Development of Carbon Molecular Sieves Hollow Fiber Membranes based on Polybenzimidazole Doped with Polyprotic Acids with Superior H₂/CO₂ Separation Properties

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Award number: DE-FE0031636

Project period: 10/1/18 to 9/30/21

Program manager: Andrew O’Palko

Project Objective: Develop CMS hollow fiber membranes with H₂ permeance of 1000 GPU and H₂/CO₂ selectivity of 40 at 200-300 °C, enabling membrane-based systems capturing 90% CO₂ from coal-derived syngas with 95% CO₂ purity at a cost of electricity 30% less than baseline capture approaches.

<table>
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<th>Team Members</th>
<th>Federal Share</th>
<th>Cost-share</th>
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Project Scope in Each Budget Period

**BP 1 Materials development (10/1/18 – 3/31/20; 18 months)**

- Optimize CMS materials with an $H_2$ permeability of 200 Barrers and $H_2/CO_2$ selectivity of 40 with simulated syngas; and
- Optimize the hollow fiber membranes based on PBI doped with polyprotic acids.

**BP 2 Membrane development (4/1/20 – 9/30/21; 18 months)**

- Optimize membranes achieving the targeted $H_2/CO_2$ separation performance;
- Test membranes using simulated syngas containing $H_2S$, CO and water vapor;
- Determine the efficiency of the membrane reactors for the WGS reaction; and
- Conduct the techno-economic analysis.
CO₂ separation is energy-intensive and expensive

Lower cost and more energy efficient separation technology is needed.
MTR’s Membrane Process Design


Diagram:
- **1.** Hot, shifted syngas
- **2.** Liquid CO₂
- **3.** N₂ sweep
- **4.** Fuel gas to combustion turbine
- **5.** Inert purge

Diagram components:
- H₂-selective membrane
- Heat exchanger
- Condenser
- Liquid pump
- Turbo expander
MTR’s Techno-Economic Analysis

![Graphs showing membrane area, total plant cost, and increase in LCOE in relation to H2 permeance and membrane H2/CO2 selectivity.]

Membrane: Energy-efficient Separation

Solution-diffusion model

(1) Sorption on upstream side
(2) Diffusion down partial pressure gradient
(3) Desorption on downstream side

Productivity - Permeability

\[ P_A = S_A \times D_A \]

Purity - Gas selectivity

\[ \alpha_{\text{H}_2/\text{CO}_2} = \frac{P_{\text{H}_2}}{P_{\text{CO}_2}} = \left( \frac{S_{\text{H}_2}}{S_{\text{CO}_2}} \right) \times \left( \frac{D_{\text{H}_2}}{D_{\text{CO}_2}} \right) \]

**Permeability/Selectivity Tradeoff**

<table>
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<tr>
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<th>Critical temperature (K)</th>
<th>Kinetic diameter (Å)</th>
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<tr>
<td>$\text{H}_2$</td>
<td>33</td>
<td>2.89</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>304</td>
<td>3.3</td>
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$$\frac{S_{\text{H}_2}}{S_{\text{CO}_2}} << 1 \quad \text{and} \quad \frac{D_{\text{H}_2}}{D_{\text{CO}_2}} >> 1$$

- Polybenzimidazole (PBI) (Celazole®)

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**2008 Upper bound at 35 °C**

- Commerical Polymers: PSF, Matrimid, PPO
- Commercial Polymers: CA, PSF, Matrimid, PPO
Polymeric Membranes for H₂/CO₂ Separation

Our Approach: Carbonizing PBI/acid to Enhance H₂/CO₂ Separation Performance

**Poly(benzimidazole) (PBI)**
- Commercially available
- High $T_g$ (417 °C), $T_d$: 550 °C

![Diagram of H₂/CO₂ separation performance](image)

- Upper bound at 150 °C
- Commercially interesting materials
- PBI, Matrimid, CMS

![Chemical structures](image)

- Acid doping
- Pyrolysis
- CMS derived from acid doped PBI
Protocol to Prepare Carbon Molecular Sieve (CMS) Materials

Pyrolysis Protocols: 200 cc N₂/min

- Isothermal at 25 °C for 30 min
- 25 °C to 50 °C with ramp rate of 0.83 °C/min
- 50 °C to 250 °C with ramp rate of 13.3 °C/min
- 250 °C to \( (T_{\text{max}} - 15 \, ^\circ\text{C}) \) with ramp rate of 3.85 °C/min
- \( (T_{\text{max}} - 15 \, ^\circ\text{C}) \) to \( T_{\text{max}} \) with ramp rate of 0.25 °C/min
- Stay at \( T_{\text{max}} \) for 2 hours and cool down under N₂ flow

\( T_{\text{max}}: \) 600-900 °C

Super $\text{H}_2/\text{CO}_2$ Separation Performance of PBI-CMS

Pure-gas $\text{H}_2/\text{CO}_2$ selectivity vs. Pure-gas $\text{H}_2$ permeability (Barrer)

Robeson's upper bound at 2008 @25 °C

CMS@T

CMS@900

CMS@800

Upper bound at 150 °C

Pure-gas $\text{H}_2$ permeability (Barrer) vs. $\text{H}_2$ permeability (Barrer)

PBI

Proteus™
Mixed-gas $\text{H}_2/\text{CO}_2$ Separation Performance of PBI-CMS@900 at 100 °C

(a) Mixed-gas permeability (Barrer) vs. $\text{CO}_2$ partial pressure (atm)

(b) Mixed-gas $\text{H}_2/\text{CO}_2$ selectivity vs. $\text{CO}_2$ partial pressure (atm)
Stable H₂/CO₂ Separation Performance of PBI-CMS@900 at 100 °C

The graph shows the mixed-gas permeability (in Barrer) and CO₂ selectivity over a 100-hour testing period. The permeability and selectivity are plotted against testing time (in hours). The graph includes data points for dry and 0.31 mol% H₂O conditions.
Carbonization of H$_3$PO$_4$ Doped PBI

**Image Description:**
- **Left Panel:**
  - Images of PBI-(H$_3$PO$_4$)$_{0.23}$, CMS-600°C, and CMS-700°C samples with dimensions labeled.
- **Right Panel:**
  - Graph showing weight loss (%) vs. pyrolysis temperature (°C) for PBI-(H$_3$PO$_4$)$_{0.11}$.
  - Absorbance (a.u.) vs. wavenumber (cm$^{-1}$) for CMS@700, CMS@600, CMS@400, CMS@700-(H$_3$PO$_4$)$_{0.10}$, PBI-(H$_3$PO$_4$)$_{0.11}$, and PBI.
  - XRD intensity (a.u.) vs. 2-θ (degree) for CMS@700, CMS@600, CMS@400, CMS@700-(H$_3$PO$_4$)$_{0.10}$, PBI-(H$_3$PO$_4$)$_{0.11}$, and PBI.
Effect of H$_3$PO$_4$ Doping and Pyrolysis Temperature on H$_2$/CO$_2$ Separation at 100 °C

![Graph showing the effect of H$_3$PO$_4$ doping and pyrolysis temperature on H$_2$/CO$_2$ separation at 100 °C. The graph plots H$_2$ permeability (Barrer) against H$_2$/CO$_2$ selectivity. Different materials, such as CMS@600 and PBI-(H$_3$PO$_4$), are compared at various temperatures (100 °C, 150 °C, 200 °C) and pyrolysis temperatures (600 °C). The graph illustrates the separation performance and how it changes with temperature and pyrolysis conditions.]
**Hollow Fiber (HF) Membrane**

- **High membrane surface area platform**
  - The H$_2$ permeability of the PBI-based CMS membrane materials mandates ultra-thin selective layers and high surface area membrane deployment platforms.

- **Approach: PBI HF membranes carbonization to obtain PBI-CMS HF membranes**
  - Liquid-liquid demixing based spinning process developed to obtain high performance base PBI HF membranes with thin selective layer.

**LANL Lab-scale continuous HF spinning system using a custom micro-machined spinneret**

- Fiber Diameter: 200 to 500 µm
- SL Thickness: 150 to 500 nm
Goal: Development of base PBI HF membranes having variety of morphologies including selective layer thickness and support layer structure

- *In-situ* formation of an integrally skinned HF using commercially available PBI material leveraging LANL PBI spinning capability and process understanding

Initiated base PBI HF membrane fabrication and pyrolysis to obtain PBI-CMS HF membranes

- Utilized spinning conditions known to produce PBI HF membranes with thin selective layer and porous support structure
- Pyrolyzed at 580 °C for 1 hour in inert atmosphere
Path Forward

- HF fabrication, acid doping and carbonization
  - Fabrication optimization of PBI and acid doped PBI HF membranes to achieve defect minimized thin selective layer membranes
    - Milestone BP1 Q2FY20: Acid doped PBI HF membranes exhibiting $\frac{H_2}{CO_2} \approx 40$.
  - Pyrolysis condition optimization to achieve high performance PBI-CMS HF membranes with minimized porous support structure collapse during carbonization
  - Demonstrate fabrication consistency via performance demonstration of fibers from multiple, replicate spinning campaigns

- Sealing Layer Development & Integration
  - Develop and optimize post-carbonization defect seal layer deposition process for PBI-CMS HF membranes

- Demonstration and Validation of Developed Materials and Methods
  - Evaluate PBI, acid doped PBI and PBI-CMS HF membranes for $\frac{H_2}{CO_2}$ separation properties at syngas relevant process conditions
  - Conduct parametric tests of PBI-CMS HF membranes in CO and H2S containing simulated syngas at process relevant conditions
BP1 Techno-Economic Analysis (TEA)

- Cursory analysis during BP1
  - Identify key cost drivers, sensitivities for key variables
  - Identify opportunities for process optimization
  - Bottom-up analysis during BP2

- UB to provide
  - Conceptual design, process simulation and material/energy balances
  - Data on membrane permeance and selectivity

- Key data
  - Inlet pressure, membrane pressure drop
  - Compositions of product streams from membrane
  - Fate of contaminants (CO, H₂S, H₂O)
  - Membrane costs

- Develop preliminary CAPEX, OPEX and energy analysis
- Due 3/31/20
Summary

DOE/NETL

UB:
- Develop CMS membranes
- Coordinate

LANL:
- Prepare membranes
- Run parametric tests

Trimeric:
- Perform TEA

Acid doping

Acid doped PBI

Pyrolysis

CMS derived from acid doped PBI

H₂ Permeability (Barrer)

H₂/CO₂ Selectivity

Upper bound 150 °C

Commercially interesting

Matrimid

PBI

PBI-(H₃PO₄)₀.25

Acid doping

CMS

LANL approval for public release (LA-UR-18-30903)