### **Review of Historical Membrane Workshop Results**

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## **Previous Membrane R&D Needs Studies**

- Workshop reports and documents developed for DOE OIT/ITP/AMO to support the *Technology Vision2020: The Chemical Industry* (1996) as requested by the White House Office of Science and Technology Policy
  - Separation Technologies for the IOF (1998)
  - Vision2020: 2000 Separations Roadmap (1999)
  - Materials for Separations Technologies: Energy and Emission Reduction Opportunities (2004)
  - Hybrid Separations/Distillation Technology: Research Opportunities for Energy and Emissions Reduction (2005)
  - Separation Technology R&D Needs for Hydrogen Production in the Chemical and Petrochemical Industries (2005)
  - Alternative, Renewable and Novel Feedstock for Producing Chemicals (2007)
  - Industrial Feedstock Flexibility Workshop Results (2009)



## General Status of Membrane Development for Industrial Applications

- Significant investment in membrane technology has occurred but with limited industrial implementation
  - NETL development of ceramic membranes with applications in fuel cells,  $\rm H_2$  separations, and O\_2 separations
  - Significant R&D investment in palladium membranes for H<sub>2</sub> recovery
- Major high energy industrial applications covered by OIT/ITP/AMO
  - Alternatives to distillation
  - Gas separations, primarily  $H_2$  and  $O_2$
  - Feedstock flexibility for chemical/petroleum industry
- Membrane systems needed for many high-energy industrial applications are limited by lack of selectivity, narrow range of useful operating conditions (thermal stability and low permeation), and high costs



## Major Barriers to Membrane Development for Industrial Applications

#### Important Properties for Emerging Membrane Systems

- Permeability
- Selectivity
- Durability (compaction)
- Resistance to fouling/fouling control
- Thermal stability
- Transport properties
- Defects, particularly at large scale
- Erosion/corrosion resistance
- Clean-in-place
- Advanced control systems
- Module design and scale-up
- Costs, particularly for high volume applications

| Intrinsic Properties   |  | System Properties   |                         |
|--|--|---|-------------------------|
| <ul> <li>selectivity</li> <li>flux/capacity</li> <li>fouling resistance</li> </ul> |  | <ul> <li>boundary layer formation and<br/>control</li> <li>permeate path carrying capacity</li> <li>limited packing density<br/>(membrane area per module<br/>volume)</li> <li>clean-in-place</li> <li>limited economies-of-scale<br/>(membrane area scale linearly)</li> </ul> |                         |
| Mechanical Properties  |  |   |                         |
|  | <u>Organic</u>                         |   | <u>Inorganic</u>        |
| <ul> <li>pressure</li> </ul>   | compaction                             |   |                         |
| <ul> <li>temperature</li> </ul>  | compaction, rate of chemical<br>attack |   | rate of chemical attack |
| • pH   | hydrolysis, rate of chemical<br>attack |   | rate of chemical attack |
| <ul> <li>microbes</li> </ul>   | biological attack and fouling          |   | biological fouling      |
| <ul> <li>solvents</li> </ul>   | compaction, swelling, dissolution      |   | dissolution             |
| <ul> <li>mechanical<br/>stress/shock</li> </ul>                                    | rupture                                |   | rupture/fracture        |
| <ul> <li>thermal<br/>stress/shock</li> </ul>                                       | rupture                                |   | rupture/fracture        |
| <ul> <li>colloids</li> </ul>   | irreversible sorption                  | 1   | irreversible sorption   |



## Membrane Systems for Distillation Applications

#### <u>Status</u>

- Systems lack selectivity, have narrow range of operating conditions, and have high costs
- Higher selectivity/flux membranes that can withstand high temperatures (80 1,200 °F); aggressive chemicals and organic mixtures with molecular sieving capabilities are needed
  - Organic membranes are not likely to withstand high distillation temperatures. Inorganic materials or inorganic/polymer composites have the highest potential, and hybrid systems may be easier to implement than total replacement of distillation equipment
- New module configuration designs, fouling control, and advanced control systems are needed to increase efficiency and reduce costs.
- Membranes are likely to be most successful in "clean" applications, i.e. gas recovery

#### General R&D Opportunity Areas

- Pilot plant demonstrations of existing materials in specific applications
- Model Predictive Control (MPC) for membrane process
- Material compatibility studies for entire systems (not just membrane materials)
- Improved membrane chemical stability
- Better scaling to reduce costs



### Membrane Systems for Distillation Applications continued

R&D Opportunities for Specific Membrane Systems

- Inorganic metal membranes
  - Refinement of the fabrication process to reduce defects in large scale membranes
  - Durability and reliability testing of the membranes
  - Erosion and corrosion resistance of membranes under long-term test conditions
  - Development of thin inorganic membrane films which will exhibit high fluxes
- Ceramic membranes
  - Develop materials that can operate with high selectivity and flux (a challenge for separation of large molecules and similar size molecules)

#### High Potential Application Areas

- Azeotrope breaking (CO<sub>2</sub> / C<sub>2</sub>H<sub>6</sub> separation)
- Pre-concentrator for distillation
- Bulk gas separations for low-temperature streams where existing polymers could be applicable
- Vent gas recovery for refining and olefin/paraffin separations
- Desalination/reverse osmosis for phosphoric acid and caustic applications



# **Membranes for Gas Separations**

<u>Status</u>

- Systems lack selectivity, have narrow range of operating conditions, and have high costs
- Most promising membrane systems for these applications are microporous metal and ceramic membranes

R&D Opportunities for Specific Membrane Materials

- Microporous metal and ceramic membranes
  - Refinement of fabrication process to reduce defects in large scale membranes
  - Development of higher flux/high temperature membranes
  - Development of metal oxide membrane materials capable of operation at <1100°F</li>
  - Improved thermal mechanical performance



## **Membranes for Gas Separations continued**

General R&D Opportunity Areas

- High temperature membranes that are selective only to O<sub>2</sub> or H<sub>2</sub>
- Low temperature O<sub>2</sub> selective membranes with permeance >100 x 10<sup>-8</sup> mole(s·m<sup>2</sup>·Pa)
- High integrity H<sub>2</sub> selective mixed matrix membranes
- Organic-inorganic hybrid membrane materials
- Improved H<sub>2</sub> selective inorganic microporous membranes
- High Potential Energy Savings Application Areas
- H<sub>2</sub> recovery in petroleum refining processes, such as catalytic cracking and hydroforming
- O<sub>2</sub> enrichment for oxygen-fueled furnaces (reducing the mass of nitrogen by 50%)



#### Membrane Systems for Feedstock Flexibility Applications Status

- Workshops have focused on feedstock flexibility for the chemical and petroleum industries: alternative bio-based feedstocks, alternative fossilbased feedstocks, and improvements in efficiency for conventional feedstocks
- Membranes are needed that can withstand processing conditions (temperatures, pH, chemicals); can cope with fouling; can selectively separate desired materials from dilute solutions; have improved permeance, selectivity, reduced costs, chemical resistance; are defect free at large scale; and have proven performance at scale

### General R&D Opportunity Areas

- Design better molecule configuration in membranes for fouling abatement
- Develop facilitated transport membranes to separate like molecules
- Develop membrane adsorbent materials (ionic liquids, olid polymeric)
- Develop smart membranes and separations systems for low concentration / high value products

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## Membrane Systems for Feedstock Flexibility continued

## R&D Opportunities for Specific Systems

- Membranes to support bio-based feedstocks
  - Membranes to increase alcohol yield, separate salts, and purify solvents
  - Scalable, low-cost commercially available membranes
  - Membranes that withstand the bio-processing conditions (temperatures, pH, chemicals), can cope with bio-system fouling, and can selectively separate desired materials from dilute solutions
- Membranes to support alternative fossil-fuel feedstocks
  - Improved air separations
- Membranes to support improvements in conventional feedstocks
  - Replace conventional distillation
  - Improved gas separations



## **Summary from Previous Workshops**

- Significant investment in membrane technology has occurred but with limited industrial implementation
- The major R&D needs are for improved selectivity, range of useful operating conditions, defect-free scale-up for large volume systems, module configuration designs, fouling control, advanced control systems, and lower costs
  - Inorganic materials or inorganic/polymer composites have the highest potential for success for many of these applications
- Research programs should focus on these technical areas for the most promising high energy applications

