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

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# Features of Membrane Reactors and Barriers to Implementation

## For a small scale hydrogen production process:

- MR is ideal for process intensification.
- MR can deliver capital & operating cost reduction.
- A *small scale* $H_2$ production process is an ideal platform for MR to demonstrate its technical and commercial viability.

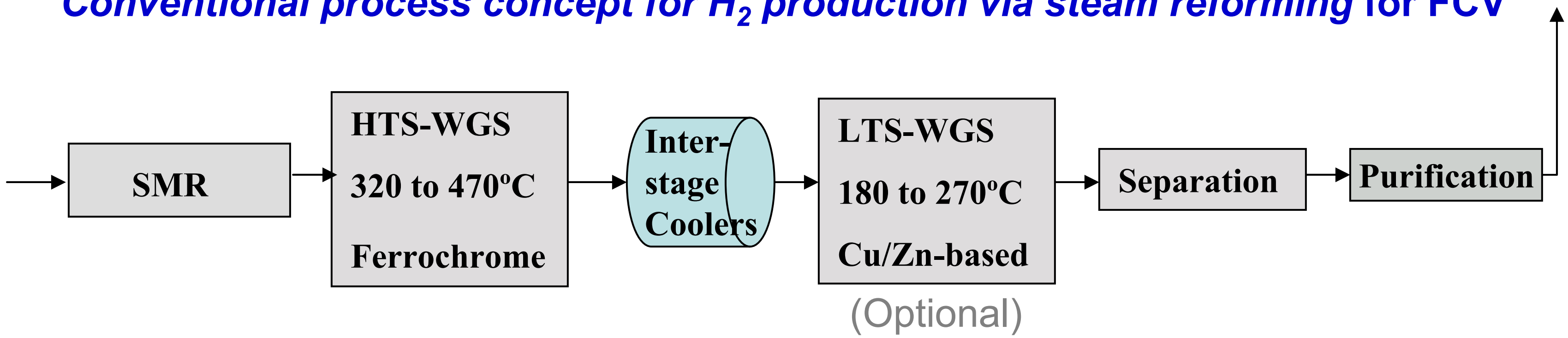
## Few commercial MR units have been installed thus far, major barriers include:

- Membrane with sufficient material stability and long term functional stability under the reaction environment – i.e., membrane has minimum tolerance.
- Membrane reactor engineering, such as heat transfer, catalyst packing density, compatibility of membrane and catalyst materials, housing/seal…
- Large scale commercially available membranes
- …..

# Potential Opportunities for Membrane Reactors

## Hydrogen Production via Steam Methane Reforming

***Conventional process concept for $H_2$ production via steam reforming*** **for FCV**




***Potential Membrane Reactor Configurations and Their Challenges***

| No. Steps | Configuration | MC | HR | Operating Features/Challenges |
|---|---|---|---|---|
| **One Step** | Reforming + WGS + Separation | 89% | 96% | >~600°C,<br>Pd membrane material stability (physical & chemical),<br>Heat transfer,<br>Large scale defect free membrane,<br>Steam effect on hydrogen permeation and material stability |
| **Two Step** | WGS (HTS) + Separation | - | - | >~350°C<br>Steam effect on hydrogen permeation and material stability |
| | WGS (LTS) + Separation | 93% | 90% | ~250°C, |

# Innovation & Uniqueness

**Unique Approach**

- Our project team focuses on reaction engineering and process development of the MR, not the membrane material development.
- Our CMS membranes demonstrate excellent chemical and material stability under the proposed reaction environment.

**Innovation**

- Although our MR is limited to the LTS range, the CO conversion was found to be fast and nearly complete with our unique MR process (HiCON).
- Unique and innovative thermal management is delivered with our membrane and membrane reactor.

**Limitation**

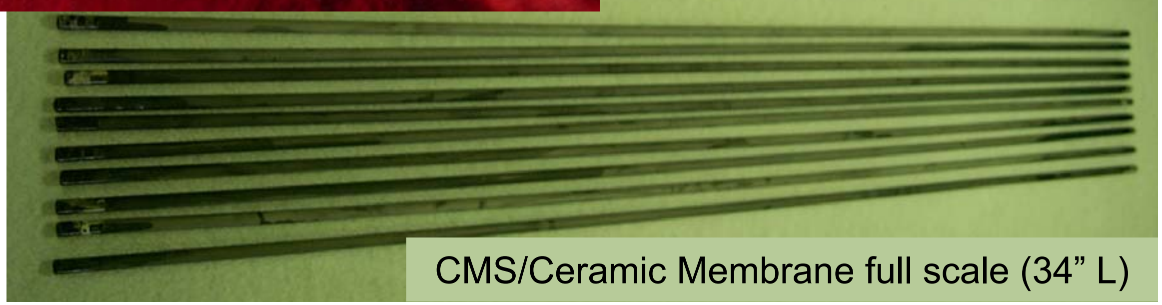
- Our microporous CMS membrane cannot deliver 99.999+% purity.

Under this project, we did develop an innovative, nearly “zero” penalty post treatment scheme to meet this objective. This polishing step can be integrated into our WGS/MR; thus, a very economical and effective approach can be implemented to achieve 99.999+% purity.

# MEMBRANES, BUNDLE AND MODULE

Pilot Scale Module of CMS/ceramic Membrane (1.5” diameter and 34”L)

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



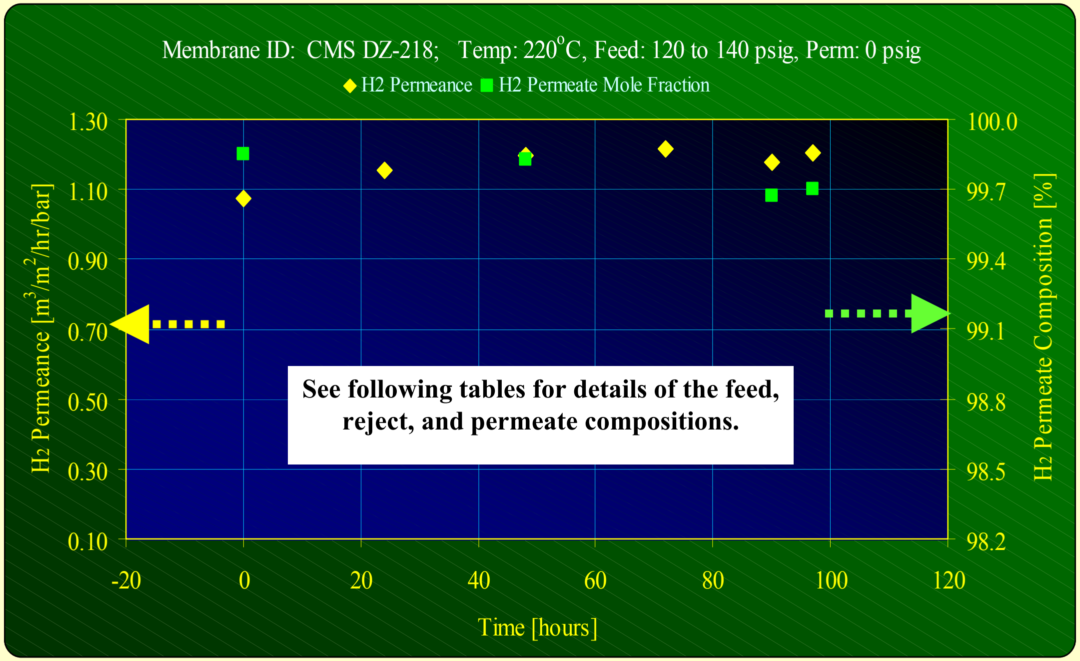
CMS/Ceramic Membrane full scale (34” L)

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

| | |
|---|---|
| Membrane Cost [$/ft$^2$] | $40 |
| Hydrogen Permeance | 19 scfh/ft$^2$ at 20 psi pressure drop (linear relationship) |
| Module Cost, including membrane [$/ft$^2$] | $60 for low pressure, $80 for high pressure applications |
| Purity and Recovery Ratio | 97-99% purity with 90% hydrogen recovery, depending on P |
| Operating Temperature [°C] | 150 to 300°C |
| Operating Pressure [psi] | 1,500 psi |

# CMS Membrane: Material Stability at a Refinery 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.




## 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% | | |

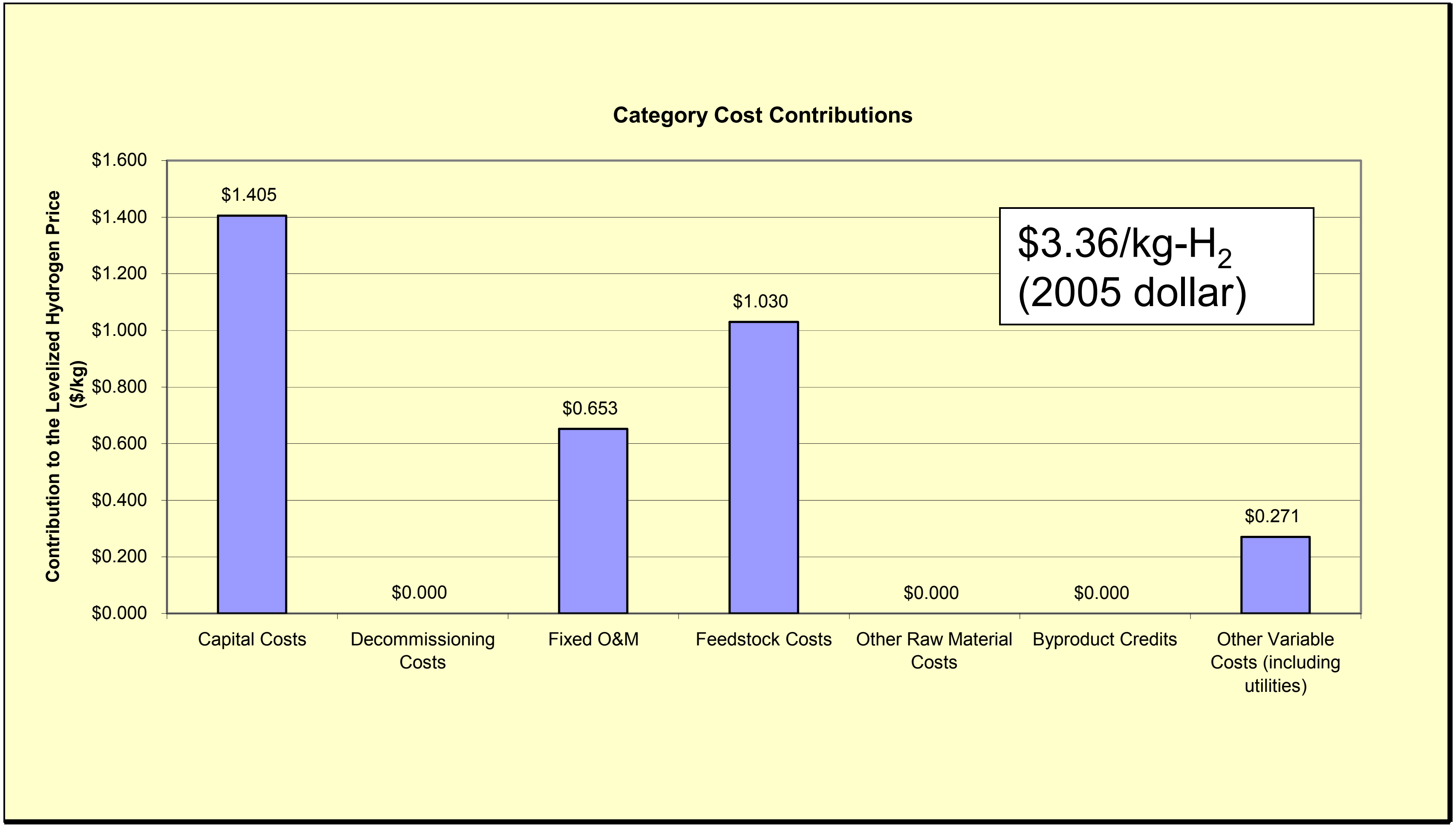
# CMS Membrane:_Material Stability at a Pilot Test - Durability

**Membrane Regeneration**

**Pure Component Permeance and Selectivity**

Test Conditions: 220ºC @ ~120 psig

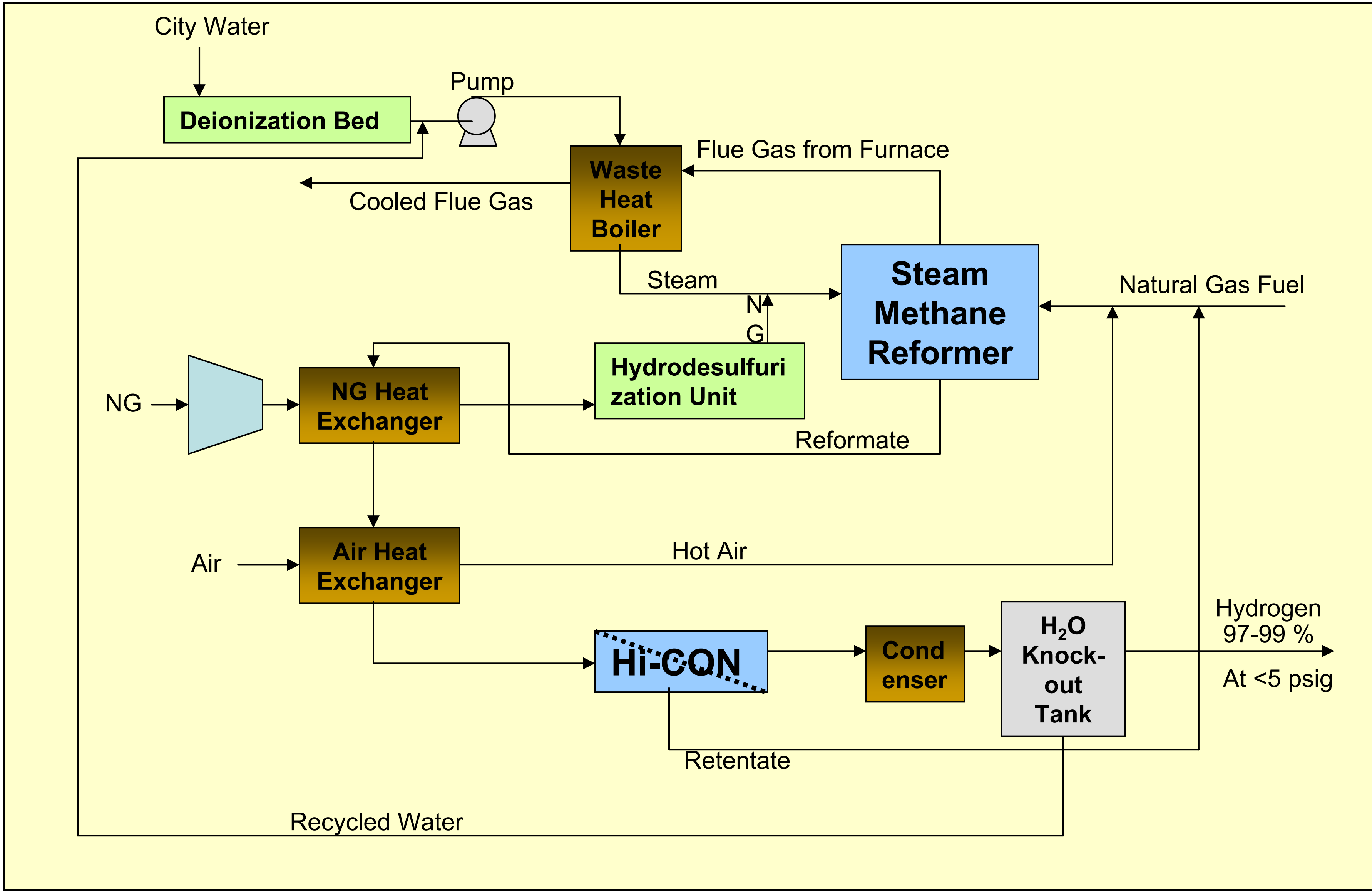
| Test Phase | $H_2$ [$m^3/m^2/hr/bar$] | $H_2/N_2$ [-] |
|---|---|---|
| Before Hydrocracker Testing | 1.27 | 75 |
| After Hydrocracker Testing | 1.22 | ND |
| After Dead Head Hydrocracker Challenge Test<br>>> ~17 hrs w/NO Reject Flow (100% Stage Cut)<br>>> Permeate flow falls from ~450 to ~3 cc/min | 0.62 | 53 |
| After Regeneration | 1.26 | 67 |


Category Cost Contributions
Contribution to the Levelized Hydrogen Price ($/kg)
$1.600
$1.400
$1.200
$1.000
$0.800
$0.600
$0.400
$0.200
$0.000
$1.405
$0.000
$0.653
$1.030
$0.000
$0.000
$0.271
Capital Costs
Decommissioning Costs
Fixed O&M
Feedstock Costs
Other Raw Material Costs
Byproduct Credits
Other Variable Costs (including utilities)
$3.36/kg-$H_2$ (2005 dollar)

# H2A Inputs

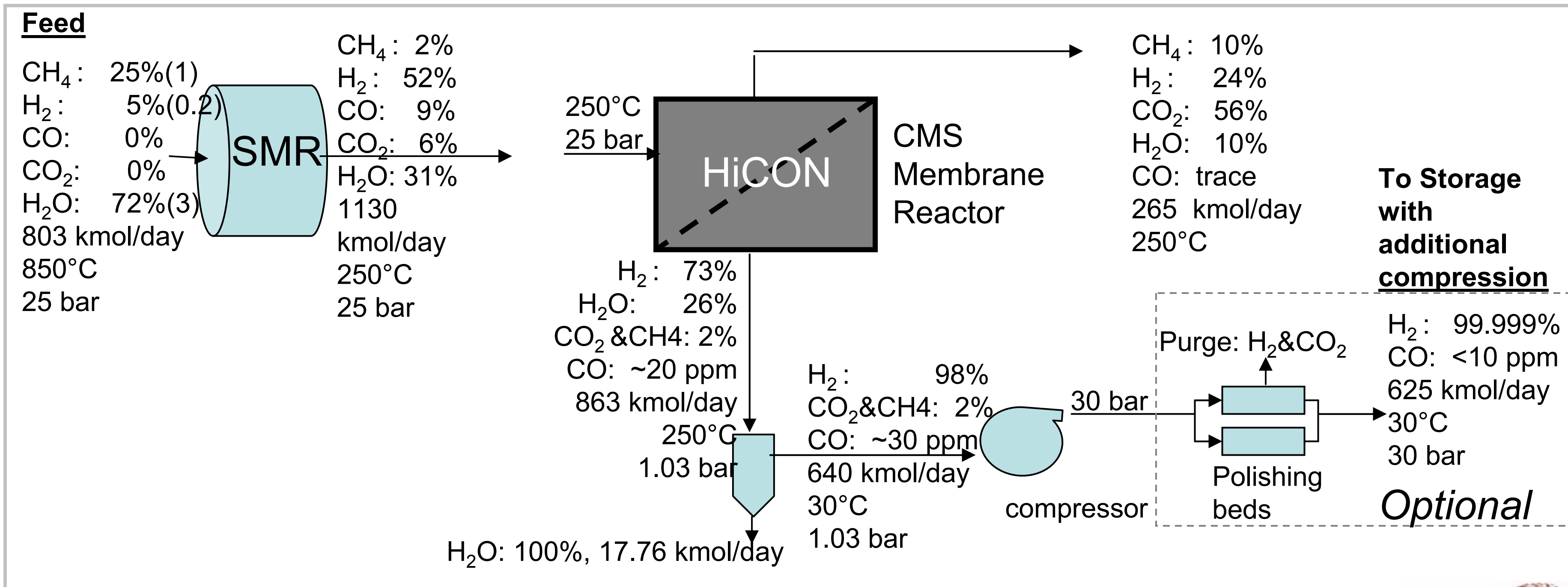
| | |
|---|---|
| • **Total production initial capital investment (installed):** | **\$1,020,000**<br>**\$1,116,000 with option** |
| • **Primary feedstock usage :**<br>**(excluding fuel usage)** | **2.4 kg NG/kg $H_2$ , or**<br>**3.4 $Nm^3$ NG/kg $H_2$ or**<br>**1.23 E+05 kJ/kg $H_2$** |
| • **Total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

# M&P HiCON for CO Conversion and $H_2$ Separation of Reformate from Steam Methane Reformer



# Distributed Hydrogen Production Process

| | |
|---|---|
| Capacity: | 1250 kg/day $H_2$ production |
| SMR: | \$472,000 |
| Membrane: | \$188,000 |
| Pretreatment for compression | \$ 50,000 |
| Polishing Beds (optional): | \$ 70,000 |
| Installation Factor: | 1.45 |
| Anticipate Foot Print Size: | ???????? |



# 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 |

**Capital Cost of Major System Components - M&P**

| | Base Cost [$] | Base Scale | | | | Scale Factor | Eq. Cost | Notes |
|---|---|---|---|---|---|---|---|---|
| ***Pre-reformer*** | | | | | | | | |
| Natural Gas Compressor | 33,000 | 5 | MW | 21,941 | mol/hr | 0.82 | 1.63E+04 | |
| Natural Gas Feed System | 2,000 | 5 | MW | 21,941 | mol/hr | 0.82 | 3.43E+00 | |
| Heat Exchanger (steel) | 7,800 | 2 | m2 | | | 0.59 | | see NG heater |
| Heat exchanger (stainless steel) | 15,500 | 2 | m2 | | | 0.59 | | see Air heater |
| Desulfurization unit | 4,800 | 0.79 | molCH4/hr | 0.79 | | 0.6 | 1.89E+04 | |
| Water Puritifcation | 2,100 | 90 | l H2O/hr | 5 | kmol/h | 0.68 | 5.99E+03 | |
| Water pump | 1,200 | 90 | l H2O/hr | 5 | kmol/h | 0.7 | 3.53E+03 | |
| Waste-heat boiler | 19,200 | 90 | l H2O/hr | 5 | kmol/h | 0.67 | 5.39E+04 | |
| Sweep gas boiler | 19,200 | 90 | l H2O/hr | 5 | kmol/h | 0.67 | | |
| NG heater | | | | | | | 2000 | heat exchanger |
| Air heater | | | | | | | 6000 | heat exchanger |
| | | | | | | | 1.07E+05 | Subtotal |
| ***Reformer*** | | | | | | | | |
| Combustion chamber (furnace) | 2,100 | 4.79 | kg H2/hr | | | 0.78 | 1.35E+04 | |
| Membraen reactor (without membran | 14,100 | 4.79 | kg H2/hr | (3x for temp diff) | | 0.7 | 2.25E+05 | |
| Catalyst (initial loading for SMR&WGS)) | | | | | | | 1.26E+05 | |
| | | | | | | | 3.65E+05 | Subtotal |
| ***Post Refomer*** | | | | | | | | |
| Hydrogen compresor | 22,000 | 4.79 | kg H2/hr | | | 0.82 | | |
| Condenser and water knock-out | 4,900 | 4.79 | kg H2/hr | | | 0.68 | 2.48E+04 | |
| Carbon dioxide compressor | 3,000,000 | 6 | MW | | | 0.7 | | |
| Dehydration equipment | 35,000 | 1180 | m3/hr | 41671 | ft3/hr | 0.7 | 2.14E+04 | |
| Cryogenic CO2 separation unit | 475,000 | 0.6 | t CO2/hr | | | 0.7 | | |
| | | | | | | | 4.62E+04 | Subtotal |
| **HiCON** | | | | | | | | |
| Membrane#1 | $800 | 1 | m2 | | | 1 | $188,975 | 25 bar feed |
| **Total Equipment Cost** | | | | | | | 7.07E+05 | |
| **Total Installed Capital Cost at 1.45 factor** | | | | | | | 1.02E+06 | |

Ref. 1: Information (except membranes) was obained from Sjardin, M., *Energy, 31* , 2523(2006); Catalysts are considered replacement cost.

# Uncertainties/Improvements

| Technology Component | Specific Uncertainties/Improvements | ECD |
|---|---|---|
| **Capital Cost vs Capacity** | ~50% of the hydrogen product cost is contributed by the capital cost recovery. / <br><br> *Refine the capital cost along with our industrial participant. Identify a throughput which can deliver most favorable capital cost contribution with our technology.* | 12/31/07 |
| **WGS/MR–experimental verification with a system approach** | The current performance of the system was generated through simulation. Previously, we have conducted bench-top study to verify the fundamentals of the unit operations. / <br><br> *An experimental study to substantiate the projected system performance is essential.* | 6/30/08 |
| **Polishing Step** | The capital and operating cost of the current polishing step was established by us. / <br><br> *A more rigorous analysis by an engineering/equipment vendor will be pursued. Also experimental study will be performed to demonstrate the feasibility to meet the purity spec.* | 6/30/08 |
| **Peripheral Application Potential** | Our HiCON process does not address the SMR step. Its potential economic impact is limited under this H2A analysis./ <br><br> *Other opportunities for our HiCON process will be identified and analyzed for future consideration, including: (i) feedstocks with substantial and complex contaminants, and (ii) hydrogen production other than reforming, such as gasification.* | 6/30/08 |

# Questions #1: Relevance to Overall DOE Objectives

- The presentation was extremely vague on the specific targets required by DOE. No cost estimates were provided. In addition, no clear flux targets were provided - just a vague comparision to metallic membranes - which appears low and in odd units.

- The temperatures being considered are low - 200+ degrees. There should be consideration to get this a bit higher - maybe into the HTS range.

- Interesting work, but not a critical piece of the puzzle for hydrogen success. Conventional WGS works pretty well and isn't overly expensive.

# Question #2: Approach to Performing R&D

- Catalyst testing and membrane development appear to be occurring along two separate paths. They need to be integrated together into a single development path

- The target CO value should be decreased to 1 ppm CO for distributed hydrogen production for dispersing to fuel cell vehicles.

- There will be other impurity level constraints in addition to CO, for these systems that must be met for the systems to be deployed.

- This process produces hydrogen at low pressure which then needs to be compressed. The ultimate measure is in the cost of hydrogen, where the hydrogen is at 300 psi.

# Question #3: Technical Accomplishments and Progress toward DOE Objectives

- The technical progress is difficult to judge. Although actual results are alluded to and appear to be included on some of the graphs, much of the work appears to be mathematical modeling. However, it is not clear which are results produced from this work and what is from the literature. It appears that the project has been minimally funded (30%) so it is not clear how much actual progress has been made.

- The use of microporous membranes will not likely give the most effective separations. The purity and percent recovery will remain a concern and the contractor has not done a lot to improve on the situation. The separation mechanism itself will likely limit these parameters.

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- The technical accomplishments to date are somewhat confusing. The stated goal is 99.999%, but reports that 97-99% clean-up was accomplished and that a non-defined adsorbent would polish the hydrogen to 99.999% with CO apparently being the principle impurity at < 10 ppm. This must be addressed

## Question #4: Technology Transfer with Industry and Universities

- Technology transfer and industry involvement appears minimal. There are some academic publications. The intro slides did list involvement of other partners, but their roles and contributions are not clear. It appears that the testing is primarily being conducted by MPT and the University of Southern California. The industry partners need to be more involved to ensure that the developed technology is worthwhile.

## Question #5: Approach to and Relevance to Proposed Future Research

- The proposed economic analysis is needed to substantiate the potential cost attractiveness of this process.

- In particular, the use of the polishing st ep needs more careful analysis, as the ultimate purification may add more to the cost than expected on the basis of a preliminary analysis.