Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas (ITM Syngas)

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Project ID: PDP15

Project Timeline

Oct'97-Apr'00	May'00-Sep'07		Oct'07-Dec'09
Phase 1	Phase 2	Phase 2 extension	Phase 3
1 2 3	4 5 6	7 8	9 10

Progress: 60% complete

Phase 1 Material and membrane development	1. Identified family of high-pressure membrane materials 2. Verified ceramic-to-metal seal performance 3. Selected planar membrane over tubular design
Phase 2 Scaleup to pilot-scale reactors (extension needed to meet all Phase 2 objectives)	4. Demonstrated stable membrane performance at elevated pressure for over 6 months 5. Tested pilot-scale planar membrane module in 24,000 SCFD* Process Development Unit (PDU) 6. Demonstrated target performance of pilot-scale membrane → 7. Test full-size membrane 8. Start operation of 1 million SCFD Sub-scale Engineering Prototype (SEP) with full-size membranes
Phase 3 Scaleup to pre-commercial demonstration	9. Start operation of 22 million SCFD Pre-Commercial Technology Demonstration Unit (PCTDU) 10. Update process economics and launch commercialization

* std. cu. ft. per day of synthesis gas

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Project Budget

Funding ($000's)	FY2004	FY2005
DOE-Fossil Energy	3,648	5,100
DOE-Energy Efficiency	200	200
Industry	4,897	6,745
Total	8,745	12,045

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Broad Industry/University Team Is Addressing DOE Technical Barriers

- Addresses DOE MYPP* Technical Barriers
  - Fuel Processor Capital Costs (A)
  - Carbon Dioxide Emissions (D)
  - Oxygen Separation Technology (AA)
- Partners

AIR PRODUCTS
ChevronTexaco
U.S. DEPT. OF ENERGY
ceramatec
ELTRON RESEARCH
SOFCo EFS
University of Pennsylvania
University of Alaska Fairbanks
PENNSTATE 1855

* Multi-Year Program Plan

Objectives

- Develop technology for the low-cost conversion of natural gas to hydrogen and synthesis gas using ion transport membranes (ITM)
  - Lower hydrogen production costs will facilitate the transition to a Hydrogen Economy
- Scale up through three levels of pilot-scale testing and precommercial demonstration
  - Scaleup covers range of distributed-scale and centralized hydrogen production
- Obtain data necessary for the final step to full commercialization of the ITM Syngas technology

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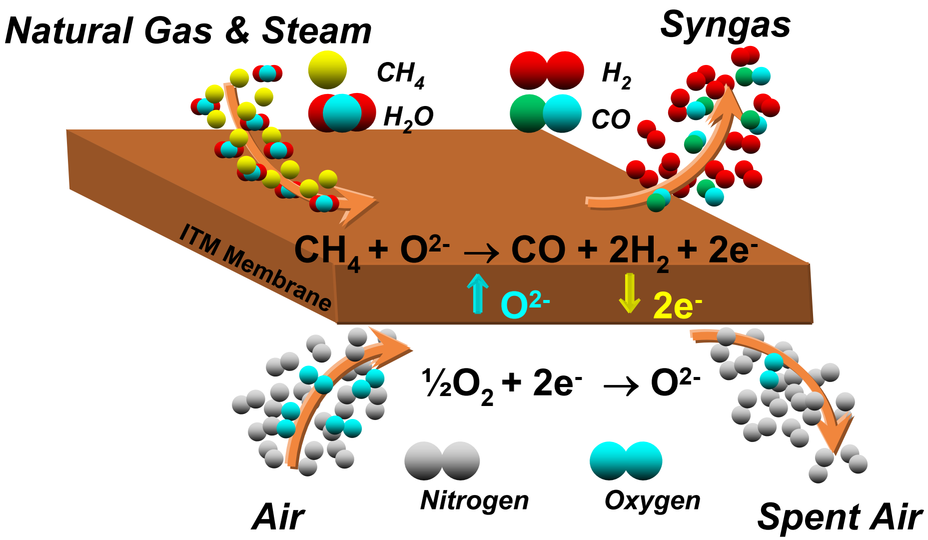
Approach

- Develop technology for the low-cost conversion of natural gas to hydrogen and synthesis gas using ITM (non-porous, multi-component, ceramic membranes)



  - Achieve significant cost savings by combining air separation and methane partial oxidation into a single unit operation.
  - Obtain high oxygen flux and high selectivity for oxygen
  - Operate at high temperatures, typically over 700°C
  - Develop membrane and reactor designs, membrane materials, and ceramic fabrication methods
  - Obtain membrane performance test data for scaleup and commercialization

ITM Syngas Membrane Materials Meet Severe Demands

- Patented composition
  - $(La_{1-x}Ca_x)_yFeO_{3-\delta}$ where $0<x<0.5$ and $1.0<y$
- Thermodynamic stability in different environments
  - High-pressure, reducing environment on the natural gas side
  - Low-pressure, oxidizing environment on the air side
- Electronic and oxygen ion conductivity to achieve economically attractive oxygen flux
- Mechanical properties to meet lifetime and reliability criteria

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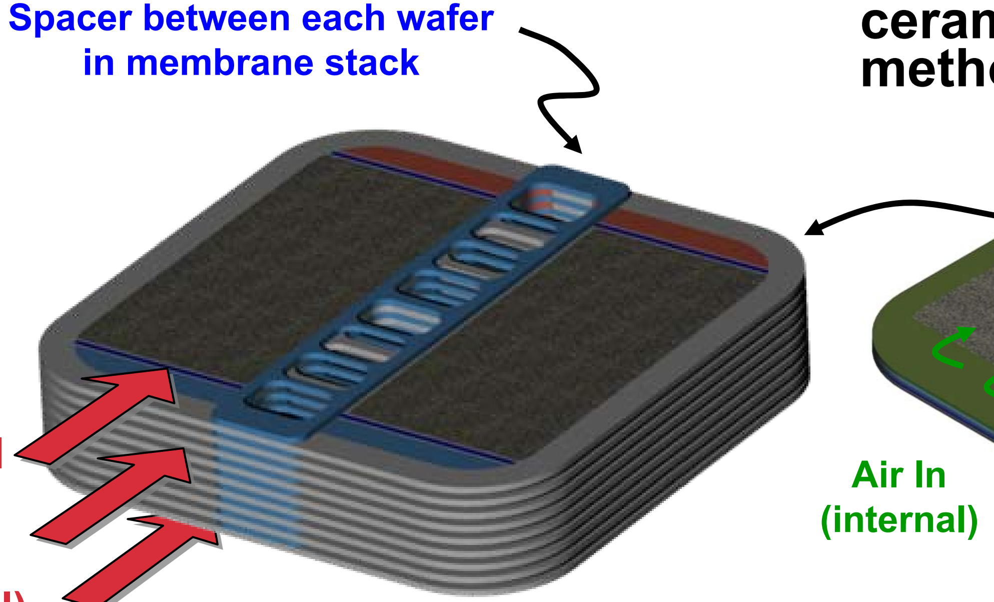
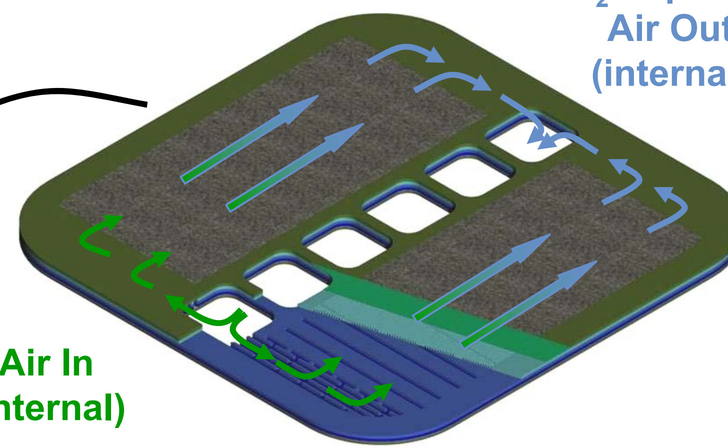
Planar Membranes Meet Performance Requirements

- Microchannel design
- Good mass and heat transfer
- Compact
- Minimizes number of ceramic-to-metal seals
- Handles high-pressure load
  - Minimize cost of air compression
- Amenable to standard ceramic processing methods



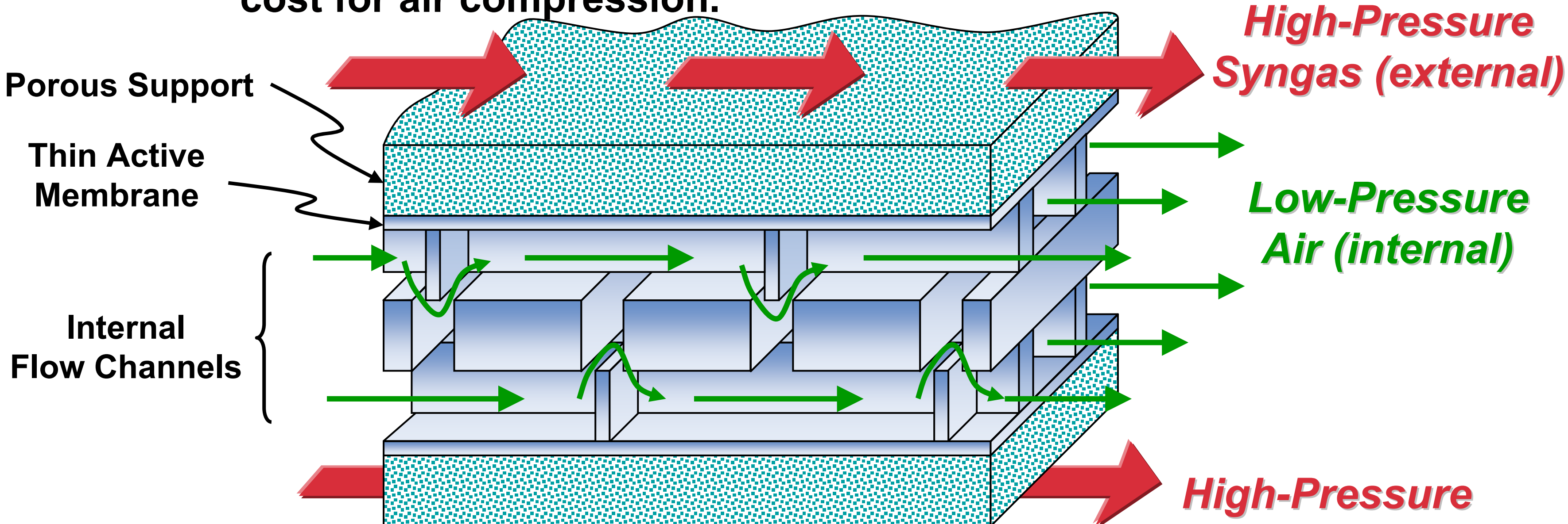
Stack of ITM Syngas Wafers



ITM Syngas Planar Wafer

Membrane Mechanical Support and Fluid Flow

- Supports pressure load
  - Porous/dense laminate structure with supports in channeled layer is in hydrostatic compression.
  - High-pressure syngas avoids additional compression downstream.
  - Low-pressure air reduces capital and operating cost for air compression.
- Meets fluid flow and mass & heat transfer requirements
  - Interconnected flow channels ensure good flow distribution and low pressure drop.
  - Channel dimensions ensure high rates of mass and heat transfer.



ITM Syngas Planar Wafer* Cross-Section

* US patent application US 2004/0186018

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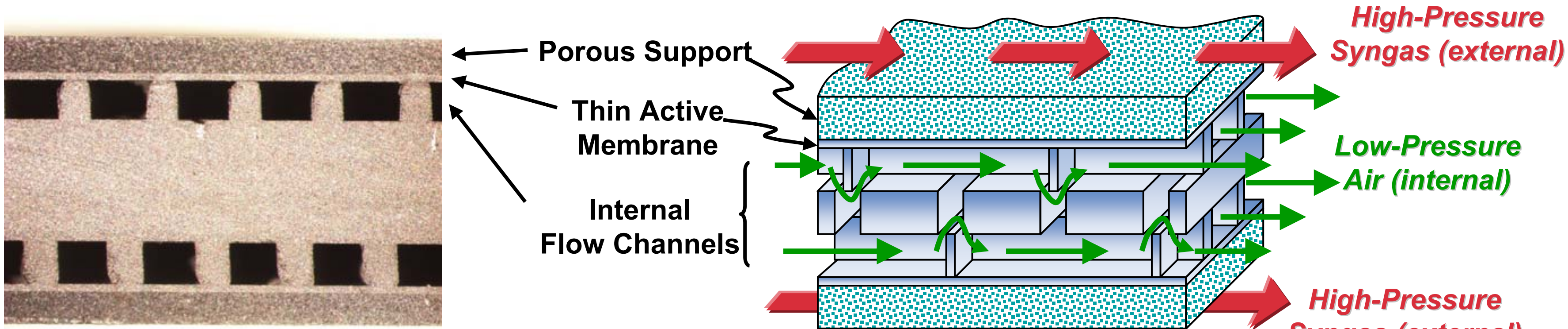
Membrane Balances Resistances

- Membrane material developed to achieve desired flux and stability*
  - $(La_{1-x}Ca_x)_yFeO_{3-\delta}$
- Thin active membrane for high oxygen ion flux
- Porous layer microstructure specified to achieve desired diffusion resistance

- Gas diffusion through porous support has much lower activation energy (E_a ~ 15 kJ/mol) than oxygen ion transport through active membrane (E_a ~ 50 - 100 kJ/mol).
  - More stable operation by limiting temperature sensitivity

* US Patent 6,492,290



(end view) (side view)

ITM Syngas Planar Wafer Cross-Section

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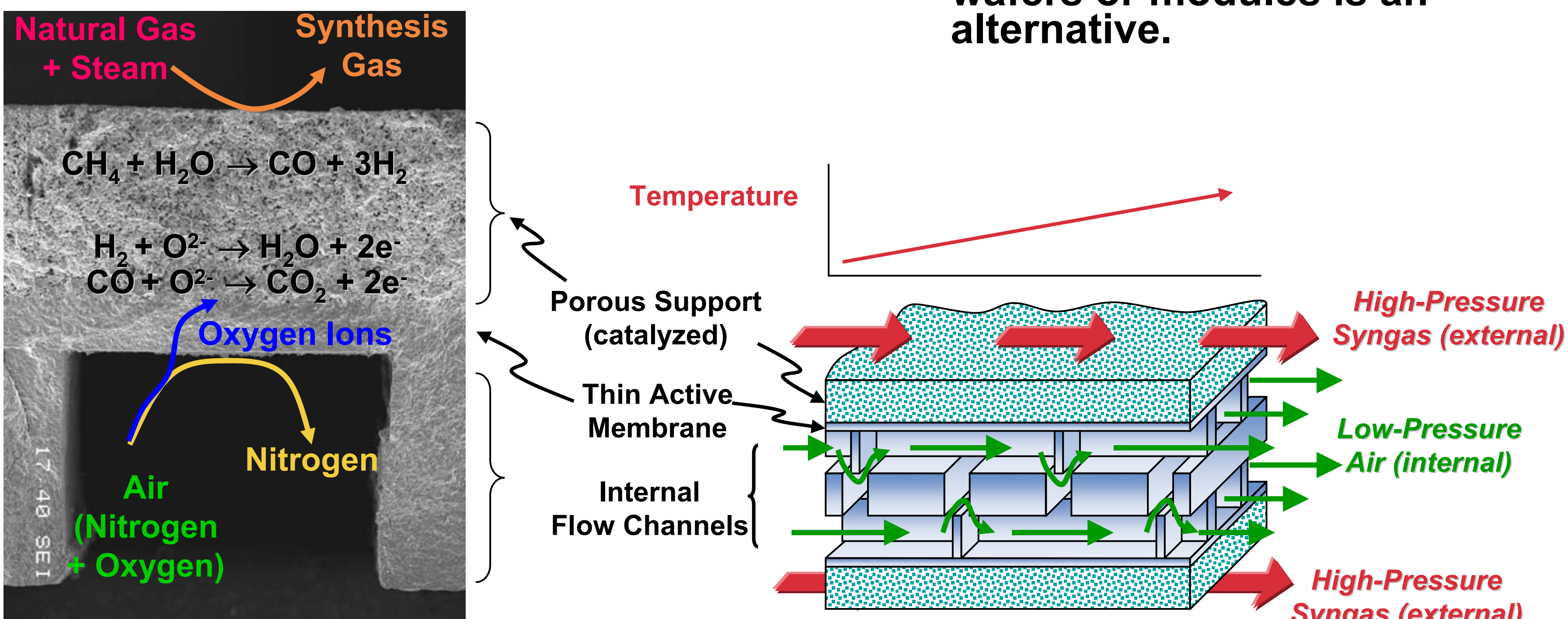
Temperature Control of Membrane

- Maintains preferred temperature profile
  - Co-current flow reduces ΔT across thin membrane.
- Catalyzed porous support layer promotes endothermic Steam Methane Reforming to balance exothermic Oxidation Reactions.
  - Catalyst placement between membrane wafers or modules is an alternative.



ITM Syngas Planar Wafer Cross-Section

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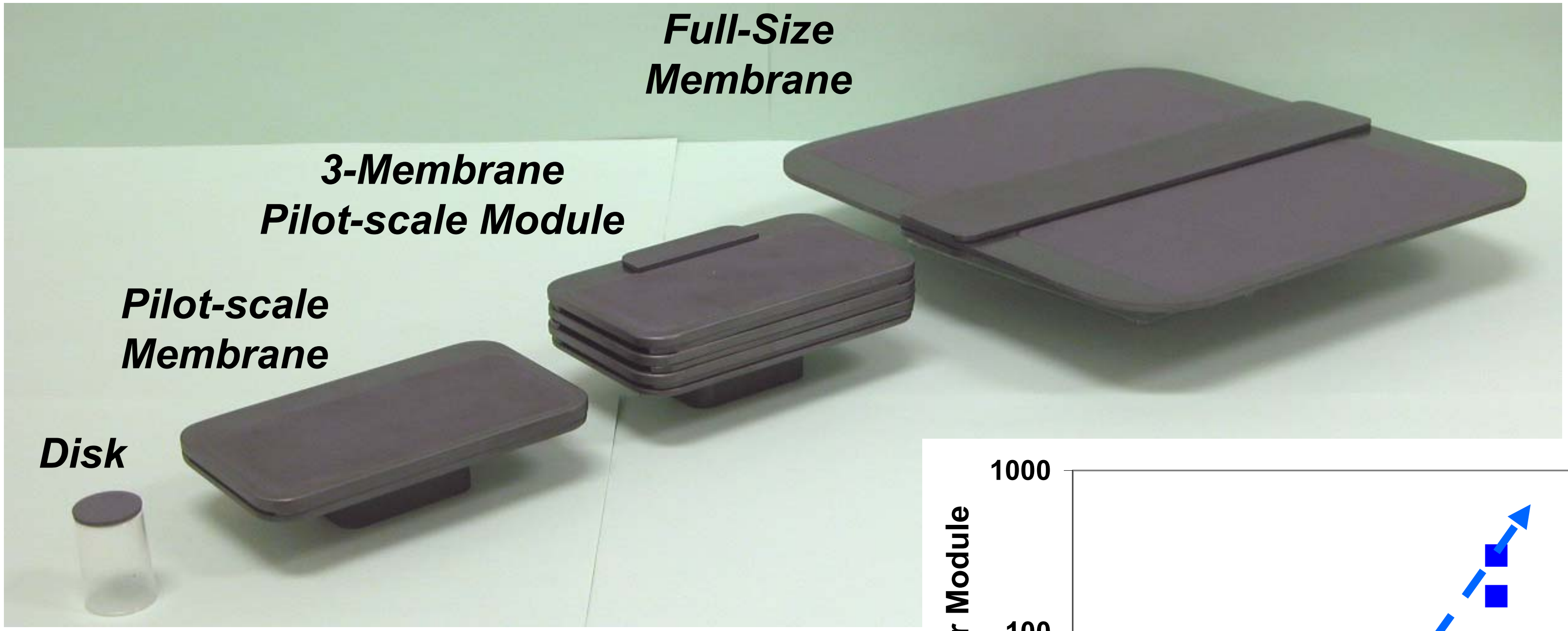
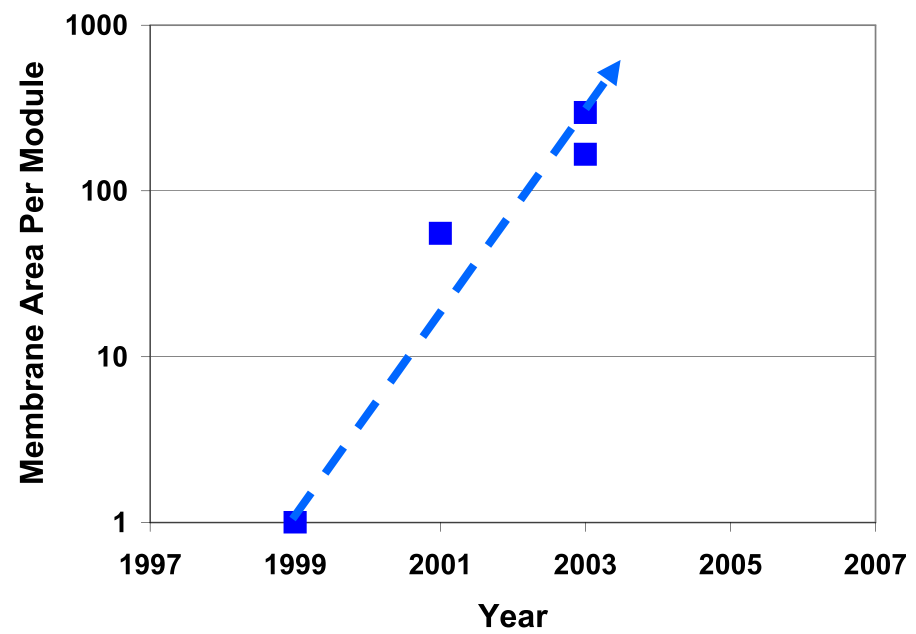
Balancing Heats of Reaction

- Endothermic Steam Methane Reforming can consume most of the heat from hydrogen oxidation.
- In reality, % of Hydrogen Oxidation heat consumed will be less than stoichiometric amount shown in table.
  - Thermodynamic and kinetic limitations of Steam Methane Reforming reaction

Reaction	$\Delta H_{850°C}$ (kJ/mol)	$\Delta H_{850°C}$ (% of H_2 oxidation)
Hydrogen Oxidation $H_2 + ½\ O_2 \rightarrow H_2O$	- 249	100%
Steam Methane Reforming $CH_4 + H_2O \leftrightarrows CO + 3\ H_2$	+ 227	- 91%
Overall Methane Partial Oxidation $CH_4 + ½\ O_2 \rightarrow CO + 2\ H_2$	- 22	9%

Planar Membrane Fabrication Has Advanced Rapidly





- Factor of 300 increase in module area since 1999
- Scalable ceramic processing methods
- Internal structures of commercial membrane tested in pilot-scale membrane
- Same material composition throughout membrane

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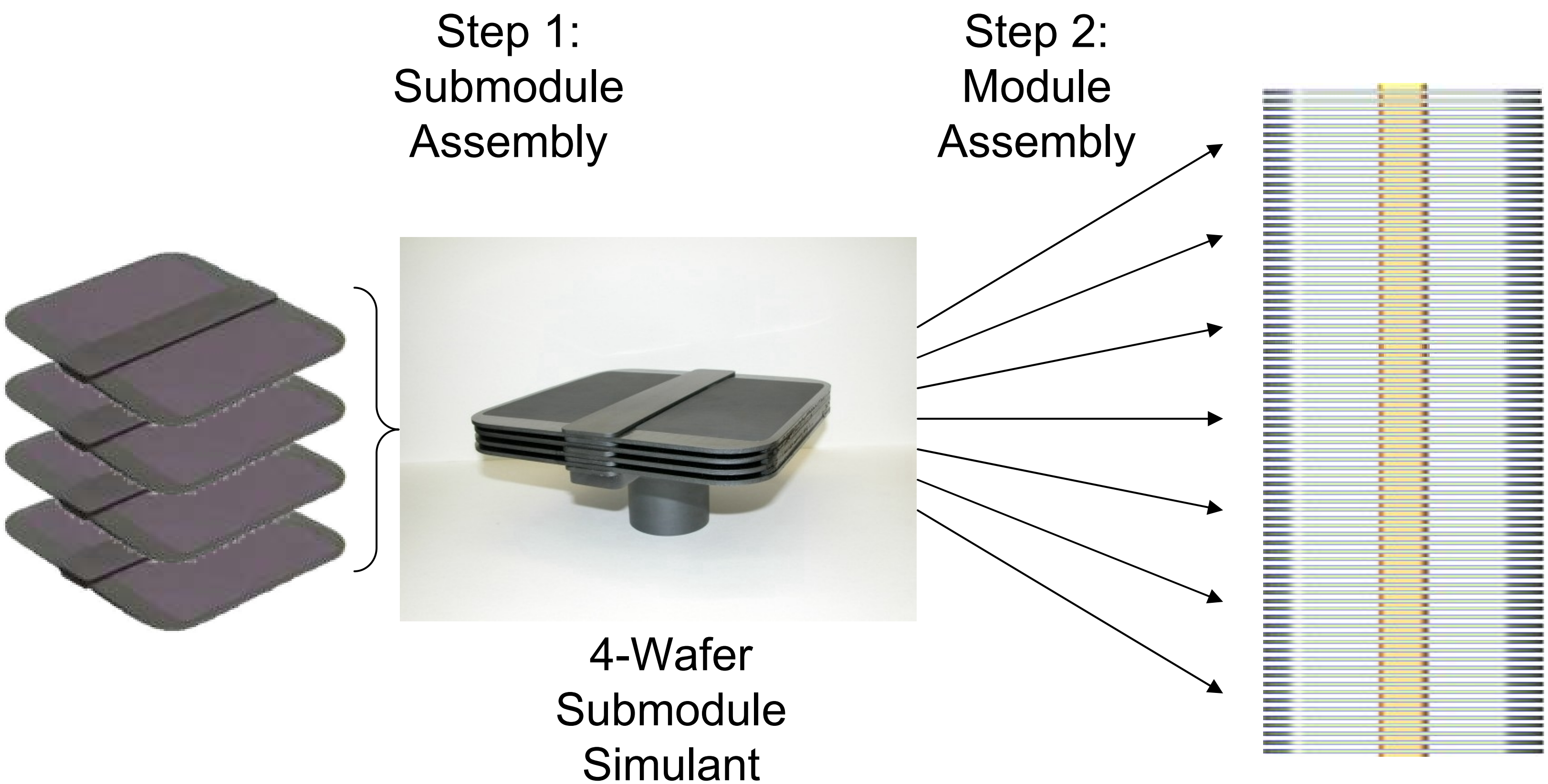
Wafer Stack Joining Method Has Been Developed

- Joining of single membranes into a module is a critical ceramic processing step.
- All-ceramic joints* have been demonstrated and have significant benefits:
  - Uniform materials
  - Match expansion behavior and reduce stress
  - Key enabling technology

Membrane Modules with All-Ceramic Joints

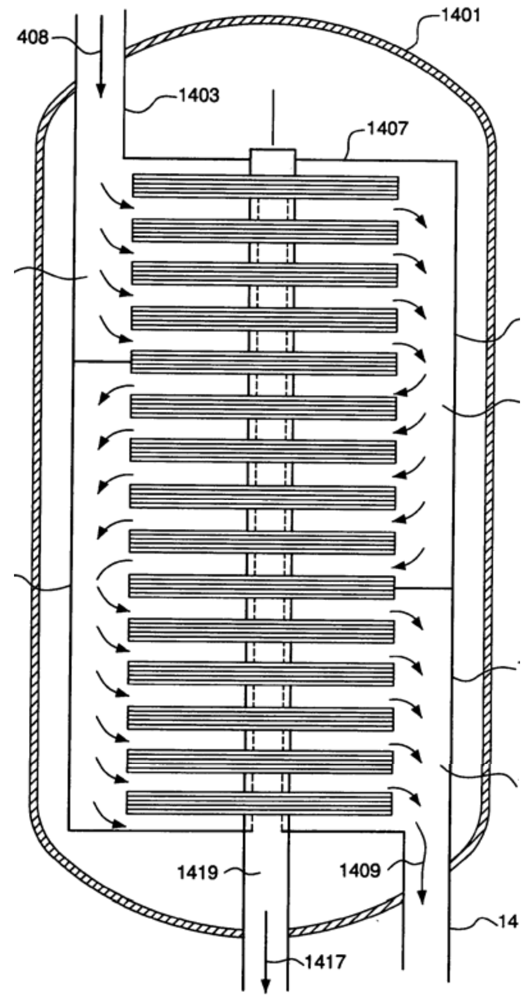
* US patent applications US 2004/0185236 and US 2004/0182306

Ceramic Joining Will Be Used to Assemble Commercial Modules from Submodules



Reactor Concept for Distributed-Scale Hydrogen Production

- Compact design
  - Multiple passes of natural gas/syngas through wafer stack
- Fewer ceramic-metal seals
  - One pair of seals per wafer stack



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Membranes Tested at Commercial Process Conditions

- Several long-term, 6-month membrane tests conducted at commercial pressure and temperature.
- Pilot-scale membranes have been operated at commercial process conditions and survive changes in operating conditions.
- Pilot-scale Process Development Unit (PDU) has demonstrated design capacity and target flux.

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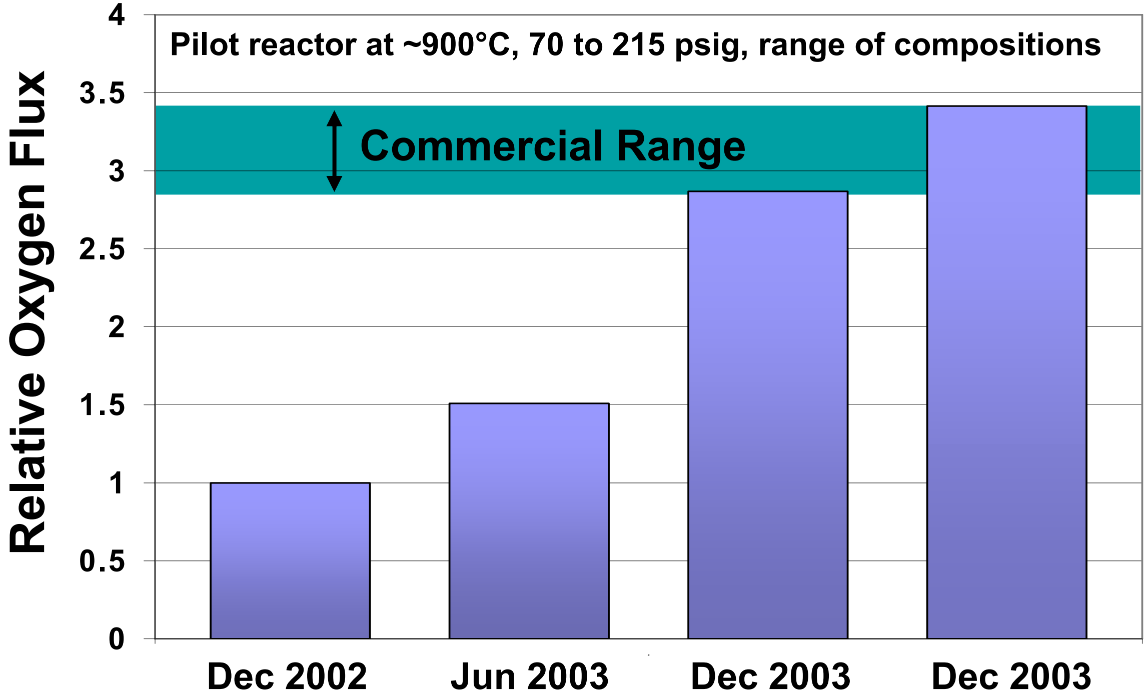
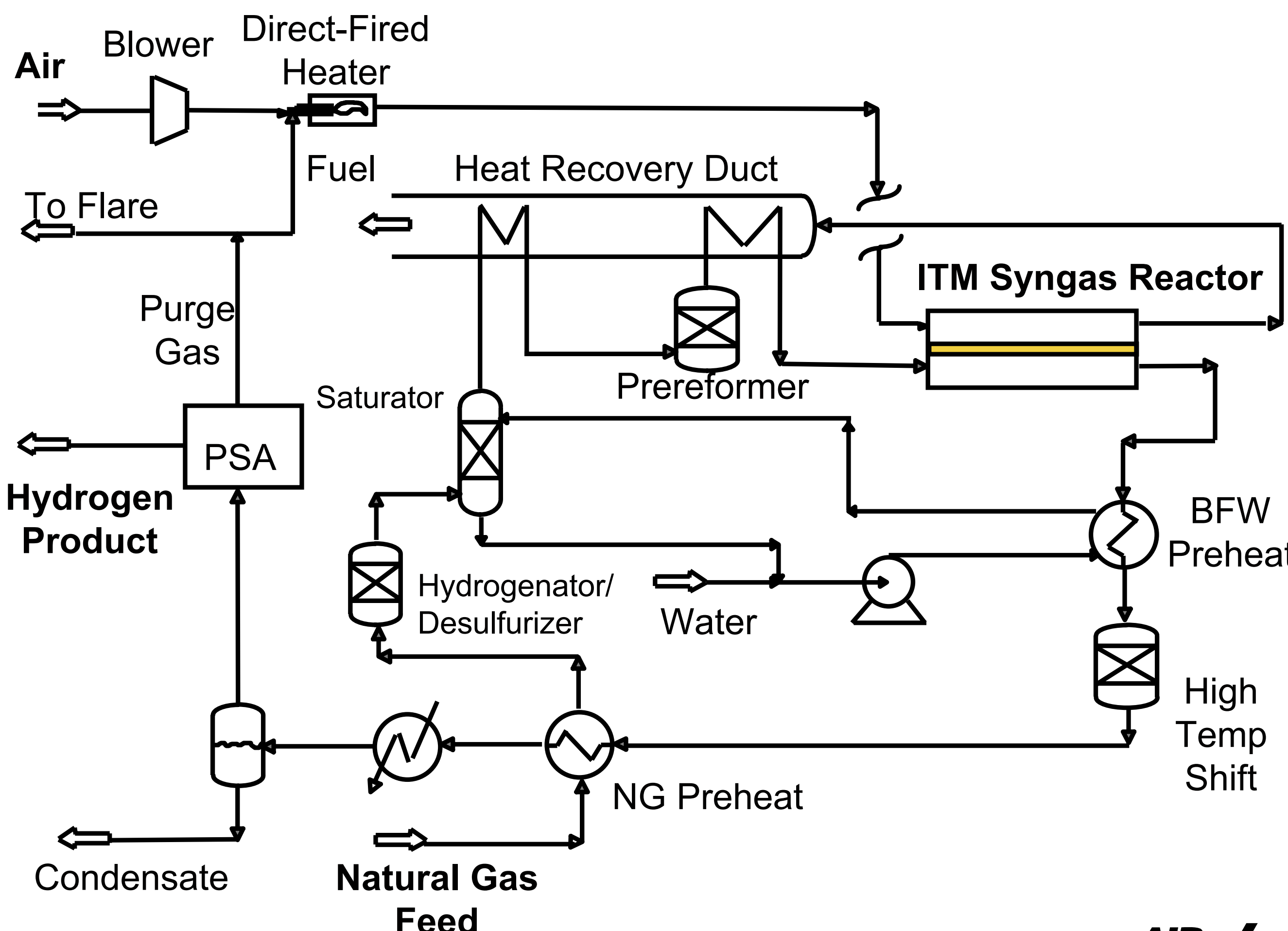
Target Fluxes Demonstrated in Process Development Unit



- Over factor of 3 increase in measured flux since 2002
- Improvements in membrane design, reactor design, and operation

Cost Reduction by Combining Oxygen Separation and Natural Gas Partial Oxidation

- **Combines oxygen separation and natural gas POX into a single unit operation**
- **Capital cost reduction for synthesis gas/hydrogen production**
- **Addresses DOE MYPP Technical Barriers "A" and "AA"**



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ITM Syngas Meets Cost Target

- DOE-HFCIT 2003 Multi-Year Program Plan cost basis
  - Hydrogen production of 860 kg/day of hydrogen (400 Nm^3/hr) is slightly higher than MYPP basis.
- ITM Syngas costs for reforming + purification are significantly below 2005 DOE target:
  - \$1.56/kg H_2 (DOE target is \$2.09/kg)
  - 39% net cost reduction in non-NG costs of reformer (DOE target is \$1.36/kg)
- ITM Syngas is a step-change technology.
- Additional cost reduction should be possible with further development of ITM Syngas technology:
  - Decreased ceramic membrane reactor costs
  - Reduced compression costs with higher pressure operation of ITM Syngas reactor
  - Process and equipment integration
  - Device simplification
  - Higher efficiency

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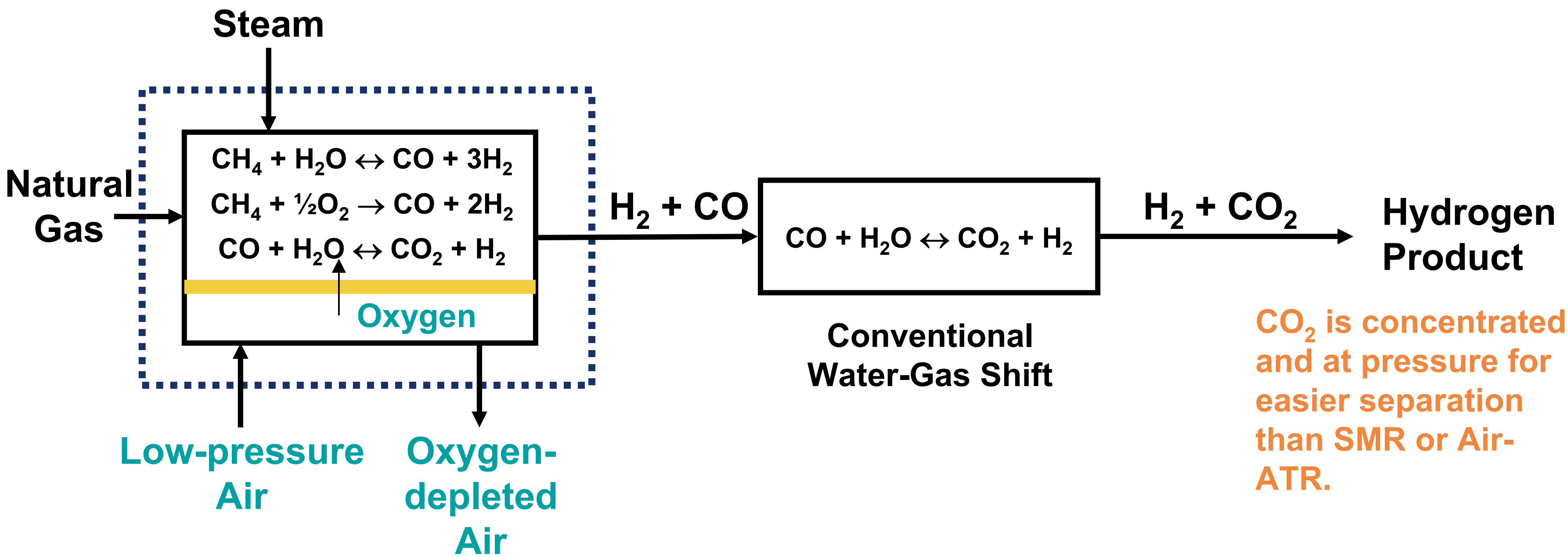
ITM Syngas Process is Amenable for 95% Carbon Capture



CO_2 is concentrated and at pressure for easier separation than SMR or Air-ATR.

Addresses MYPP Technical Barrier "D"

Process design and economic evaluation of 150-760 MMSCFD H_2 plants with CO_2 separation to provide a carbon-free "clean fuel" (250-1300 MW equivalent power) showed the potential for over 30% capital cost savings in the syngas production step and over 20% capital cost savings in the overall H_2 production/CO_2 separation plant.

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Response to 2004 Reviewers' Comments

- "Is a housing needed for the ITM module? If so, what is the arrangement?"
  - The ITM Syngas membrane module is housed in a flow duct.
  - An example arrangement is shown in this presentation.
- "Discuss whether this technology is applicable for distributed H_2 production or only large-scale production."
  - The ITM Syngas technology is applicable for large-scale production, and is competitive for distributed-scale production.
  - Economic analyses for both scales are shown in this presentation.
- "Consider showing H_2 production costs that include cost of base material, in this case, natural gas."
  - The DOE Multi-Year Program Plan specifies the basis for production costs, including cost of natural gas and utilities.

Future Work

- Remainder of FY 2005
  - Test Subscale Engineering Prototype (SEP)-size ceramic-to-metal seals
  - Implement PDU modifications to test sub-scale module of full-size planar membrane
  - Initiate engineering design of the nominal 1 million SCFD SEP plant
- FY 2006
  - Evaluate performance of on-membrane reforming catalysts at process temperature, pressure, and gas composition
  - Test full-size membranes at high pressure
  - Evaluate fabrication scaleup for featuring ceramic tape with microchannel structures

Acknowledgement

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Supplemental Slides

2004-2005 Patent Applications and Presentations

- U.S. patent application US 2004/0186018 A1, M. Carolan et al., "Planar ceramic membrane assembly and oxidation reactor system."
- U.S. Patent application US 2004/0182306 A1, D. Butt et al., "Method of forming a joint."
- U.S. Patent application US 2004/0185236 A1, D. Butt et al., "Method of joining ITM materials using a partially or fully-transient liquid phase."
- "Development of the ITM Syngas Ceramic Membrane Technology," AIChE Spring National Meeting, New Orleans, April 26, 2004.
- "ITM Syngas Ceramic Membrane Technology for Synthesis Gas Production," 7th Natural Gas Conversion Symposium, Dalian, China, June 6-10, 2004.
- "Hydrogen and Syngas Production Using Ion Transport Membranes," 8th International Conference on Inorganic Membranes, Cincinnati, OH, July 18-21, 2004.
- "ITM Syngas for GTL Economic Improvement," Energy Frontiers International Gas-to-Market Conference, Washington, DC, Sept. 29-Oct. 1, 2004.
- "ITM Syngas: Ceramic Membrane Technology for Lower Cost Conversion of Natural Gas," AIChE Spring National Meeting, Atlanta, GA, April 12, 2005.

Hydrogen Safety

- Risk
  - Potential mechanical failure of membrane module or seals, resulting in mixing of natural gas/synthesis gas and air to create a flammable mixture.
- Mitigation Measures
  - Membrane modules are designed for reliable operation for mechanical stresses encountered during operation.
  - Process and reactor control systems are being designed to maintain membrane module conditions within design envelope.
  - Methods are being developed to automatically isolate membrane modules in case of a mechanical failure.