Carbon Molecular Sieve Membrane as Reactor for Water Gas Shift Reaction

DE-FG36-05GO15092

PDP 9

Paul KT Liu
Media and Process Technology Inc.
1155 William Pitt Way
Pittsburgh, PA 15238
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Overview

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

- Barriers

☐ **Total project funding**
  - DOE Share: $1,530,713.
  - Contractor Share: $382,678.

☐ **Funding received in FY05**
$100K

☐ **Funding received in FY06**
$200K

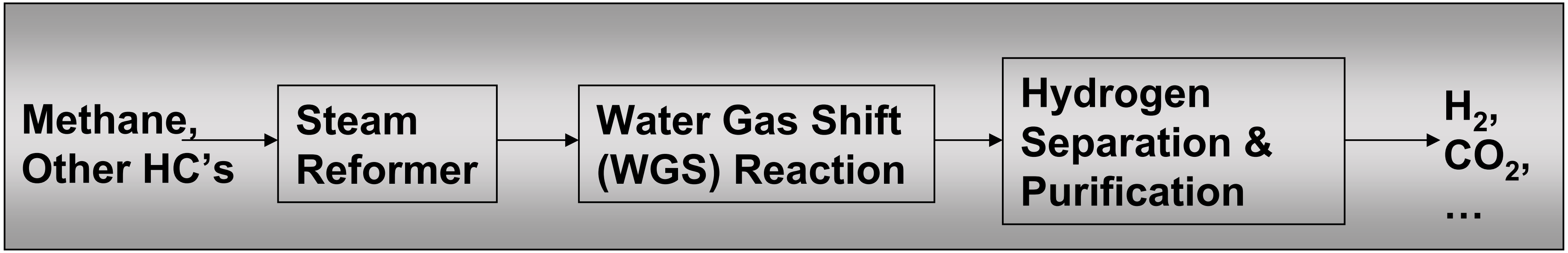
☐ No catalyst development activities due to funding reduction in FY05&06

☐ **Professor Theo T. Tsotsis**
University of Southern California,
Catalytic membrane reactor expert

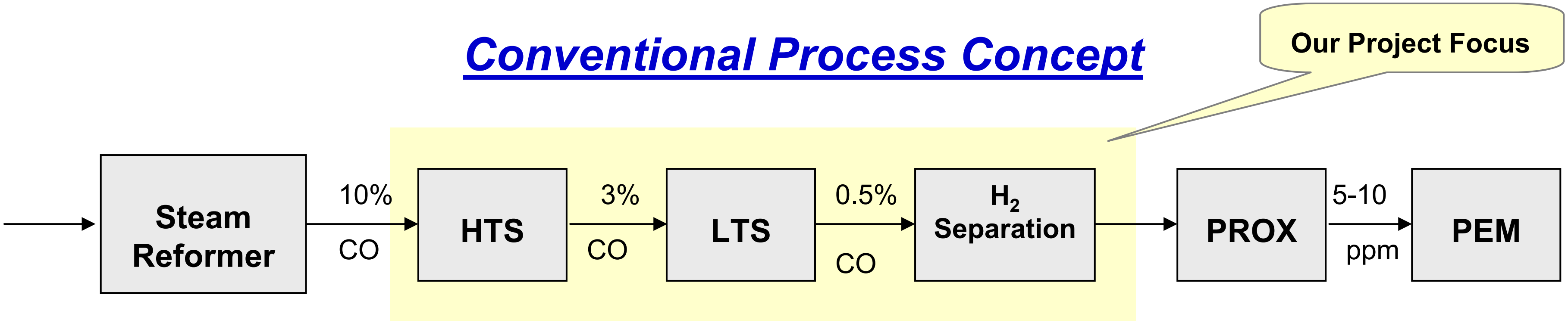
☐ **Dr. John Wind**, Chevron ETC.
End User Participant

☐ **Dr. Hugh Stitt,** Johnson Matthey
Catalyst Manufacturer

Hydrogen Production from Steam Reforming



Conventional Process Concept

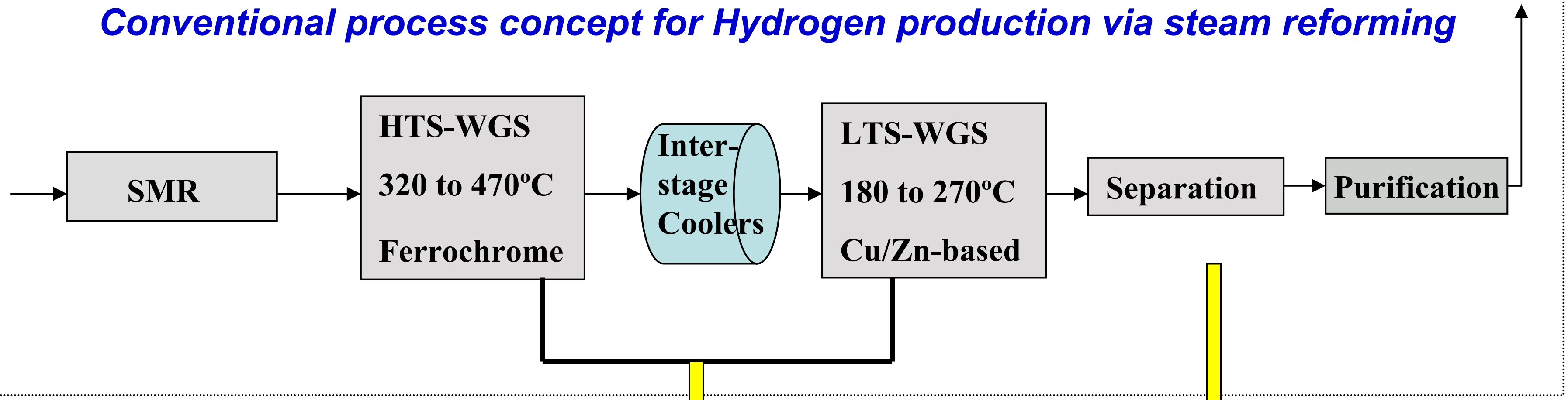


$$CO + H_2O \longrightarrow CO_2 + H_2$$

HTS: High Temperature Shift; LTS: Low Temperature Shift; PROX: Preferential Oxidation; PEM: Fuel Cell

Project Objective:
Process Intensification & Production Efficiency Enhancement for Distributed Hydrogen Production Use

Conventional process concept for Hydrogen production via steam reforming



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

2. Integrate separation/ purification into the reaction step

A "single stage" combining shift reaction, hydrogen separation and purification with built-in thermal management

Overall Technical Approach

1. Bench-Scale Verification (1st to 15th month)	2. Pilot Scale Testing (16-24th Month)	3. Field Demonstration (25 to 36th month)
1.1 Evaluate membrane reactor: use existing membrane & catalyst via math simulation	2.1 Prepare membranes, module, and housing and catalyst for pilot 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	3.2 Site preparation and installation
1.3 Validate membrane reactor performance & economics	2.3 Perform economic analysis and tech evaluation	3.3 Perform field test
	2.4 Prepare field testing	3.4 Conduct system integration study
		3.5 Finalize economic analysis & refine performance simulation

▨ Technology development team 🟨 End user participant

Technical Approach – Yr I

- ❑ **Evaluate Existing Components for Proposed Membrane Reactor (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 low steam concentrations*
      - – *Reaction kinetic expression under the proposed operating temperature and pressure*.
    - *Membrane reactor configuration study*
  - ✓ Membrane Reactor Process Evaluation
    - *Refining 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 MR Evaluation**
  - ✓ Refine membrane performance to meet the performance criteria defined above
  - ✓ Fabricate an MR and establish peripheral hardware for lab study
  - ✓ Perform bench-top experimental study to demonstrate the proposed LTS-WGS-MR and verify the mathematical model established.

- ❑ **Technology Verification, Validation and Preliminary Economic Analysis by End Users**
  - ✓ Evaluate membrane performance simulating actual streams available at refinery
  - ✓ Refine mathematical model based upon pilot test results
  - ✓ Conduct economic analysis

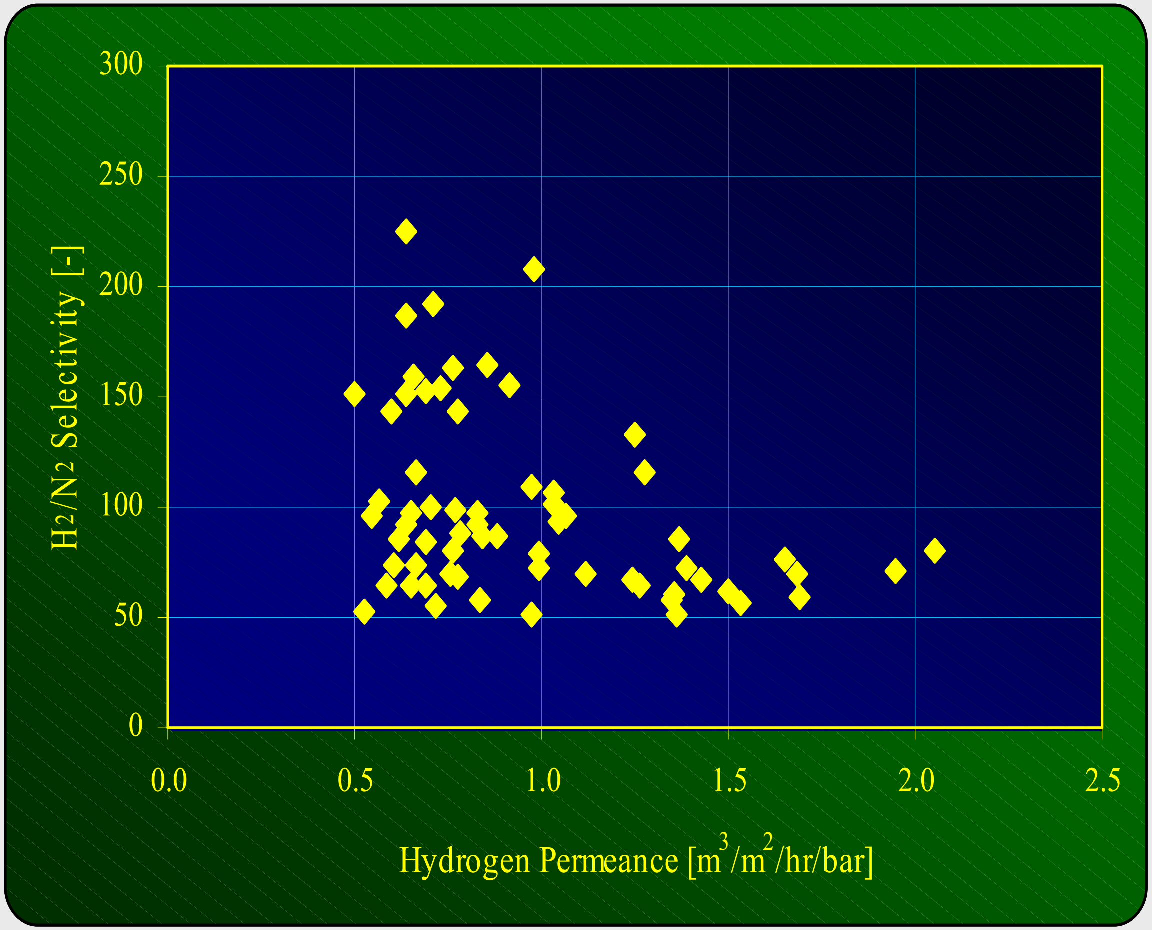
OVERALL TECHNICAL ACCOMPLISHMENTS/PROGRESS

- Our existing CMS membrane has demonstrated the **material stability**, i.e., thermal, hydrothermal and chemical, required for the proposed LTS/WGS reaction environment.
- A wide range of separation performance, i.e., hydrogen **permeance** of 0.5 to >2 $m^3/m^2/hr/bar$ and hydrogen **selectivity** of 50 to >100, has been generated, which is **adequate** for the proposed LTS/WGS applications.
- Our CMS membrane has demonstrated an excellent **steam permeance** (parallel to H_2 permeance), which offers an additional control variable to optimize the WGS-MR reaction, and manage the exothermic heat generated from WGS.
- Our bench-top reactor study exhibited **96% CO conversion using H_2O/CO ratio of 1.1** (vs 82% based upon thermodynamics), which matches well with the simulation results. CO contamination is <1,000 ppm and >95% hydrogen recovery can be achieved according to simulation.
- **Prototype membrane and membrane reactor (pilot scale)** have been successfully fabricated based upon our commercial membranes and housing. This MR will be used for the pilot scale test to be conducted next year.

In short the membrane and catalyst have been qualified for the proposed LTS/WGS/MR. The initial membrane reactor data supports the benefits of production efficiency improvement and process intensification potential. The bench-top membrane reactor study will be completed in this project year. A prototype membrane reactor based upon our existing commercial membrane has been fabricated for the pilot test.

TECHNICAL ACCOMPLISHMENTS/PROGRESS:

1.1 evaluate existing membranes: full-scale membranes (30"L) prepared



The specification of our CMS membranes is >0.5 $m^3/m^2/hr/bar$ and H_2/N_2 > 50 at 120°C. Evidently, the performance of our membranes produced thus far well exceeds this minimum specification. In general, the selectivity in the low 50's can be produced for the permeance of >>1-2 $m^3/m^2/hr/bar$, while selectivity >>100 can be obtained for the permeance in the range of 0.5 -1 $m^3/m^2/hr/bar$. This range of performance is adequate for the proposed reactor application.

TECHNICAL ACCOMPLISHMENTS/PROGRESS:

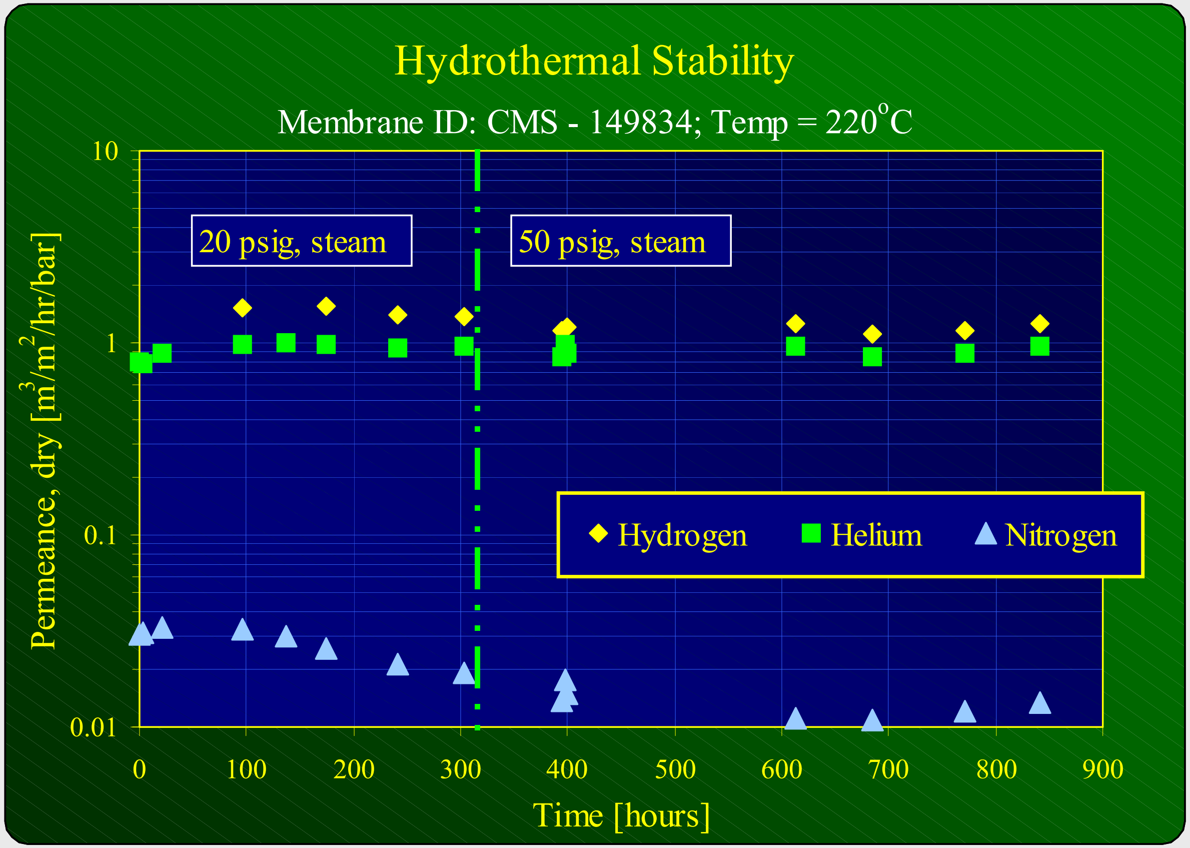
1.1 evaluate existing membranes: water permeances

Temperature [ºC]	Pressure [psig]	Water Flux [kg/m^2/hr]	Water Permeance [m^3/m^2/hr/bar]	Hydrogen Permeance [m^3/m^2/hr/bar]
DZ-149				
130	20	5.3	1.9	0.49
170	20	4.3	1.5	0.78
220	20	2.5	1.2	1.36
NN-25				
130	30	7.7	3.4	2.36
NN-404				
150	15	6.1	7.4	1.97

The excellent water permeance (parallel to its hydrogen permeation) as shown above provides us an effective, independent and unique tool to optimize the water (as a reactant) content in the reactor and to implement the thermal management in-situ.

TECHNICAL ACCOMPLISHMENTS/PROGRESS

1.1 evaluate existing membranes: performance stability under the proposed environment



Long term thermal, hydrothermal and chemical stability demonstrated in both bench and field tests.

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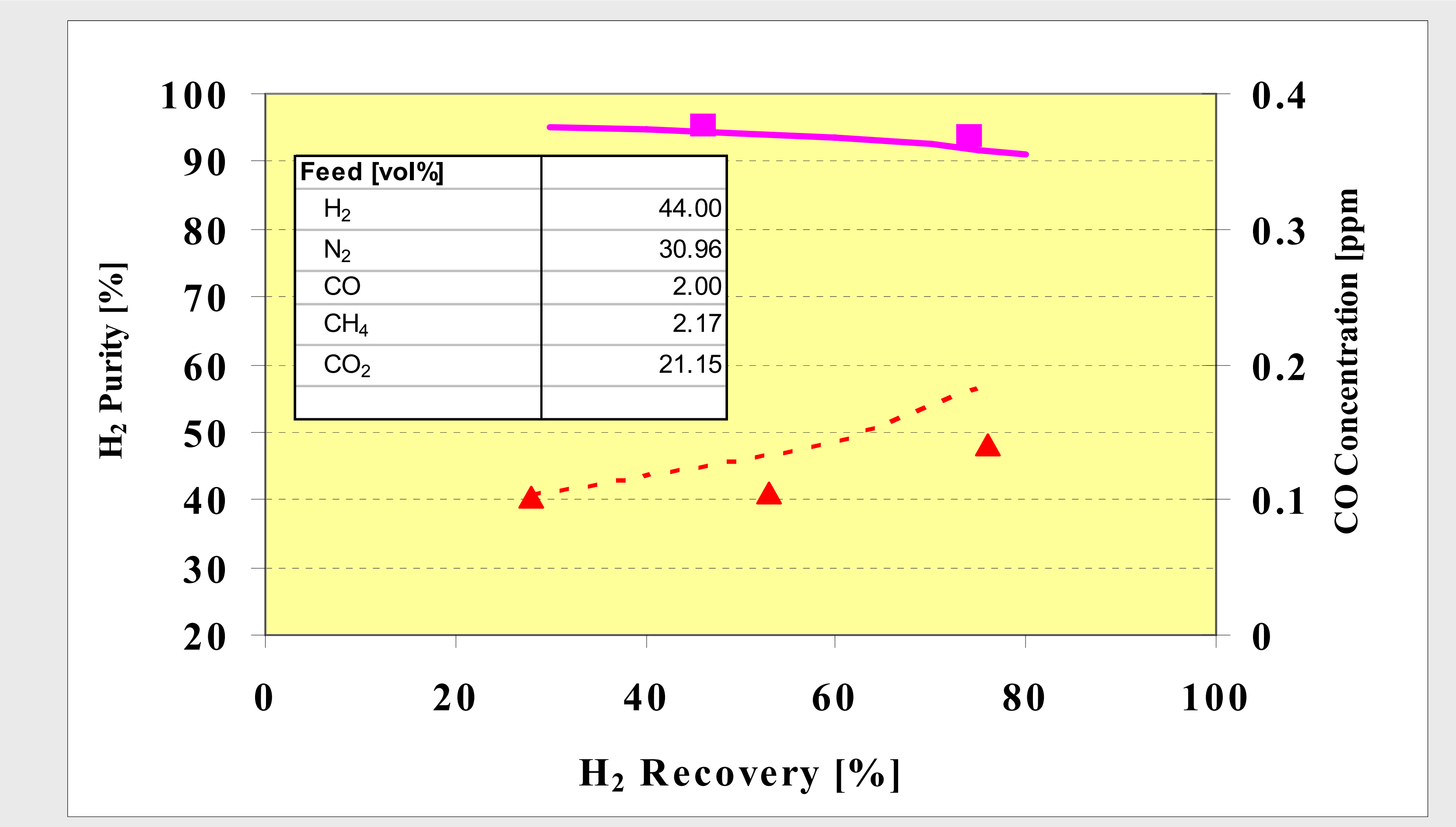
TECHNICAL ACCOMPLISHMENTS/PROGRESS:

1.2 experimental verification: separation of synthetic reformate

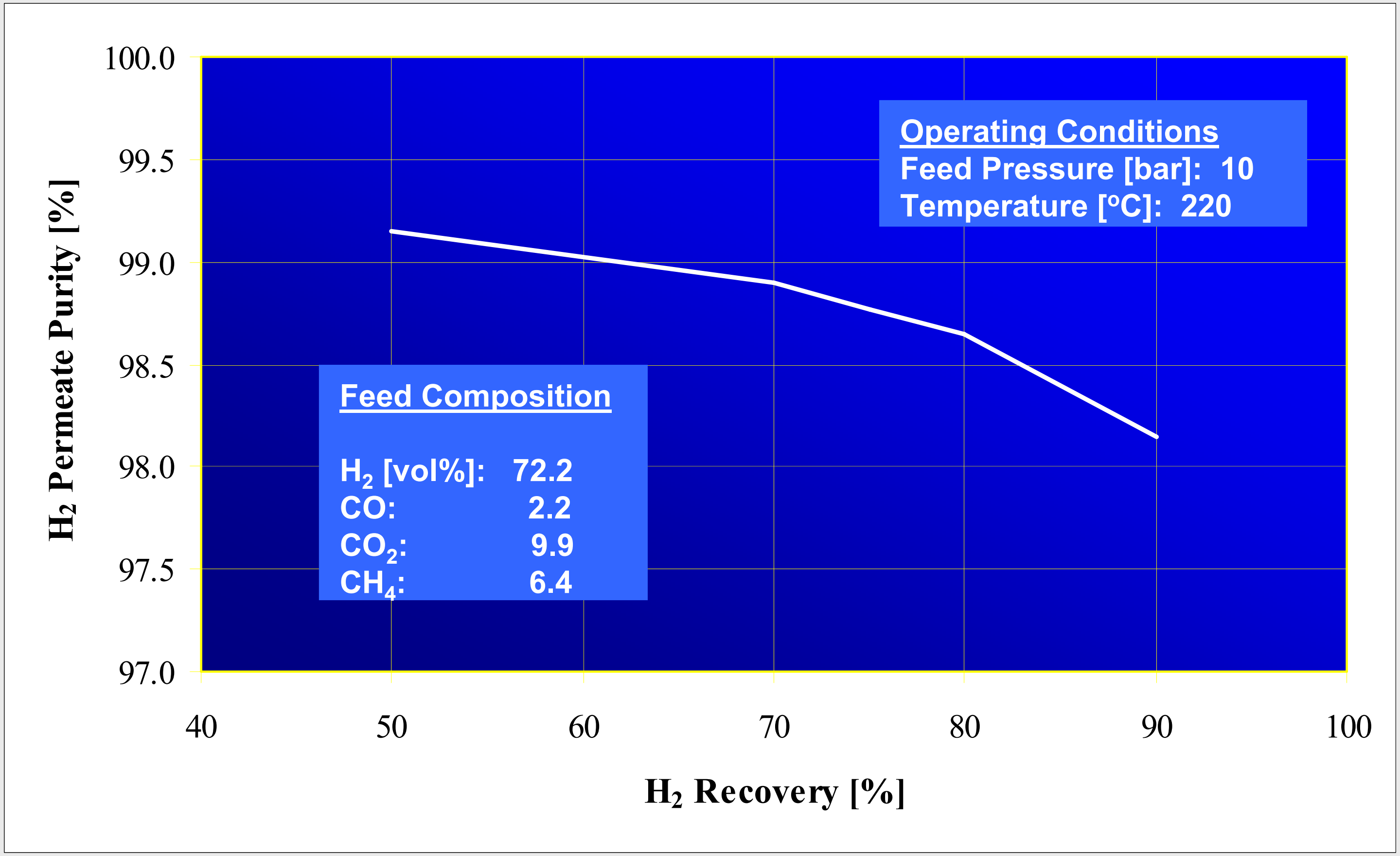


Feed [vol%]	
H_2	44.00
N_2	30.96
CO	2.00
CH_4	2.17
CO_2	21.15

The performance of our CMS membrane was demonstrated in mixture separation using a synthetic reformate shown above. Further, our mathematical model can reliably predict the permeate composition vs H_2 recovery.

TECHNICAL ACCOMPLISHMENTS/PROGRESS:

1.2 experimental verification: separation of a representative stream in LTS/MR



Operating Conditions

Feed Pressure [bar]: 10
Temperature [°C]: 220

Feed Composition

H_2 [vol%]: 72.2
CO: 2.2
CO_2: 9.9
CH_4: 6.4

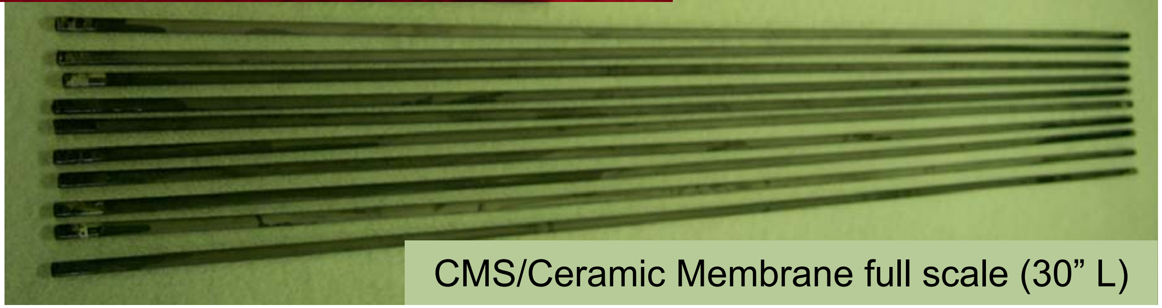
Our simulation shows that high purity hydrogen can be produced for a wide range of hydrogen recovery from a representative synthetic reformate

TECHNICAL ACCOMPLISHMENTS/PROGRESS:

1.2 experimental verification: pilot and full-scale CMS membrane and module preparation

Pilot Scale Module CMS/Ceramic Membrane (1.5” diameter and 30”L)

Our commercial ceramic membrane modules for gas (left) and liquid (below) applications



CMS/Ceramic Membrane full scale (30” L)

Pilot scale CMS module and full-scale CMS membrane tubes have been successfully fabricated and evaluated. These membranes and modules were adapted from our existing commercial ceramic membrane products and modules. Thus, the membrane and reactor for the pilot scale test and full-scale demonstration can be developed without difficulty.

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TECHNICAL ACCOMPLISHMENTS/PROGRESS:

1.2 experimental verification: via bench-scale reactor

T = 250°C

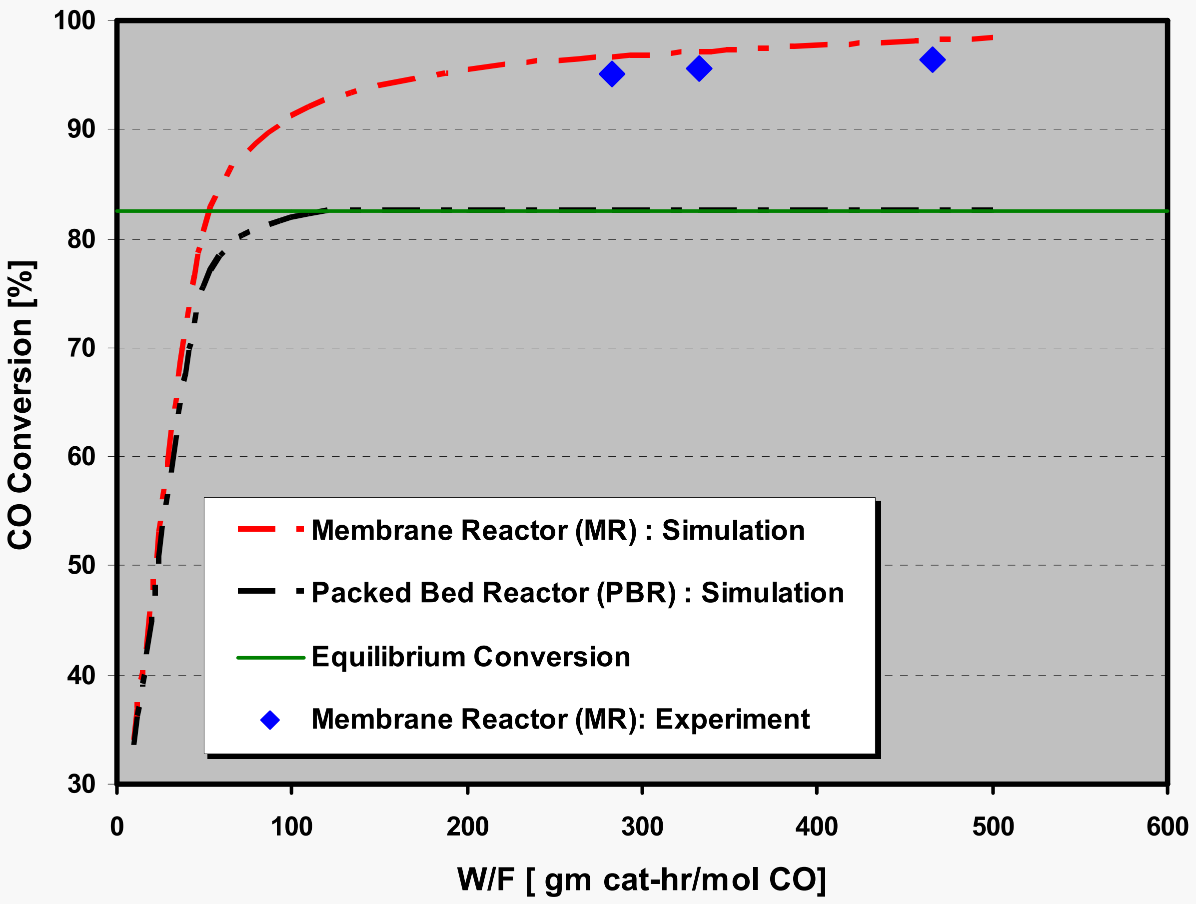
P_{feed} = 3 bar

P_{perm} = 1 bar

Feed Composition:
H_2:H_2O:CO = 4:1.1:1

Permeance $[m^3/m^2/hr/bar]$:
H_2: 1.67,
CO: 0.04,
H_2O: 2.02

Sweep Ratio: 0.1

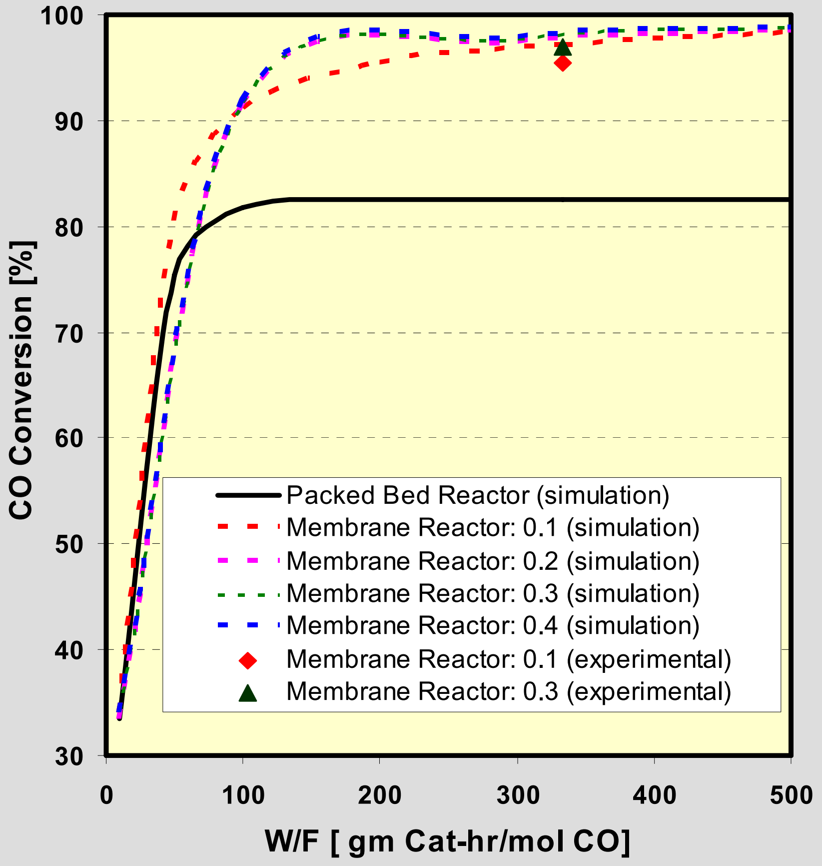


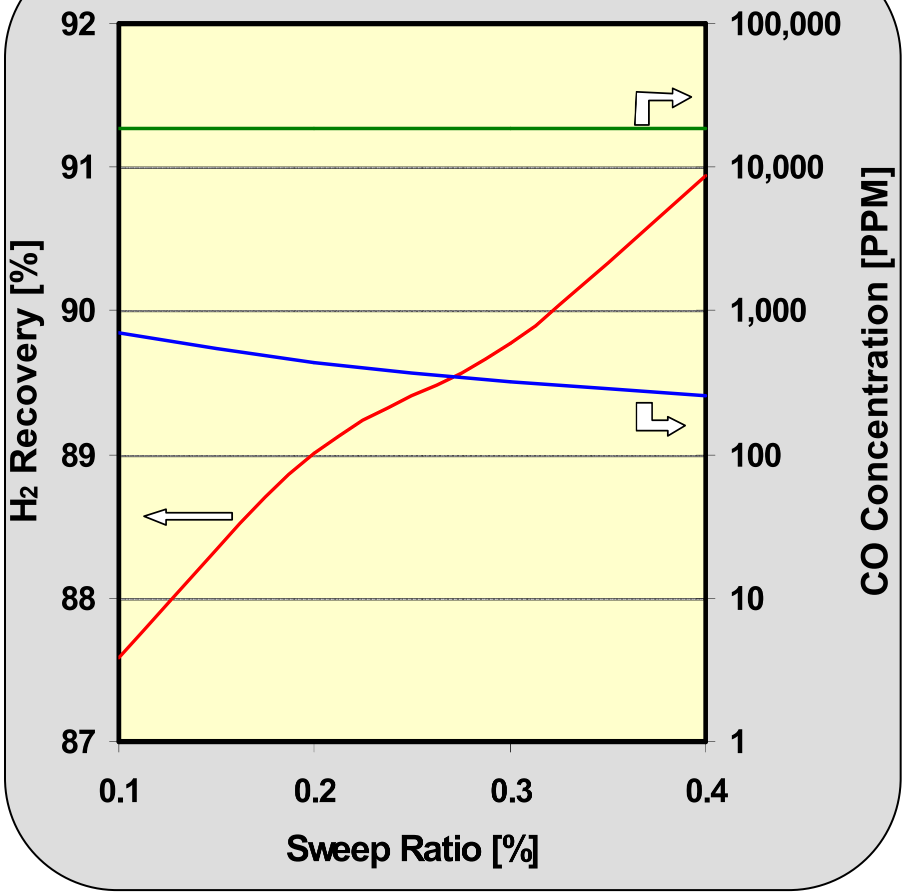
Membrane reactor shows ~14% enhancement in CO conversion over the equilibrium using a typical reformate as feed and a nearly stoichiometric H_2O to CO ratio. Our simulation results match well with the experimental results obtained thus far.

TECHNICAL ACCOMPLISHMENTS/PROGRESS:

1.2 experimental verification: membrane reactor performance evaluation (simulation)

Feed: CO:H2O:H2=1:1.1:4, 250ºC, 3 bar, H_2 permeance = 2.02 m^3/m2/hr/bar, H_2/CO = 53





The sweep ratio of 0.3 appears sufficient. 90% hydrogen recovery and <500 ppm CO can be produced vs 20,000 ppm CO for the packed bed according to the simulation.

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Future Work

Remainder of FY 2006

- Complete mathematical simulation
  - incorporating temperature profile to simulate the non-isothermal single stage reactor,
  - demonstrate the temperature control strategy via steam permeable CMS membrane, and
  - complete experimental study to verify the model prediction.
- Confirm gas separation efficiency using a pilot scale (about 1 m^2) reactor.
- Validate the performance results and meet the economic projection by end user.

FY 2007 & 2008

- Conduct pilot scale LTS-WGS-MR test using the pilot scale membrane reactor developed in FY2006 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.
- Prepare and conduct a field test to demonstrate the distributed hydrogen production process and economics by our end user participant.

SUMMARY

Why Membrane Reactor (MR)

MR has been identified as an innovative process concept because it can enhance production efficiency and streamline the unit operation requirement.

Commercialization Barriers of MR

- No membranes have demonstrated their adequacy in terms of functional performance and material stability. These requirements are dependent upon the reaction candidate.
- No MR configuration and hardware have been offered suitable for field usage.

Our Project Team Mission

Our project team composed of a membrane manufacturer, a catalyst manufacturer, an end user and an academic institute is well positioned to overcome this barrier.

Our Focus and Accomplishments

- Qualified each technical component of the MR for one-stage WGS, we have
  - Evaluated the full-scale membrane performance.
  - Confirmed the material stability under a simulated environment.
  - Experimentally verified a high degree of CO conversion
  - Demonstrated its significant enhancement over the conventional reactor.
- Demonstrated the technical feasibility of the hardware aspect of the MR.

Combining the positive results from (i) the qualification of the technology components and (ii) the verification of commercially viable MR hardware, we are confident in moving the MR technology to the next phase of the pilot scale study.

Publications and Presentations

1. R.J. Ciora Jr. and P.K.T.Liu, “Carbon Molecular Sieve Membranes for Gas Separations”, AIChE Spring National Meeting, Atlanta, GA, (2005).