Carbon Molecular Sieve Membrane as Reactor/Separator for Water Gas Shift Reaction

DE-FG36-05GO15092

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Date: June 11, 2008

PDP25

Overview

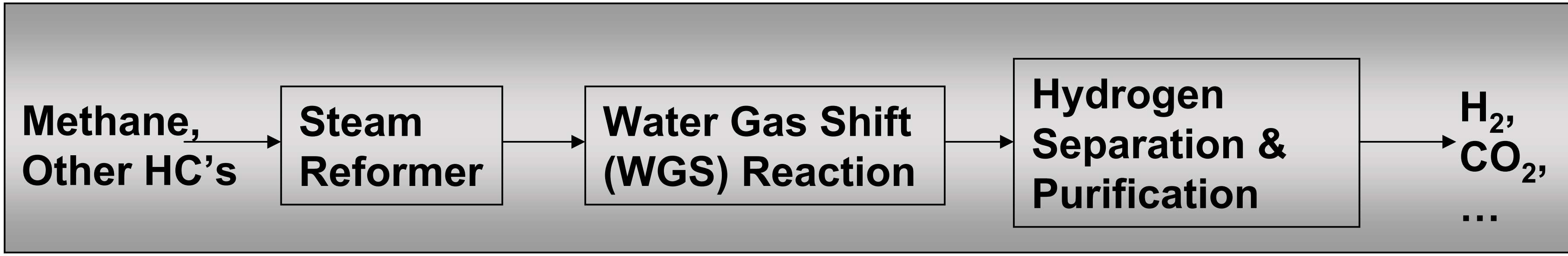
- **Project Start Date**
  7/1/05
- **Project End Date**
  6/30/07
  (1 yr no cost extension submitted)
- **Percent Complete**
  85%

- Delivery of 99.999% H_2 with high H_2 recovery ratio is difficulty through a membrane-based process
- Demonstration of the membrane reactor-based process in a significant scale
- Economic analysis for production cost

- **Total project funding**
  - DOE Share: $1,530,713.
  - Contractor Share: $382,678.
- **Previous Funding received:**
  $100K(FY05), $225K(FY06), $566K(FY07)
- **Funding received in FY08**
  $325K
- No catalyst development activities due to funding limitation in the beginning of the project

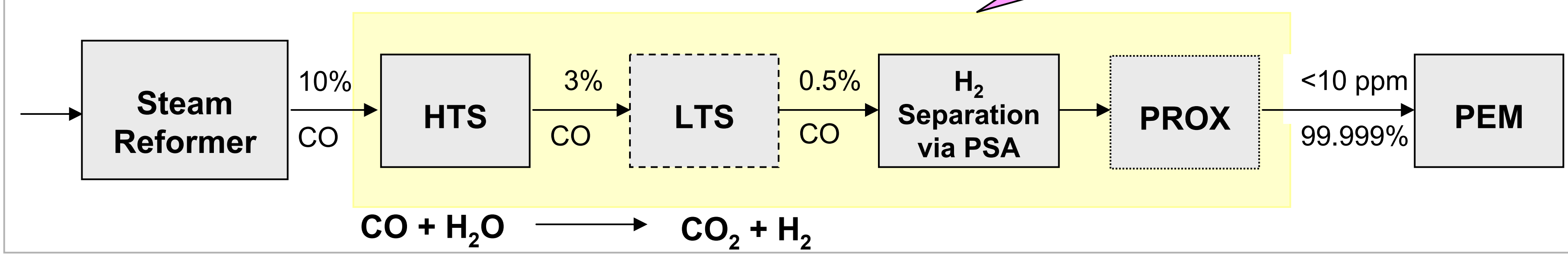
- **Professor Theo T. Tsotsis**
  University of Southern California,
  Catalytic membrane reactor expert
- **Dr. Babak Fayyaz-Najafi**
  Chevron ETC,
  End User Participant
- **Dr. Hugh Stitt,** Johnson Matthey, Catalyst Manufacturer

Hydrogen Production from Steam Reforming



Our Project Focus
Improve Production Efficiency and Streamline Unit Operations involving CO Conversion/H_2 Separation & Purification

Conventional Process Concept



HTS: High Temperature Shift
LTS: Low Temperature Shift
PROX: Preferential Oxidation
PEM: Proton Exchange Membrane Fuel Cell

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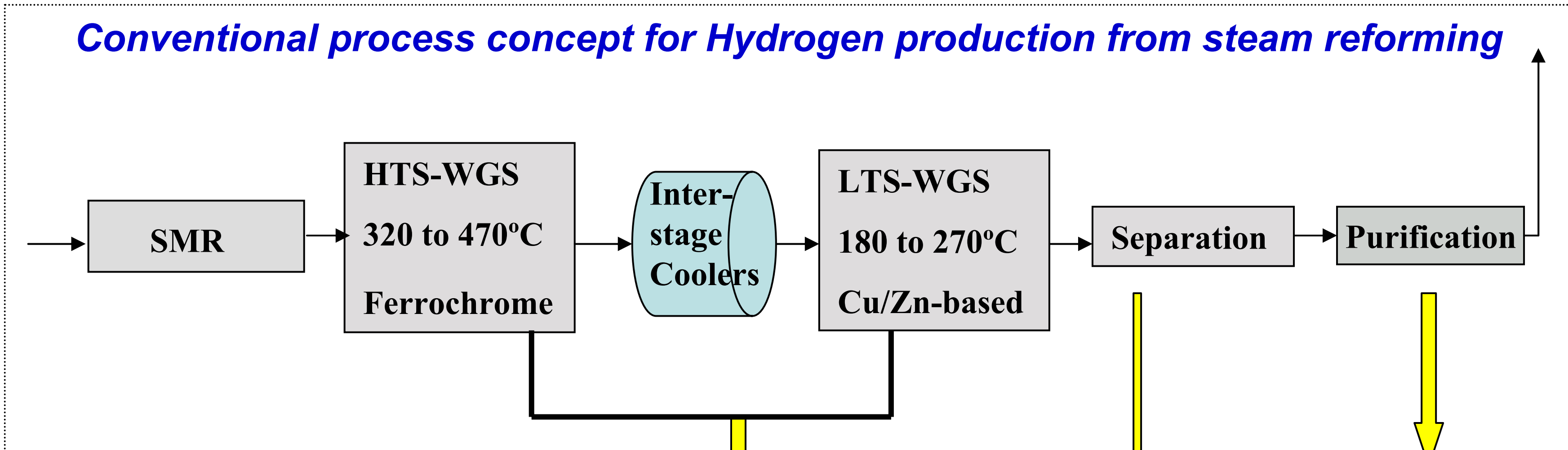
OVERALL TECHNICAL STRATEGY



*1. Reduce HTS/LTS reactors & inter-stage coolers into a single stage **LTS** operation*

*2. Process synthesis to overcome the dilemma of **high H_2 purity vs high H_2 recovery ratio** for a membrane-based process*

*3. Develop a low cost polishing step **compatible** with our proposed MR process to meet 99.999% purity.*

Overall Technical Approach

1. Bench-Scale Verification (Yr I&II, Phase I)	2. Pilot Scale Testing* (Yr III, Phase I)	3. Field Demonstration (Phase II)
1.1 Evaluate membrane reactor: use existing membrane & catalyst via math simulation	2.1 Prepare membranes, module, and housing for pilot-scale testing	3.1 Fabricate membranes and membrane reactors and prepare catalysts
1.2 Experimental verification: use upgraded membrane & existing catalyst via bench unit	2.2 Perform pilot scale testing and demonstration	3.2 Prepare site and install reactor
	2.3 Perform economic analysis & technical evaluation	3.3 Perform field test
		3.4 Conduct system integration study
1.3 Validate membrane and membrane reactor performance & economics	2.4 Prepare field testing	3.5 Finalize economic analysis &refine performance simulation

Technology development team (grey) — End user participant (yellow)

*current stage of the project

Distributed hydrogen production

Objectives and Technical Approach for Yr III

Based upon the lab results obtained from Yr I&II in the performance of our membrane and membrane rector, we have focused on below in Yr III:

- **Process Synthesis to**
  - deliver 99.999% H_2 purity
  - achieve capital cost reduction, and
  - overcome intrinsic deficiencies of membrane and membrane reactor technologies;
- **Establishing PDU testing facility at USC and pilot demonstration and field testing unit at M&P to**
  - verify the performance based upon process simulation, and
  - provide experimentally substantiated inputs for H2A analysis
  - perform H2A analysis

TECHNICAL ACCOMPLISHMENTS – Yr III

❑ Process Synthesis for Distributed H_2 Production based upon WGS/MR

A distributed hydrogen production process has been synthesized based upon our WGS/MR + Polishing to produce hydrogen with high overall conversion (80-85%) and 99.999% purity.

❑ High H_2 Recovery vs High H_2 Purity is no longer a Choice

Based upon the lab experimental results, our simulation indicates 90% hydrogen recovery at 99% purity is achievable with our HiCON process. A PDU unit has been assembled to experimentally verify this simulation by the end of Yr III.

❑ Production of 99.999% with Operating-Cost Free Polishing Step

Our experimental result demonstrated that 99.999% purity H_2 was produced with an adsorption-based polishing step. Through integration with the HiCON process, this polishing step can be operated without additional operating cost.

❑ Process Flow Diagram and Heat Integration with PRO/II

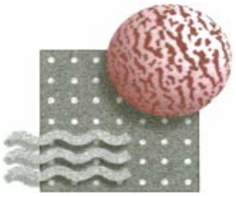
PRO/II design package was used for the development of the process flow diagram based upon our HiCON process. The finalized design with optimized heat integration will be used as input for H2A analysis.

❑ Performing H2A Analysis

A preliminary H2A analysis has been performed based upon our simulation result. Once the experimental results from the PDU unit become available, we will finalize the process flow diagram and the H2A analysis.

❑ Assembly of Pilot Testing Unit

A stand-alone pilot testing unit is under construction, which will be used for in-house pilot testing (under Phase I) and field demonstration (under Phase II if budget is available).



M&P Ceramic MEMBRANES - Low cost

Our Commercial Ceramic Membranes/Bundles and their Substrate

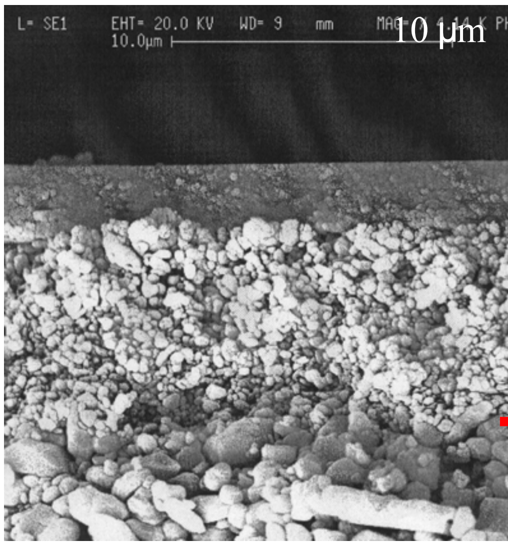
Proposed module for gas phase applications

The low cost ceramic membrane was used as substrate for the hydrogen selective membrane developed for this project.

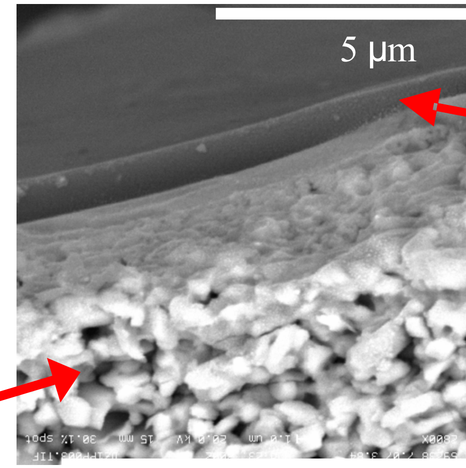
M&P Emerging Inorganic Membranes

M&P's Core Technology: Thin film deposition on porous substrates

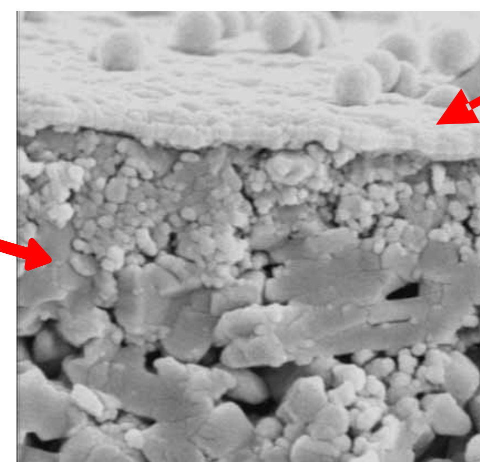
Inorganic Substrate



Ceramic
Substrate



Carbon
molecular
sieve
(porous)



Palladium
(dense)

Emerging membranes used by our proposed hydrogen production process

Limitation of membrane-based separation and reactor process

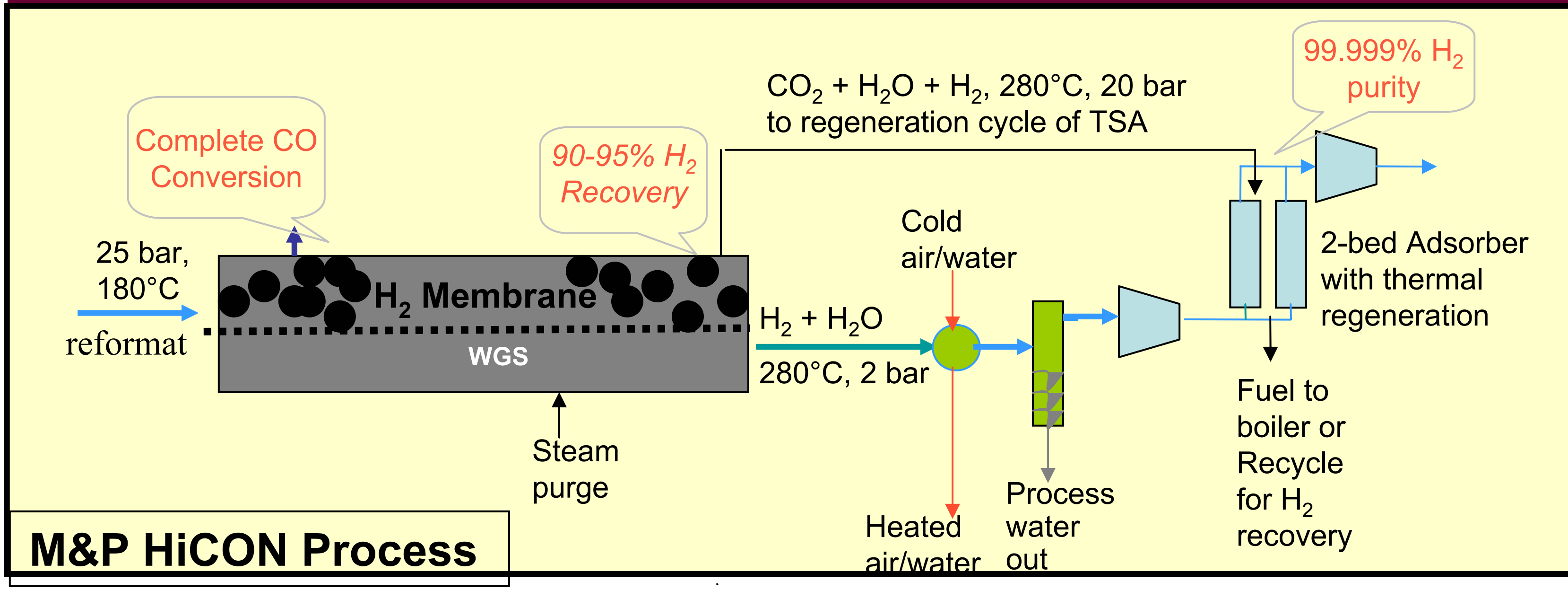
- High H_2 purity vs high H_2 recovery vs High recovery efficiency are incompatible
- 100% conversion is theoretically possible, but practically unattainable

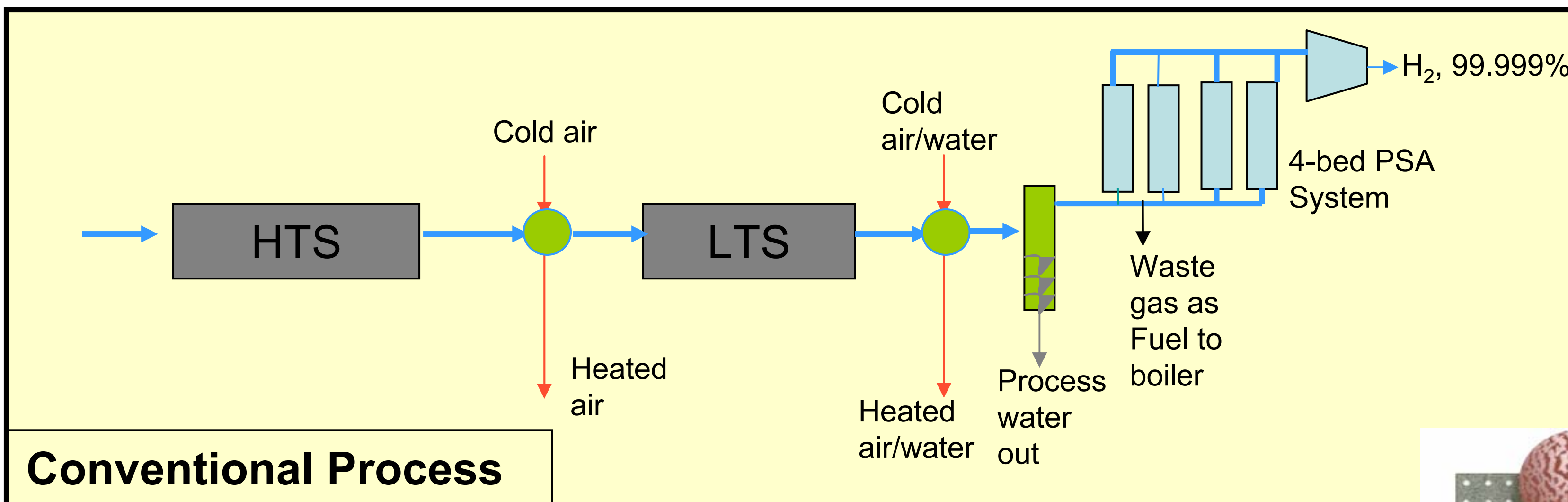
e.g., $CO + H_2O \longleftrightarrow CO_2 + H_2$

How did we overcome these deficiencies via membrane properties process synthesis ?

- Using a uniquely formulated membrane for enhancing conversion to achieve nearly complete conversion
- Using adsorption as a no (operating) cost polishing step in order to achieve high purity with high recovery.
- Additional recovery potential of the unrecovered hydrogen from the reject of our membrane process.

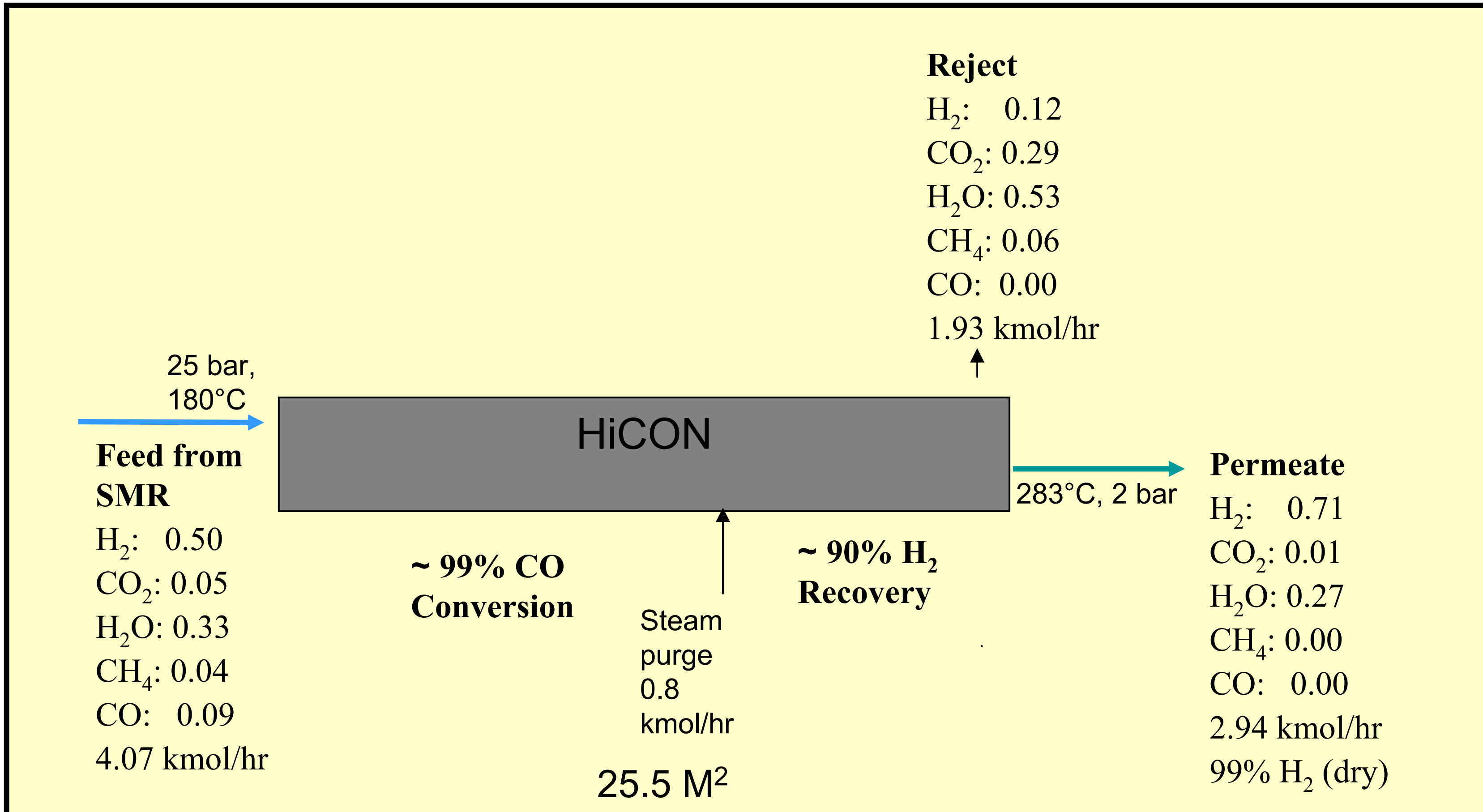
HICON Process: CO Conversion, H_2 Recovery and Polishing Step





Stream composition, size, temperature & pressure
And membrane surface area requirement

Basis: 100 kg/day production



Membrane reactor is under adiabatic operation (i.e., no temperature control is required).

Experimental study: production of 99.999% H_2 via Polishing Step

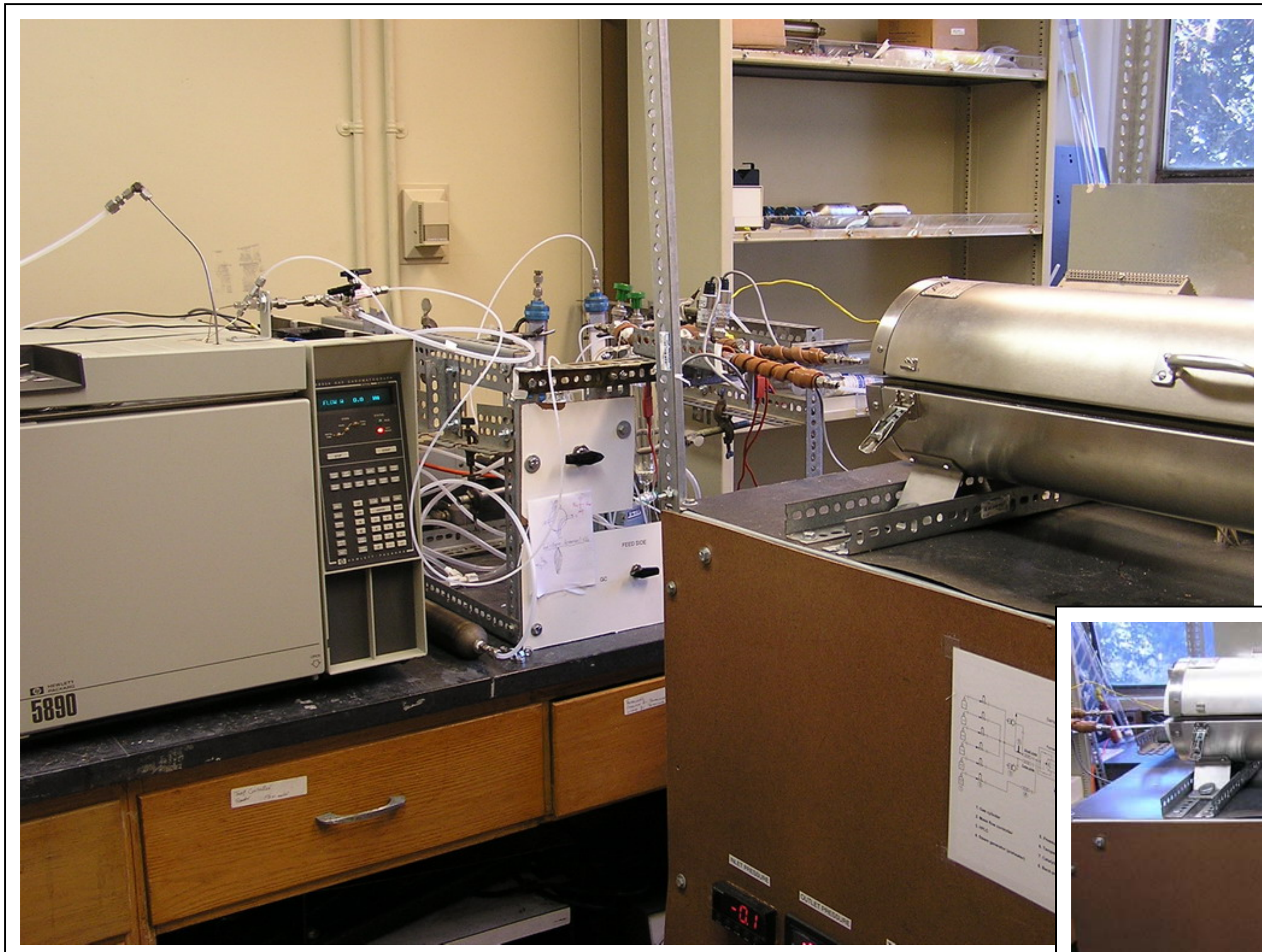
Experimental Results				**Projected for Actual Operating Condition**			
Adsorbent Dosage	38	gm					
Adsorer	3/4"ID x 10"L						
Flow rate	3	cc/sec					
Pressure	80	PSI		Feed Pressure	308.7	psig (20 bar)	
Composition	95.41%	H2		equi. Comp [%]	98.592		
	4.59%	CO2			1.408		
Effluent				Influent	Effluent		
time (min)	H2 Purity (%)	CO2 % in gas	% Error **	% H2 Purity	P, CO2, psia	%CO2 Impurity	% H2 Purity
2	100	NOCO2 Detected		98.592	0.000	0.000	100.000
5	100	NOCO2 Detected		98.592	0.000	0.000	100.000
10	99.992	0.008	0.080	98.592	0.008	0.002	99.998
15	99.913	0.087	0.058	98.592	0.082	0.027	99.973
25	99.934	0.066	0.028	98.592	0.063	0.020	99.980
35	99.956	0.044	0.049	98.592	0.042	0.013	99.987
75	99.906	0.094	0.107	98.592	0.089	0.029	99.971

**% error is calculated from the GC calibration data

99.999% purity was produced using a synthetic feed from Our HiCON process.

Process Development Unit at USC

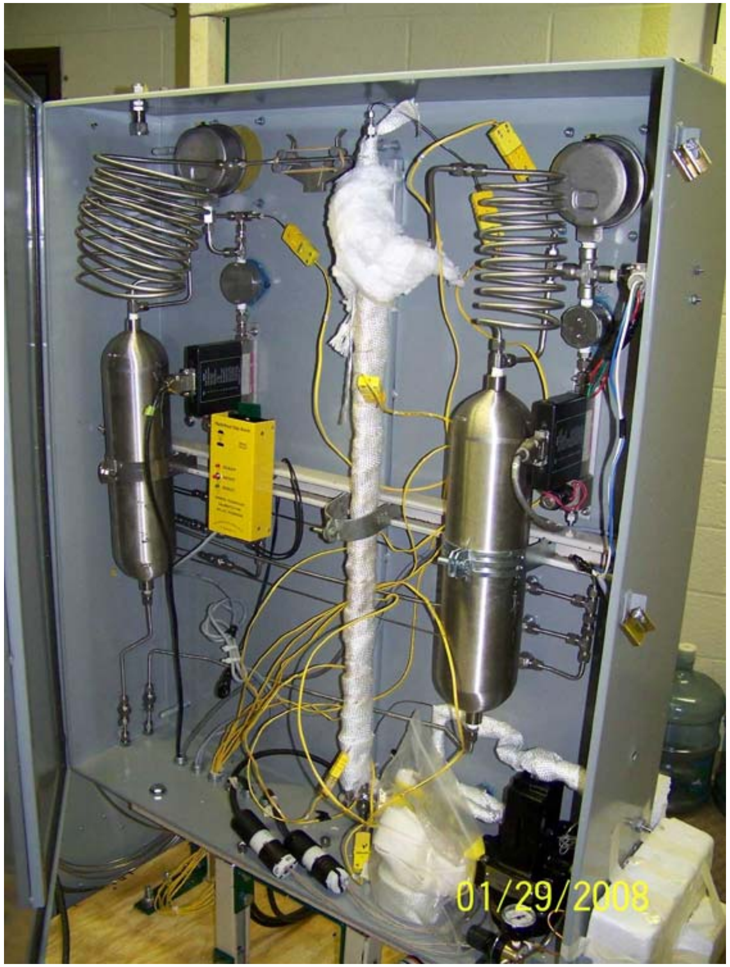
using
30"L full-scale
Single Tube
Membrane Reactor



This facility is completely installed and is currently under operation. This facility will provide experimental data generated from a full scale membrane tube for process simulation and H2A analysis. Experimental data will be available during the meeting

M&P HiCON Process

Demonstration and Field Testing Unit



Control Panel

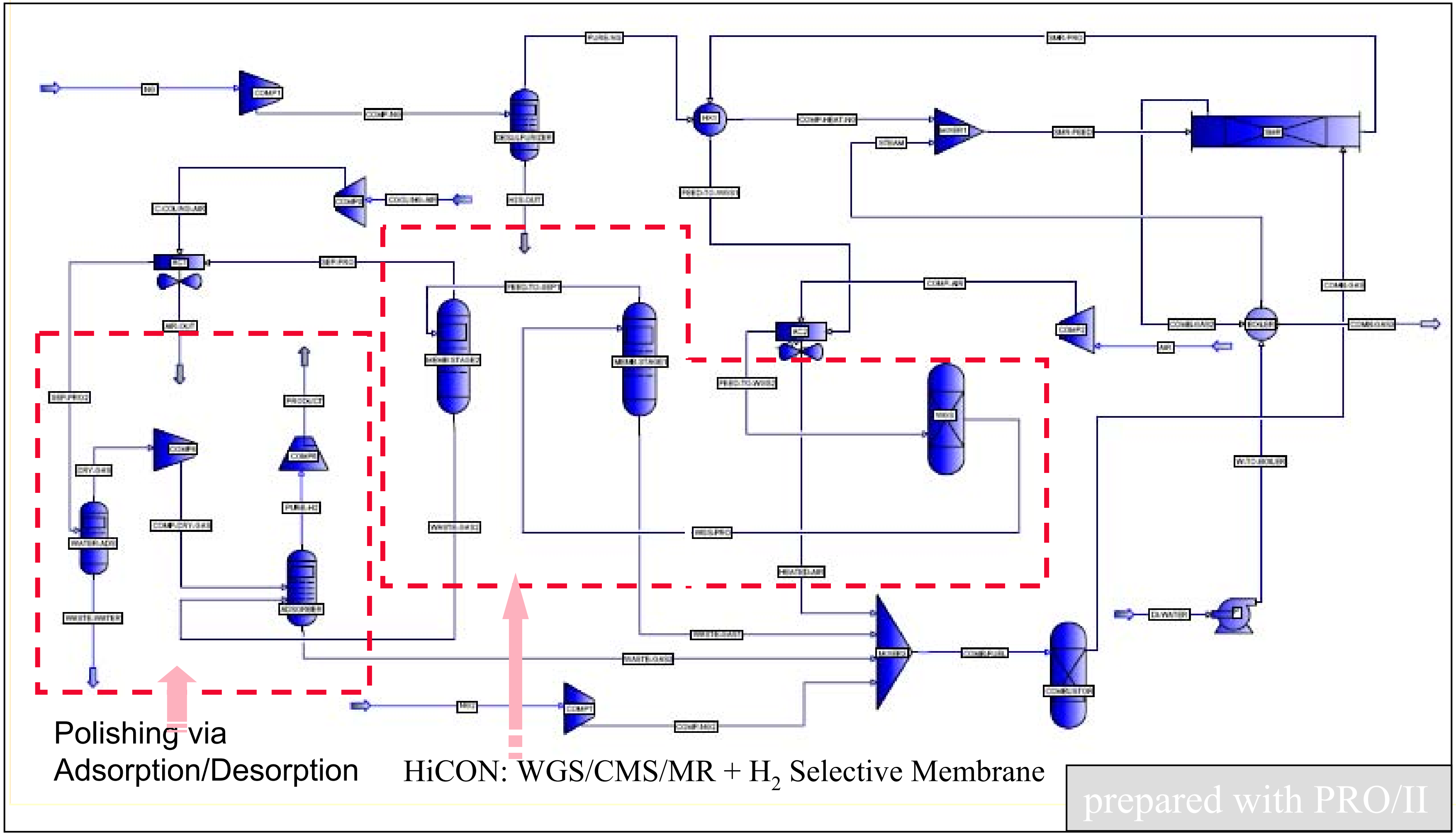
Main Unit

L: inside

R: overview

This unit is currently under construction. This unit will be used for demonstrating the HiCON Process, a process for hydrogen production beyond the reformer.

Our HiCON Process Flow Diagram



Process simulation and heat integration are actively pursued by us using PRO/II. Saxon Engineering has been retained for engineering evaluation and capital cost estimate. The results will be fed to H2A analysis.

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H2A Inputs

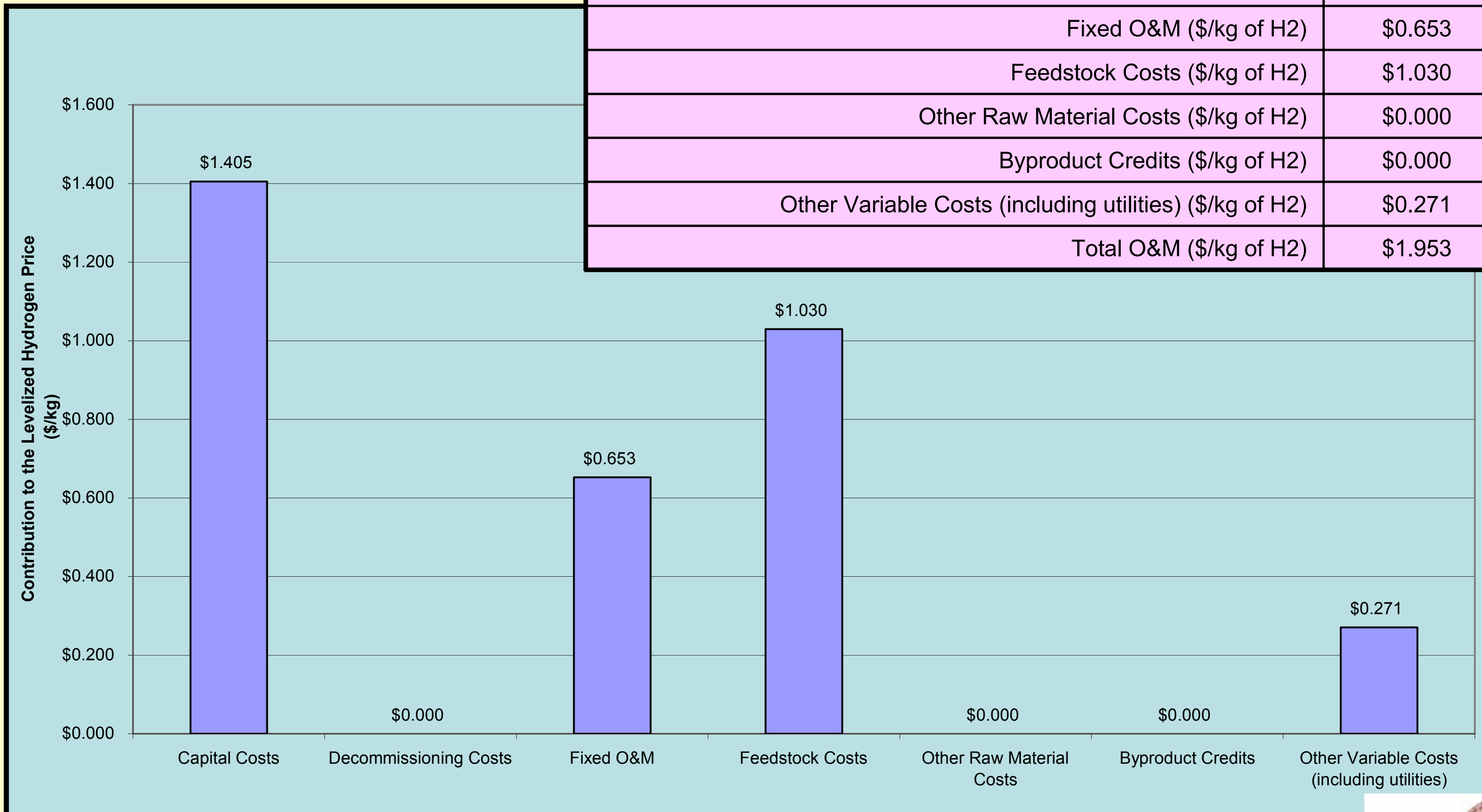
• Total production initial capital investment (installed):	$1,020,000 $1,116,000 with option
• Primary feedstock usage : (excluding fuel usage)	2.4 kg NG/kg H_2 , or 3.4 Nm^3 NG/kg H_2 or 1.23 E+05 kJ/kg H_2
• Total other energy usage:	0.50 kWh/kg H_2 for NG Compression, and 2.70 kWh/kg H_2 for H_2 Compression, and 0.7 Nm^3/kg H_2 for Fuel Usage 3.50 E+04 kJ/kg-H_2 Total
• Total yearly operating costs excluding energy:	$0.67/kg H_2 excluding utilities

INPUT AND OUTPUT FOR ENERGY & WATER

Energy efficiencies for individual process steps	Values	Basis
Production System Feedstock Consumption (kJ Feedstock (LHV)/kg of H2)	146595.6	9.31 kmol/hr for 52.1 kg-H2/hr. This feedstock includs the use of methane as fuel in addition to the use of methane as feedstock for H2.
Production Unit Hydrogen Efficiency (%)	83.7%	93% Methane conversion and 90% H2 recovery
Production Electricity Consumption (kWhe/kg of H2)	0.497	25900 watt/52.1 kg-H2/hr for NG compression, 3 stages
Hydrogen Leak from Production System (%)	0%	
Production Step Efficiency (%)	82.3%	
Compression, Storage and Dispensing Feedstock Consumption (kJ (LHV)/kg of H2)	0.0	
Compression, Storage and Dispensing Electricity Consumption (kWhe/kg of H2)	2.7	according to Ariel, 9 stages, <270F
Hydrogen Leak from Compression, Storage and Dispensing Systems (%)	0%	
Compression, Storage and Dispensing Step Efficiency (%)	92.0%	based upon LHV of H2
Total H2 Leak (%)	0%	
Total System Efficiency (%)	75.7%	
Process water consumption (L/kg of H2)	8.1	3:1 ratio, 23.4 kmol/hr, credit from retentate not accounted for yet

Hydrogen Selling Price and Cost Contribution (year 2005$)

Hydrogen Selling Price and Cost Contributions (Year 2005 $)	
Required Hydrogen Cost ($(Year 2005)/kg of H2)	$3.358
Capital Costs ($/kg of H2)	$1.405
Decommissioning Costs ($/kg of H2)	$0.000
Fixed O&M ($/kg of H2)	$0.653
Feedstock Costs ($/kg of H2)	$1.030
Other Raw Material Costs ($/kg of H2)	$0.000
Byproduct Credits ($/kg of H2)	$0.000
Other Variable Costs (including utilities) ($/kg of H2)	$0.271
Total O&M ($/kg of H2)	$1.953



Upgrading via optimization with PRO/II is continuing. Updated results will be available in our poster.

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Future Work

Remainder of FY 2008

- **Complete PDU testing using a single, full-scale hydrogen selective membrane and synthetic feed to generate performance database for H2A analysis.**
- **Complete pilot scale testing to demonstrate the optimized HiCON process.**
- **Complete the H2A economic analysis for hydrogen production via the developed HiCON process.**

FY 2009 and Beyond

- **Depending upon the budget availability, the field demonstration with the pilot scale unit as originally planned will be pursued.**

Other Potential Opportunities of HiCON Process

- HiCON via CMS/MR is uniquely suitable for gasified products (such as from biomass) containing high CO, and/or sulfur and other poisons.
- Our HiCON can deliver H_2 product at 99% purity with 90 to 95% recovery for the downstream polishing step.
- Purification with simple adsorption/thermal regeneration at no operating cost to meet the PEM feedstock spec. This option overcomes the barrier associated with the membrane-based technology.

ACKNOWLEDGEMENT

US DOE Project Managers

- Rick Farmer, Sara Dillich, Arlene Anderson
- Jill Grubber, Carolyn Elam

Our Project Team Members

- Theo T. Tsotsis, University of Southern California
- Babak Fayyaz-Najafi & John Wind, Chevron ETC
- Hugh Stitt, Johnson Matthey
- Richard J. Ciora, Jr. Media and Process Tech Inc.