Hydrogen Production via a Commercially Ready Inorganic Membrane Reactor

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PDP9

Overview

- **Project Start Date**
  10/1/03
- **Project End Date**
  9/30/06
- **Percent Complete**
  70%

- Barriers

- Total project funding
  - DOE Share: $720,000.
  - Contractor Share: $180,000
- Funding received in FY04
  $246,034
- Funding received in FY05
  $ 237,221

- **Professor Theo T. Tsotsis**
  University of Southern California,
  Catalytic membrane reactor expert
- **Pall Corporation**, supplier of stainless steel porous substrate
- **Dr. Richard Kleiner**, consultant

Hydrogen Production from Coal Gasifier Off-Gas

Coal → Gasifier → Water Gas Shift (WGS) Reaction → H_2, CO_2, …

Conventional Process Concept

Texaco

Oxygen Blown Gasifier

~1300ºC, ~70 bar

CO:	**39%**
H_2:	**27%**
CO_2:	**13%**
H_2O:	**18%**
H_2S:	**1%**

→ **Hot Gas Clean up** → **HTS-WGS*** 320 to 470ºC, Ferrochrome → **LTS-WGS*** 180 to 270ºC, Cu/Zn-based → **Separation and Purification** →

$\Delta H^o_{298} = -41.17\ kJmol^{-1}$

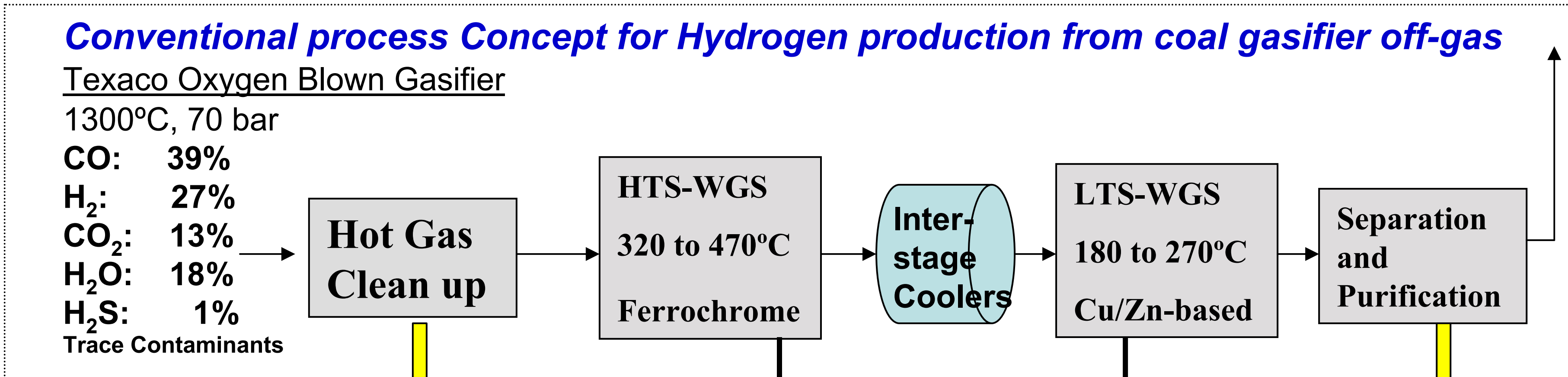
Trace Contaminants

alkali vapor,
ammonia,
HCl,
HCN,
particulates

*HTS: high temperature shift
*LTS: low temperature shift
*WGS: water gas shift reaction

Project Objectives:

Process Intensification & Production Efficiency Enhancement



1. Avoid cleanup at high temperature which remains to be demonstrated

2. Reduce HTS/LTS reaction & Inter-stage Coolers into a single stage operation

3. Integrate separation/ purification into the reaction step

A "single stage" for hydrogen production and CO_2 sequestration without requirement of gas cleanup at high temperature

Technical Approach

- **Evaluate <u>Existing</u> Technologies for Proposed Single Stage LTS-WGS-MR.**
  - Membrane Reactor Hardware Evaluation
    - Membrane evaluation under the proposed operating condition:
      - hydrogen permeance, and selectivity
      - Thermal, hydrothermal and chemical stability
    - Catalyst evaluation under the proposed operating condition:
      - Reaction rate (W/F) and stability in the environment of high CO and low steam concentrations
      - Reaction kinetic expression under the proposed operating temperature and pressure.
  - Membrane Reactor Process Evaluation
    - Developing mathematical model to simulate the proposed one stage process
    - Conducting simulation to define a suitable membrane performance and operating condition (isothermal).
    - Incorporating temperature as a variable for heat transfer consideration (non-isothermal)
    - Developing steam delivery/water quenching as in-situ temperature control strategy.

- **Perform Bench-Top LTS-WGS-MR Evaluation**
  - Refine membrane performance to meet the performance criteria established above
  - Fabricate a bench-top membrane reactor and establish peripheral hardware for bench-top evaluation
  - Perform bench-top experimental study to demonstrate the proposed LTS-WGS-MR and verify the mathematical model established.

- **Perform Pilot-Scale LTS-WGS-MR Testing**
  - Design and fabricate pilot scale membrane reactor module using existing ceramic substrate as a low cost option
  - Develop stainless steel supported membrane and reactor as a very large scale applications
  - Perform pilot scale testing using both ceramic and stainless steel supported membranes and a synthetic feed stream.

- **Prepare Field Testing for Next Phase Study**
  - Refine mathematical model based upon pilot test results
  - Conduct process development/optimization and economic analysis.
  - Present process and economics to potential customer for Identifying a test site with a slip stream available.

TECHNICAL ACCOMPLISHMENTS/PROGRESS/RESULTS

- Overall -

Developed a single stage WGS unit operation via our proposed LTS-WGS membrane reactor (MR), specifically,

- **The CMS membrane has been proven to be stable in the expected LTS-WGS-MR environment.**
- **Existing commercial catalyst (Zn/Cu-based) has been experimentally proven effective and efficient under the condition of the proposed single stage LTS-WGS-MR process.**
- **It has been identified that the unique water permeability of our membranes offers an effective tool for in-situ heat management of the WGS reaction.** (Work in progress to be completed by the end of Yr II.)
- **Low temperature required for existing gas clean-up technology is adequate for the proposed LTS temperature (~180ºC).**

Thus, high purity hydrogen (≤ 0.1 to 0.2% CO) can be produced from coal gasifier off-gas via a compact, single-stage process using existing gas cleanup technology, commercial catalyst, and our hydrogen selective inorganic membrane.

MAJOR ACCOMPLISHMENTS - specifics

A. Experimentally verified the suitability of our hydrogen selective inorganic membranes for the proposed single stage LTS-WGS operation; specifically

- A1. Excellent hydrogen permeance and selectivity under the proposed temperature, pressure, and composition of the reactor.
- A2. Long term thermal, hydrothermal and chemical stability demonstrated in both bench and field tests.

B. Evaluated the benefit of the proposed LTS-WGS-MR

- B1. Conducted bench-scale experimental study to demonstrate the proposed process and
- B2. verified mathematical model developed which will be used for Yr III process development and optimization.

C. Determined the performance of our proposed single stage LTS-WGS process, specifically:

- C1. 88- 98% CO conversion (vs 82- 88% of packed bed).
- C2. Hydrogen product with CO contamination of ≤0.2% depending upon the permeate sweep ratio.
- C3. CO_2 rich stream ready for sequestration.

Our experimental and simulation results demonstrate that the proposed compact, singe stage process offers a potential to produce efficiently a high purity hydrogen product.

D. Membrane and Membrane Reactor hardware Development

D.1 Successfully fabricated pilot scale CMS membrane supported on ceramic substrate. Module with 1.5" diameter was successfully tested at 200ºC with multiple thermal cycling.

D.2 Deposited CMS membrane layer on the stainless steel substrate. However, the hydrogen permeance and selectivity are lower than those on the ceramic substrate. Further performance improvement is currently underway.

Responses to Previous Year Reviewers' Comments

- This is the first year review for this project.

Why not High Temperature Shift (HTS) ?

- Hot gas clean-up technology is essential to practice HTS without cooling and then re-heating the stream. Unfortunately the technology has yet to be completely developed. Industry has recently moved away from hot gas clean-up.

- Excess steam usage (e.g., H_2:CO≥4:1) was reported to (i) avoid coking at the entrance of the reactor for HTS, and (ii) permit this exothermic reaction under the adiabatic condition without overheat. Excess steam usage also reduces the reaction rate.

- Using the conventional technology, such as wet scrubbers, the gas stream can be cleaned at 180°C is suitable for LTS using existing commercial catalysts. Thus, steam contained in the stream will not be condensed.

HTS-WGS-MR process concept is contingent upon the development and demonstration of the hot gas cleanup technology, while LTS-WGS-MR uses the commercially available cleanup technology.

Why Membrane Reactor (MR) ?
vs Conventional Packed Bed Reactor

Advantages – General

- **Process intensification**: integrating reaction and separation into a single stage.
- **Improving Production Efficiency**: increasing the conversion and/or yield for reactions limited by thermodynamic equilibrium, such as WGS.

Advantages – Specific to WGS and LTS

- **No excess steam is required**: MR relies on the in-situ removal of product(s) to shift the reaction away from equilibrium, not excess steam as in the conventional reactor. Excess steam usage decreases the energy/power generation efficiency.

M&P Hydrogen Selective Carbon Molecular Sieve (CMS) Membranes for LTS-WGS

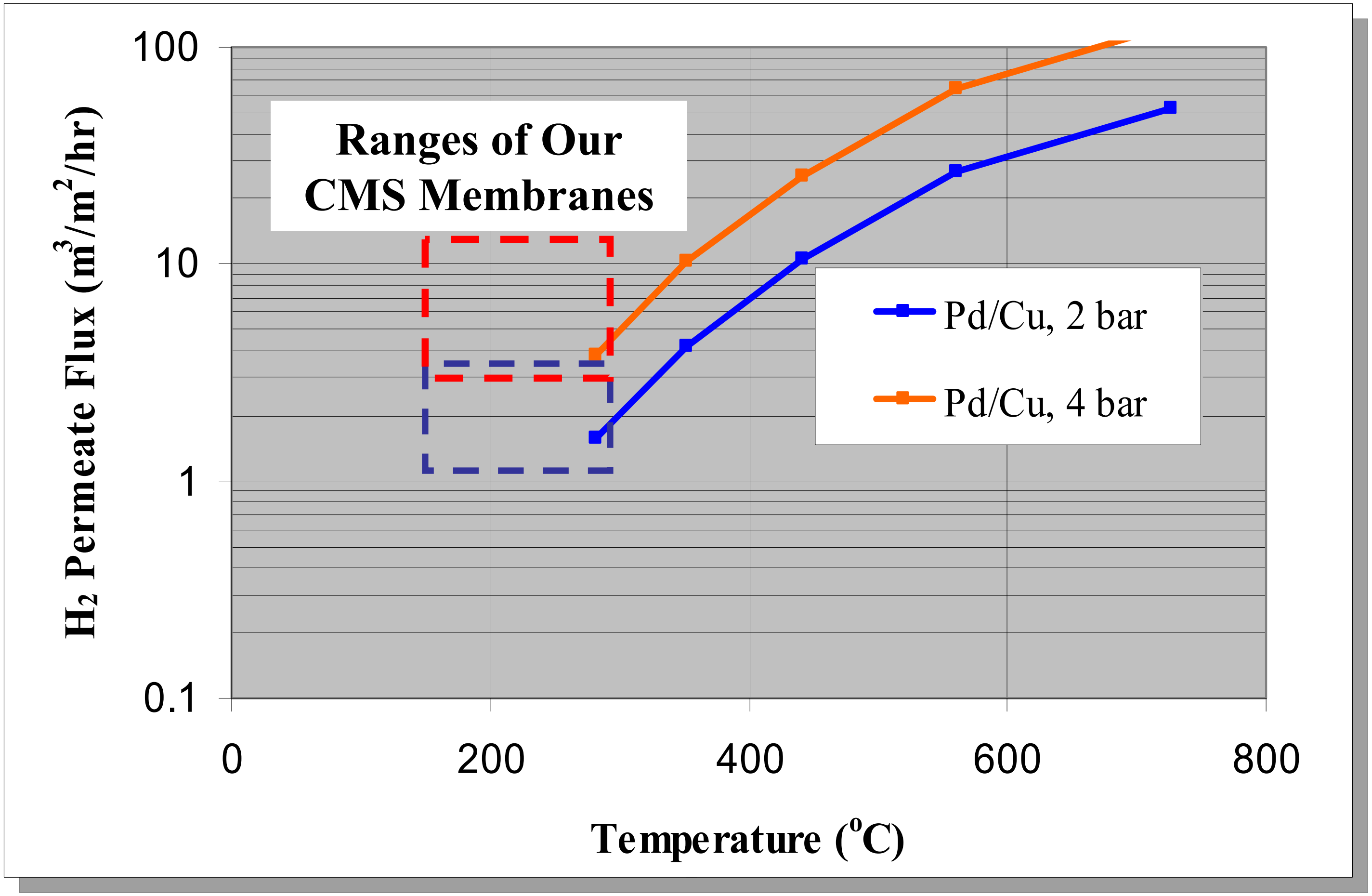
Typical Performance of Selected Membranes

Part ID	Temperature [ºC]	H_2 [$m^3/m^2/hr/bar$]	H_2/N_2 [-]	H_2/CH_4 [-]	H_2/H_2O [-]
DZ-218	220	1.1	80	130	-
NN-02	220	1.9	45	85	-
NN-22	250	4.2	62	77	2.8

Excellent hydrogen permeance and selectivity at the temperature range for LTS-WGS. In addition, the membrane demonstrates exceptional unique steam permeance as high as hydrogen's, which permits the LTS-WGS via MR become technically feasible.

HYDROGEN PERMEANCES of CMS vs Pd/Cu MEMBRANES

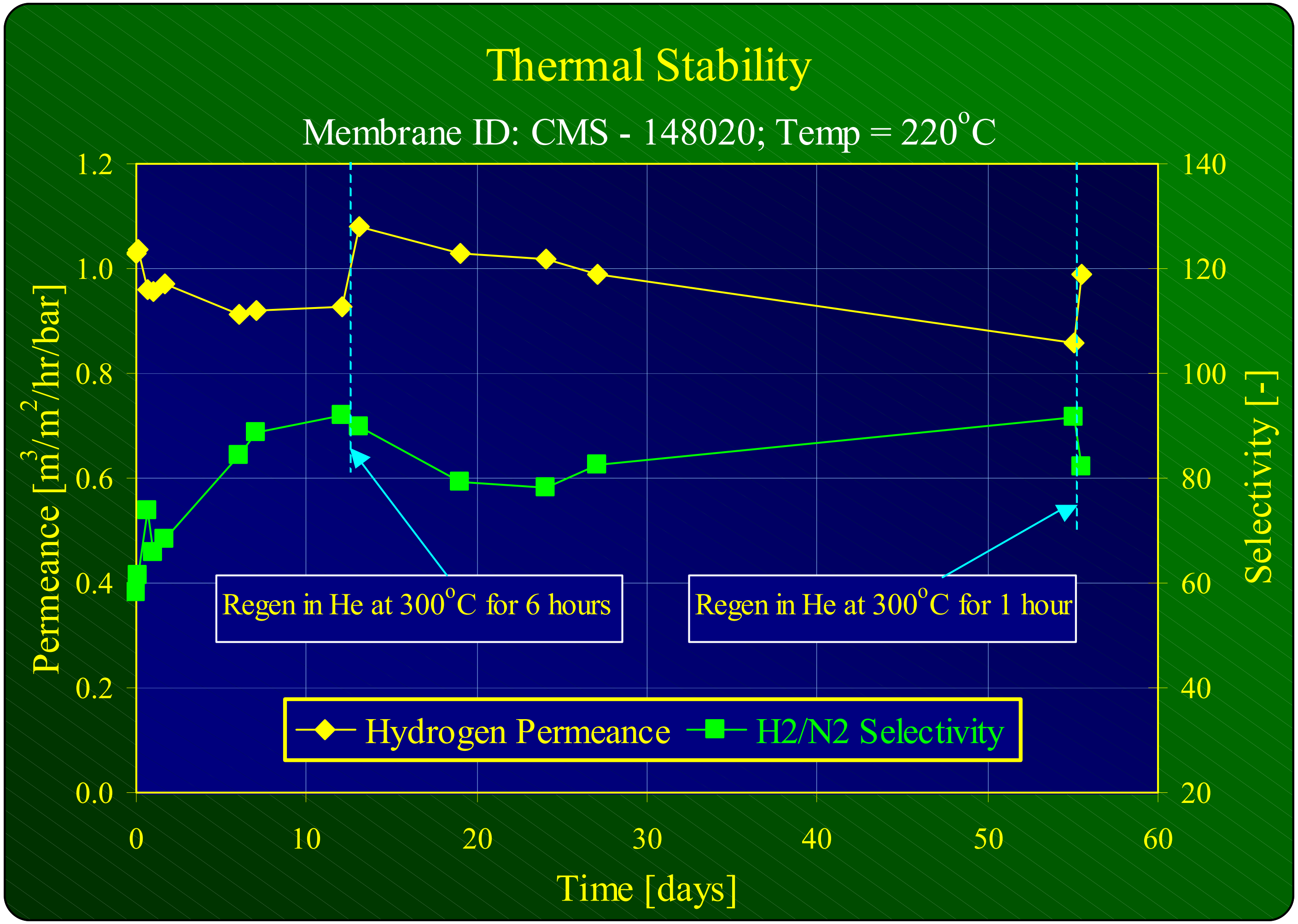
- *Benchmarking* -



- Assuming 1 micron thickness of Pd/Cu membrane,
- Permeate flux data source: Morreale, B.D., etc, *JMS,* 241(2004) 219
- Feed Pressure as indicated, Permeate Pressure: 1 atm

Our CMS hydrogen selective membrane shows higher hydrogen permeance than the Pd alloy membrane for the LTS-WGS operating temperature range.

Thermal Stability and Regenerability



Hydrogen permeance is stable at 220ºC for 55 days and regenerable as shown here.

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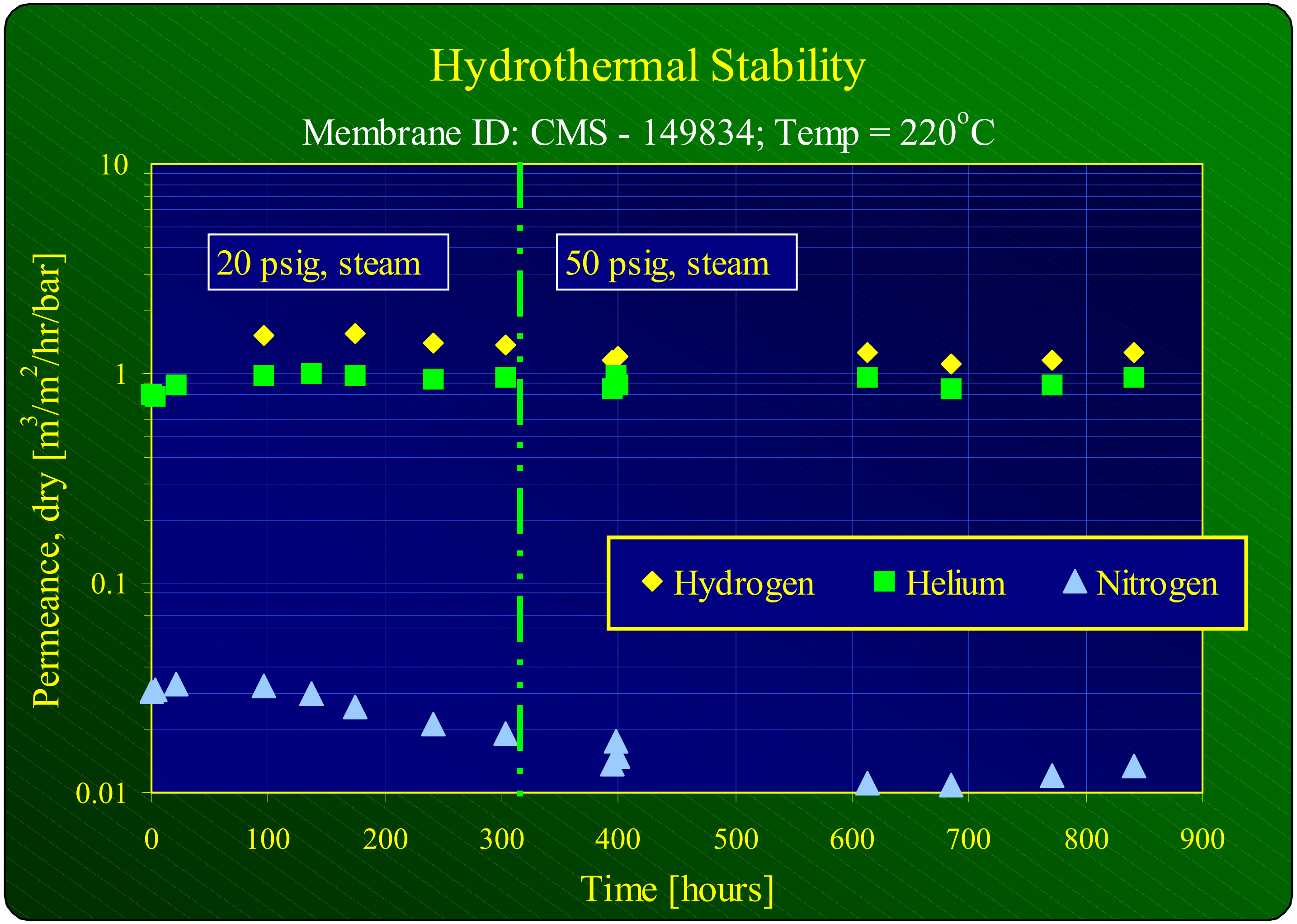
Hydrothermal Stability of M&P CMS Membranes



Hydrogen permeance is stable at 220°C and 20 to 50 psi steam for ~850 hrs.

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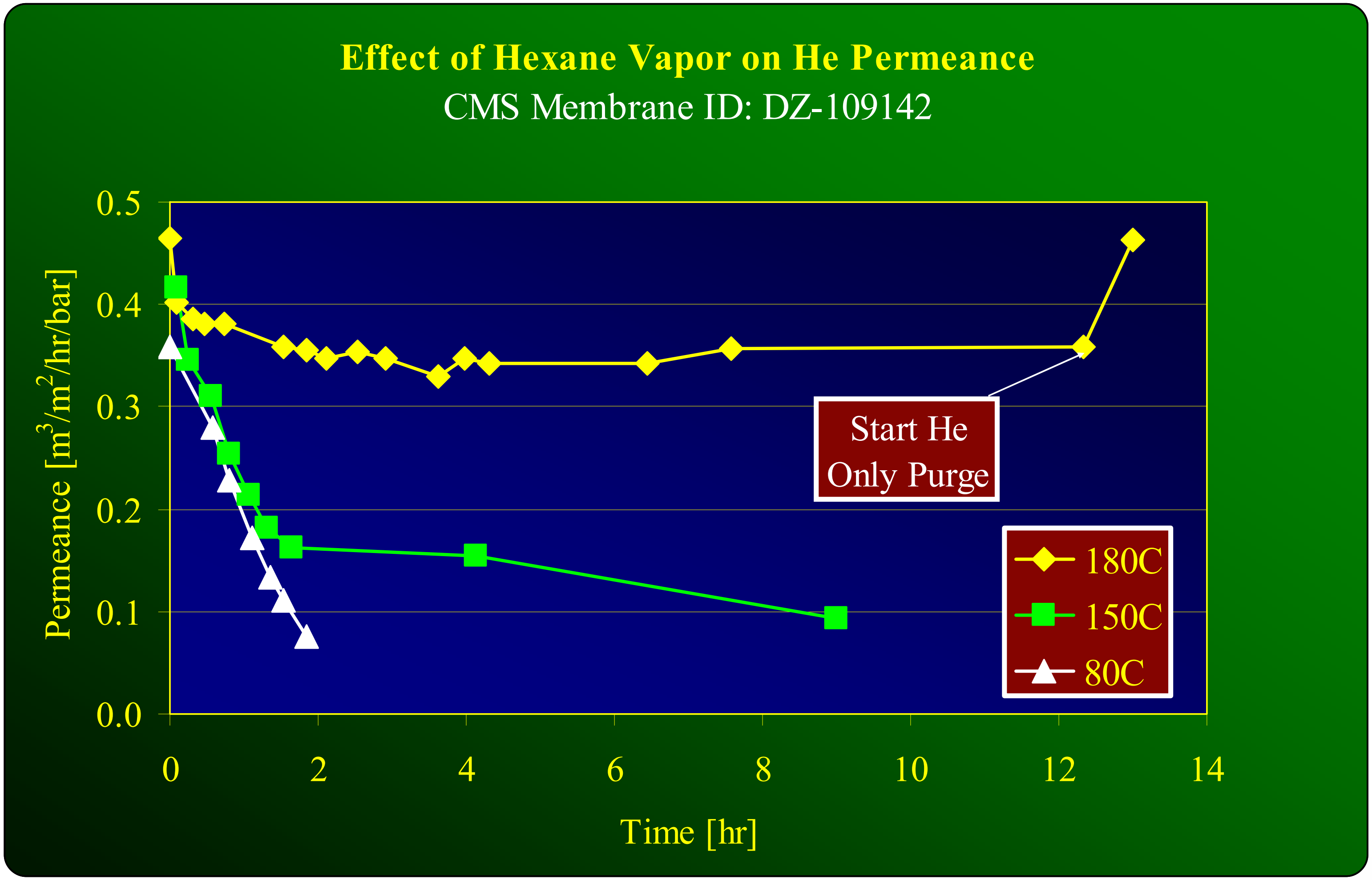
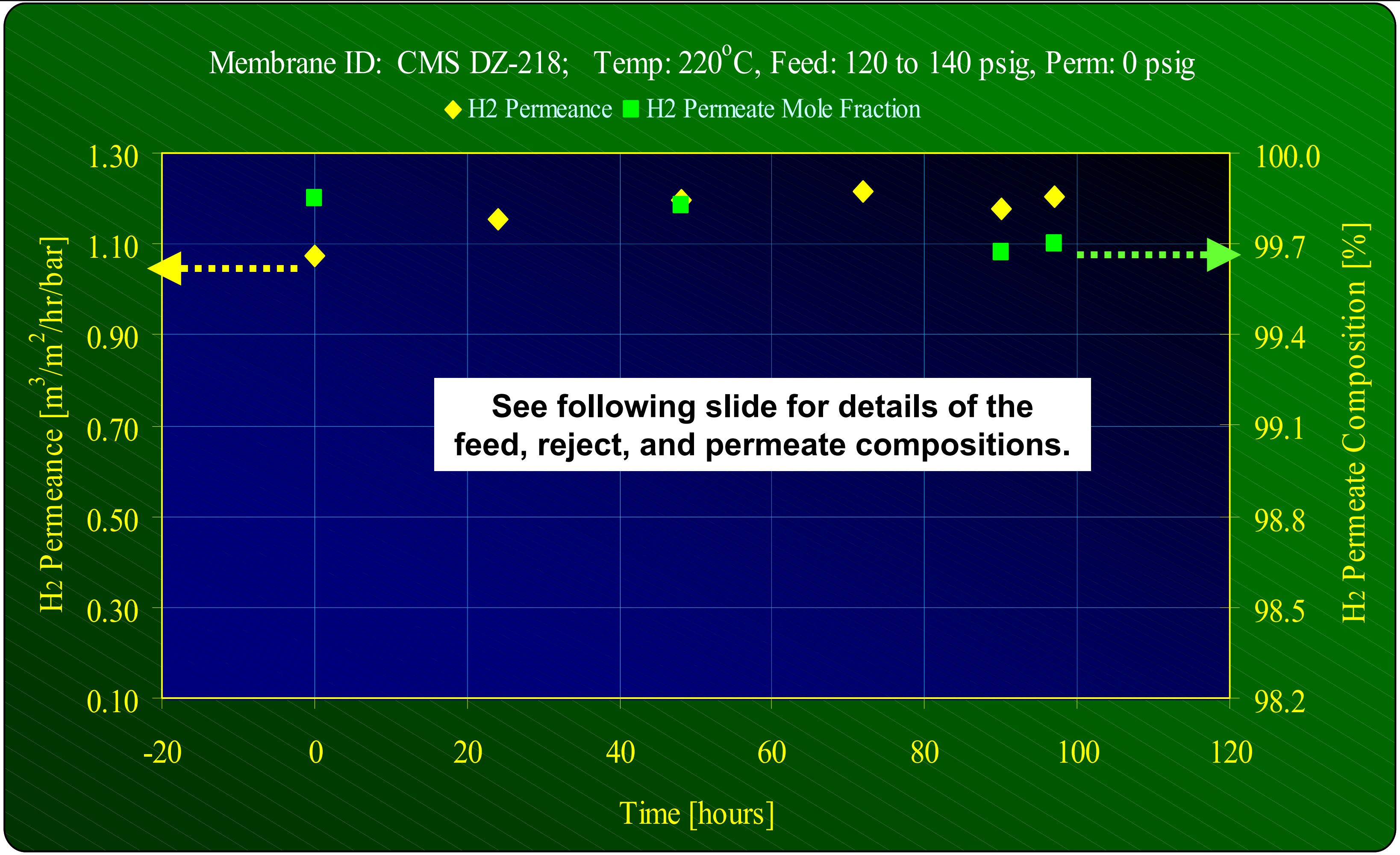
Resistance to Organic Vapor Poison



Organic vapor poison can be inhibited and regenerated at a higher temperature as shown above.

M&P HYDROGEN SELECTIVE MEMBRANES- *Field Experience*

H_2 Recovery from VGO Hydrocracker Purge Stream at a Refinery Site



During this 100 hr field test, our membrane shows excellent H_2 permeance and selectivity in the presence of H_2S, ammonia and hydrocarbons.

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Gas Stream Compositions and Stage Cut and H_2 Recovery for the VGO Hydrocracker Pilot Test

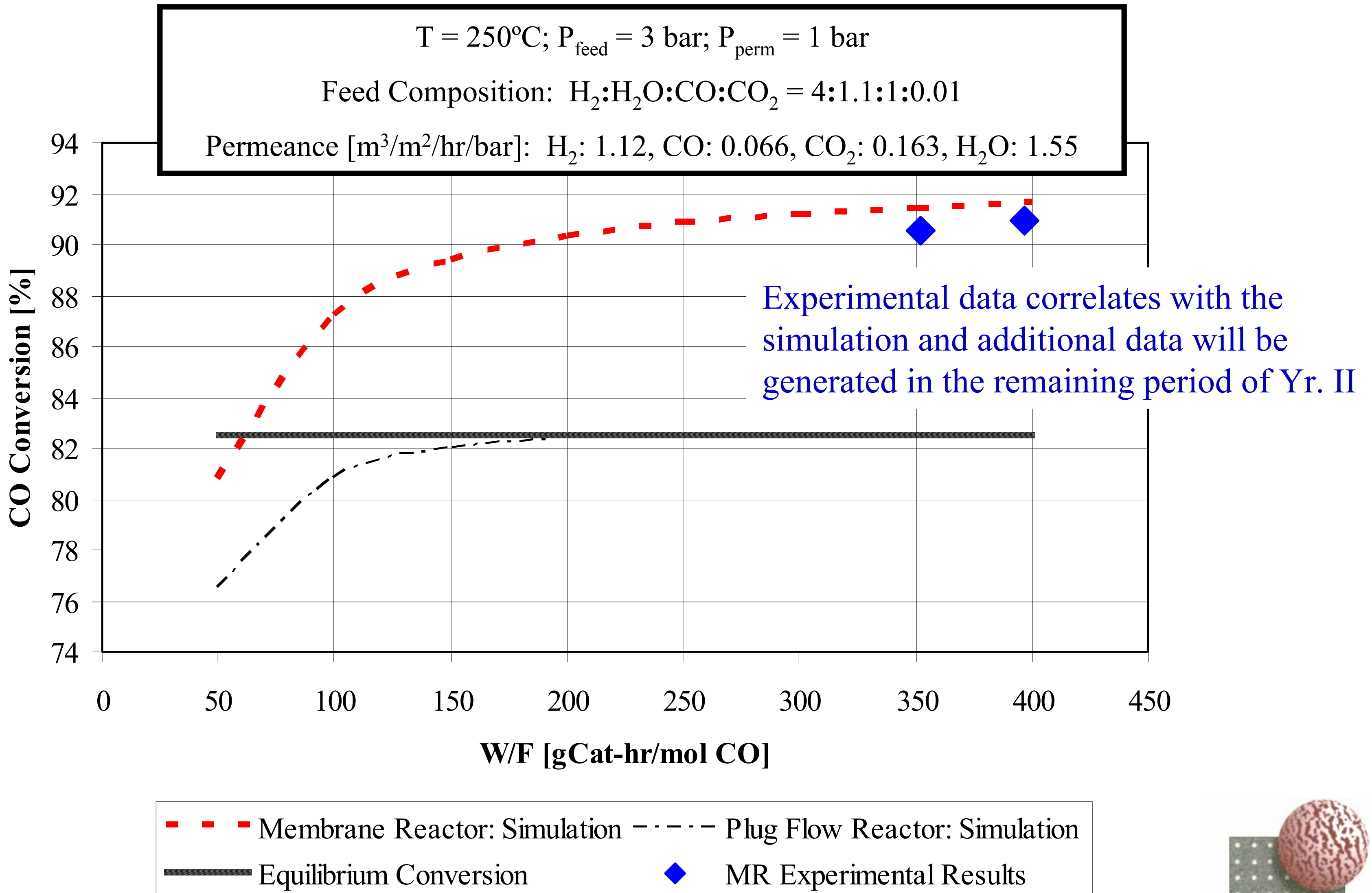
(See previous slide for membrane performance details)

At time = 3 hours				
Gas	Composition [%]			H_2/Slow Selectivity
	Feed	Reject	Permeate	
H_2S	5.2	32.0	0.03	163
H_2	89.9	38.9	99.88	1
C_1	2.1	12.2	0.08	123
C_2	0.88	5.4	0.01	~600
C_3+	1.88	11.6	ND	>1,000
Stage Cut			85%	
H_2 Recovery			92%	

At time = 100 hours				
Gas	Composition [%]			H_2/Slow Selectivity
	Feed	Reject	Permeate	
H_2S	4.8	24.5	0.16	74
H_2	90.8	50.6	99.70	1
C_1	1.9	9.9	0.06	123
C_2	0.81	4.2	0.01	~600
C_3+	1.66	10.7	ND	>1,000
Stage Cut			80%	
H_2 Recovery			85%	

LTS-WGS USING OUR CMS MEMBRANES AS MR

Experimental vs Simulation Results



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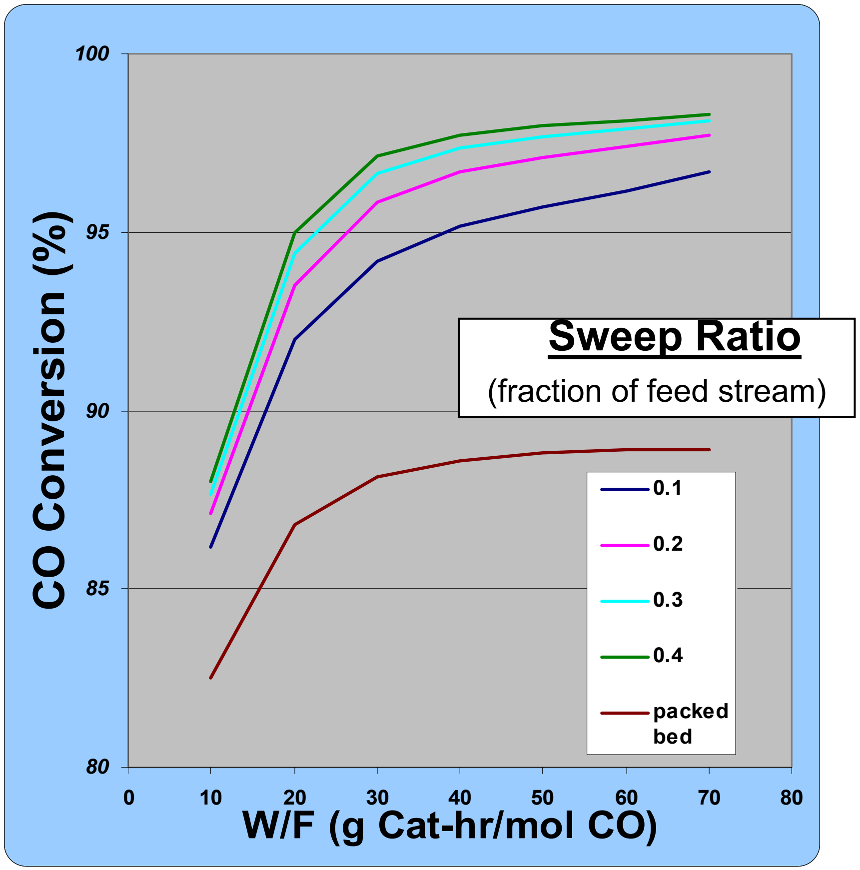
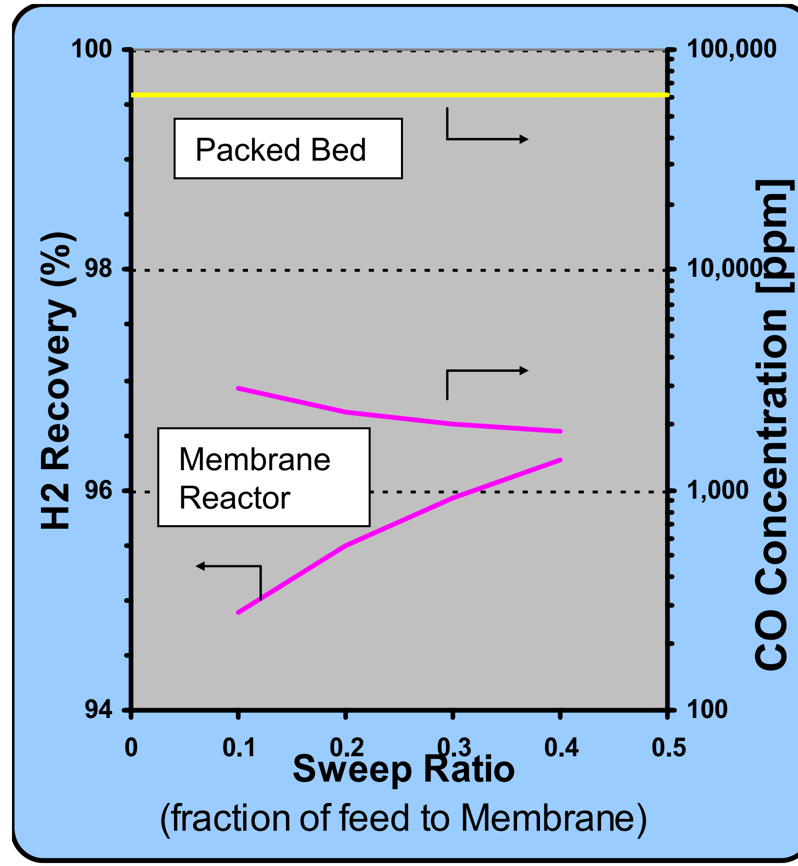
Membrane Reactor vs Packed Bed Reactor for LTS-WGS

Feed: $CO:H_2O:H_2:CO_2$=1:1.1:0.7:0.33, 250ºC, 15 bar, Permeate = 3 bar, H_2 permeance = 4 m^3/m2/hr/bar, H_2/CO = 100





88 - 98% CO conversion can be achieved with the MR in comparison with 82 - 89% by the conventional packed bed. The sweep ratio of 0.3 appears sufficient. 96% hydrogen recovery and <2,000 ppm CO can be produced vs 60,000 ppm CO for the packed bed. Optimization will begin once the rate parameters are verified with the bench top experimental study by the end of Yr II.

Membrane Reactor Configuration Development

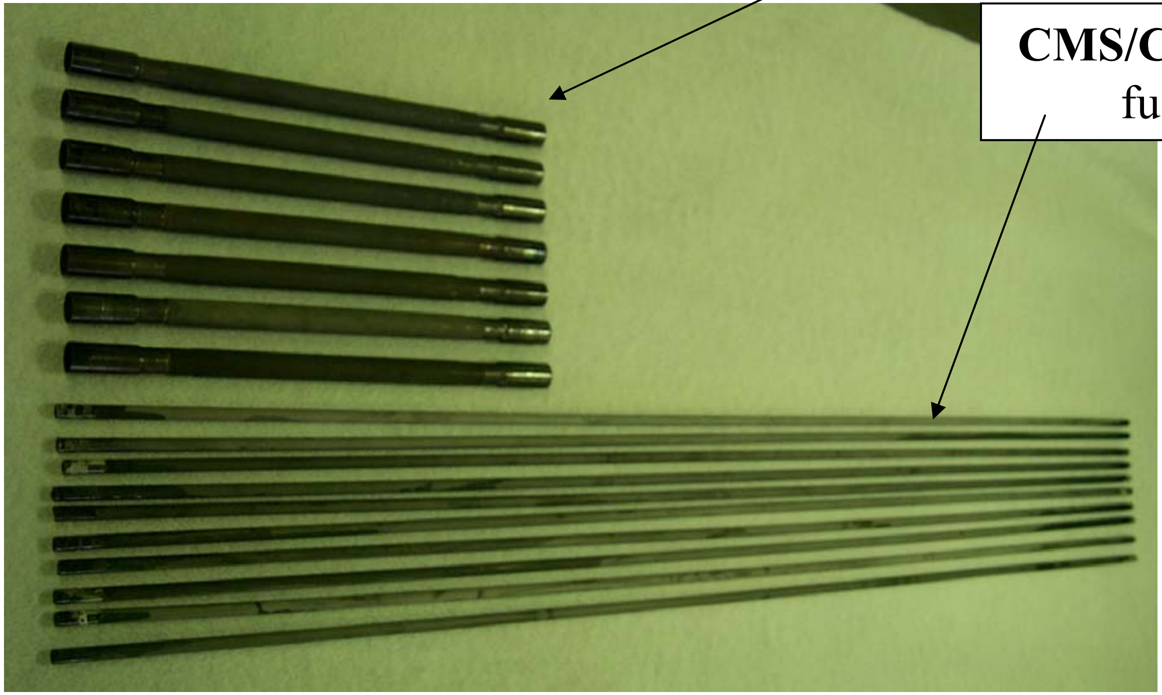
Option #1: a low cost solution

- Using our commercial porous tubular ceramic membranes as substrate
- Deposited with our carbon molecular sieve membrane
- Shell-and-tube design
- Using our existing ceramic membrane modules and housing.

Option #2: a product for very large scale applications

- Using tubular stainless steel membranes (Pall's AccuSep) as substrate
- deposited with our carbon molecular sieve membrane
- Shell-and-tube design
- Using Pall's mega-scale stainless steel module.

M&P CMS Membranes on Ceramic and Stainless Steel Substrates
- single tubes -



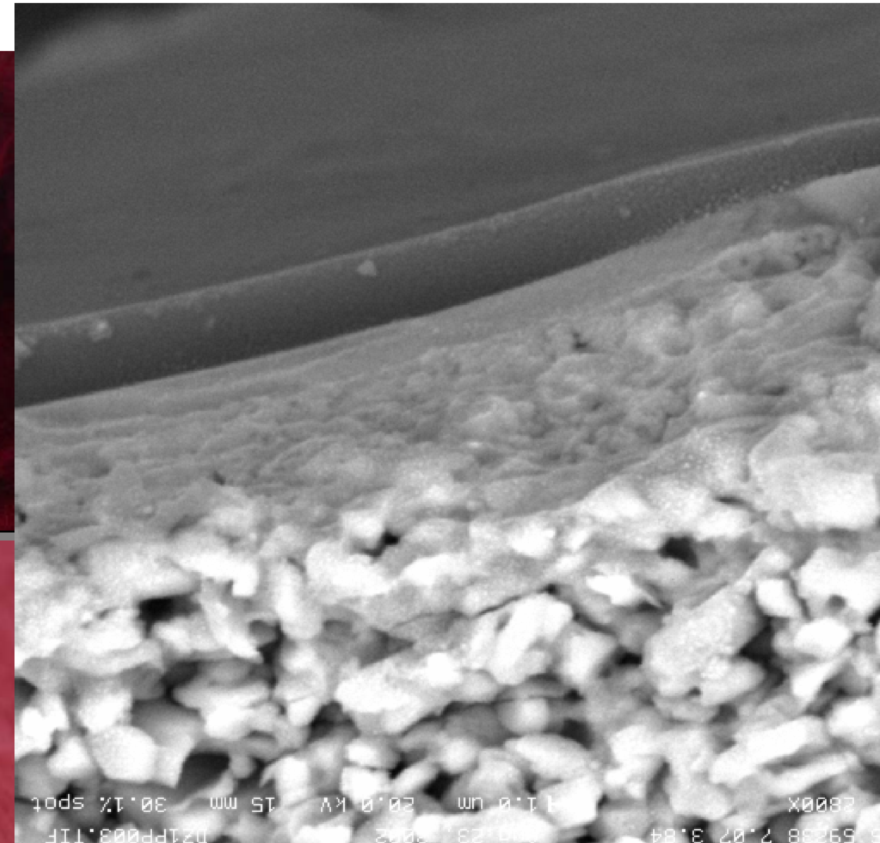
CMS/SS Membrane
lab scale (10" L)

CMS/Ceramic Membrane
full scale (30" L)

CMS Membrane with Our Commercial Ceramic Membranes as Substrate and Module – *low cost option*

M&P Commercial ceramic membrane modules

M&P pilot scale hydrogen selective membrane bundle



CMS Membrane on ceramic substrate

CMS/ceramic membrane modules have been fabricated as shown here.

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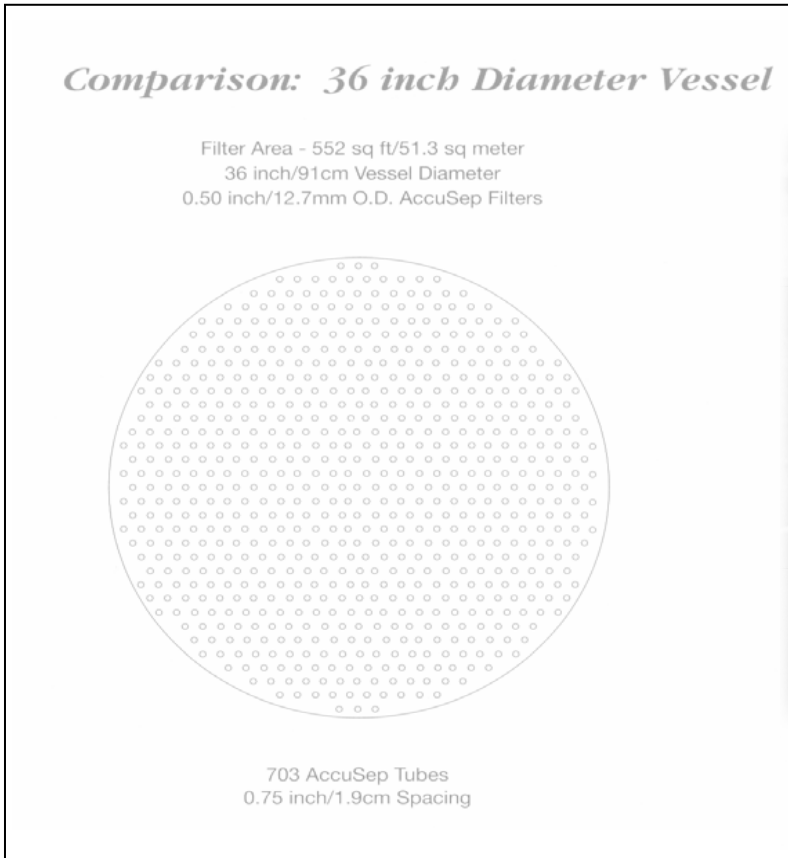
CMS Membrane with Pall Stainless Steel Substrate
– for Very Large Scale Applications -



Accusep Membranes - An Enabling Product Platform

AccuSep Inorganic Membranes can revolutionize the purification and separation processes found within the refining, petrochemical, food, beverage and power generation industries.

Pall has undertaken several joint development programs with universities, government labs, and industry for:

- Hydrogen Separation/Recovery
- Carbon Dioxide Removal
- Olefin Recovery from Paraffins
- Oxygen/Nitrogen Separation

AccuSep membranes are so versatile, they provide the ideal platform for creating unique separation and purification process.

Material	Surface Area (M^2/Module)	Cost ($/$M^2$)
Stainless Steel	57	>1,000
Ceramic	2-8	600* - 1,500

* Represented by our low cost ceramic membrane

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CMS Membrane Performance

- on Pall AccuSep Stainless Steel Substrate -

Typical Performance of Selected Membranes

Part ID	Temperature [ºC]	H_2 [$m^3/m^2/hr/bar$]	H_2/N_2 [-]	H_2/CH_4 [-]
DZp-34	120	0.49	20	22
DZp-x4	220	0.72	19	18
DZp-208	180	4.1	18	18

1. Technical feasibility of the CMS membrane on the stainless steel substrate has been proven.
2. The performance is not as good as on a ceramic substrate, although specific problems that limit the performance and specific solutions have been identified.
3. During the remaining period of Yr II and during Yr III, these solutions will be implemented to deliver significantly improved CMS membrane performance on this substrate.

Future Work

Remainder of FY 2005

- ❑ Complete mathematical simulation
  - ➢ incorporating temperature profile to simulate the non-isothermal single stage reactor
  - ➢ demonstrate the heat management strategy via our unique membrane.
  - ➢ Perform experimental study to verify the model prediction.
- ❑ Fabricate a pilot scale (about 1 m^2) reactor.

FY 2006

- ❑ Conduct a pilot scale LTS-WGS-MR operation using both Option #1 and #2 configurations to demonstrate the product purity and throughput on a long term basis.
- ❑ Refine mathematical simulation with the pilot test results for process optimization and economic analysis.
- ❑ Identify a field test site to demonstrate the pilot scale operation using the actual gasifier off-gas as a follow-up activity after the completion of the current phase of the project.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

During the year III, a pilot scale test will be performed, which involves a stream of 1liter/min containing ~37% CO and ~20% H_2 simulating the coal gasifier off-gas. Since

- H_2 is flammable
- CO is odorless,
- Its TLV is extremely low,
- The reactor system is too bulky to be housed in the hood,

We consider this is the most significant hydrogen hazard associated with this project.

Hydrogen Safety

Our approach to deal with this hazard is:

- The reactor will be housed in a steel barricade, which is purged with nitrogen constantly.
- The purge stream will be monitored for its flammable content to early detect any leak from the reactor.
- The room will have both CO and flammable gas monitors.
- In case of accident, the explosion will be confined within the barricade.
- The off-gas will be vented through a dilution stack at 50 to 1 ratio.

Publications and Presentations

1. Ciora, R.J., Fayyaz, B., Liu, P.K.T., Suwanmethanond, V., Mallada, R., Sahimi, M., and Tsotsis, T.T. "Preparation and Reactive Applications of SiC Membranes," *Chem. Eng. Sci.,* 59, 4957(2004).
2. R.J. Ciora Jr. and P.K.T.Liu, "Nanoporous Hydrogen Selective Membranes for Water-Gas-Shift Reaction", 20th Annual Intl. Pgh. Coal Conference, Pgh, PA, (2003).
3. R.J. Ciora Jr. and P.K.T.Liu, "Carbon Molecular Sieve Membranes for Hydrogen Separations and Production", 21st Annual Intl. Pgh. Coal Conference, Osaka, Japan, (2004).
4. R.J. Ciora Jr. and P.K.T.Liu, "Carbon Molecular Sieve Membranes for Gas Separations", AIChE Spring National Meeting, Atlanta, GA, (2005).
5. R.J. Ciora Jr. and P.K.T.Liu, "Results from Bench and Pilot Scale Testing that Demonstrate the Superior Performannce and material Stability of Inorganic Membranes over Polymeric Membranes and Competing inorganic Membranes: Applications in Hydrogen recovery"", to be presented at 22nd Annual Intl. Pgh. Coal Conference, Pittsburgh, PA, (2005).
6. Fayyaz, B., Harale, A., Park, B.G., Liu, P.K.T., Sahimi, M., and Tsotsis, T.T., Design Aspects of Hybrid Adsorbent-Membrane Reactors (HAMR) for Hydrogen Production," *In Press Ind. Eng. Chem. Res.*