Coal to Hydrogen: A Novel Membrane Reactor for Direct Extraction

> Francis Lau and Shain Doong
Gas Technology Institute
Des Plaines IL
francis.lau@gastechnology.org

GCEP Energy Workshops

April 26-27, 2004

Francis C. Arrillaga Alumni Center, Stanford University

GAS TECHNOLOGY INSTITUTE

- Independent Not-for-Profit R&D and Training Organization
  - 18-acre campus
  - 350,000 ft^2 facility
  - Labs, test facilities, library, classrooms, offices
- Energy & Environmental Topics
- Fossil and Renewable Energy Focus

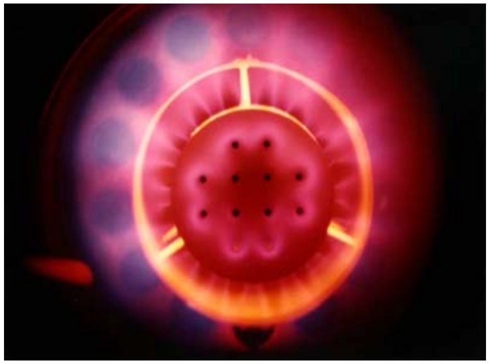
Exploration & Production

Pipeline Materials

Fuel Cells

Distributed Generation

Gasification



Combustion

Project Goal

Develop a novel membrane gasification reactor for low cost production of hydrogen from coal

Project Team

- Gas Technology Institute
- University of Cincinnati (Dr. Jerry Lin)
- University of Florida (Dr. Eric Wachsman)

Project Sponsors

- DOE/NETL
- DCEO/ICCI
- AEP

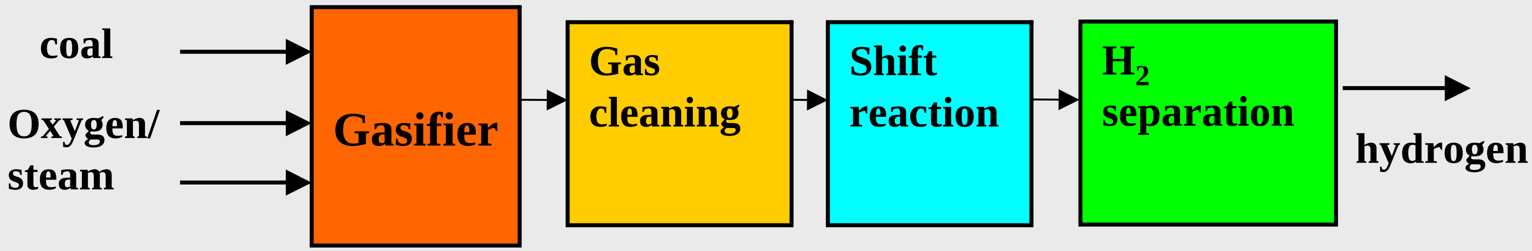
Industrial Advisors

- American Electric Power, utility
- Wah Chang (Allegheny), metals, palladium membrane
- Schott Glass, sealant, hydrogen membrane
- ProTek: high temperature membrane manufacturing

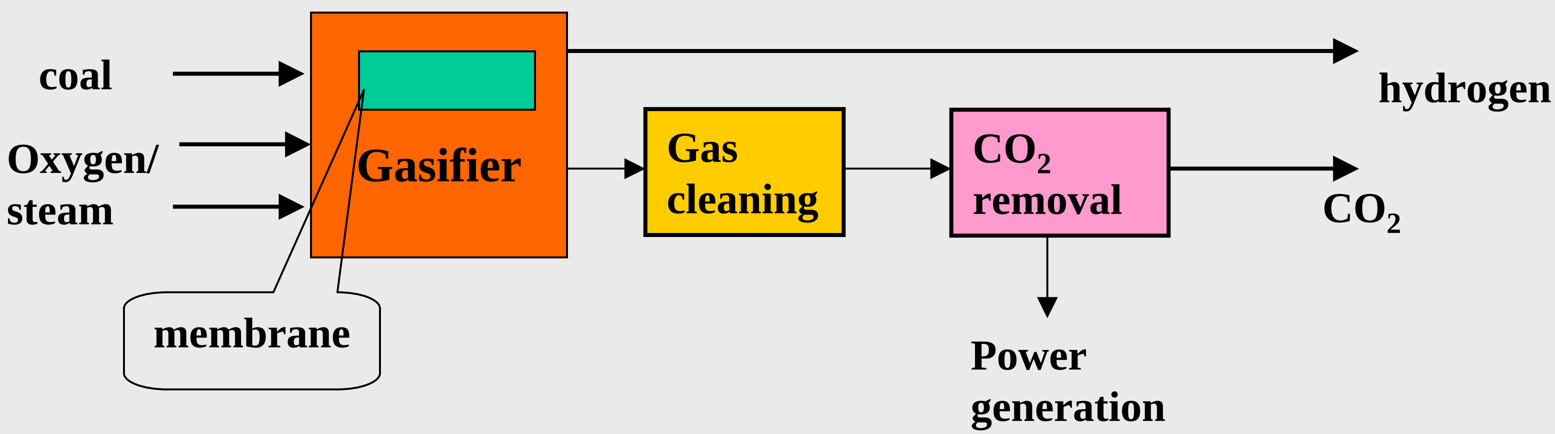
gti[SM]

Hydrogen from Coal via Gasification

Conventional gasifier



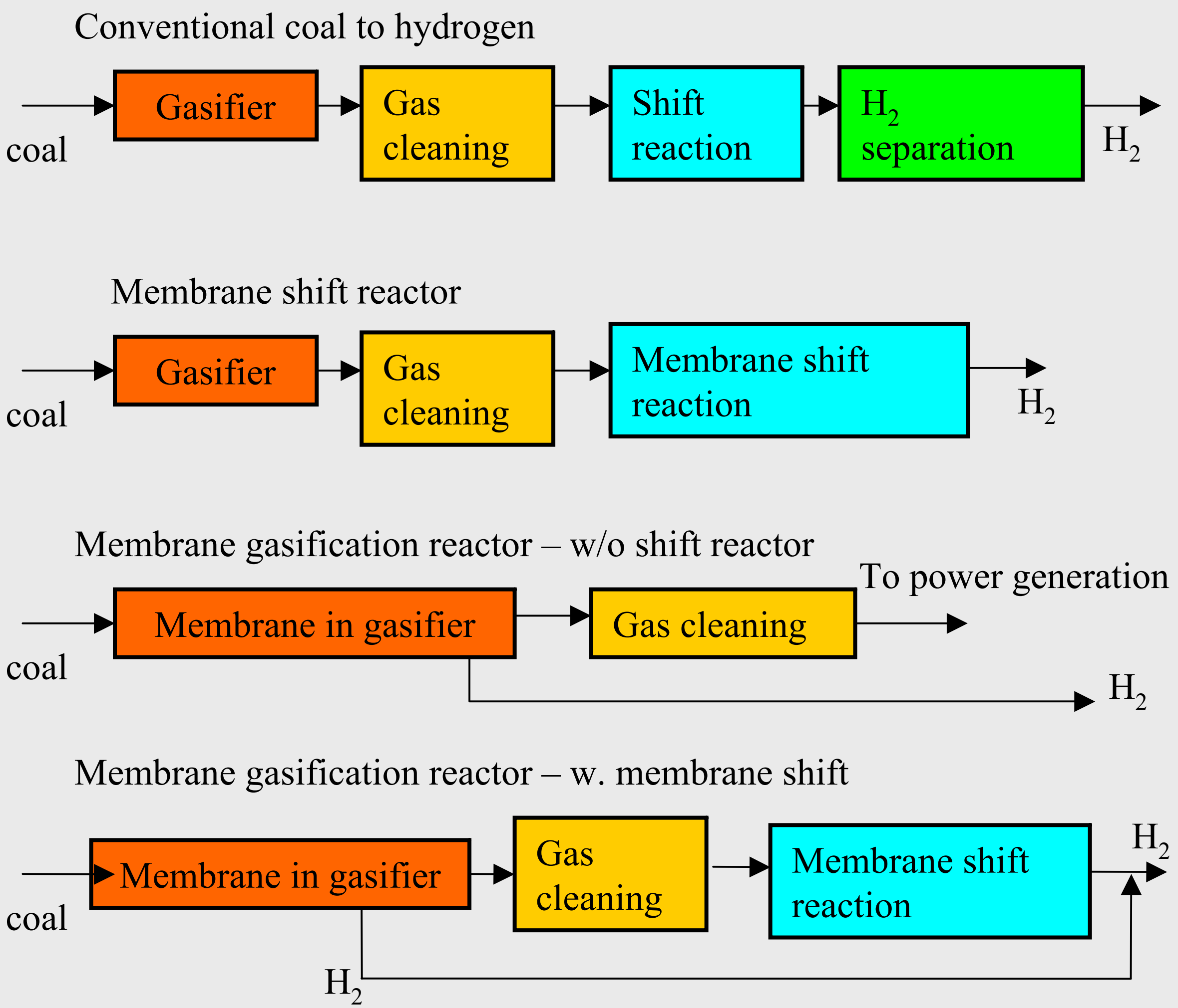
Membrane gasification reactor



Potential Benefits of Membrane Reactor for Hydrogen Production from Coal

- **High H_2 production efficiency:**
  - Preliminary thermodynamic analysis indicates over 30 - 50% improvement in H_2 production efficiency over the current gasification technologies
- **Low cost:**
  - reduce/eliminate downstream processing steps
- **Clean product:**
  - no further conditioning needed, pure hydrogen
- **CO_2 sequestration ready**:
  - simplify CO_2 capture process
- **Power co-generation**:
  - utilization of non-permeable coal syngas

Comparison of Process Options for Hydrogen from Coal



For same coal feed

Process option	H_2 product	To gas cleaning
Conventional coal to hydrogen	100	100
Membrane shift reactor	129	100
Membrane gasification reactor – w/o shift reactor	130	60
Membrane gasification reactor – w. membrane shift	150	60

gti

Mass Balance for Process Options for Hydrogen from Coal

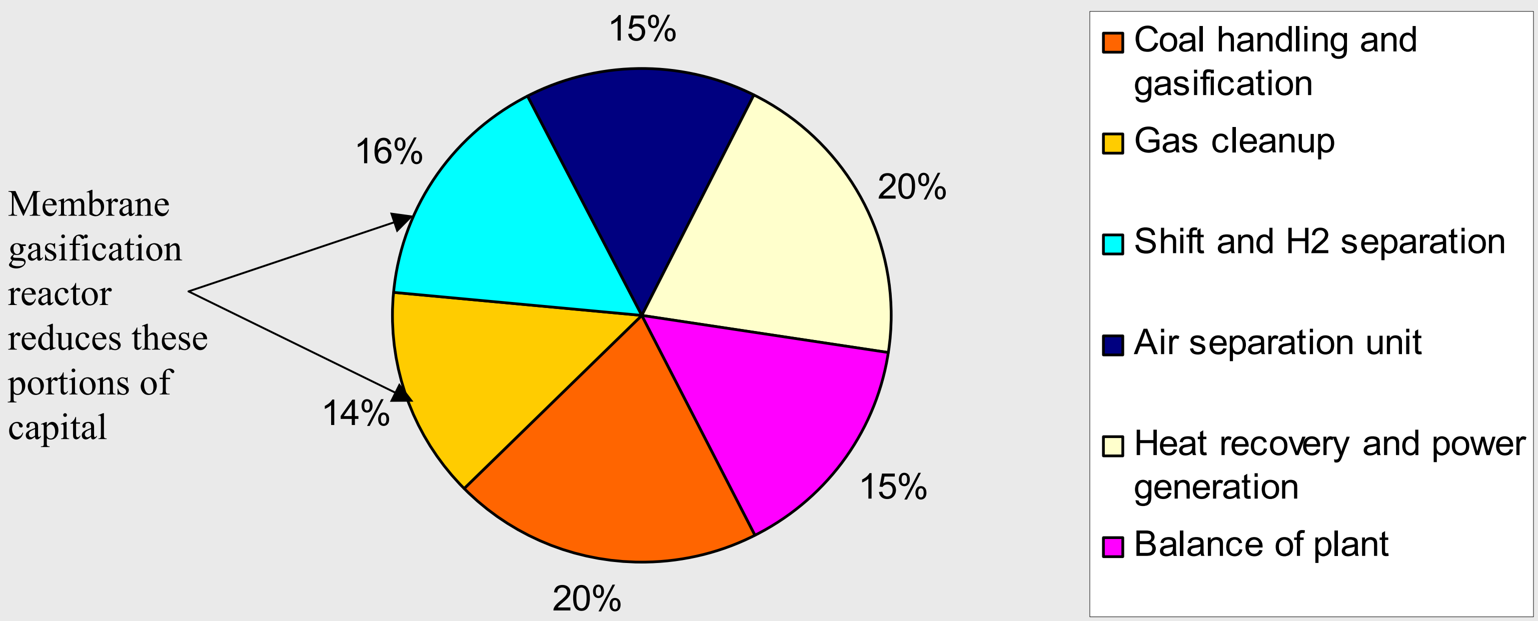
Process	1	2	3	4
Hydrogen product, mole	100	129	130	150
Residual gas, mole				
H_2	25	1	4	2
CH_4	5	5	0	0
CO	6	0	18	0
CO_2	90	96	83	101
H_2O	26	21	27	10

- **Membrane reactor increases hydrogen production by**
  - **Eliminate loss in PSA (Pressure Swing Adsorption) tail gas**
  - **More CO shift** $H_2O+CO = CO_2+H_2$
  - **Reform CH_4** $CH_4+H_2O = CO+3H_2$

1. Conventional coal to hydrogen
2. Membrane shift reactor
3. Membrane gasification reactor – w/o shift reactor
4. Membrane gasification reactor – w. membrane shift

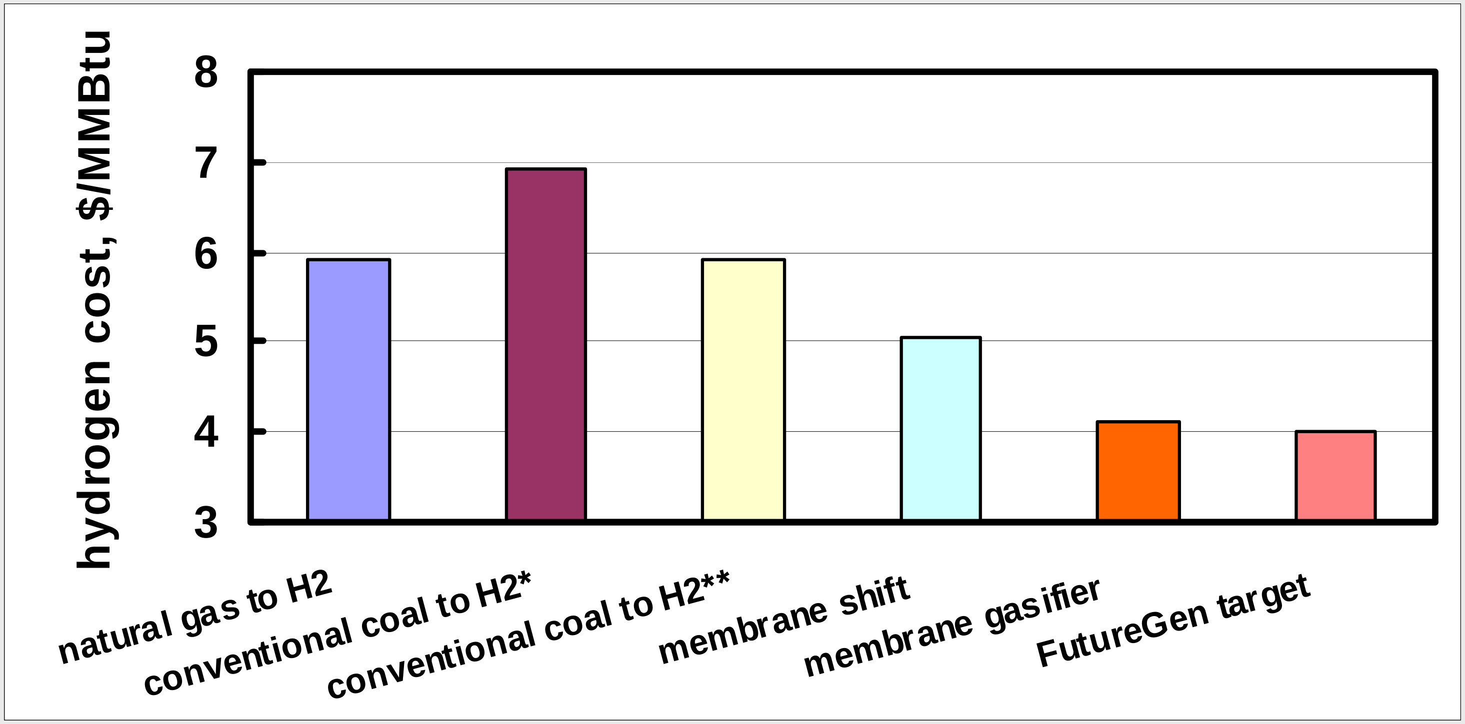
gti

Typical Capital Cost Breakdown for Hydrogen Production from Conventional Coal Gasification



- Cost of hydrogen from coal: 75% capital, 25% coal and O&M

Membrane Gasification Reactor Offers a Low Cost Option for Hydrogen from Coal



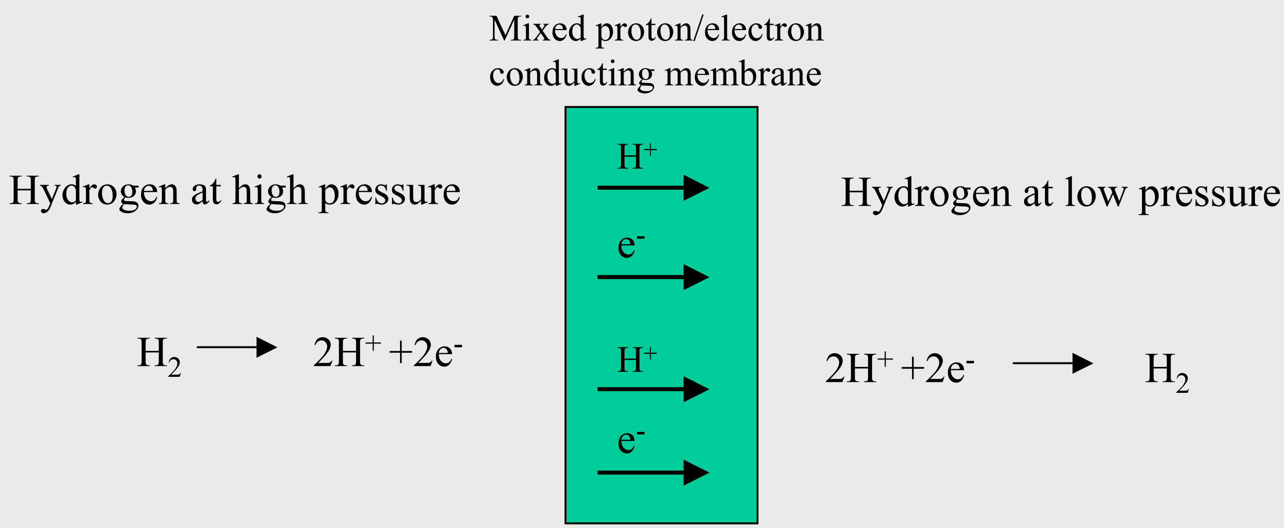
*With CO_2 Capture. ** Without CO_2 Capture.

- Data based on a study by Parsons Infrastructure and Technology Group, Inc. "Hydrogen Production Facilities Plant Performance and Cost Comparisons", Final Report DOE Contract DE-AM26-99FT40465, March 2002 (Natural gas: $3.15/MMBtu, Coal: $1.00/MMBtu)
- H_2 cost of membrane gasifier case is based on the 50% increase in hydrogen production with 20% increase in capital for membrane module.

gti

Advanced Ceramics Identified as Candidate Membrane Materials

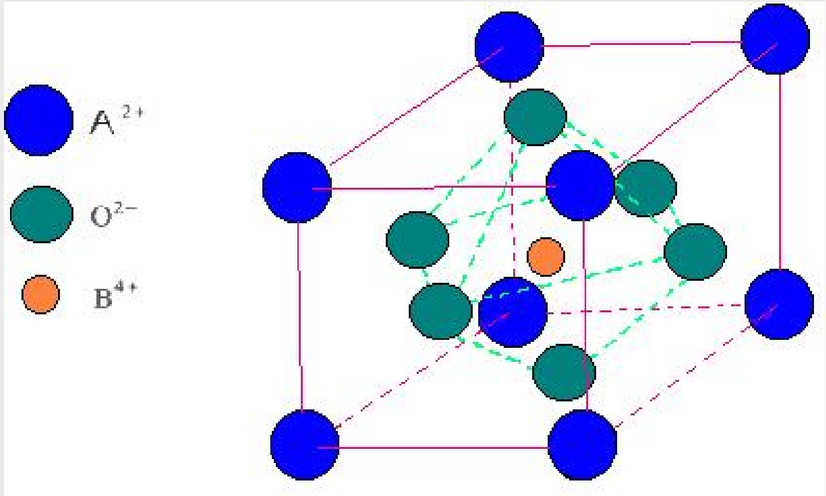
> Certain perovskite-based oxides possess both proton and electron conductivities at high temperatures (500~ 1200°C).



Ceramic Material of Perovskite Type Identified as a Leading Candidate Membrane for H_2 Separation

- $ABO_{3-\alpha}$ (α oxygen deficiency)
- Conduct both ions (proton or oxide) and electrons
- Proton forms an OH group
- For use in H_2 separation
  - A : Ba or Sr
  - B : Ce
  - B-site dopants :

    Y, Yb, Nd, Gd, Eu, ….



- Adding a metal phase to the ceramic matrix – cermet
  - To improve electronic conductivity

gti

Literature Review on High Temperature Hydrogen Separation Membrane - Mixed Ionic-Electronic Conductor

Team	Flux, cc/min/cm^2	thickness, mm	T, C	membrane
U. of Cincinnati	0.04	1.6	900	$SrCe_{0.95}Tm_{0.05}O_{3-\alpha}$
Nagoya U. (Japan)	0.056	1	900	$SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$
Wachsman (US patent)	0.05	2	600	$BaCe_{0.95}Gd_{0.15}O_{3-\alpha}$
Wachsman (US patent)	0.42	2	600	$BaCe_{0.95}Eu_{0.15}O_{3-\alpha}$
Argonne	0.072	1	800	$SrCe_{0.95}Y_{0.05}O_{3-\alpha}$
UC Berkeley	1.3	0.002	680	$SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$
Argonne	20	0.4	900	cermet
Eltron	4	0.2	950	cermet

gti[SM]

High Temperature H_2 Membrane Material Development

> Target flux performance: 50 cc/cm²/min

> Current approach:

  - Operating at higher pressure, higher temperature with thinner membranes
  - Addressing chemical stability and durability of membrane materials

> Test membranes prepared in-house and by others (U. of Florida and U. of Cincinnati)

> Ceramic membrane development program

  - GTI's capability to make solid oxide fuel cell membrane
  - funded by Illinois Clean Coal Institute (ICCI)

> Membrane testing for permeation

  - Existing unit, low pressure, < 950°C
  - New high pressure unit, 1100°C and 1000 psi

gti

Initial Membrane Materials to be Tested

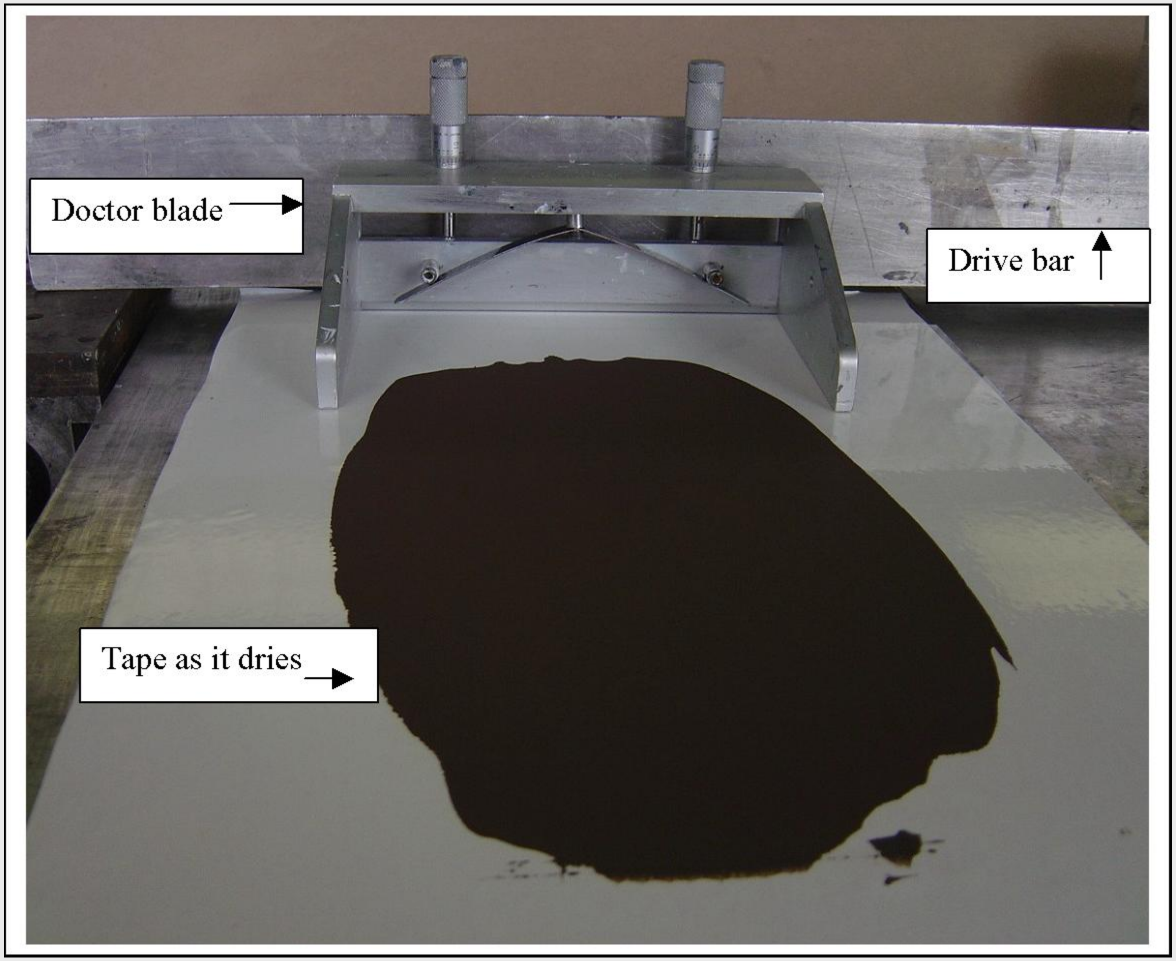
> $BaCe_{0.8}Y_{0.2}O_{3-\alpha}$ (BCY)
  – 25 µm, supported on a porous BCY layer (400 µm total)

> $SrCe_xTm_{1-x}O_{3-\alpha}$ (SCTm)
  – 2 mm

> $SrCe_xEu_{1-x}O_{3-\alpha}$ (SCEu)
  – 10-25 µm

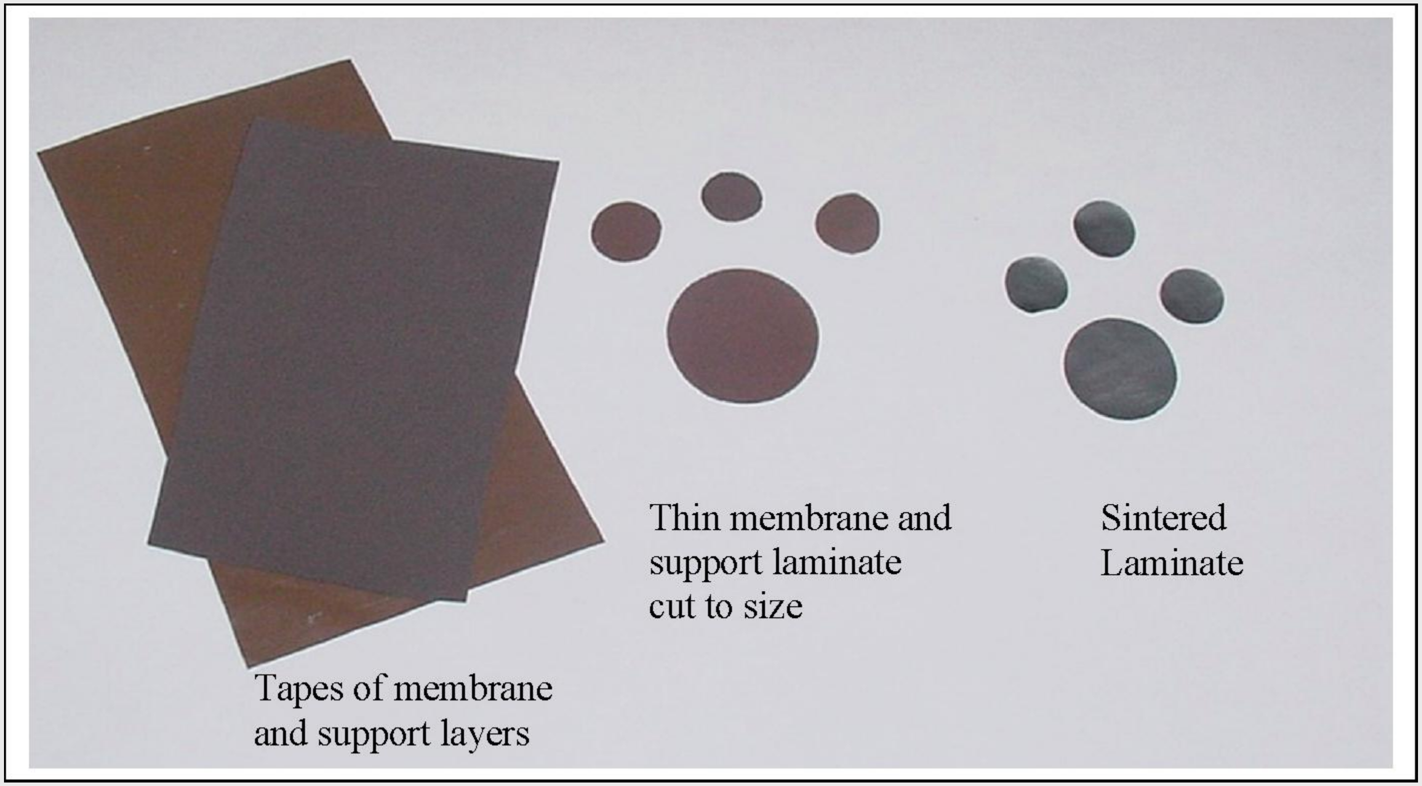
> Ni/Pd/BCY dual phase membrane

Thin Membranes Prepared by Tape-Casting Technique

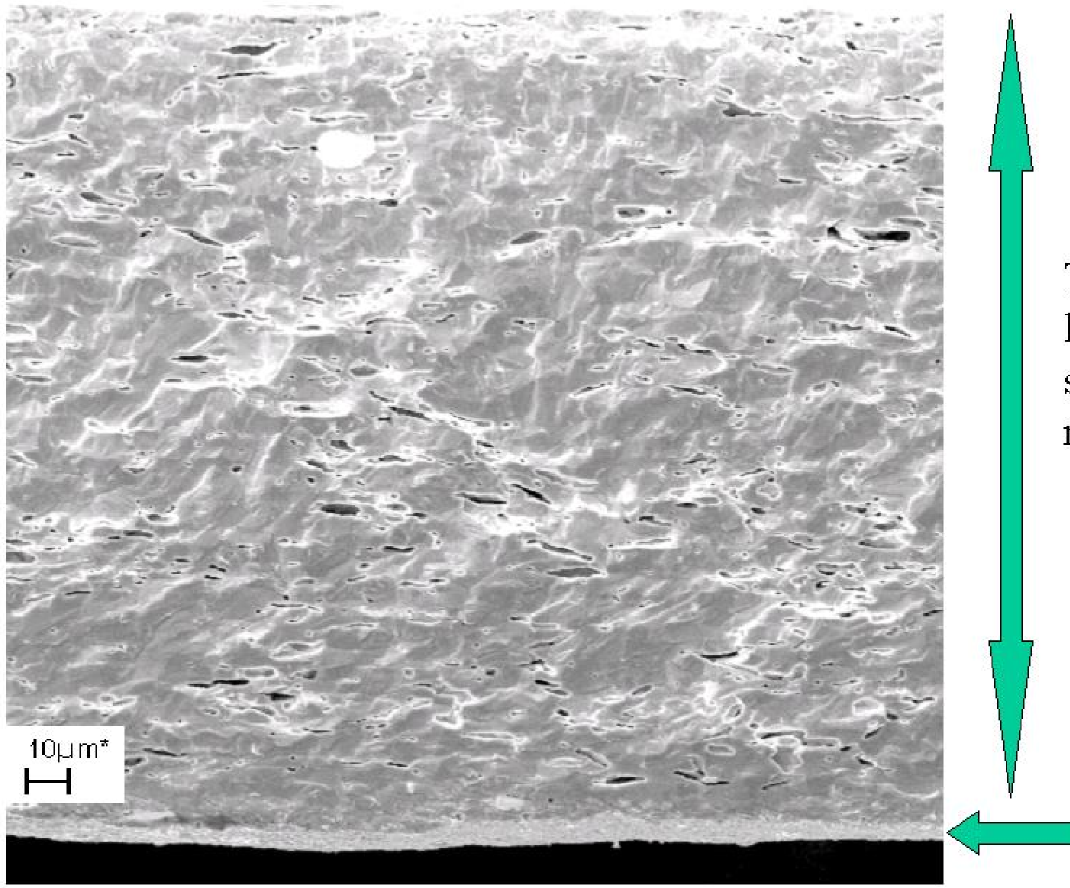


gti

Supported Thin Film Ceramic Membranes



GTI's Supported Thin Ceramic Membrane
- SEM Picture

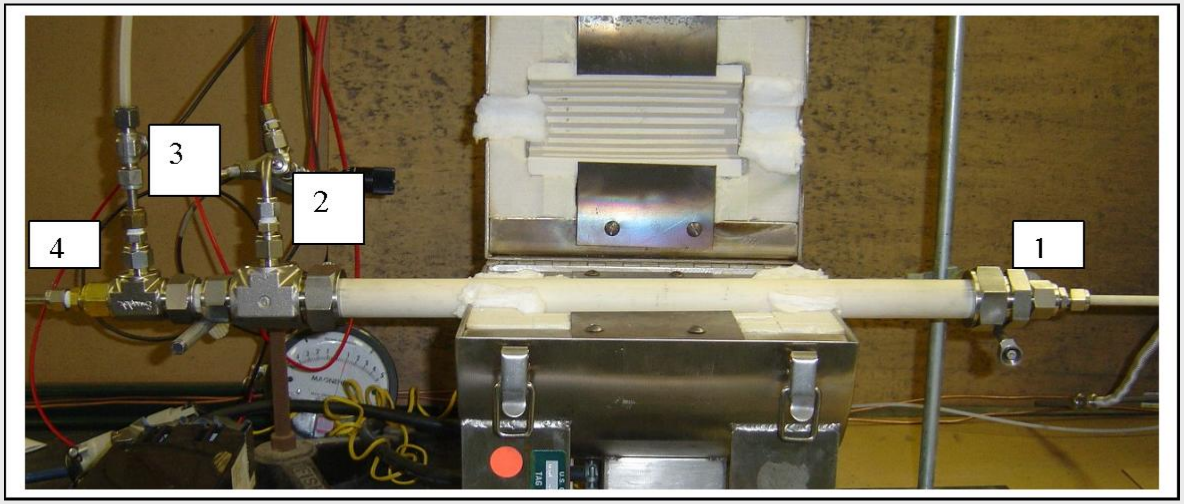


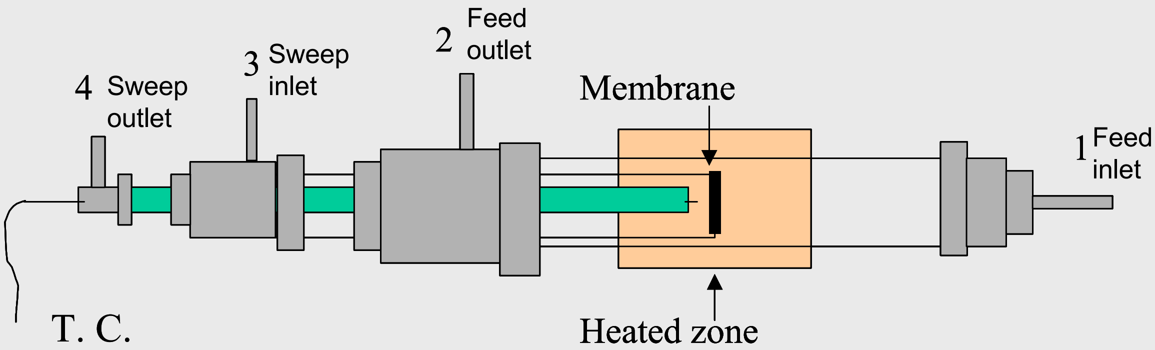
This thick porous layer is the support for the membrane.

This thin dense layer is the membrane.

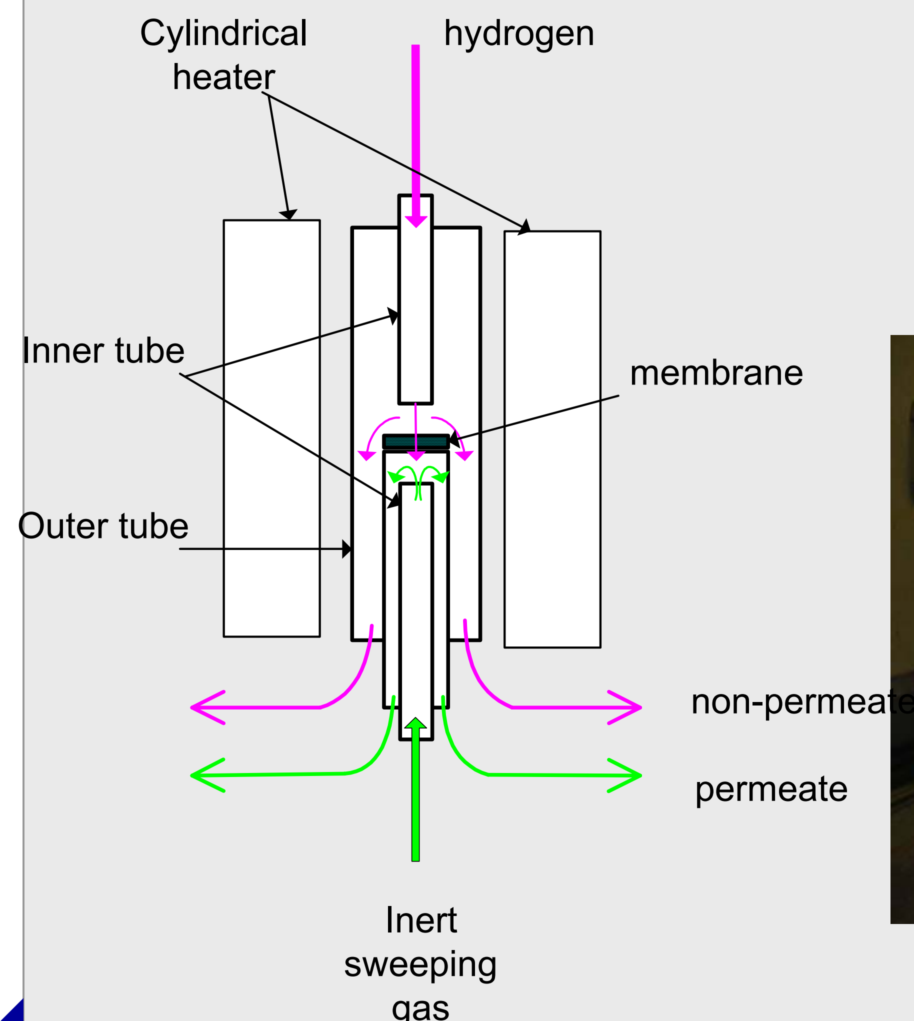
GTI's Membrane Permeation Apparatus

- ambient pressure and 1000^{o}C

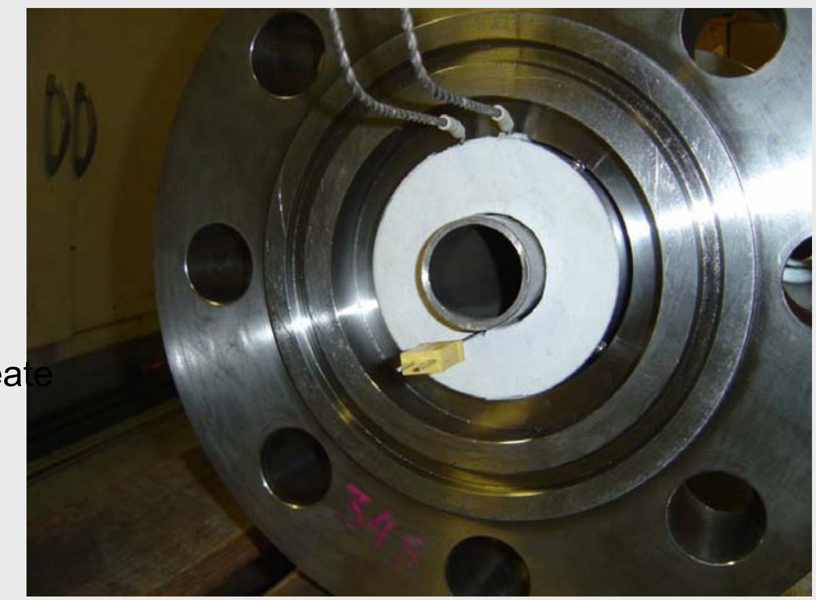




Design of High Temperature/High Pressure Hydrogen Permeation Unit

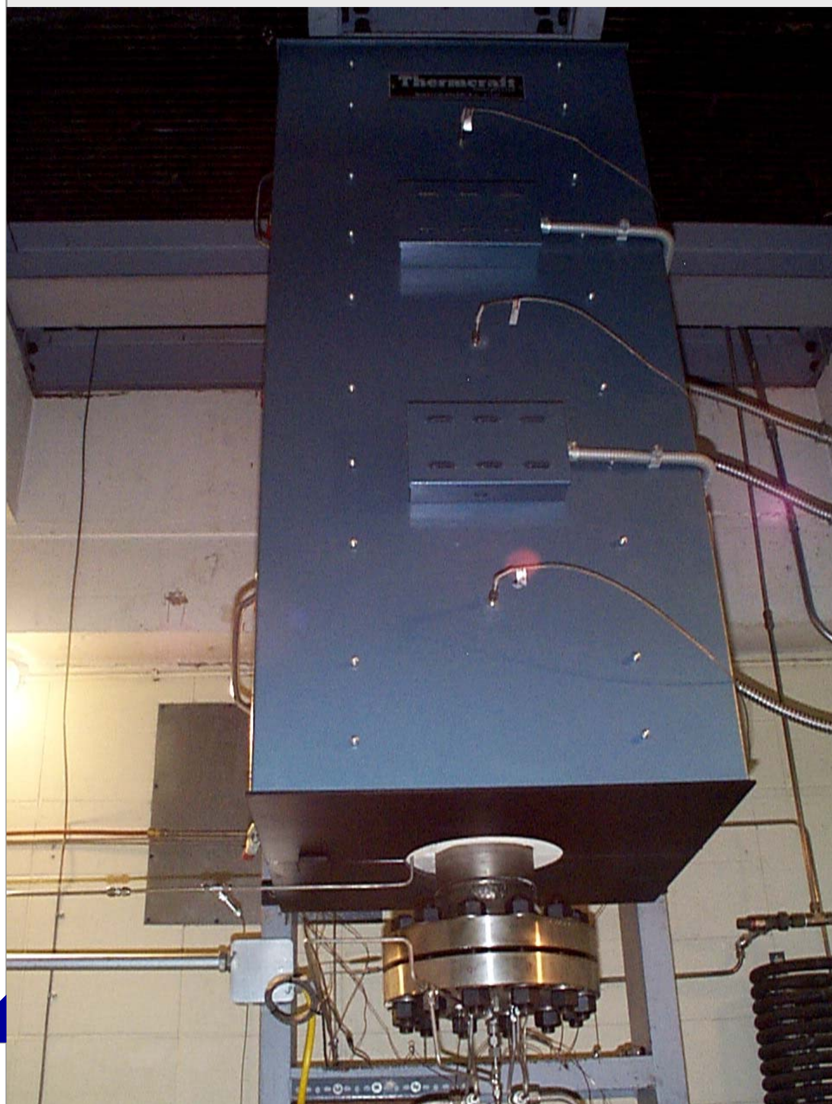


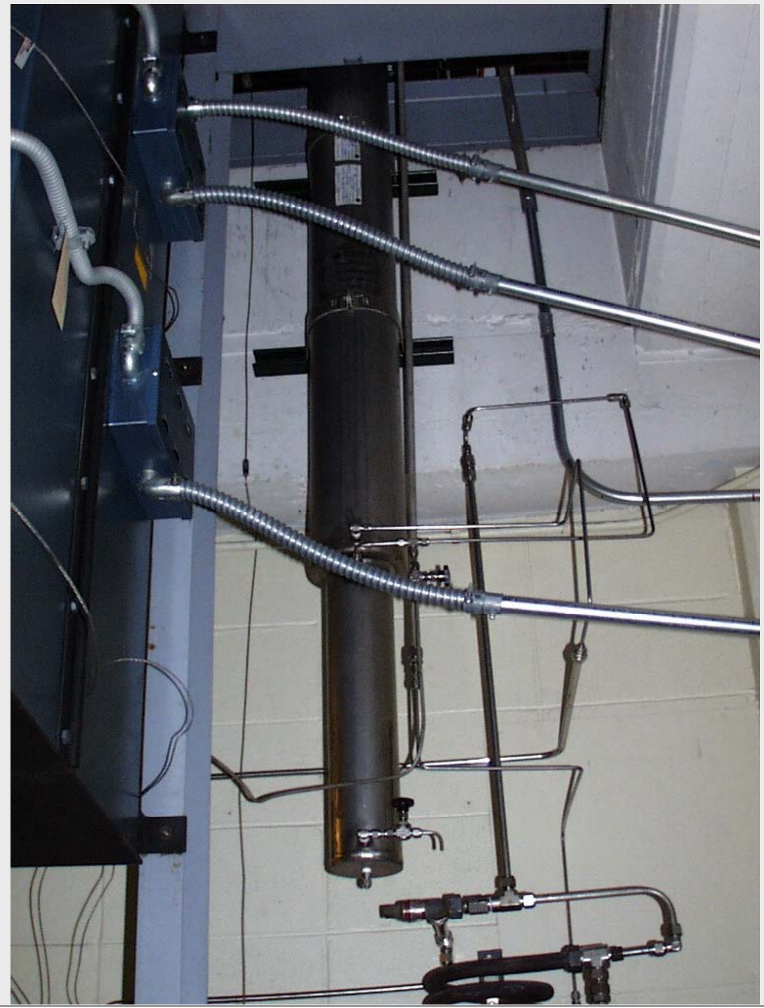
- Membrane diameter:1.25”
- Max Temp: 1100°C
- Max Pressure:1000 psi



GTI High temperature/High Pressure Permeation Unit

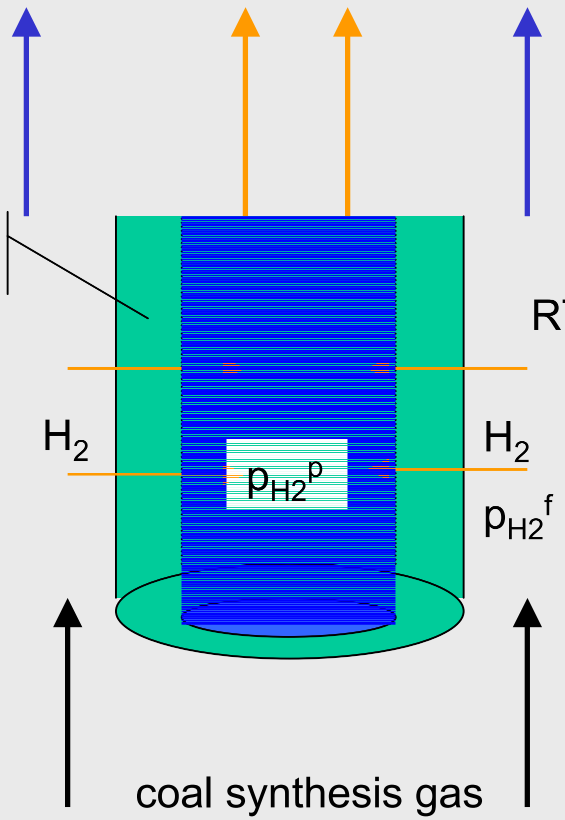
High Pressure Bench-scale Reactor





gti

Membrane Gasification Modeling -Matching reaction kinetics and hydrogen permeation rate



noncatalytic gas phase rxn

$H_2O+CO = CO_2+H_2$

$CH_4+H_2O = CO+3H_2$

$(CH_4+CO_2 = 2CO+2H_2)$

700-400 °F approach to equilibrium for reforming reactions

J_{H2} (hydrogen flux) =

$RT/F^2\sigma_H[(p_{H2}^{f})^n-(p_{H2}^{p})^n]A/L$

n: 0.25-0.5

σ_H: proton conductivity

A: membrane area

L: thickness

gti

Potential Technical Issues and Barriers

> Chemical stability under CO_2 environments for Ba and Sr cerate perovskites

> Tolerance to other contaminants, sulfur, chlorine, carbon deposit, etc.

> Steam may increase oxygen conductivity and reduce proton conductivity

> Higher temperature (>1000C) favors oxygen (oxide) transport than proton transport

> Interfacial polarization for very thin membrane, may need catalyst layer to facilitate hydrogen dissociation

gti

GTI Flex-Fuel Test Facility

Capacity: 10 – 20 tpd coal, 20 to 40 tpd biomass

Plug and Play: Feed and gas conditioning systems

gti

GTI FlexFuel Test Facility

Gasifier

Primary Cyclone

Roadmap of Membrane Gasification Reactor Development