*Distributed Reforming of Renewable Liquids via Water Splitting using Oxygen Transport Membrane (OTM) **

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... for a brighter future

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Objective & Rationale

Objective:

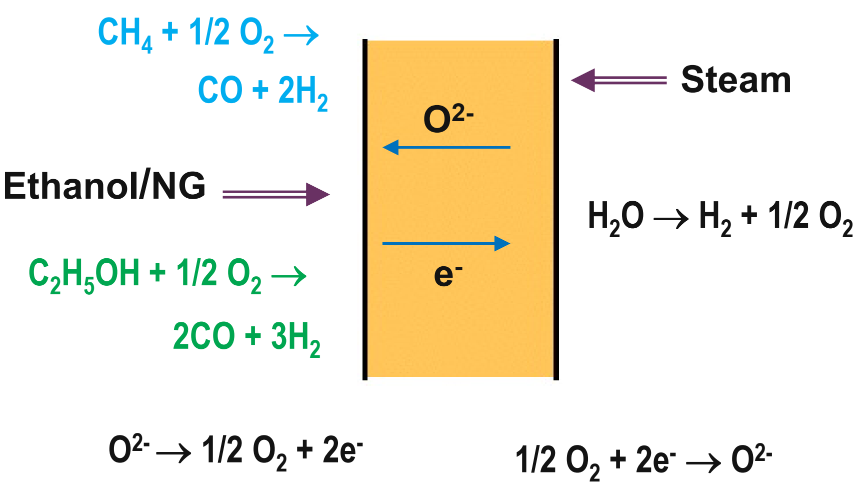
- Develop compact dense ceramic membrane reactors that enable the efficient and cost-effective production of hydrogen by reforming renewable liquid fuels using pure oxygen produced by water splitting and transported by an OTM.

Rationale:

- Membrane technology provides the means to attack barriers to the development of small-scale hydrogen production technology. This is critical to the development of hydrogen infrastructure for refueling of hydrogen powered vehicles.

- Specific areas where this membrane technology provides crucial benefits include:
  - Improved reforming & separation efficiencies
  - Incorporation of breakthrough separations technology
  - Intensification & consolidation of the number of process steps
  - Reduced foot-print area

Reforming of Fuels via Water Splitting using OTM



-Fuel is reformed using oxygen that is formed by water splitting and transported by the membrane.

-H_2 is produced on both sides of the membrane.

Predominant products of ethanol reforming: H_2, CO, CO_2, CH_4, H_2O

- No electrical circuitry/power supply
- Non-galvanic
- Single material (no electrodes)

Barriers Addressed by this Project (DOE – MYPP)

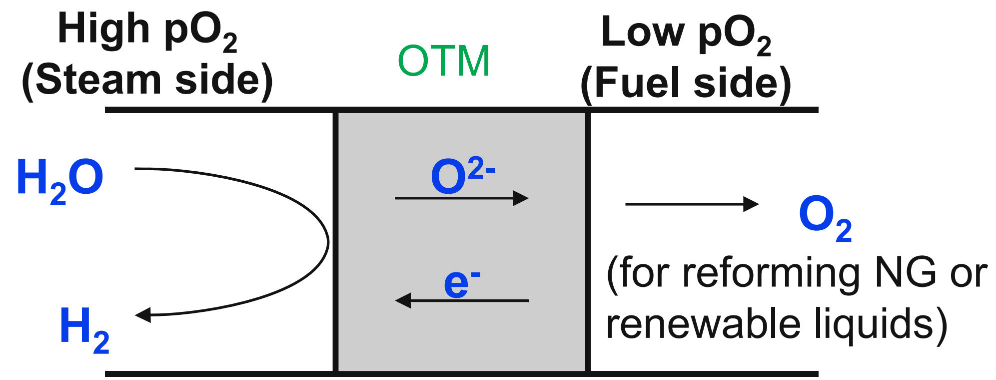
- A – Reformer capital cost
  - Process intensified by combining unit operations
  - High energy efficiencies
- B – Reformer manufacturing costs
  - Skid mounted units can be produced using currently available low-cost, high-throughput manufacturing methods
  - Compact design reduces construction costs
- C – Operation & maintenance costs
  - Uses robust membrane systems that require little maintenance
- D – Feedstock issues
  - Feedstock flexible; membrane provides pure oxygen needed for reforming

Membranes being developed also address cross-cutting barriers – Separations

Durability (barrier K), Impurities (barrier L); Selectivity (barrier N); Operating Temperature (barrier O); and Flux (barrier P).

Reforming via Water Splitting using OTM

- Oxygen is removed by membrane.
- Non-galvanic (no electrodes/ electrical circuitry)



Dense mixed (oxygen ion-electron) conductor (500-900°C)

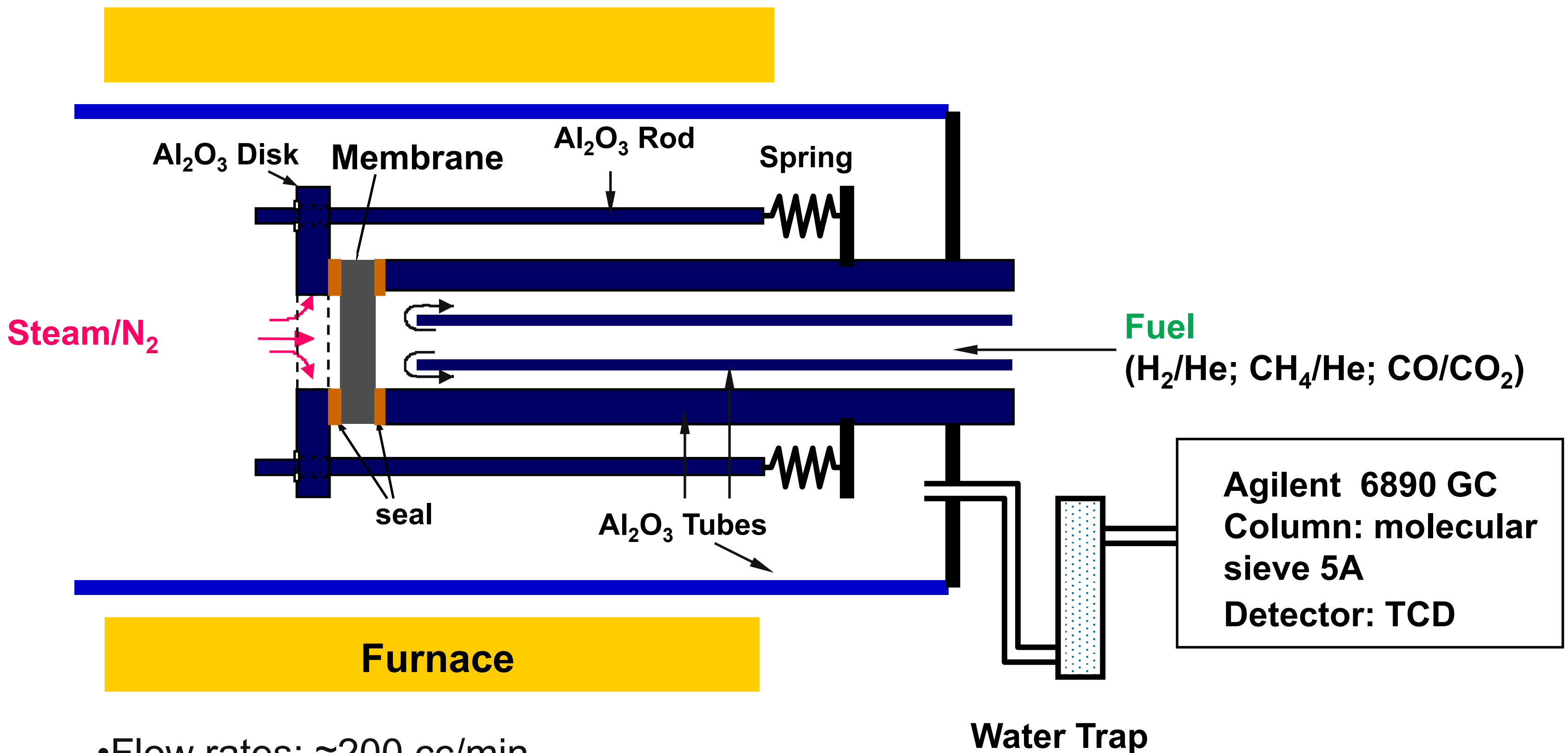
$$H_2O \Leftrightarrow H_2 + 1/2\ O_2$$

- Very low concentrations of H_2 and O_2 are generated even at relatively high temperatures (0.1 and 0.042% for H_2 and O_2, respectively, at 1600°C).
- Significant amounts of H_2 & O_2 can be generated at moderate temperatures if the reaction is shifted toward dissociation by removing either O_2, H_2, or both.

$$K = \frac{P_{H_2} P_{O_2}^{\frac{1}{2}}}{P_{H_2O}}$$

U. Balachandran et al., Int. J. Hydrogen Energy, <u>29</u>, 291, 2004; U.S. Patent 7,087,211, Aug. 8, 2006.

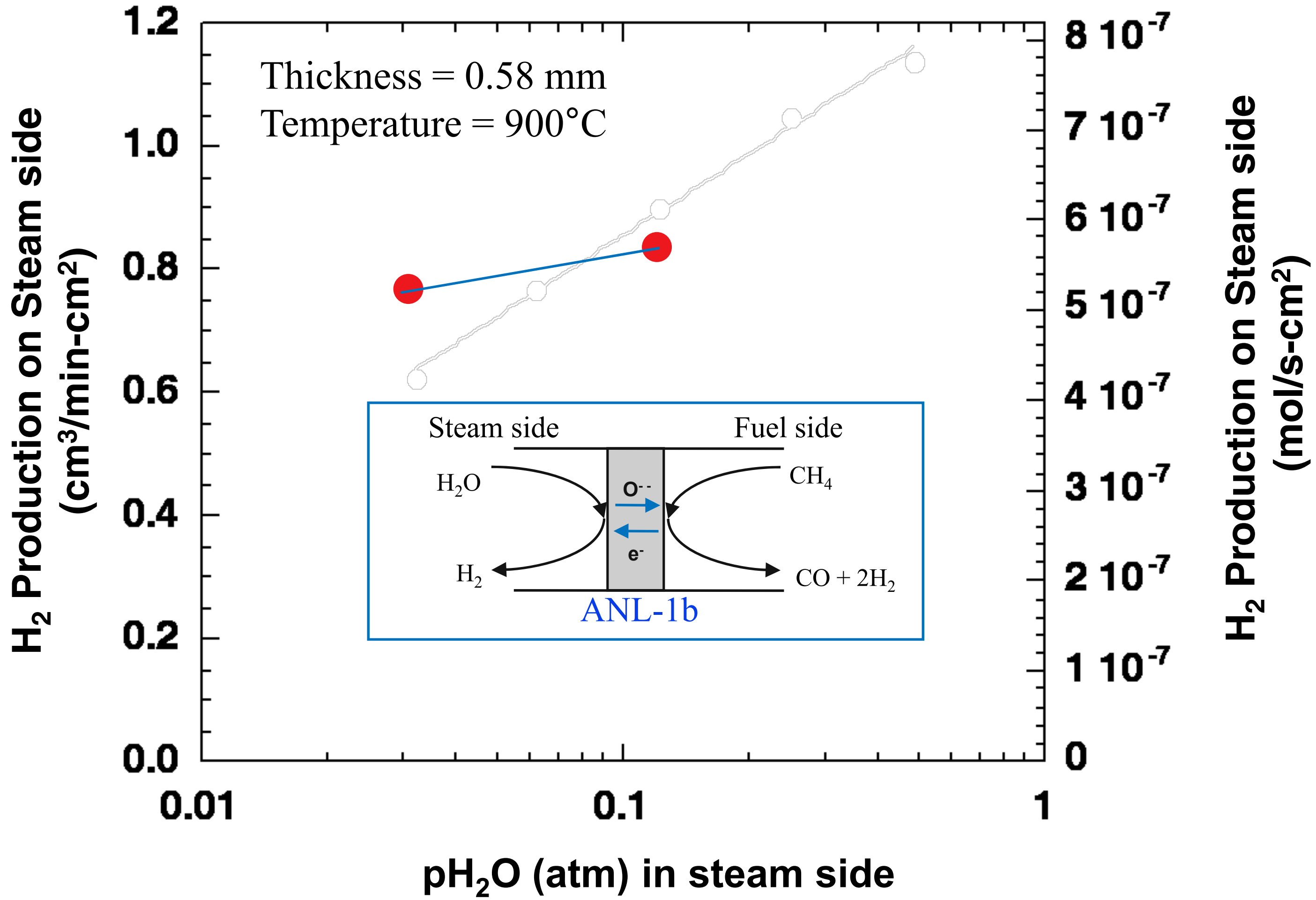
Schematic of Experimental Setup – Ambient pressure
Disk-type Membrane



- Flow rates: ≈200 cc/min
- OTM sample size: ≈20 mm dia.
- Feed concentration: 5% CH_4/He; 10% CO/CO_2
- H_2 production rate: ≈18 cc/min/cm^2
- Temperature: 500 - 900°C

Reforming of NG using OTM via Water Splitting (Fuel side = 5% methane/bal. N_2)

H_2 produced on the CH_4 side = 0.64 cm^3 (STP)/min-cm^2)



Performance Metrics

- Near term – focus on OTM material development
  - Flux, temperature, stability, mechanical properties
  - Membrane fabrication, catalyst(s) incorporation
  - H2A analysis using updated OTM performance
  - Ethanol reforming using a small tubular OTM membrane reactor

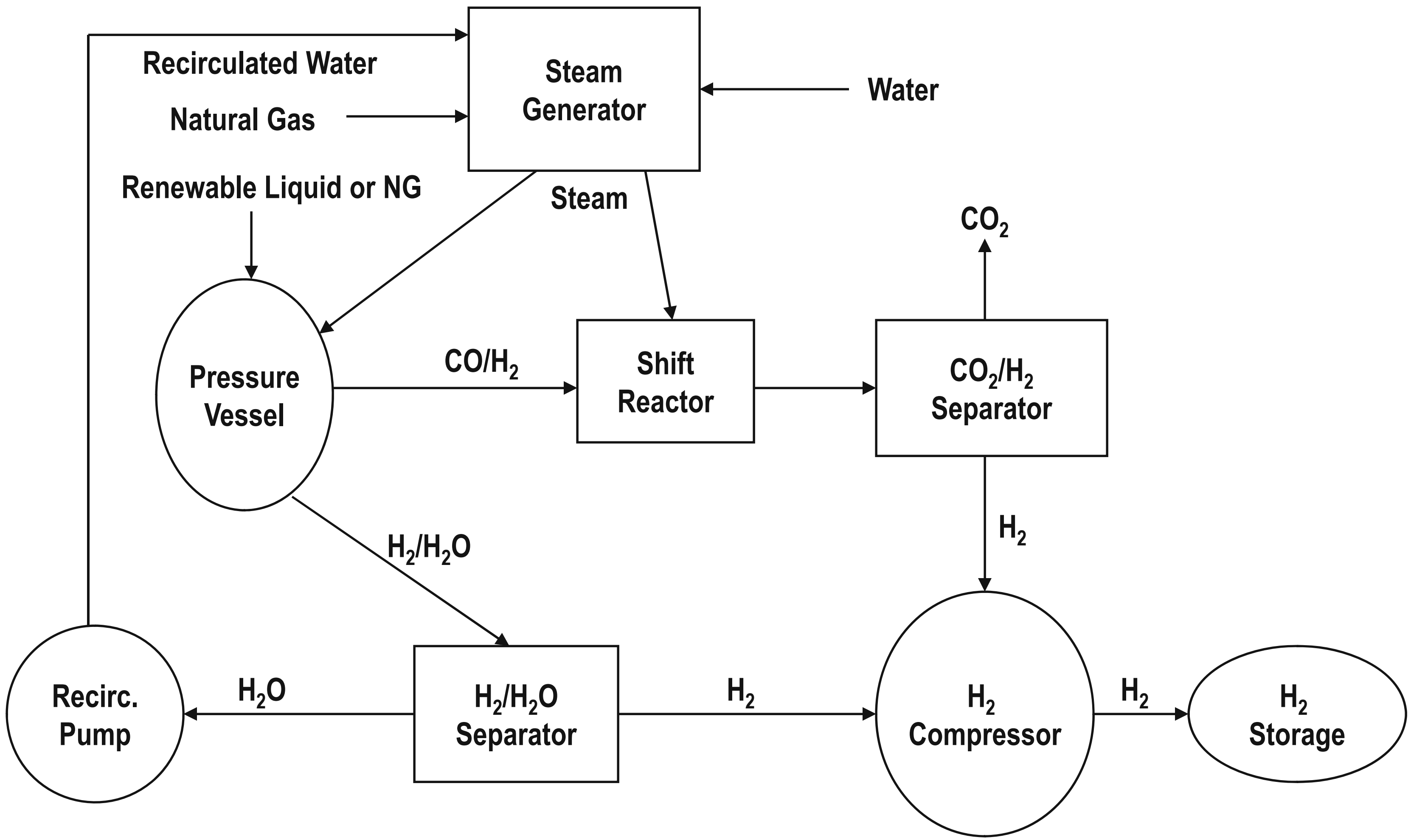
- Mid term – focus on membrane reactor design & prototype reactor testing
  - Bench-scale membrane reactor for ethanol reforming
  - Long-term stability tests
  - Defining optimum operability conditions
  - Scale-up issues & preliminary membrane reactor design
  - Update H2A analysis using data from bench-scale reactor testing

- Longer term – technology transfer
  - Process demonstration unit
  - Sub-scale engineering prototype

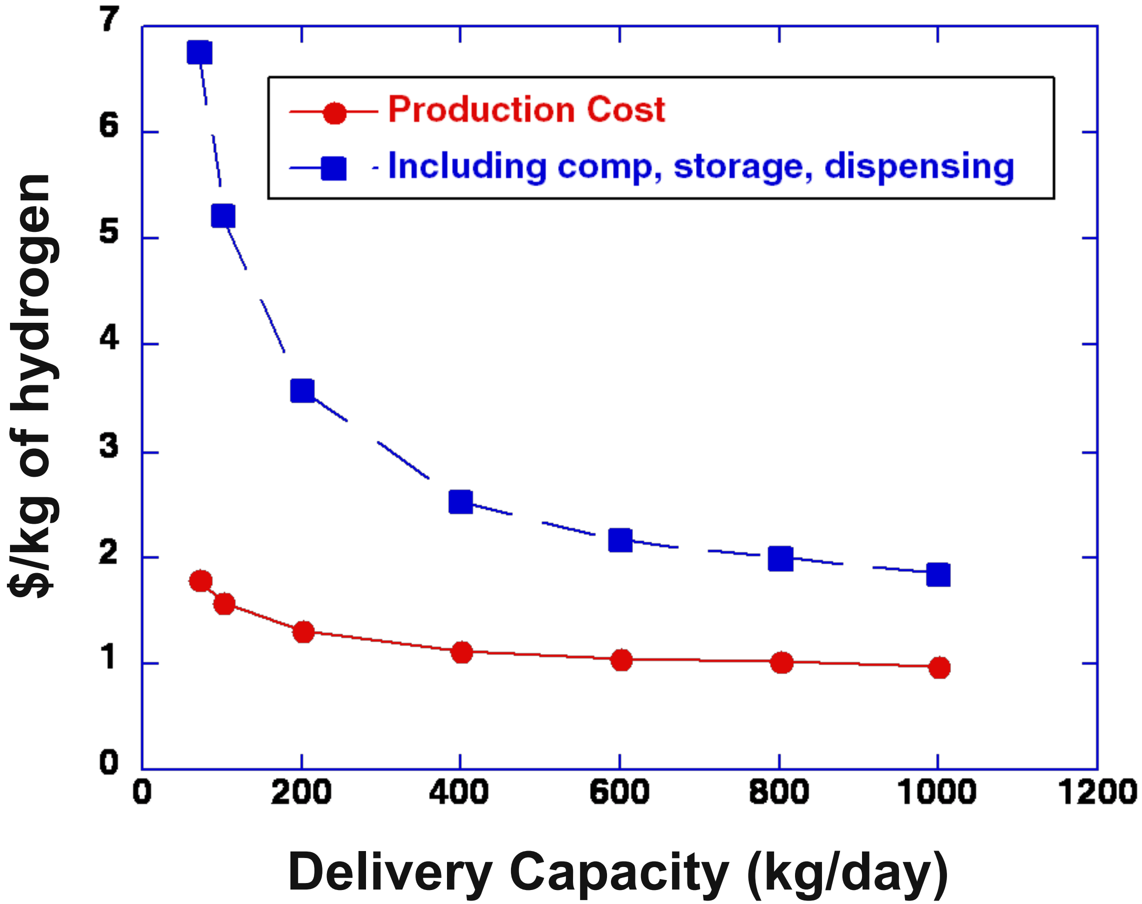
Challenges and Options

- Preventing coke formation. [Ethanol will thermally decompose into methane, ethylene, formaldehyde, and carbonaceous deposits (coke)]. Possible approaches:
  - Higher temperature operation (>800°C)
  - Mixing steam with ethanol
- Fabricating of membrane modules for “real-world” applications
  - Life cycle analysis
    - *Demonstrate mechanical integrity in prototype forms (mechanical property measurement)*
    - *Evaluate failure limits of materials by finite-element analysis*
    - *Evaluate chemical stability by performing long term tests*
- Enhancing H_2 yield of the reformer
  - Incorporate hydrogen transport membrane to remove H_2 and thereby circumvent thermodynamic equilibrium limits
- Incorporating catalysts to promote desired reactions
  - Interact with catalyst development effort
- Controlling the mixing of ethanol vapor & oxygen
  - Membrane reactor design by simulation & modeling studies

Flow Diagram for Hydrogen Production by Reforming Methane/Renewable Liquids Using OTM Membrane via Water Splitting



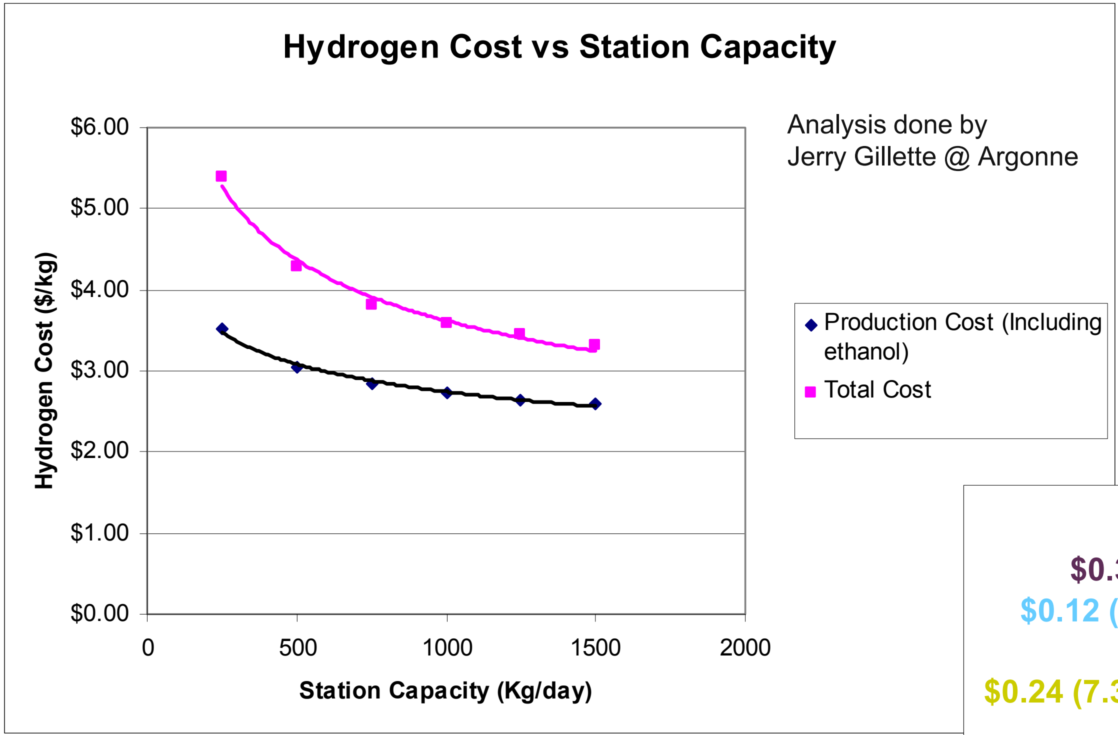
Hydrogen Cost vs. Station Capacity (Reforming of NG using OTM via Water Splitting)



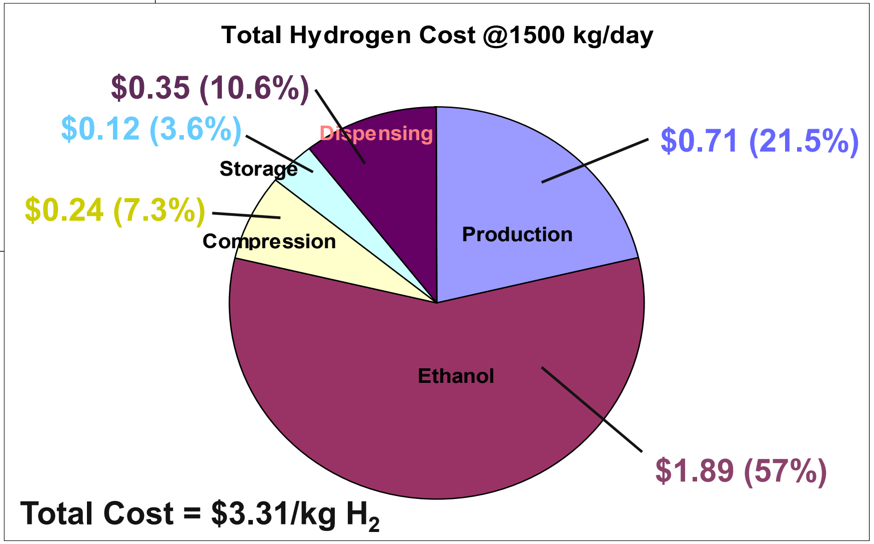
Station Size (kg/day)	Production Cost ($/kg)	Total Cost ($/kg)
70	1.79	6.76
100	1.58	5.23
200	1.31	3.58
400	1.13	2.54
600	1.05	2.16
800	1.01	2.00
1000	0.98	1.85

Analysis done by Jerry Gillette @ Argonne

Hydrogen Cost vs. Station Capacity (Reforming of Ethanol using OTM via Water Splitting)

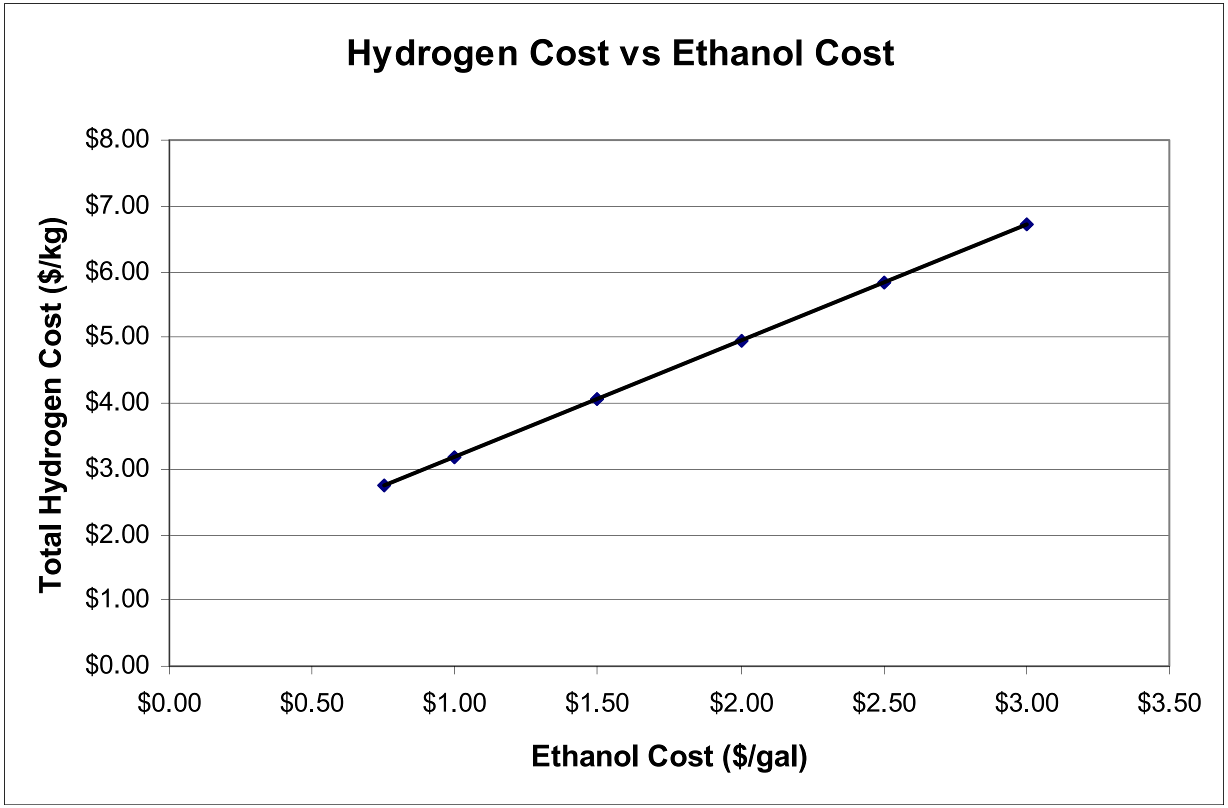


Station Size (kg/day)	Production Cost Incl. Ethanol ($/kg)	Total Cost ($/kg)
250	3.52	5.39
500	3.04	4.29
750	2.84	3.81
1000	2.73	3.59
1250	2.65	3.44
1500	2.60	3.31



- Total capital investment per station: $3.2 M (1500 kg H_2/day)
- Annual operating cost of $1.8 M of which $1 M is for ethanol (@$1.07/gal)
- Energy Efficiency (not including electricity): Energy out in the form of H_2/Energy in Ethanol + Energy in NG to produce steam = 68%

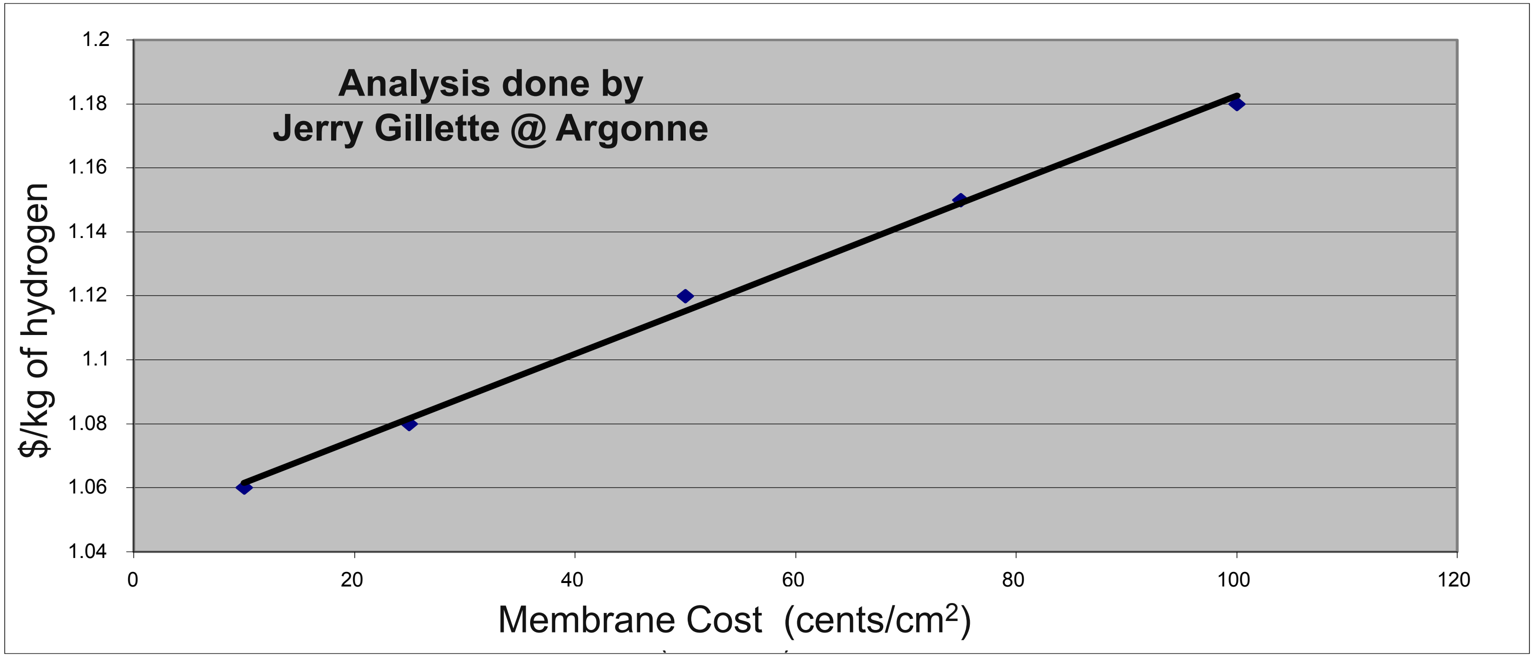
Total Hydrogen Cost vs. Ethanol Cost – Reforming of Ethanol using OTM via Water Splitting (@1500 Kg/day)



Ethanol Cost ($)	Total H_2 Cost ($/kg)
0.75	2.75
1.00	3.19
1.50	4.07
2.00	4.96
2.50	5.84
3.00	6.72

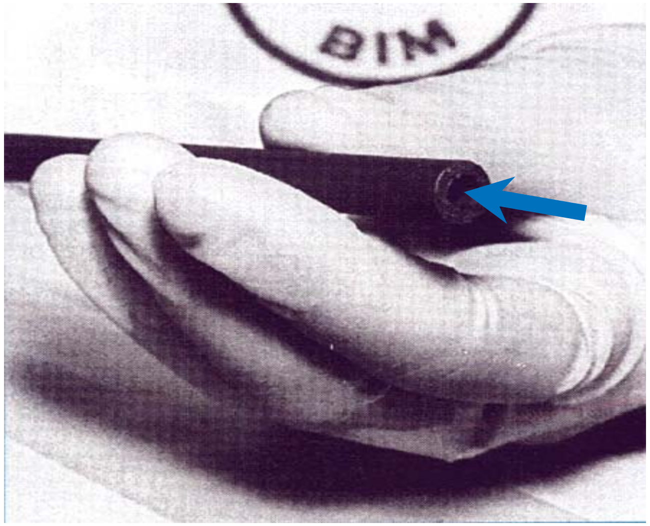
Analysis done by
Jerry Gillette @ Argonne

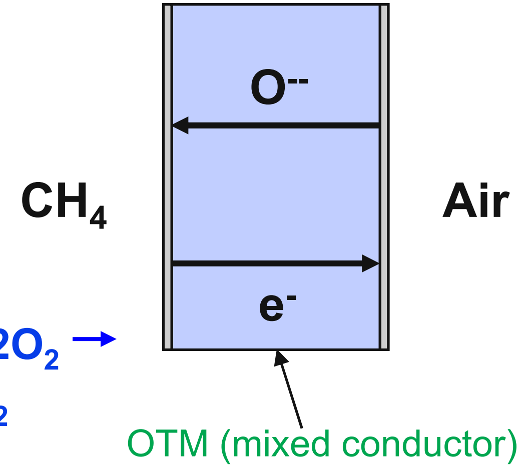
H_2 Production Cost vs. Membrane Cost @ 500 kg/day (Reforming of NG using OTM via Water Splitting)



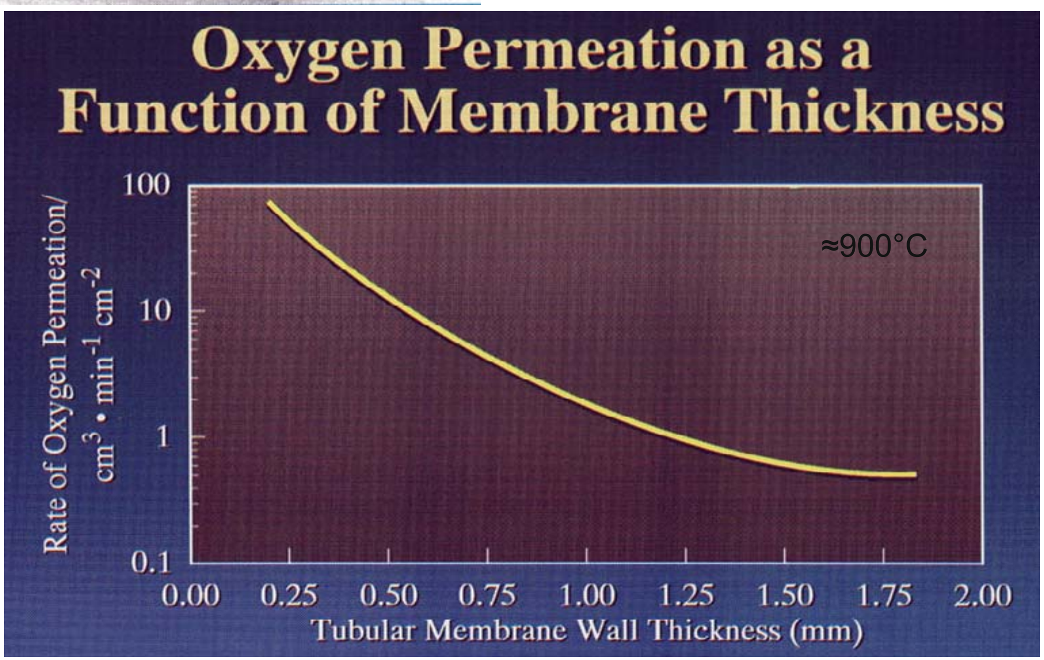
Membrane Cost ($/cm²)	($/ft²)	H_2 Production Cost ($/kg)
0.10	93	1.06
0.25	231	1.08
0.50	463	1.12
0.75	693	1.15
1.00	925	1.18

OTM for high pressure steam reforming of ethanol (S. Ahmed)



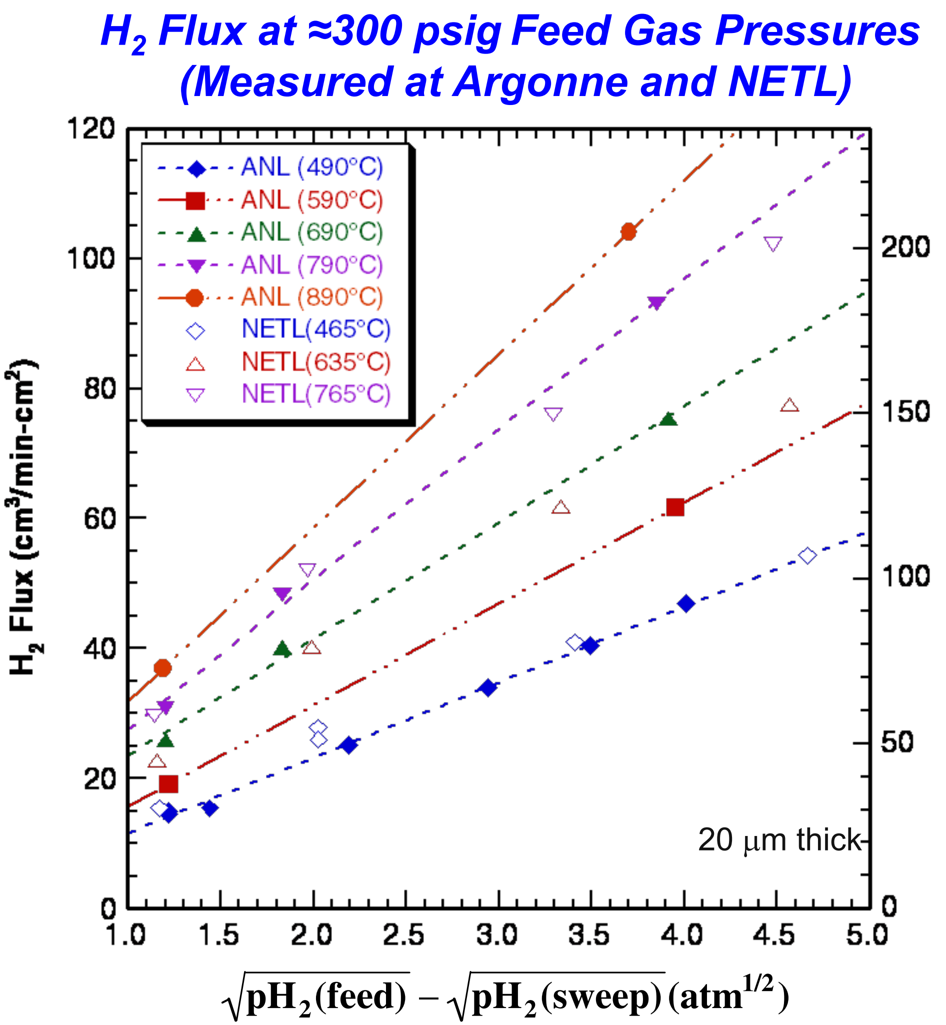


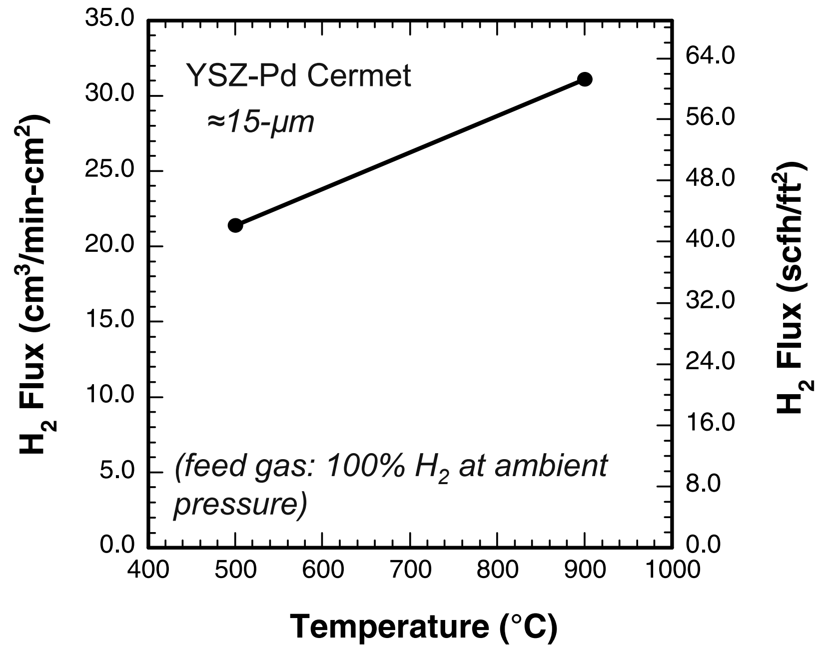
$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$



- No electrical circuitry/power supply
- Non-galvanic
- Single material (no electrodes)

HTM Membrane: H_2 Flux Measured at Ambient & High Feed Gas Pressures (≈300 psig)





High pressure measurements were made on ≈0.8-mm-thick cermet membrane, and were scaled to 20 µm thickness for comparison. Extrapolated values fall in line with values measured at high pressures at both Argonne and NETL.

Measurements at NETL were made by M. Ciocco and R. Killmeyer

SUMMARY

- Oxygen transport membrane (OTM) materials for distributed reforming of renewable liquids via water splitting are being developed.

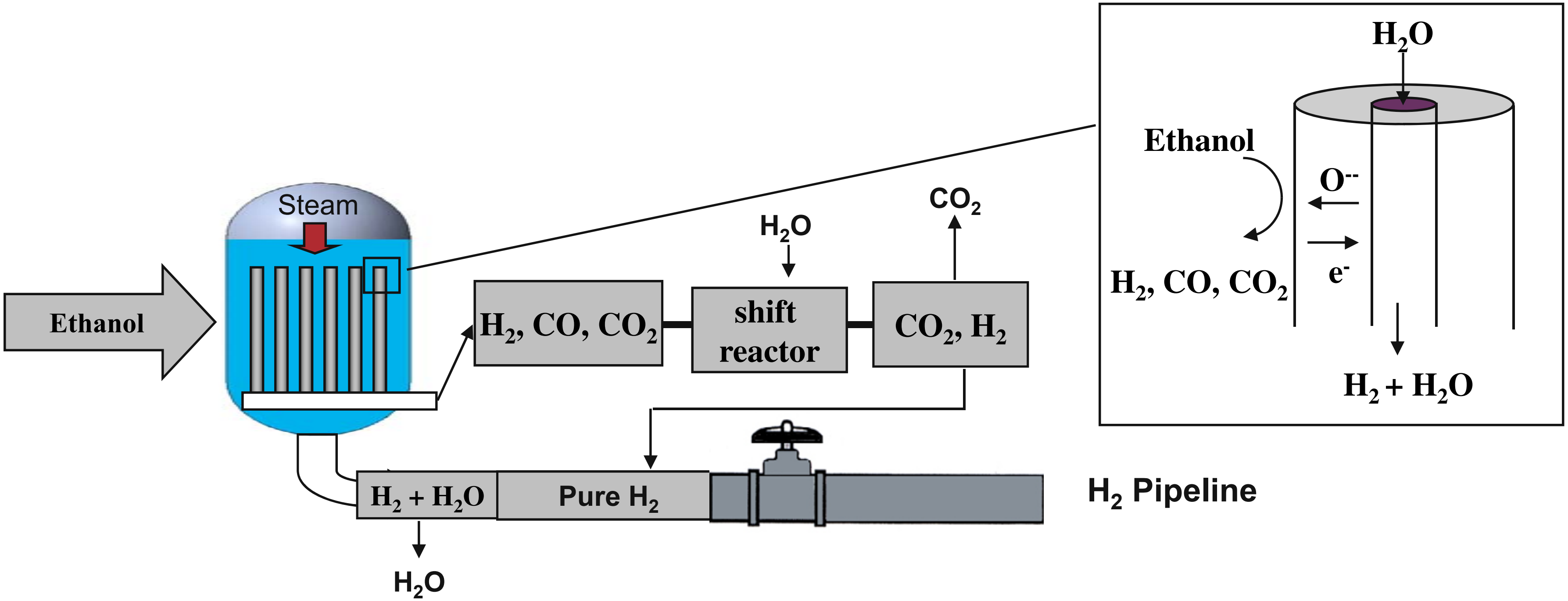
- Hydrogen production rate of ≈18 cm^3 (STP)/min-cm^2 was measured at 900°C.

- Production rate increased with increasing steam pressure, increasing pO_2 gradient, and with decreasing membrane thickness.

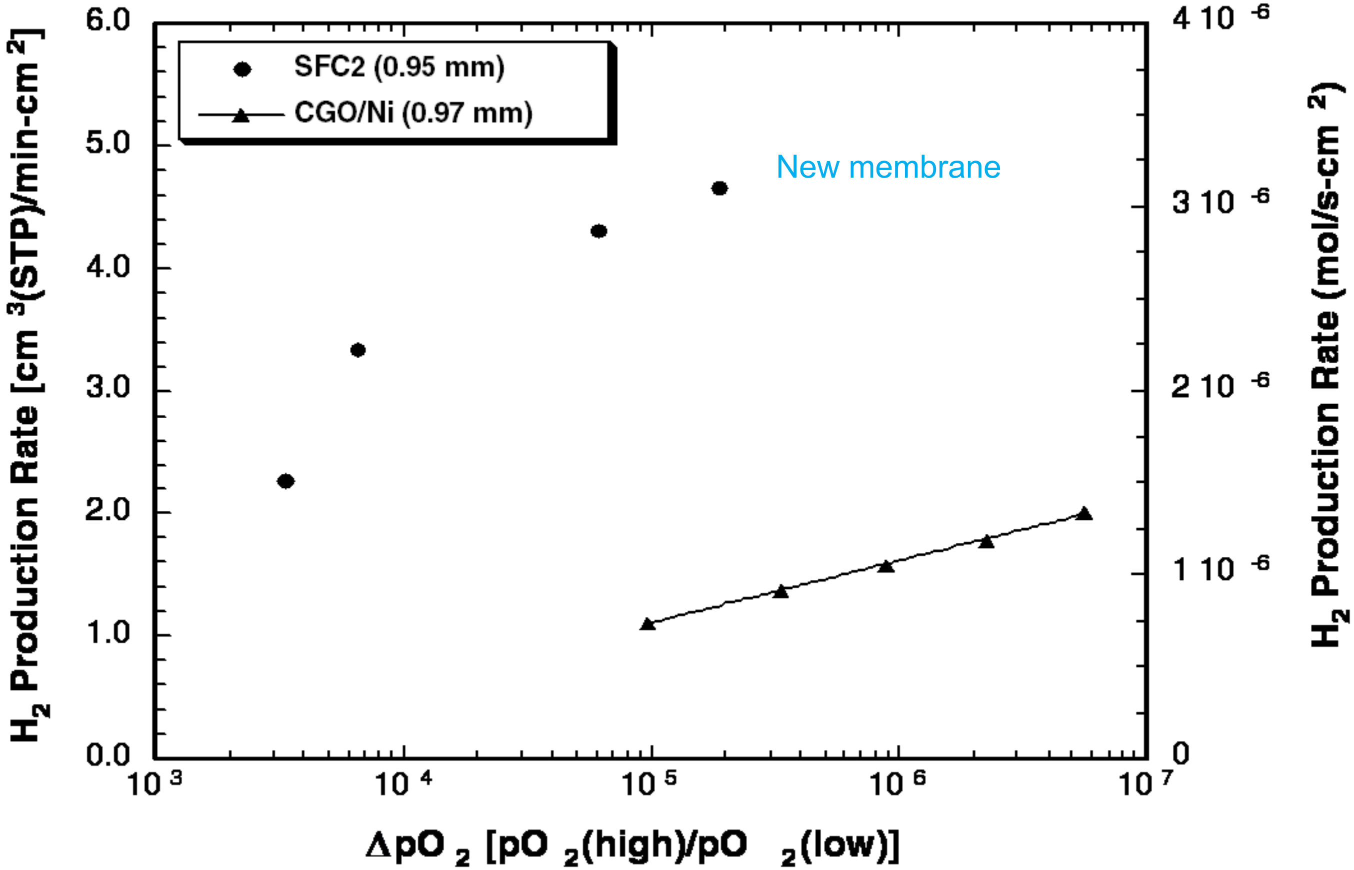
- Preliminary H2A analysis showed the following results for a station capacity of 1500 kg/day of H_2:
  - H_2 production cost including cost of ethanol (@$1.07/gal) = $2.60/kg
  - Total cost of H_2 (including costs of production, ethanol, compression, storage, & dispensing) = $3.31/kg
  - Total cost of H_2 increased from $3.19 to $4.96/kg when cost of ethanol increased from $1 to $2/gal
  - Total capital investment per station = $3.2 M
  - Annual operating cost of $1.8 M of which $1 M is for ethanol @$1.07/gal

Back-up Slides

Schematic of Distributed Reforming of Renewable Liquids using OTM via Water Splitting



H_2 production rate vs. pO_2 differential across the membrane (T = 900°C)

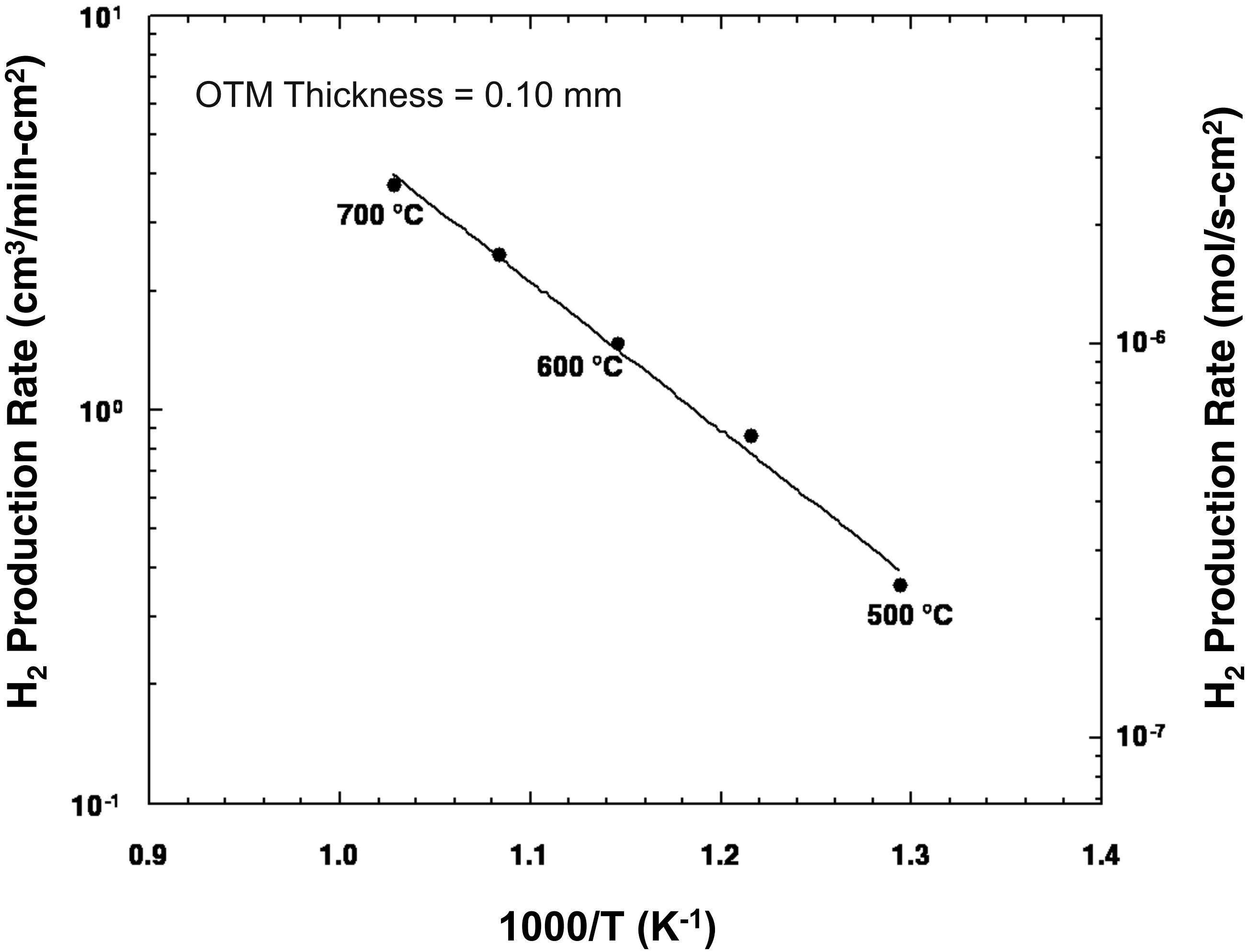


≈20-µm thick new membrane on porous support exhibited H_2 production rate ≈18 cc/min/cm²

In this model experiment, H_2 instead of CH_4 was used on the fuel side to calculate the effect of pO_2

Decreasing membrane thickness should enhance H_2 production rate

Dependence of Hydrogen Production Rate on Temperature of OTM



In this model experiment, H_2 instead of CH_4 was used on the fuel side to study the effect of temperature.