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

DE-FG36-05GO15092

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PD7

Overview

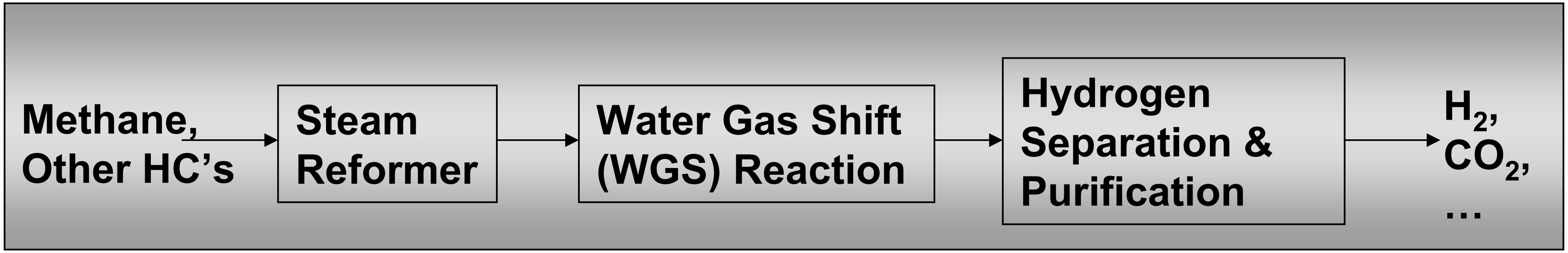
- **Project Start Date**
  10/1/03
- **Project End Date**
  9/30/07
- **Percent Complete**
  80%

- Delivery of 99.999% H_2 with high H_2 recovery ratio
- Fabrication of membranes/ module suitable for large scale reactor operation
- Demonstration of the membrane reactor process in a significant scale

- **Total project funding**
  - DOE Share: $1,530,713.
  - Contractor Share: $382,678.
- **Funding received in FY05 & FY06**
  $300K
- **Funding received in FY07**
  $200K
- No catalyst development activities due to funding limitation

- **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

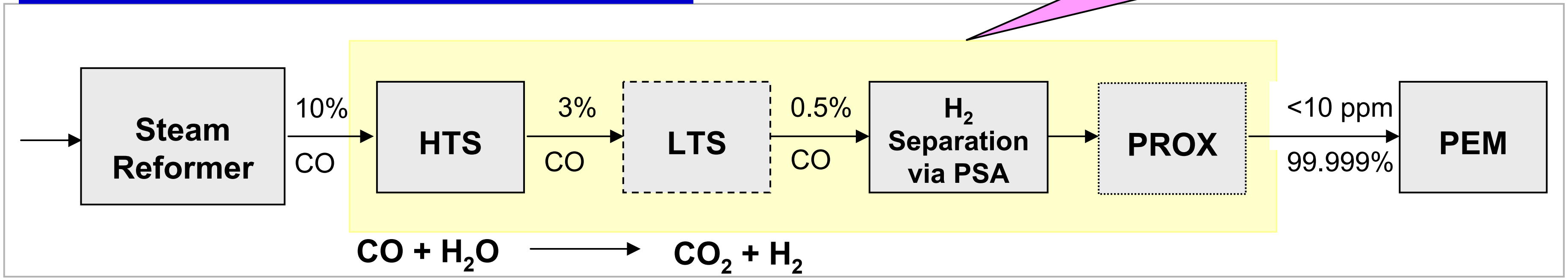
Hydrogen Production from Steam Reforming


Methane, Other HC's → **Steam Reformer** → **Water Gas Shift (WGS) Reaction** → **Hydrogen Separation & Purification** → H_2, CO_2, …

Our Project Focus

Streamline Unit Operations involving CO Conversion/H_2 Separation & Purification

Conventional Process Concept



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

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

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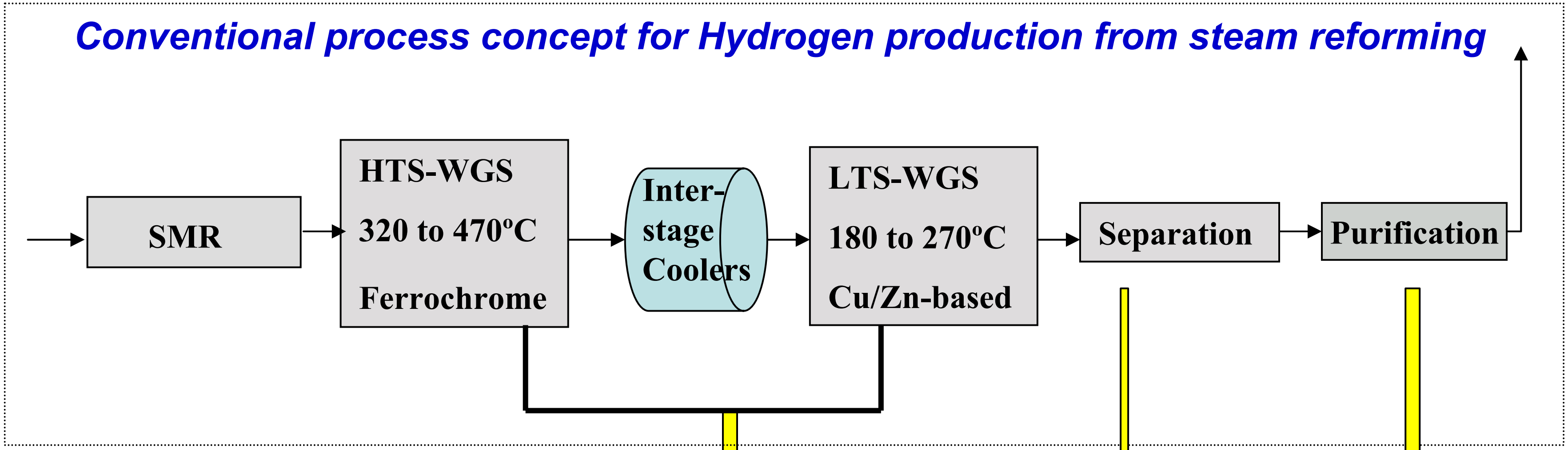
OVERALL TECHNICAL STRATEGY



Conventional process concept for Hydrogen production from steam reforming

SMR

HTS-WGS
320 to 470°C
Ferrochrome

Inter-stage Coolers

LTS-WGS
180 to 270°C
Cu/Zn-based

Separation

Purification

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

*2. Integrate H_2 separation into the reaction step to deliver **high purity H_2 with high recovery ratio***

*3. Develop a cost acceptable polishing step **compatible** with our proposed MR process.*

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 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 Prepare site and install reactor
1.3 Validate membrane and membrane reactor performance & economics	2.3 Perform economic analysis & technical 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 II

☐ Perform <u>Bench-Top MR</u> Evaluation

✓WGS Catalyst evaluation under the proposed operating condition

✓Perform MR experiment to verify the prediction of H_2 purity, H_2 recovery and residual CO contaminant by our mathematical model in addition to CO conversion, which was verified in Year I.

☐ Tailor <u>Membrane Performance</u> for Proposed MR-based H_2 Production Process.

✓Refine existing H_2 selective membranes required for the MR selected for scale-up.

- *hydrogen permeance, and selectivity over CO and CO.*

☐ Perform <u>Process Optimization</u> via Simulation for Economics Analysis

✓Identify an optimized MR configuration and operating condition to match the reformer technology developed by our end user participant (Chevron).

✓Identify a post treatment configuration to deliver >99.999% hydrogen with <10 ppm CO.

☐ Conduct <u>Pilot Test</u> to Verify the Optimized Process

✓Using a simulate stream and a full-scale (34"L) single membrane tube for this pilot test.

☐ Conduct <u>Technology Validation and Economic Analysis</u> by End User

✓Evaluate membrane performance

✓Refine mathematical model based upon pilot test results

✓Conduct economic analysis

TECHNICAL ACCOMPLISHMENTS – Yr II

❑ Experimental Verification of Mathematical Model

Our MR experimental study has delivered H_2 purity, H_2 recovery ratio, and residual CO contaminant level consistent with prediction by our model. In addition, the effect of reactor temperature has been verified experimentally.

❑ Development of A MR-based H_2 Production Process – HiCON

The HiCON process has been developed for the small scale reformer developed by our end user participant (Chevron). A nearly complete CO conversion (i.e., 99+%) can be realistically achieved in contrast to ~70% conversion by HTS and ~95% by HTS + LTS with the conventional reactors.

❑ Optimization via Simulation

Process optimization study demonstrates that 97-99% H_2 purity and 98-75% H_2 recovery can be accomplished.

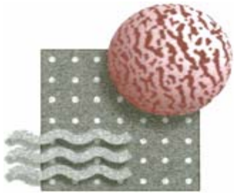
❑ Development of A Simple & Cost Effective Polishing Step

Instead of PROX, a simple adsorptive process can be installed as a polishing step for HiCON. Thus, 99.999% H_2 purity and <10 ppm CO can be accomplished. Our preliminary economic analysis indicates nominal cost, e.g., 2-4¢/kg H_2,.

❑ Facility & Safety

A barricade has been established ready for performing the proposed HiCON process at a pilot scale.

In short, we have completed the bench top experimental study and mathematical simulation. The HiCON process has been developed to meet the PEM fuel spec. We are now ready for pilot testing to be performed during the remaining FY2007.

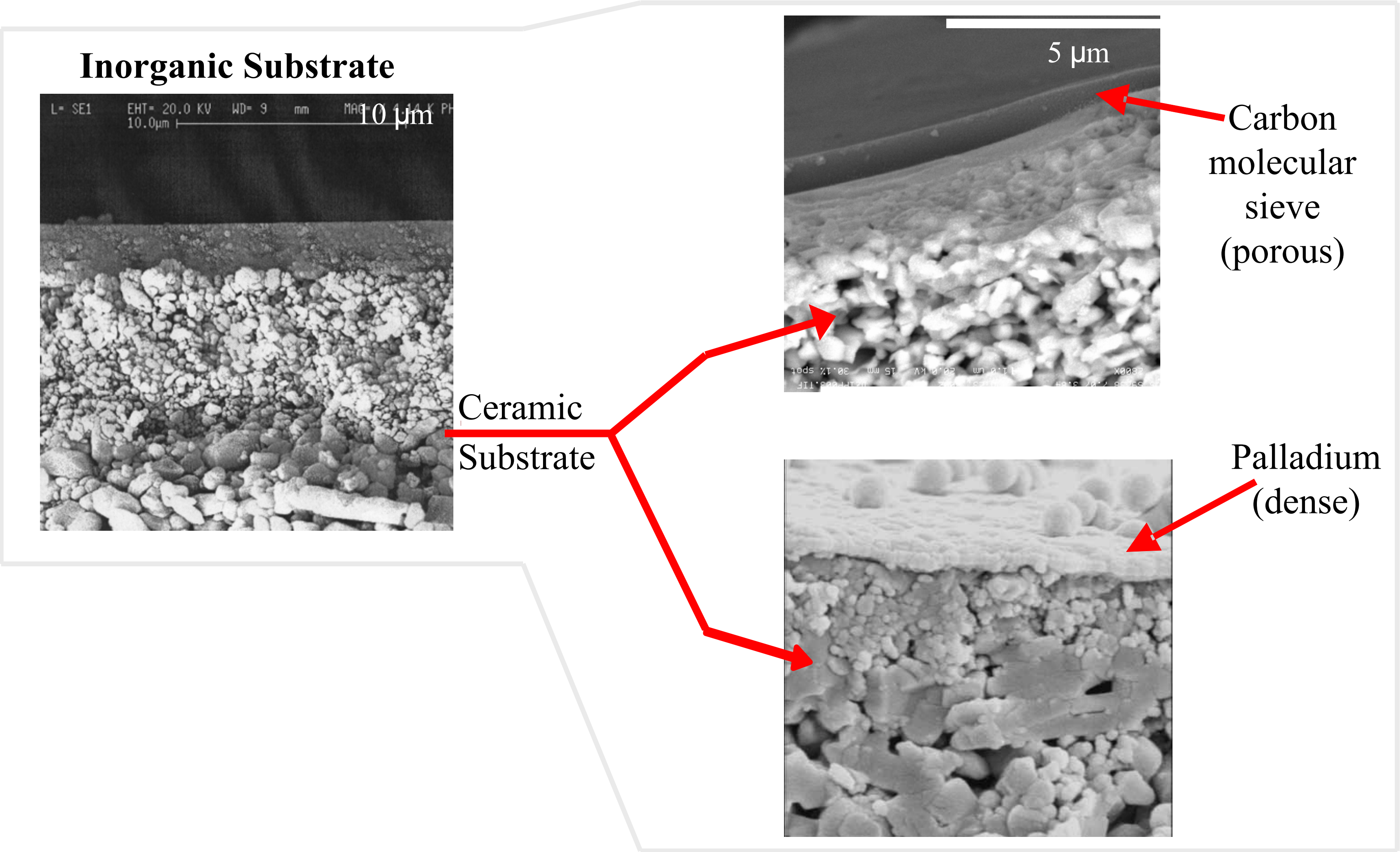


M&P Ceramic MEMBRANES - Low cost

Our Commercial Ceramic Membranes/Bundles and their Substrate

M&P Emerging Inorganic Membranes

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



Inorganic Substrate

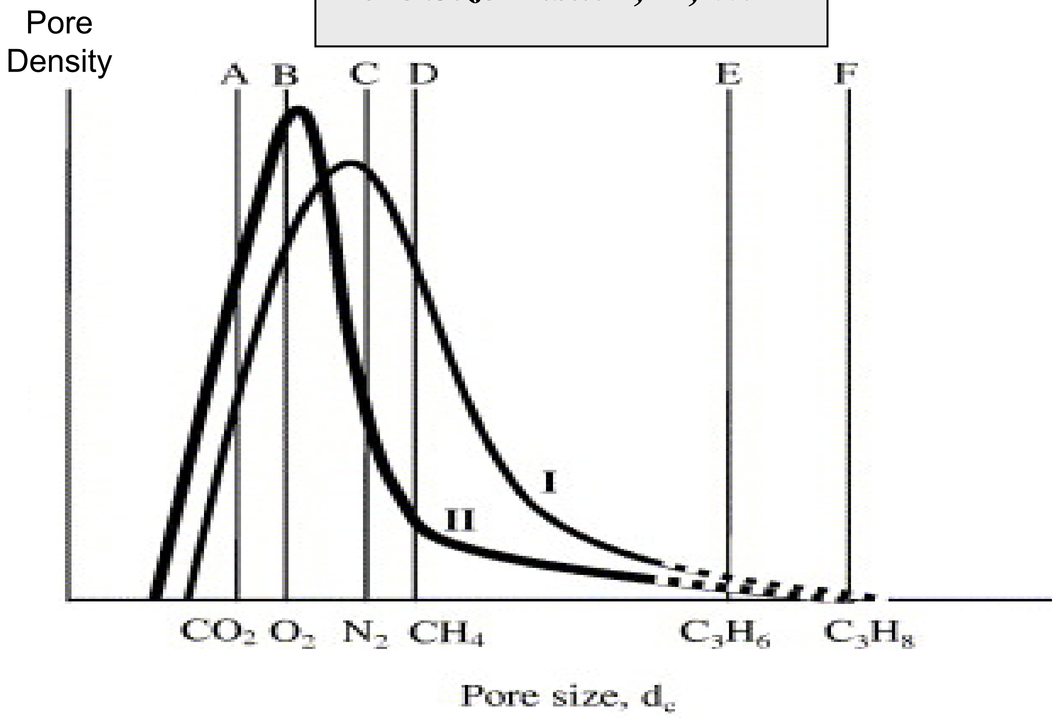
Ceramic Substrate

Carbon molecular sieve (porous)

Palladium (dense)

Carbon Molecular Sieve (CMS) Membranes

Typical CMS Membrane Pore Size Dist.: I, II, …



Unique Features

- ***Operating Temperature***
- ***Selectivities***
- ***Material Stability***

CMS Membrane Performance Upgrading – Yr II

Accomplishment: Enhanced H_2/CO & H_2/CO_2 selectivities without sacrificing H_2 permeance

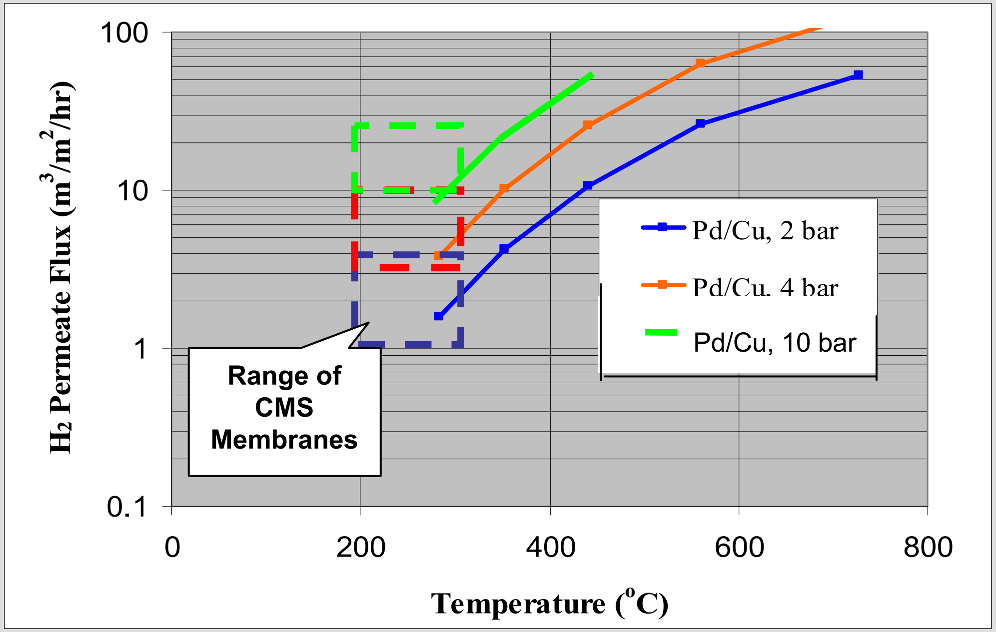
M&P CMS H_2 Selective Membrane

Typical Hydrogen Permeance:
1-3 $m^3/m^2/hr/bar$ at 220°C

Typical Selectivities:

Gas Molecules	Kinetic Diameter [Å]	Selectivity over N_2 at 220°C
H_2	2.89	1
CO_2	3.30	10 to 40
N_2	3.64	40 to >80
CO	3.76	50 to >90
CH_4	3.80	60 to >100

CMS vs Pd Alloy Membranes

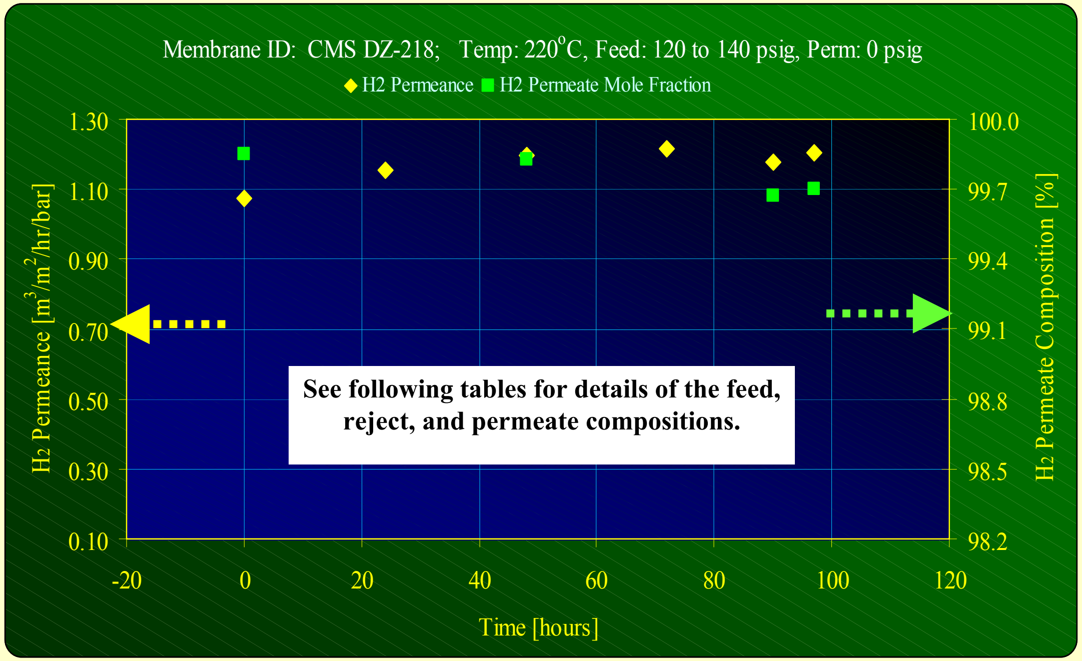


- Assuming 1 micron thickness of Pd/Cu membrane,
- Permeate flux data source: Morreale, B.D., etc, *JMS,* 241(2004) 219
- Feed Pressure as indicated, Permeate Pressure: 1 atm

During Yr II we have tailored our CMS membrane with the properties above to suite the proposed MR application requirements. Its thermal, hydrothermal and chemical stability under the proposed application environment was demonstrated in Yr I.

CMS Membrane: Material Stability at a Pilot Test

Membrane performance is stable in a 100 hour challenge test conducted at a refinery pilot facility using VGO hydrocracker off-gas in the presence of significant H_2S, NH_3, and higher hydrocarbon contamination.



See following tables for details of the feed, reject, and permeate compositions.

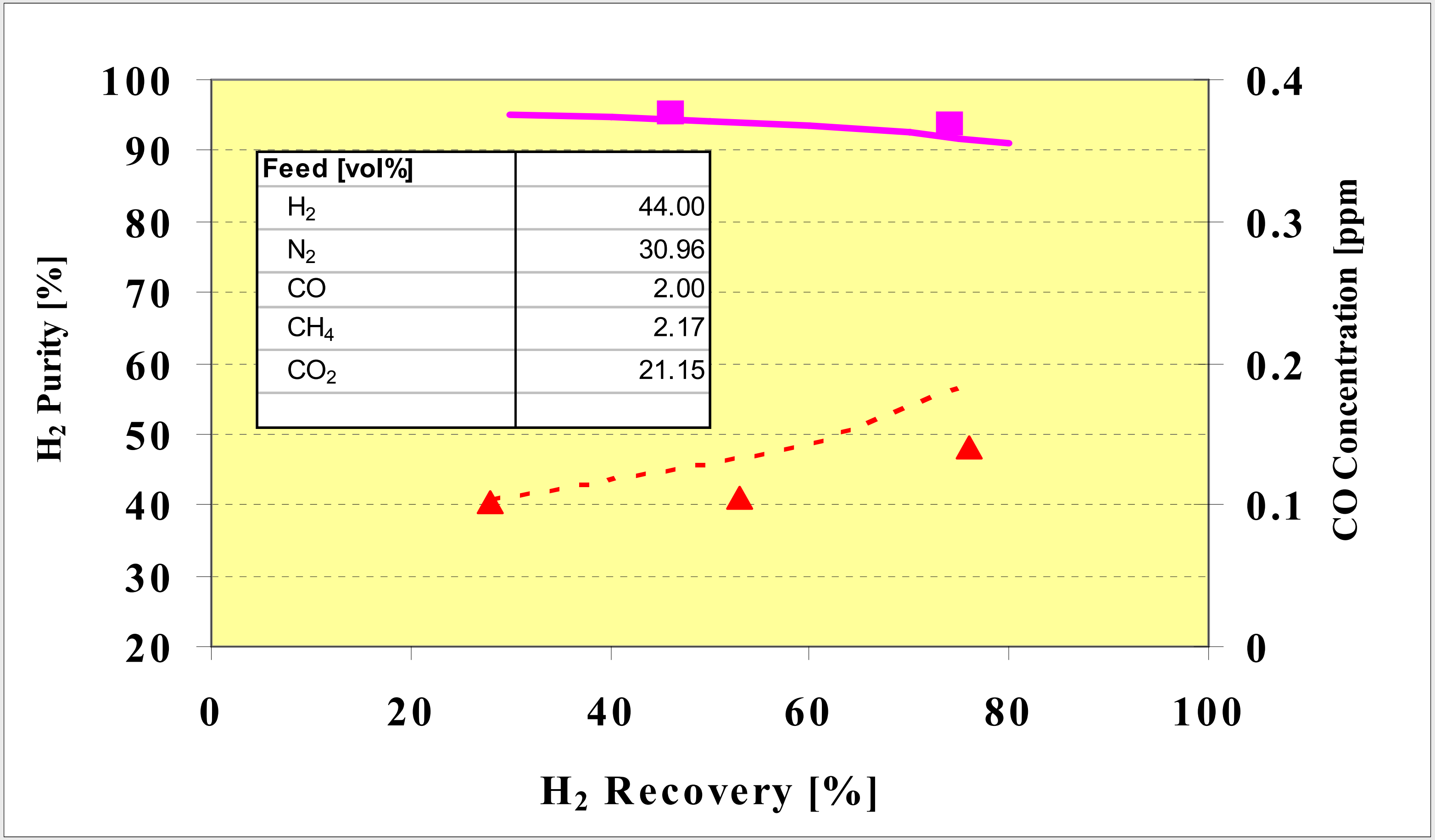
Gas Stream Compositions, Stage Cut and H_2 Recovery During the VGO Hydrocracker Pilot Test

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%**		

Experimental Verification:

Mixture Separation vis CMS Membranes



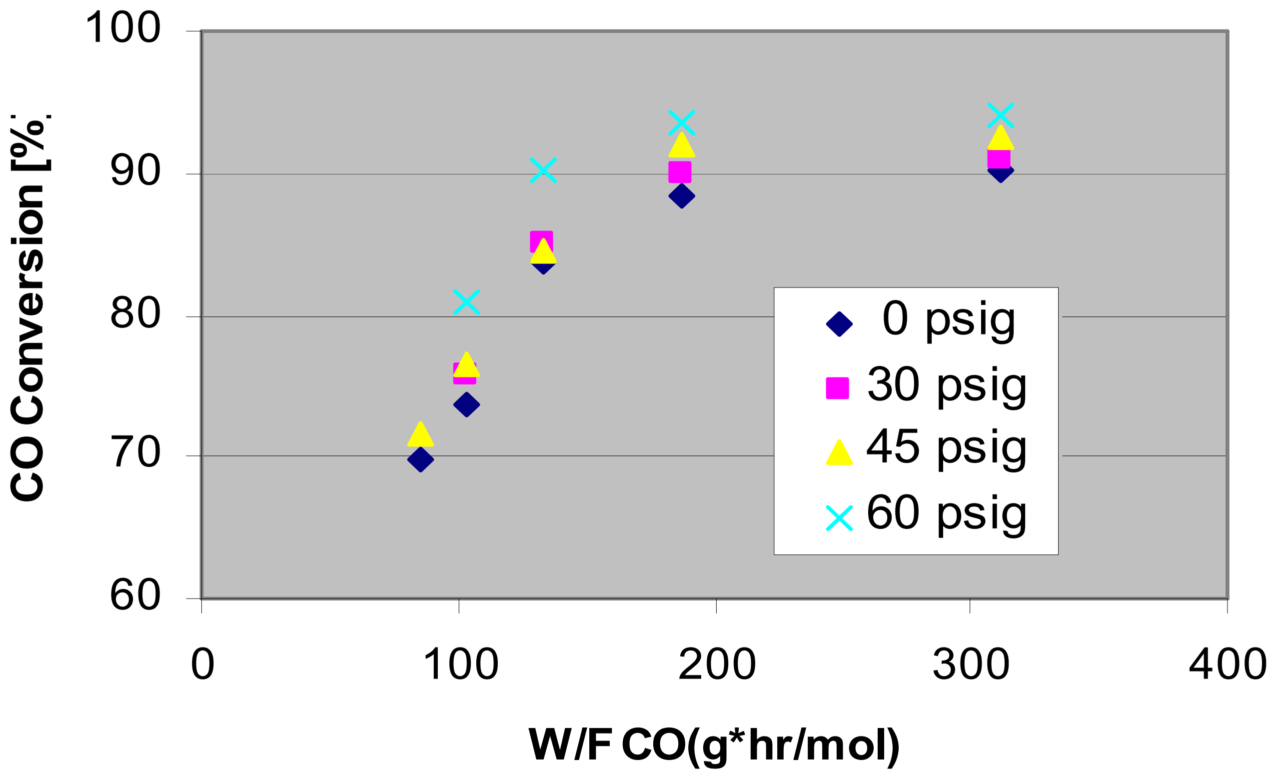
Feed [vol%]	
H_2	44.00
N_2	30.96
CO	2.00
CH_4	2.17
CO_2	21.15

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.

Water Gas Shift Reaction Kinetic Study

Cu/Zn catalyst: CO Conversion vs Pressure

$T = 250^{o}C$, $P_{feed} = 1$ to 5 atm, Feed Composition: $H_2:H_2O:CO:CO2 = 5:3:1:0.5$



$$\text{Rate} = k_0*(1-\text{Beta})*(P_{CO})*(P_{H2O})^{1.8}(P_{CO2})^{-1.4*}(P_{H2})^{-0.5*}P_t^{-0.8}$$

Rate constant suitable for the proposed application environment was determined, which has been used for our simulation study.

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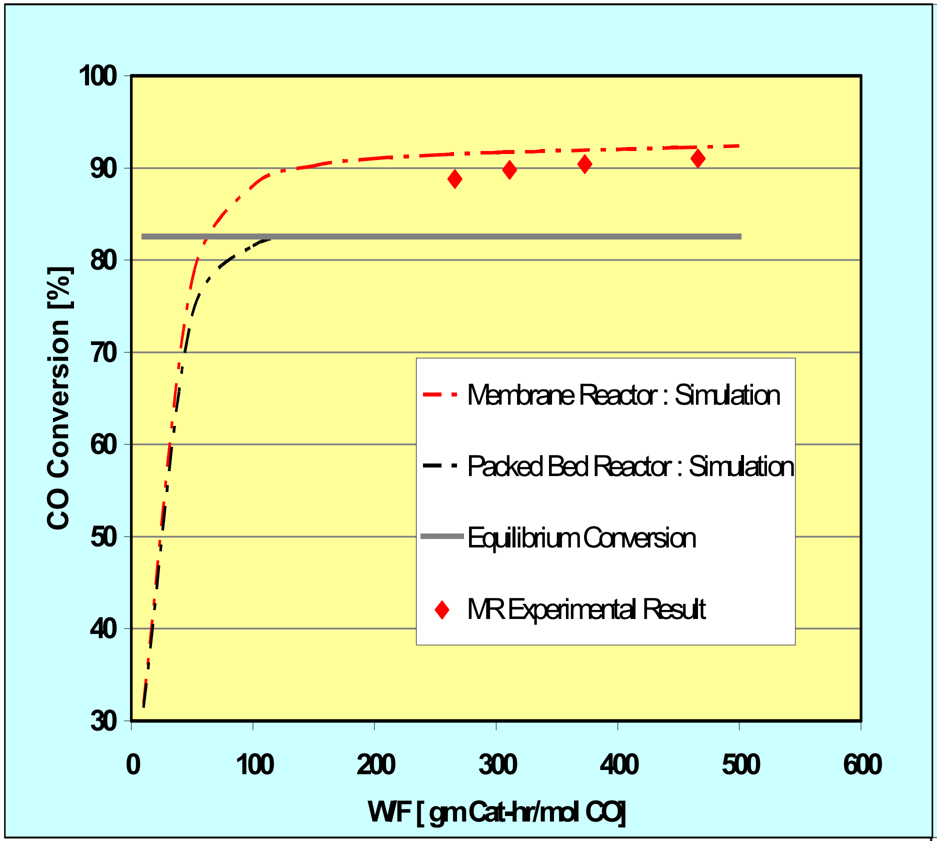
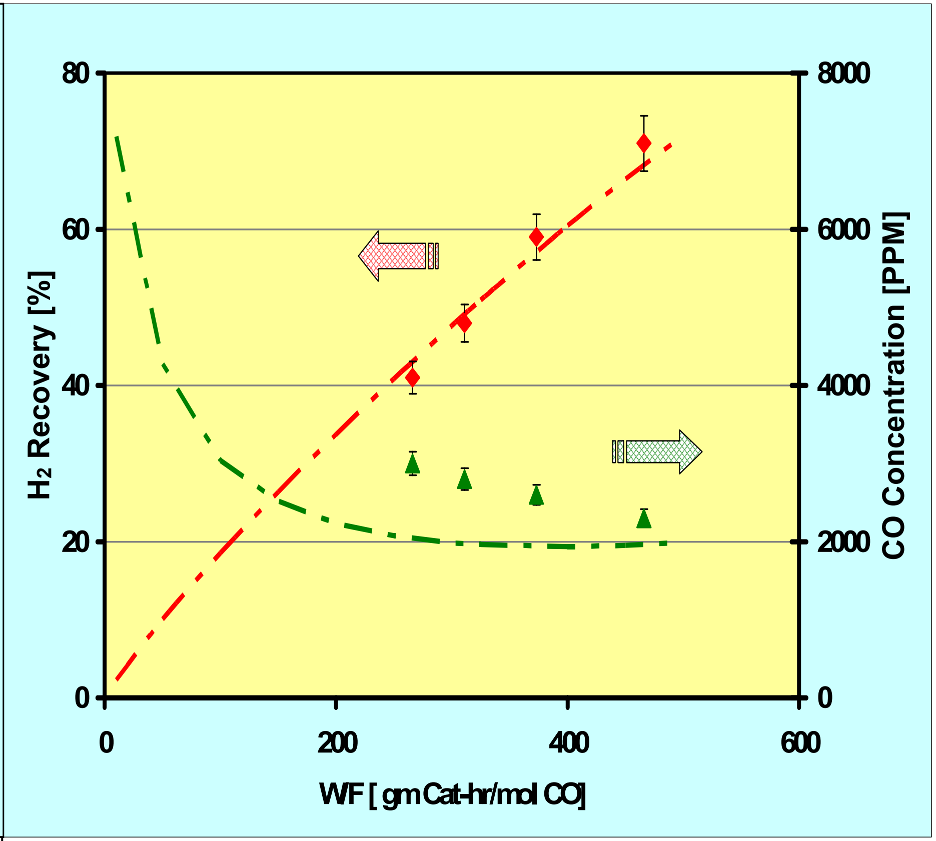
Bench Top Membrane Reactor Study: Experimental vs Simulated





CO Conversion vs W/F

H_2 Recovery, CO Concentration vs W/F

W/F: Ratio of Catalyst Dosage to Feed FlowRate

Our prediction on CO conversion, H_2 recovery and CO residual level was verified with experimental results obtained from our bench top membrane reactor.

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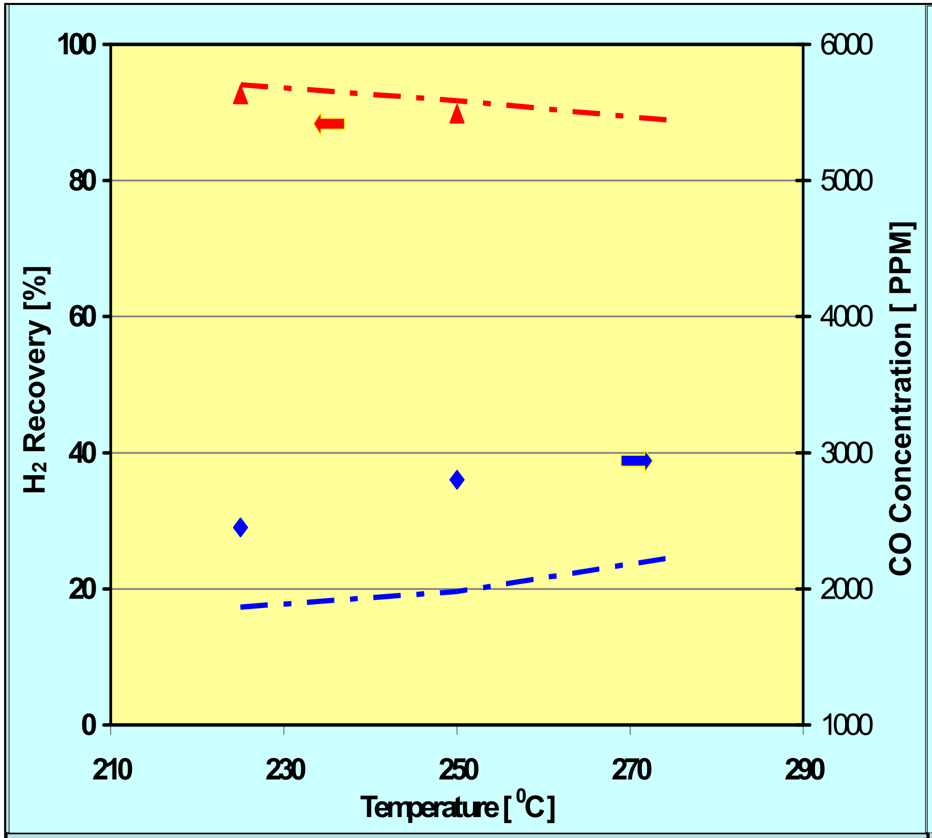
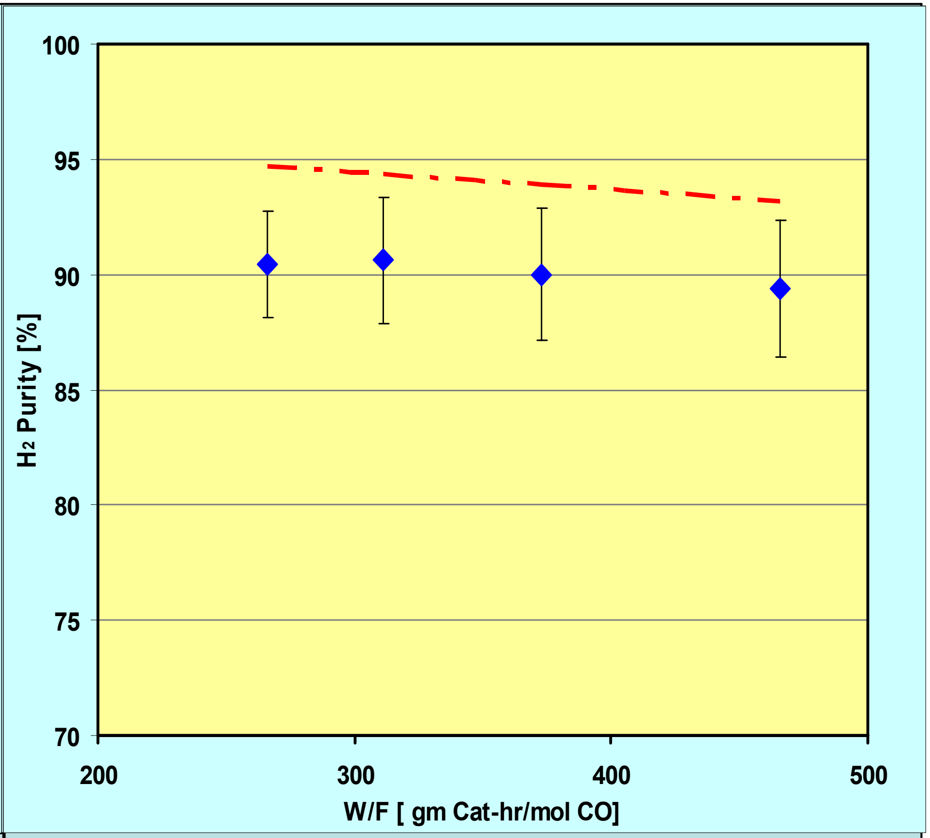
Bench Top Membrane Reactor Study

Experimental vs Simulated & Verification of Mathematical Model



H2 Recovery & CO Conc. vs W/F



H_2 Purity vs W/F

Our prediction on H2 purity and effect of temperature was verified with experimental results obtained from our bench top membrane reactor.

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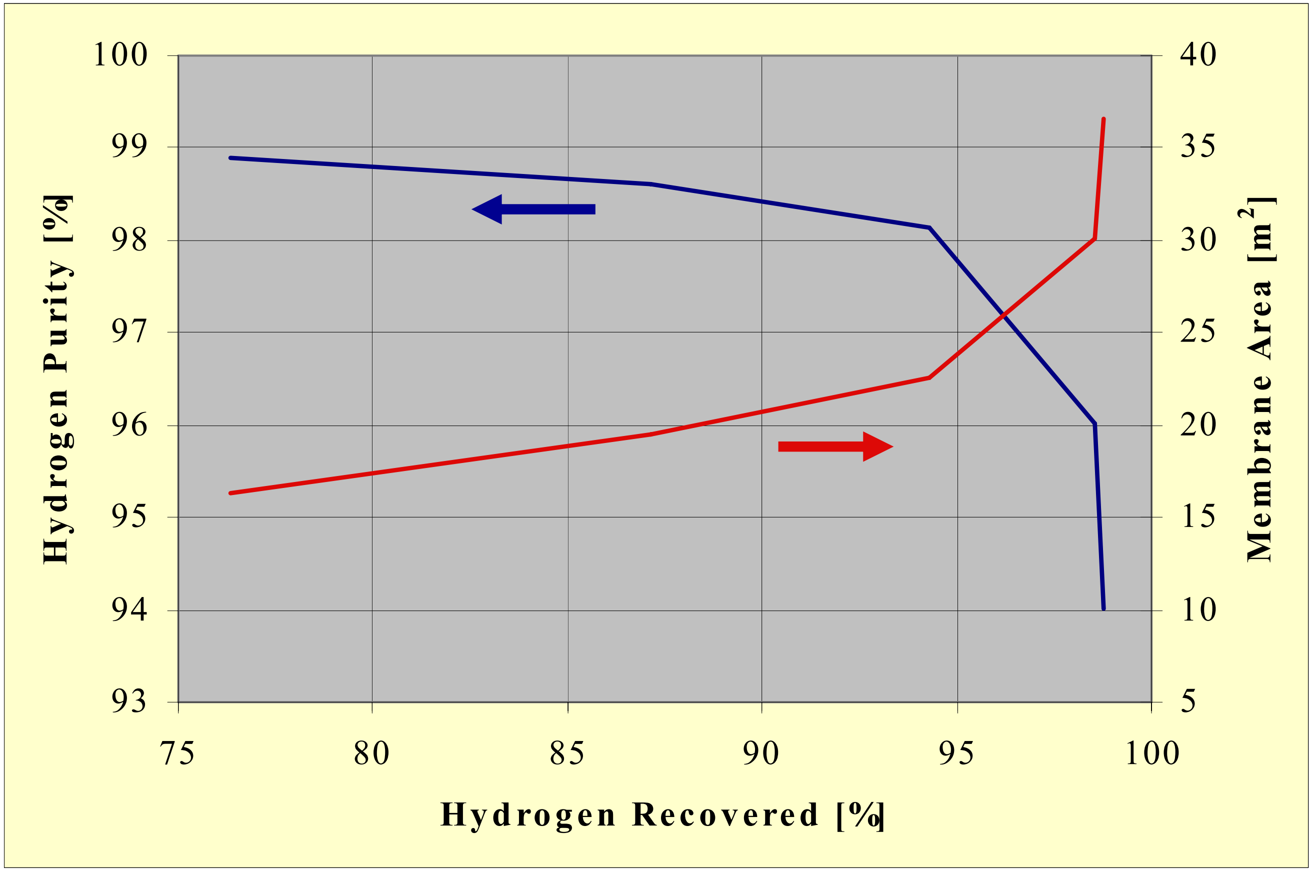
Performance of Our Proposed Membrane Reactor Process

via Mathematical Simulation, basis: 100 kg/day H_2 feed



Our proposed HiCON can deliver 96-99% H_2 purity with 98-77% H_2 recovery with a modest membrane surface area requirement.

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Preliminary Economic Analysis: Post Treatment Capital and Operating Cost

Target: 99.999% purity H_2 Basis: 1500 kg/day H_2 production

Case A: Temperature Swing Adsorption (TSA) Integrated with Membrane Reactor			
Adsorption temperature [C]			50
Pressurization cycle [min]			5
Adsorption Cycle [min]			175
Temperature Swing Regeneration [min]			180
Feed Purity [%]	99	97	93
Adsorber ID [in]	12.6	15.7	19.8
Adsorber Height [ft]	11.8	19.9	29
Capital Cost* [$]	134,598	214,249	333,304
Capital Recovery Cost [¢/Kg H_2]	4.1	6.5	10.1
Hydrogen Yield [%]	~100	~100	~100

Bulk Hydrogen Cost

at Production Point via Methane Steam Reforming

$1 – 2.4/Kg H_2 for 22-600 tons/day with $3.5-7/GJ NG

* Example of Capital Cost Estimate: for 99% purity case

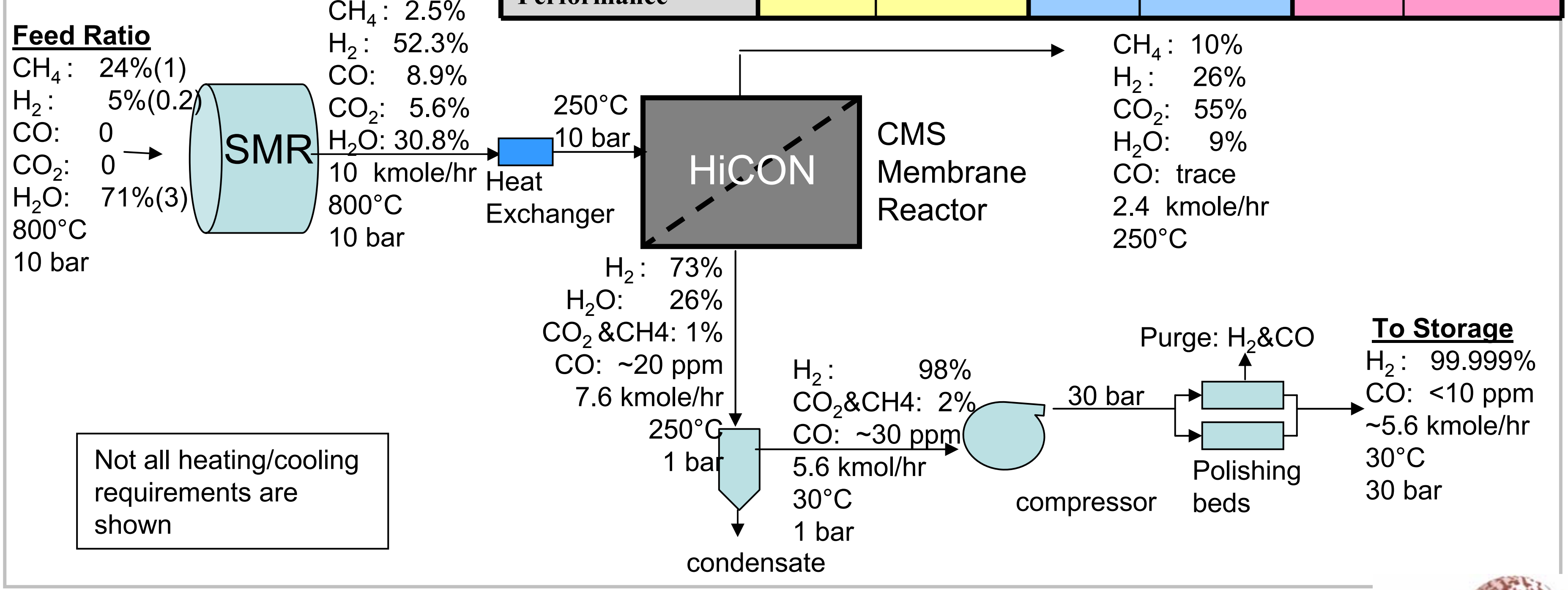
For Quantity of 4 Adsorbers	
Purchase Price of Pres Vessels, fob	$42,032
Purchase Price of Zeolite, fob	$2,162
Purchase Price of Support, fob	$39
Delivery	$2,212
Installation	$51,090
Purchased, Deliverd & Installed	$97,535
Piping, Valving & Instumentation	$19,507
Total Fixed Capital Investment	$117,042
Other One-Time Costs	$17,556
Other One-Time Costs	$134,598
Not including heating equipment for TSA.	

Our preliminary analysis indicates that the incremental cost for the developed post treatment scheme is very insignificant

Distributed Hydrogen Production Process

HiCON

Schemes Unit Operations	Scheme #1		Scheme #2		Scheme #3	
	H_2 Purity [%]	H_2 Recovery Ratio [%]	H_2 Purity [%]	H_2 Recovery Ratio [%]	H_2 Purity [%]	H_2 Recovery Ratio [%]
Membrane Reactor/Separator (HiCON)	98.5	90	97.0	97	93.0	98
Polishing Step	99.999	100	99.999	100	99.999	100
Cumulative Performance	99.999	90	99.999	97	99.999	98



Feed Ratio
CH_4: 24%(1)
H_2: 5%(0.2)
CO: 0
CO_2: 0
H_2O: 71%(3)
800°C
10 bar

SMR

CH_4: 2.5%
H_2: 52.3%
CO: 8.9%
CO_2: 5.6%
H_2O: 30.8%
10 kmole/hr
800°C
10 bar

Heat Exchanger

250°C
10 bar

HiCON

CMS Membrane Reactor

CH_4: 10%
H_2: 26%
CO_2: 55%
H_2O: 9%
CO: trace
2.4 kmole/hr
250°C

H_2: 73%
H_2O: 26%
CO_2 &CH4: 1%
CO: ~20 ppm
7.6 kmole/hr
250°C
1 bar

condensate

H_2: 98%
CO_2&CH4: 2%
CO: ~30 ppm
5.6 kmol/hr
30°C
1 bar

compressor

30 bar

Purge: H_2&CO

Polishing beds

To Storage
H_2: 99.999%
CO: <10 ppm
~5.6 kmole/hr
30°C
30 bar

Not all heating/cooling requirements are shown

It appears that our HiCON process is able to deliver nearly 90% hydrogen recovery with 99+% purity accoarding to our simulation.

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BENCHMARKING: EXISTING PSA/PROX

Product Stream from Our Enduser Reformer : 10 bar, 10-3% CO

Our HiCON Process

CH_4 : 1
H_2 : 0.2
CO: 0
CO_2: 0
H_2O: 3
800°C
10 bar

SMR

Small scale

CH_4 : 2.5%
H_2 : 52.3%
CO: 8.9%
CO_2: 5.6%
H_2O: 30.8%
800°C
10 bar

Membrane Reactor

WGS (LTS)

H_2 Separation

H_2 : 98%
CO_2&CH4:2%
CO: ~30 ppm
30°C
1 bar

Post Treatment

Simple Adsorption

99.999% H_2
<10 ppm CO

Benchmarking

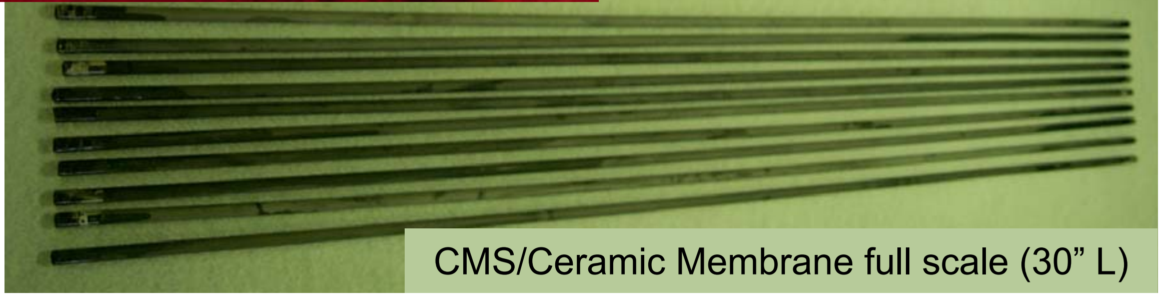
Performance Criteria	Conventional/PSA	OUR HiCON
CO Conversopm [%]	75 - 95	99
H_2 Recovery [%]	70 - 85	~90
Product, H_2, pressure [psi]	150	15
Reject, CO_2, pressure [psi]	15	150
Capital Cost [$]	TBD	TBD

Economic analysis is under preparation currently, and will be presented in the meeting.

MEMBRANES, BUNDLE AND MODULE PREPARATION

Pilot Scale Module of CMS/ceramic Membrane (1.5" diameter and 30"L)

Our full-scale ceramic membrane module (3 - 4" dia, prototype) for gas applications



CMS/Ceramic Membrane full scale (30" L)

These membranes and modules were adapted from our existing commercial ceramic membrane products and modules.

- **The pilot scale module is currently under a pilot test for hydrogen recovery.**
- **The full-scale single tube (30"L) will be used for our pilot scale MR test in FY2007.**

M&P CMS H_2 SELECTIVE MEMBRANES – PILOT TEST

Engineering Demonstration Facility, Startech Environmental Corp.

2 ton/day Plasma Conversion System (based upon MSW)

200 SCFM PCG
(plasma converted gas)

__Performance Results__

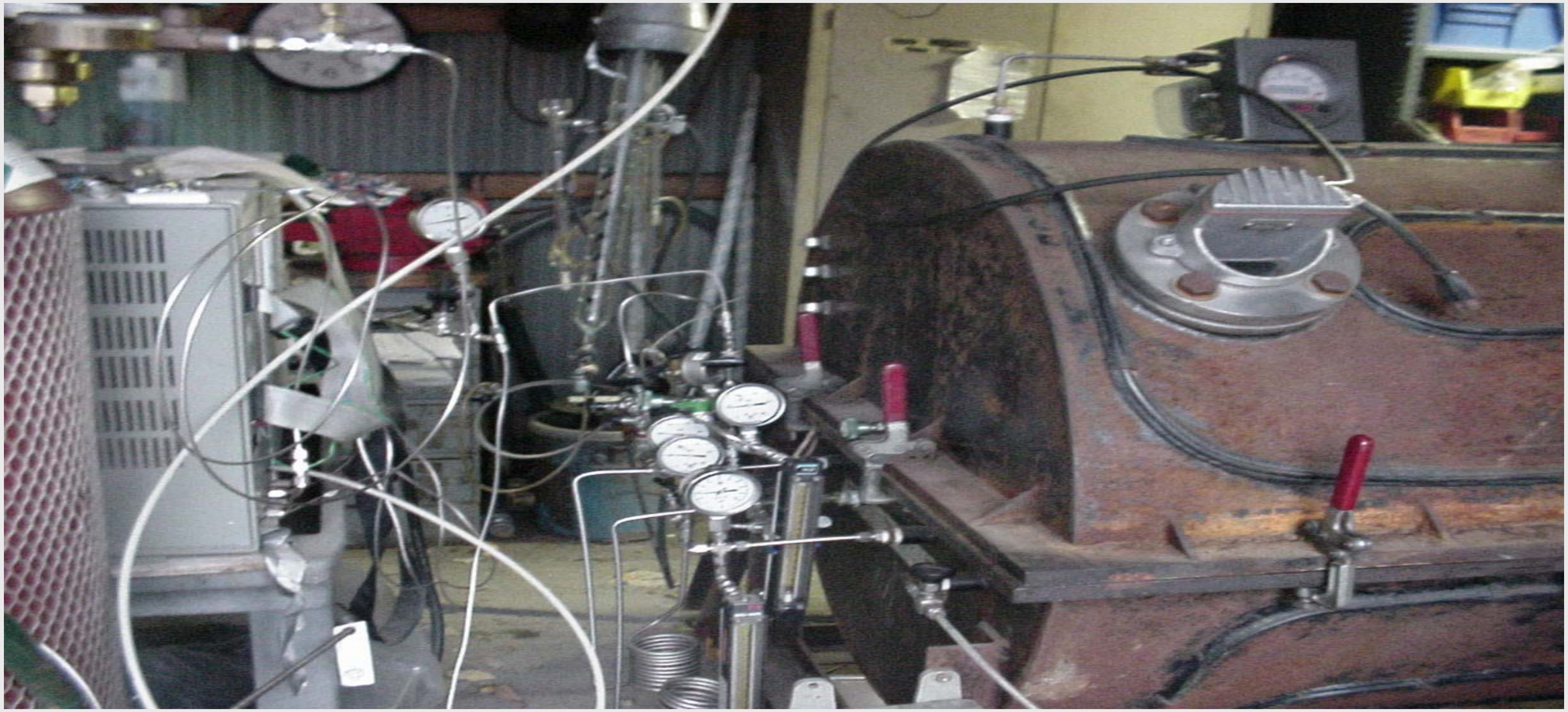
50/50 H2/CO at 18 SCFM and ~100°C

87/13 H2/CO at 82% H2 Recovery for Stage 1 at 9.5 barg

>99% H2 at 93% H2 Recovery for Stage 2 at 6.8 barg

MEMBRANE REACTOR: PILOT SCALE TESTING FACILITY

for a Full-Scale (34"L)Single Tube Membrane Reactor



We have designed and constructed this barricade to perform the membrane reactor study involving high temperature and high pressure CO & H_2. The single full-scale membrane tube (34"L) as a reactor is housed within this barricade. Its temperature is controlled in-situ by an electric tube furnace. Unique safety features include:

- The barricade can be constantly purged with inert gas. Any leak in H_2 and CO can be detected via the purge gas analysis.
- The barricade has a water leg to allow the surge under the worst case scenario: explosion.

Future Work

Remainder of FY 2007

- Complete pilot scale testing using a single, full-scale hydrogen selective membrane and synthetic feed to demonstrate the optimized HiCON process.
- Complete the preliminary economic analysis for hydrogen production via the developed HiCON process by our end user.

FY 2008 and Beyond

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

SUMMARY

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 the commercialization barriers associated with the membrane reactor while the distributed hydrogen production is an ideal platform to showcase the MR technology.

Our Accomplishments

- We have completed the bench top experimental study and mathematical simulation to demonstrate our HiCON process to deliver **99+%** CO conversion with **97-99%** purity and **98-75%** H2 recovery via a simple MR process, uniquely suitable for the distributed hydrogen production.
- Although membranes are not ideal to deliver **99.999% purity with trace CO contaminant**. Our study indicates that a cost acceptable post treatment unique to our proposed process can achieve this target. This in conjunction with our HiCON process offers a practical and economically viable process to meet the stringent feed quality requirement for PEM.
- We have established a **pilot scale testing facility** for performing a pilot scale test to verify the optimized HiCON process using a full-scale membrane tube with synthetic feed, which is expected to be completed by the end of FY 2007.

In short, with the budget available, we anticipate to complete the minimum tasks required to take this HiCON process to the next step for field demonstration.

ACKNOWLEDGEMENT

US DOE Project Managers

- Arlene Anderson
- 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.