:

1292 F (700°C) gasifier
1292 F (700°C) membrane and reformer
7410 m^2 membrane needed
0.2 bar permeate pressure

Results:

115% of molecular H_2 recovered from gasifier outlet
7410 m^2 membrane needed
Cost $1.82/kg

PSA Case:

80% of molecular H_2 recovered from gasifier outlet
Cost $2.00/kg

Technical Accomplishments and Progress: Detailed Capital Cost (ASPEN Results) Estimation

	Preliminary, 2005 MM$	Updated in FY12, 2005 MM$
Feed	18.8	20.3
Gasifier	12.0	12.9
Gas Processing	14.7	18.9
Membrane	30.3	29.6
Air Compression	21.9	23.6
H_2 Compression	3.3	3.5
Steam System	4.9	5.3
Utilities	11.4	12.2
Buildings	6.4	6.4
Total	123.7	132.7
Total, excluding H_2 compression to 1000 psi	118.0	129.2

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Technical Accomplishments and Progress: Utilities estimation

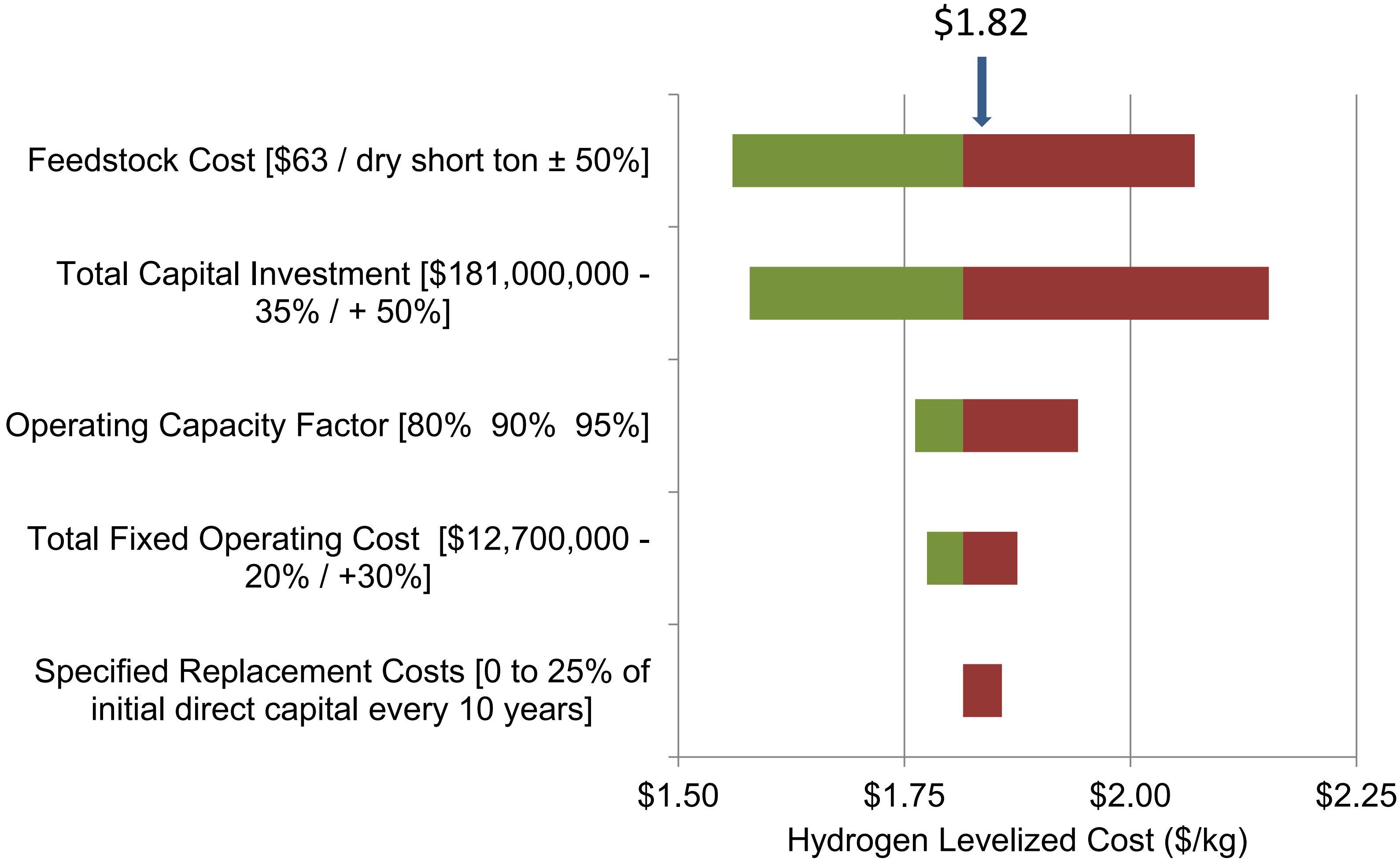
	Power, kw	
	PSA	8J
Feed handling & drying	742	742
Gasification, reforming	3636	980
Compression, S removal	26058	26856
Shift, PSA	159	0
Membrane	0	0
H_2 Compression final	4190	5543
H_2 Compression to 315 psi		25688
Steam system	662	156
Power generation	-29974	-52484
Cooling water	1152	539
Miscellaneous	3660	3660
Total	10285	11680
Total ex H_2 comp to 1000 psi	6095	6137

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

Cost Component	H2 Cost, $ 2007 /kg
Capital Cost	0.68
Decommissioning	0.00
Fixed O& M	0.20
Feedstock Cost	0.51
Other Raw Material	0.11
By-Product Credits	0.00
Other Variable Costs	0.32
Total	**1.82**

Technical Accomplishments and Progress: Sensitivity Analysis



Cost dominated by feedstock and capital equipment

Technical Accomplishments and Progress: Conclusions for Economic Analysis

- 2012 Membrane Case (8J) has recovery of 115% of H_2 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 (<700ºC)

  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

	PSA			Membrane		
	Preliminary	V2.2	v3	Preliminary (7F)	V2.2 (8J)	v.3 (8J)
H2, $/kg	1.17	1.47	2.00	1.17	1.28	1.82

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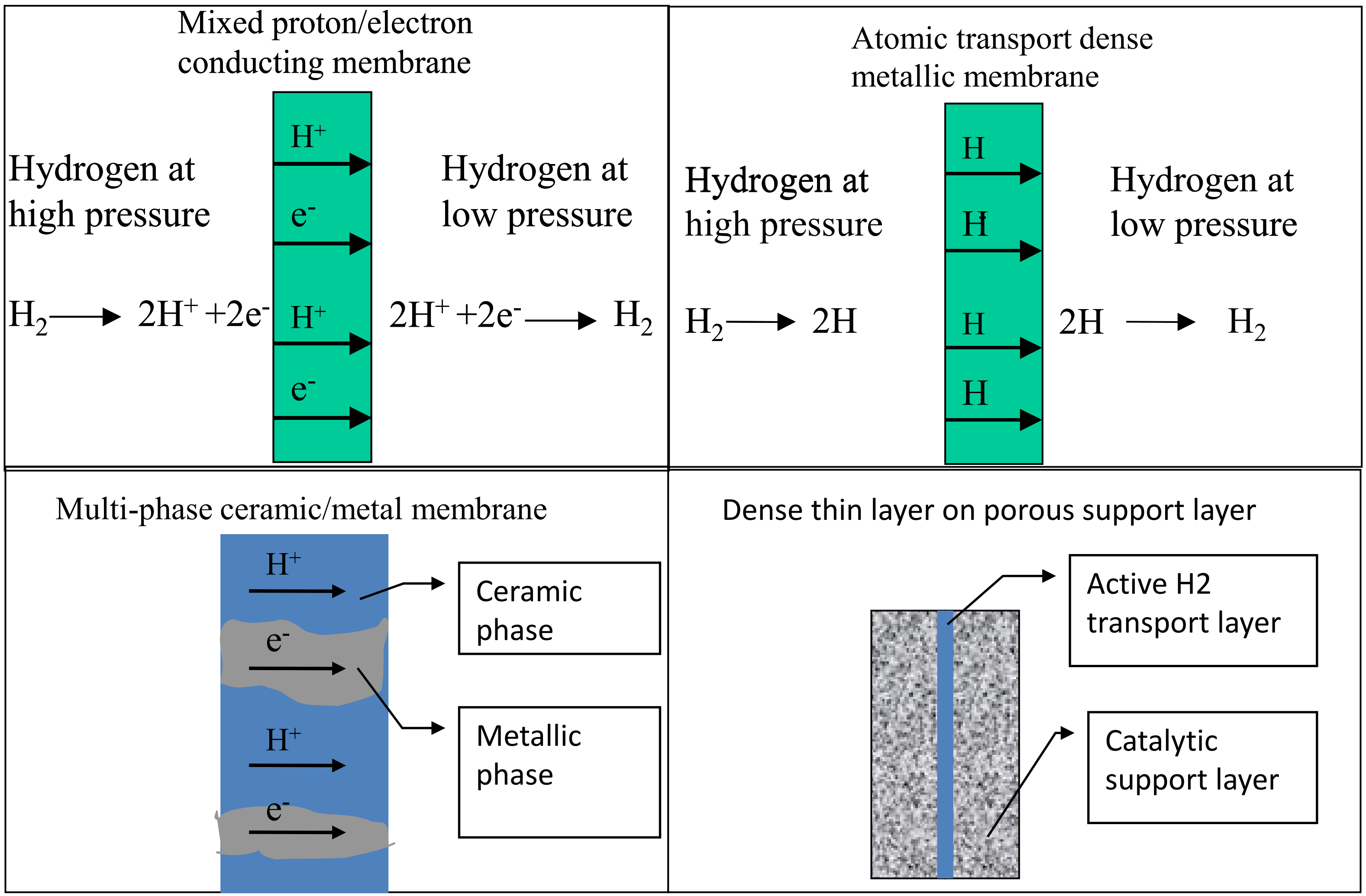
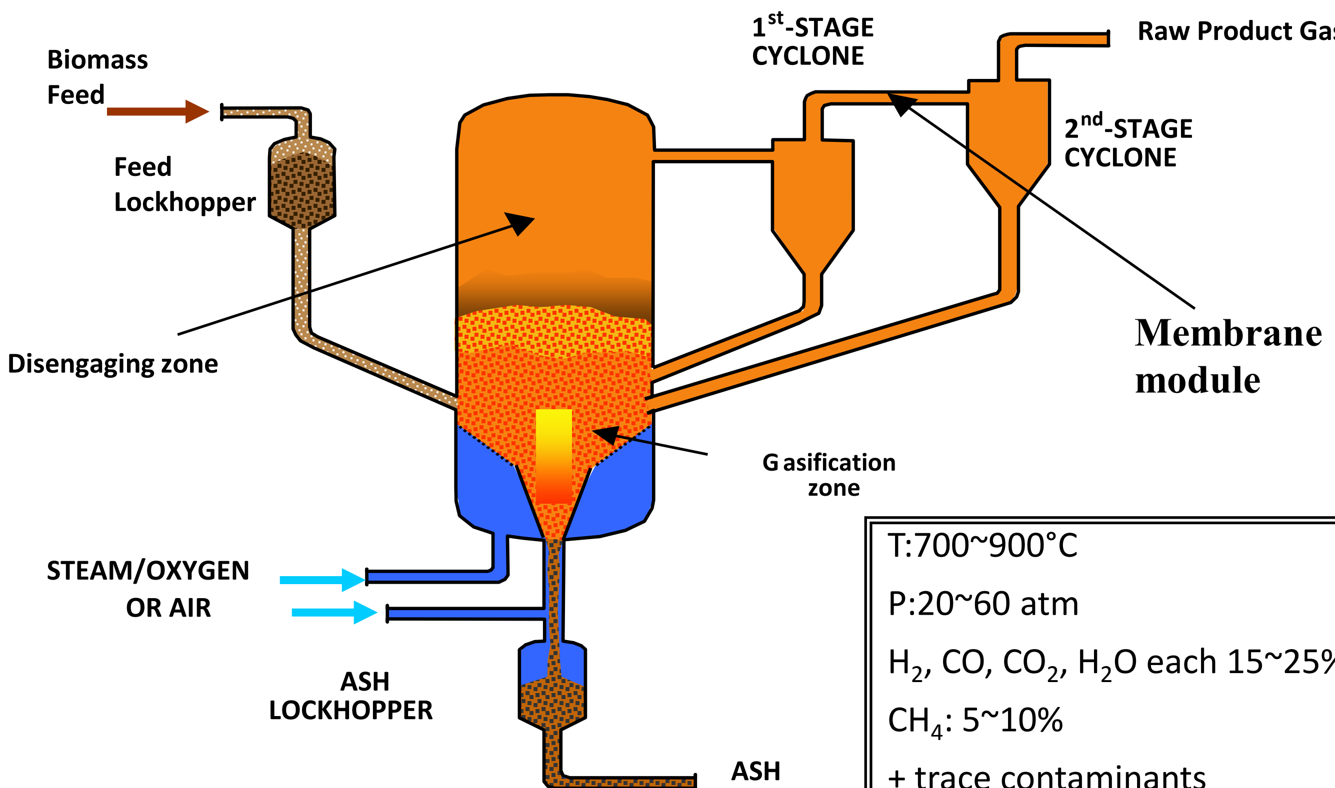
Technical Back-Up Slide

Advanced Inorganic Membranes for Biomass Gasification Application



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%

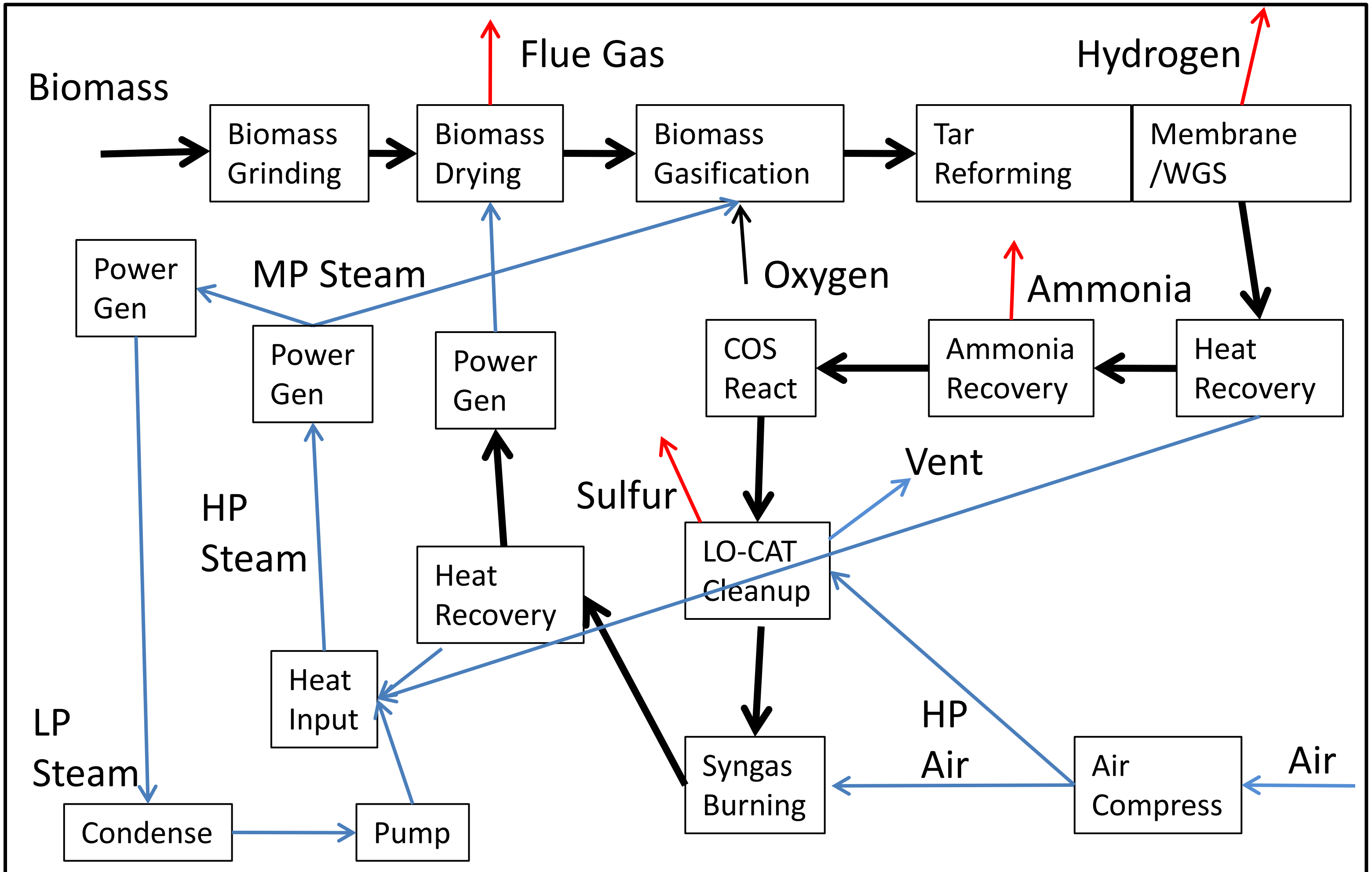
+ trace contaminants

Technical Accomplishments and Progress: Potential Sites for Membrane Module

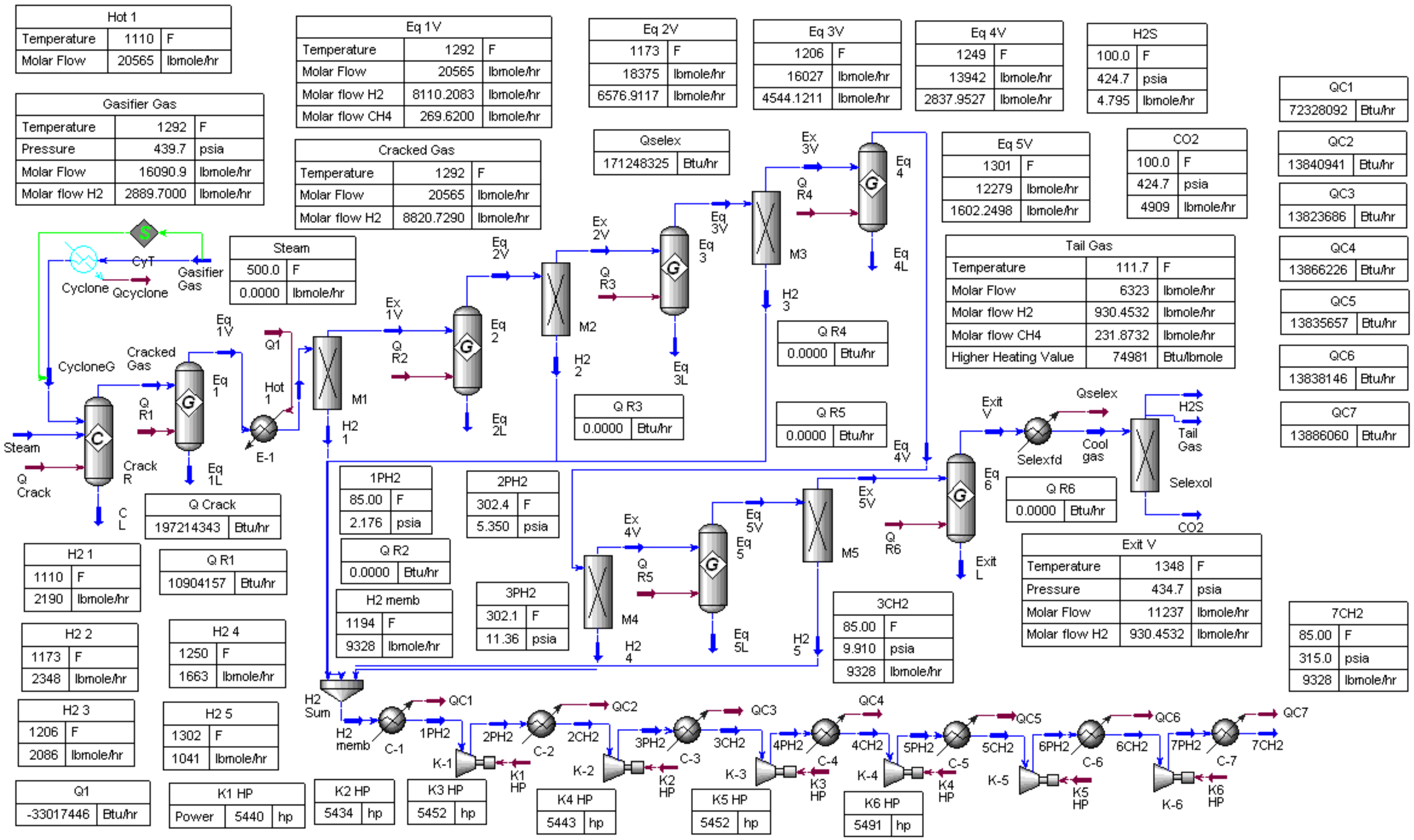
Auburn University

Gas Technology Institute-FFTF

Technical Accomplishments and Progress: Process Flow Diagram



Technical Accomplishments and Progress: Case 8J



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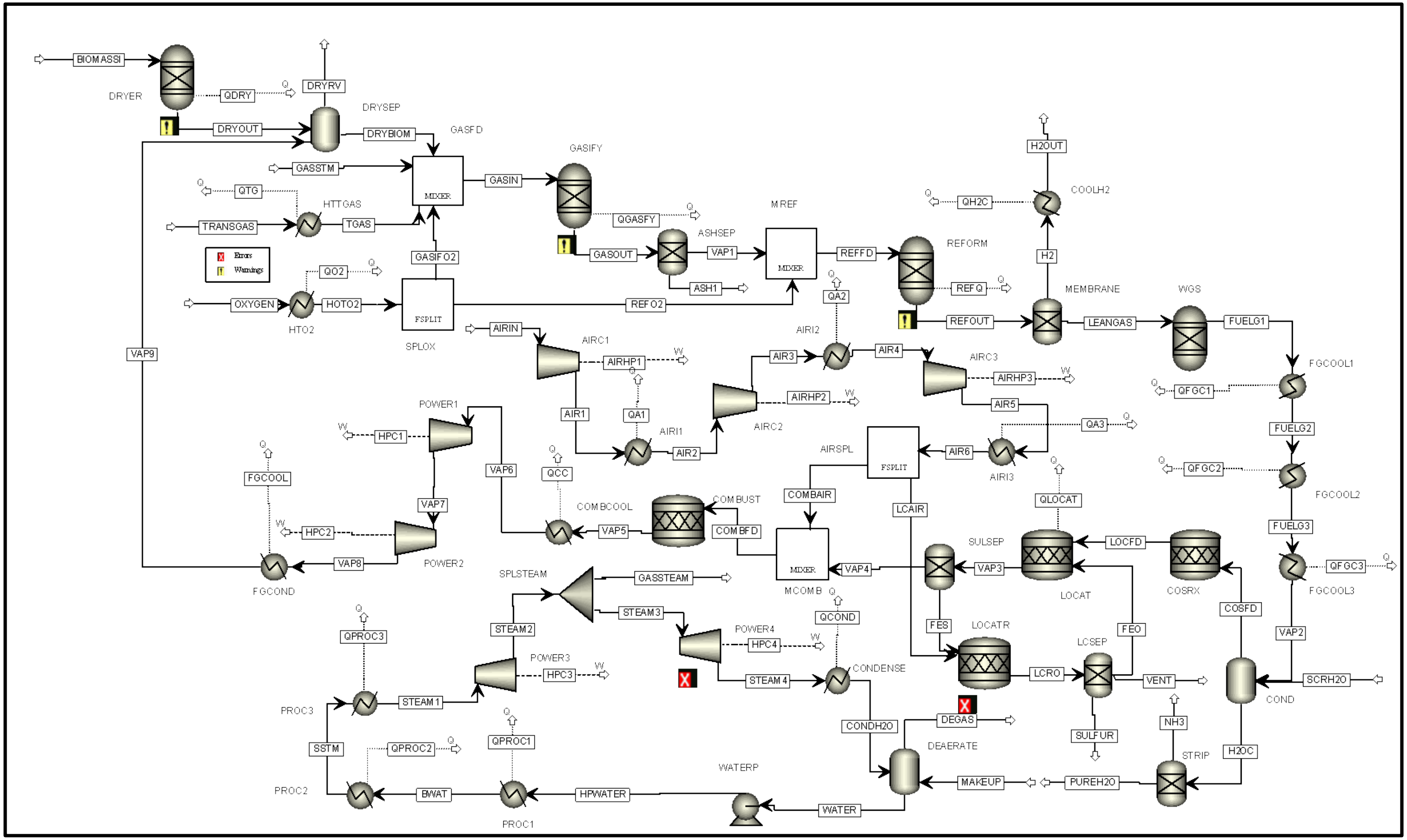
Technical Accomplishments and Progress: Aspen Plus® Model



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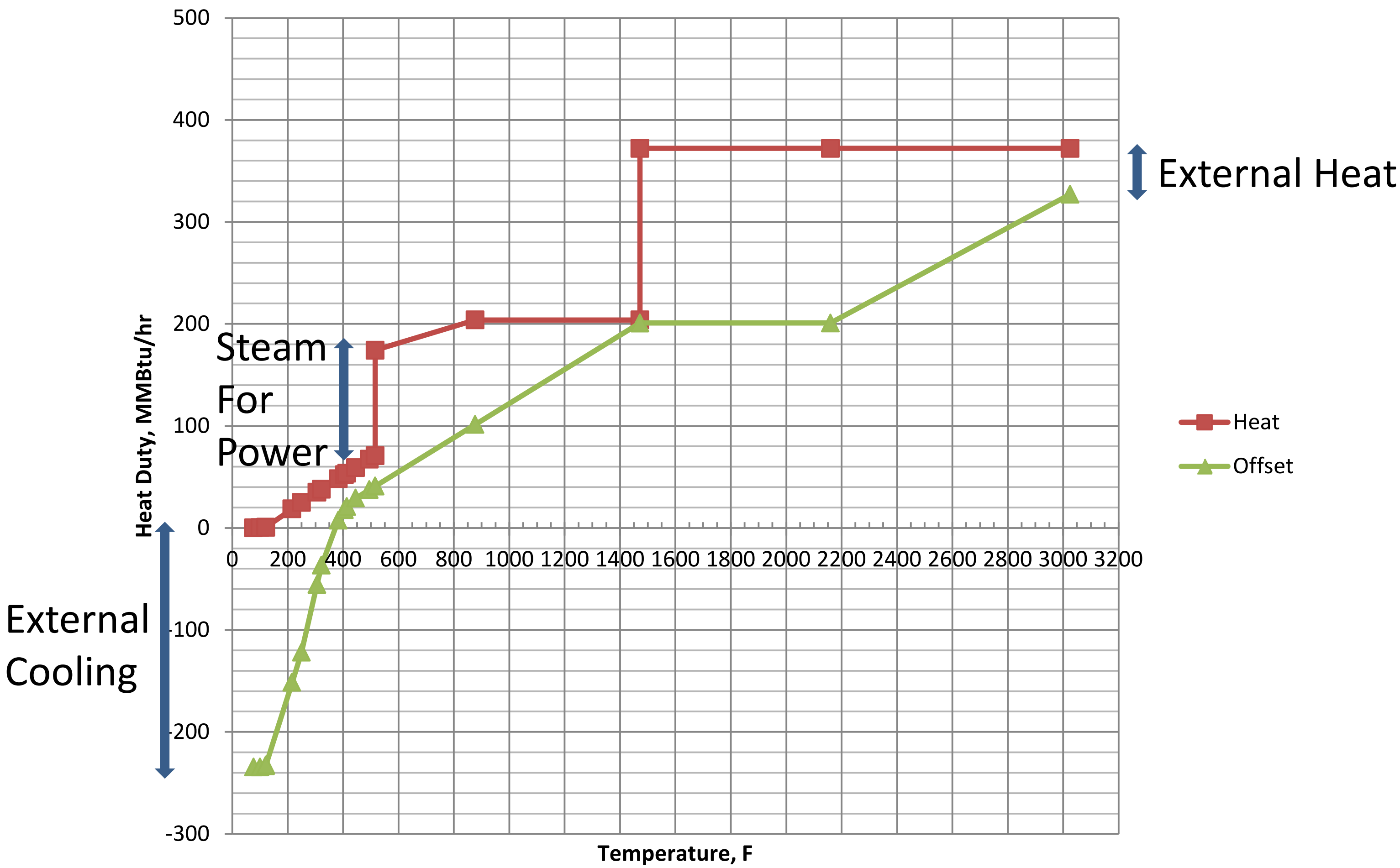
Technical Accomplishments and Progress: Pinch Analysis



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