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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University at Buffalo, State University of New York

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings August 2 through August 31, 2021
Project Overview

– Overall Project Performance Dates: 10/1/18 to 9/30/21
– Project Participants: University at Buffalo (UB), State University of New York; Los Alamos National Laboratory (LANL); Trimeric Corporation
– Funding (DOE and Cost Share)

<table>
<thead>
<tr>
<th>Team Members</th>
<th>Federal Share</th>
<th>Cost-share</th>
<th>Total</th>
<th>Roles</th>
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<tr>
<td>UB</td>
<td>$534,999</td>
<td>$202,225</td>
<td>$737,224</td>
<td>Materials development</td>
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<tr>
<td>LANL</td>
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<td>$200,000</td>
<td>Membrane development</td>
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<tr>
<td>Trimeric</td>
<td>$65,000</td>
<td>$0</td>
<td>$65,000</td>
<td>Techno-economic analysis</td>
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<td><strong>$799,999</strong></td>
<td><strong>$202,225</strong></td>
<td><strong>$1,002,224</strong></td>
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Overall Project Objectives: Develop CMS hollow fiber membranes with H$_2$ permeance of 1000 GPU and H$_2$/CO$_2$ selectivity of 40 at 200-300 ºC, enabling membrane-based systems capturing 90% CO$_2$ from coal-derived syngas with 95% CO$_2$ purity at a cost of electricity 30% less than baseline capture approaches.

- **Milestone 1:** CMS films with H$_2$ permeability of 200 Barrer and H$_2$/CO$_2$ selectivity of 40;

- **Milestone 2:** Hollow fiber membranes (HFM) based on PBI doped with polyprotic acids exhibiting H$_2$ permeance of 1,000 GPU and H$_2$/CO$_2$ selectivity of 40.
Project Schedule and Milestones

BP 1 Materials development (10/1/18 – 3/31/20; 18 months)
• Optimize CMS materials with an H₂ permeability of 200 Barrer and H₂/CO₂ selectivity of 40 with simulated syngas;
• Optimize the hollow fiber membranes based on PBI doped with polyprotic acids.

BP 2 Membrane development (4/1/20 – 9/30/21; 18 months)
• Prepare and optimize CMS hollow fiber membranes with an H₂ permeance of 1,000 GPU and H₂/CO₂ selectivity of 40 at 200-300 °C;
• Test membranes using simulated syngas containing H₂S, CO and water vapor;
• Determine the efficiency of the membrane reactors for the WGS reaction;
• Conduct the techno-economic analysis (TEA).
CO$_2$ separation is energy-intensive and expensive

GEE IGCC/Selexol 543 MWe plant (Case 2)

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$ capture</th>
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<tbody>
<tr>
<td>Power consumption</td>
<td>50 MWe</td>
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<tr>
<td>Capital cost</td>
<td>$252 MM</td>
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</table>

Lower cost and more energy efficient separation technology is needed.
### Permeability/Selectivity Tradeoff

<table>
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<tr>
<th></th>
<th>Critical temperature (K)</th>
<th>Kinetic diameter (Å)</th>
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<tbody>
<tr>
<td>H₂</td>
<td>33</td>
<td>2.89</td>
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<tr>
<td>CO₂</td>
<td>304</td>
<td>3.3</td>
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</table>

\[
\frac{S_{H_2}}{S_{CO_2}} << 1 \quad \text{and} \quad \frac{D_{H_2}}{D_{CO_2}} >> 1
\]

![Polybenzimidazole (PBI) (Celazole®)](image)

- Commercially available
- High \( T_g \) (417 °C), \( T_d \) : 550 °C
Our Approach to Meet Milestones: Carbonization of Polyprotic Acid Doped PBI
Polymeric Membranes for $\text{H}_2/\text{CO}_2$ Separation

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

$T_{max}$: 600-900 °C
Meeting Milestone I: H₂ permeability of 200 Barrer and H₂/CO₂ selectivity of 40

![Graph showing H₂ permeability and H₂/CO₂ selectivity for PBI-H₃PO₄ CMS@600 and PBI-H₄P₂O₇ CMS@600](image-url)
Stable H₂/CO₂ Separation Performance of PBI-PPA CMS@600 at 150 °C

![Graph showing mixed-gas permeability and selectivity](image)
Fabrication of PBI CMS HFM

Base PBI HFM

Carbonized PBI HFM

Diagram and images illustrating the fabrication process of PBI CMS HFM.
Improve Separation Performance of PBI CMS HFMs

1. Defect-Sealing

- Selective Layer
- Defect-Sealing Layer
- Fiber
- Porous Support Layer

Defects: Knudsen Flow $\frac{H_2}{CO_2} = 4.69$

2. Acid doping and carbonization

Symmetric – Low Permeance
Asymmetric – High Permeance
Meeting Milestone 2: $\text{H}_2$ permeability of 1000 GPU and $\text{H}_2/\text{CO}_2$ selectivity of 40

$\text{H}_2/\text{CO}_2$ selectivity: 57
Activated Diffusion Dominant Gas Transport Phenomena
Membrane Reactor and Testing Platform for WGS Reaction
Optimize Performance of Hollow Fiber Membranes

Ceramic-support PBI-PPA Carbon molecular sieve (CMS) composite membranes

Diagram showing the relationship between hydrogen permeance (GPU) and H₂/CO₂ selectivity at 100 °C. Points labeled S1, S2, S3, and S4 are plotted on the graph.
Activity of Commercial Catalysts

A. 30 psig, CO/N₂: 10/90

- CO conversion (%) vs. Temperature (°C)

B. 250 °C, CO/N₂: 10/90

- CO conversion (%) vs. Feed pressure (psig)

C. 250 °C, 30 psig

- CO conversion (%) vs. H₂/CO vol. ratio
MTR’s Membrane Process Design

MTR’s Techno-Economic Analysis

(a) Membrane area (m$^2$) vs. $H_2$ permeance (GPU) with $H_2/CO_2$ selectivity: 15, 90% CO$_2$ capture.

(b) Total plant cost ($million) vs. $H_2$ permeance (GPU) with $H_2/CO_2$ selectivity.

Increase in LCOE (%) vs. Membrane $H_2/CO_2$ selectivity with $H_2$ Permeance: 300 GPU, 600 GPU, 900 GPU.

Selexol$^TM$ DOE target.

Membrane reactors other techn. improvement.

**TEA: Process to be Simulated**

**TEA Focus:** effect of key membrane improvements on CO₂ capture design and costs

- **Improved permeability and selectivity:** Reduce CO₂ processing costs downstream of membrane
- **Increased operating temperature (200-300°C vs 150°C):** Reduce cost of cooling gas upstream of the membrane

Incorporating membrane performance into process model:

Source: MTR, Final Report to DOE-NETL for DE-FE0001124, December 2011
Plans for Future Testing/Development/Commercialization

LANL: syngas evaluations in a pencil module

Pre-mixed syngas w or w/o H₂S

H₂O

Steam Generator

Temperature Controlled

Gas Pre-heater

Condensers

To pressure controller, flow & composition measurement

<table>
<thead>
<tr>
<th>Feed composition</th>
<th>Test 1</th>
<th>Test 2</th>
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<tbody>
<tr>
<td>H₂ (%)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>CO₂ (%)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>H₂O (%)</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>CO (%)</td>
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<td>1</td>
</tr>
<tr>
<td>H₂S (ppm)</td>
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<td>20</td>
</tr>
<tr>
<td>Total Feed Pressure (psia)</td>
<td>200</td>
<td>200</td>
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<tr>
<td>Temp (°C)</td>
<td>200-350</td>
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Plans for Future Testing/Development/Commercialization

UB: characterize membrane reactors for $\text{H}_2/\text{CO}_2$ separation

Trimeric: conduct TEA (Impact on COE; Comparison to DOE reference Selexol case)
Summary

DOE/NETL

UB:
Develop CMS membranes
Coordinate

LANL:
Prepare membranes
Run parametric tests

Trimeric:
Perform TEA

Los Alamos
National Laboratory
EST. 1943

H2/CO2 Selectivity

Upper bound
150 °C

Commercially interesting

PBI

Acid doping

Pyrolysis

Acid doped PBI

CMS derived from acid doped PBI
University at Buffalo (UB):
Dr. Haiqing Lin (PI)

**Project efforts:**
- Prepare, optimize and characterize PBI doped with polyprotic acids;
- Prepare, optimize and characterize CMS materials;
- Prepare and optimize hollow fiber membranes based on PBI and PBI doped with polyprotic acids;
- Characterize H₂/CO₂ separation properties;
- Conduct parametric tests of membranes for H₂/CO₂ separation;
- Evaluate the CMS membranes for WGS reactors.
Organization Chart

- Los Alamos National Laboratory (LANL), Carbon Capture and Separations for Energy Applications (CaSEA) Laboratory

**Team members**
- Rajinder P. Singh (co-PI)
- Jeremy C. Lewis
- JongGuen Seong
- Kathryn A. Berchtold

**Project efforts:**
- Prepare and optimize hollow fiber membranes based on PBI and PBI doped with polyprotic acids;
- Characterize $\text{H}_2/\text{CO}_2$ separation properties;
- Conduct parametric tests of membranes for $\text{H}_2/\text{CO}_2$ separation;
Organization Chart

Trimeric Corporation (Trimeric)

- Privately-owned consulting firm located in Buda (Austin), Texas

Team members
- Andrew Sexton
- Katherine Dombrowski

Project efforts:
- Perform Process Technical Analysis;
- Evaluate Economic Potential of Membrane Process Compared to Other Capture Technologies.
# Project Timetable

<table>
<thead>
<tr>
<th>Tasks</th>
<th>2018</th>
<th>2019</th>
<th>2020</th>
<th>2021</th>
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<td>Oct-Dec</td>
<td>Jan-Mar</td>
<td>Apr-Jun</td>
<td>Jul-Sep</td>
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<td>Project Management and Planning</td>
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<tr>
<td>Hollow fiber membranes with H₂/CO₂ selectivity of 40</td>
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<td>CMS hollow fiber membranes with an H₂ permeance of 1,000 GPU and H₂/CO₂ selectivity of 40</td>
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<td>Final Techno-Economic Analysis</td>
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Membrane: Energy-efficient Separation

Solution-diffusion model

Productivity - Permeability

\[ P_A = S_A \times D_A \]

Purity - Gas selectivity

\[ \alpha_{H_2/CO_2} = \frac{P_{H_2}}{P_{CO_2}} = \left( \frac{S_{H_2}}{S_{CO_2}} \right) \times \left( \frac{D_{H_2}}{D_{CO_2}} \right) \]

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

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

Stable H$_2$/CO$_2$ Separation Performance of PBI-CMS@900 at 100 °C