Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

Lie Meng and Jerry Y.S. Lin*

Arizona State University

DOE Award:
DE-FE0026435

2018 NETL CO₂ Capture Technology Project Review Meeting
August 14, 2018, Pittsburgh, Penn
Overview

**Timeline**

- Project start date: **Oct. 1, 2015**
- Project end date: **Jan. 31, 2019**
- Budget Periods:
  - I: 10/1/2015-7/30/2017
  - II: 8/1/2017-1/31/2019

**Budget**

- Total project funding
  - DOE $2,760,797
  - Cost-share: $689,963
  - Total: $3,450,760

**Research Area**

2B2: Bench-Scale Pre-Combustion CO₂ Capture Development and Testing

**Partners**

- Arizona State University (ASU)
- University of Cincinnati (UC)
- Media and Process Technology, Inc (MPT)
- Nexant, Inc.
- University of Kentucky Applied Energy Research Center
Project Objectives

To demonstrate a bench-scale zeolite membrane reactor (ZMR) for WGS reaction of coal gasification gas for hydrogen production for integration with IGCC power plant.

To evaluate the performance and cost-effectiveness of this new membrane reactor process for use in 550 MW coal-burning IGCC plant with CO$_2$ capture.
Zeolite Membrane Reactor for Water-Gas Shift Reaction for CO₂ Capture

Zeolite Membrane Requirements:

- Operate at 350-550°C
- Chemically stable in H₂S, thermally stable at ~500°C
- H₂ permeance > 1x10⁻⁷ mol/(m².s.Pa) (>300 GPU) with H₂/CO₂ selectivity > 10
DOE Project: Zeolite Membrane Reactor for Pre-Combustion CO$_2$ Capture

Task description

CO + H$_2$O = CO$_2$ + H$_2$

Project Manager
Andrew Jones

PI: Jerry Y.S. Lin

PI: Junhang Dong

PI: Richard Ciora

PI: Gerald Choi

Media and Process Technology Inc.
MFI-type Zeolite
Structure and property

MFI-type Zeolite (Silicalite-1 or ZSM-5)

- Molecular sieving at high temperatures
- Highly chemically and thermally stable (up to 700°C)

Surface and cross-section SEM images of (a, b) templated synthesized random oriented MFI membrane, and (c, d) template-free synthesized random oriented MFI membranes (from Lin lab)

- Tailorable structure
Tubular MFI-type Zeolite Membranes
Membrane preparation and property

in-situ crystallization

CCD modification*

Al₂O₃ tubular support
MFI zeolite membrane
Modified zeolite membrane

OD = 5.7 mm; ID = 4.7 mm
Pore size < 100 nm

25°C: H₂/CO₂ = 0.1-0.4
450°C: H₂/CO₂ = 4.0-5.0

25°C: H₂/CO₂ = 1.5-3.0
450°C: H₂/CO₂ = 10-45

*Catalytic Cracking Decomposition of Methyl-diethoxysilane (MDES)
Scope of work

1) Scaling up ZMRs from lab-scale to bench-scale for combined WGS reaction and H₂ separation

2) Conducting a bench-scale study using these ZMRs for hydrogen production for IGCC with CO₂ capture.

Goal is to demonstrate effective production of H₂ and CO₂ capture by the bench-scale zeolite membrane reactor from a coal gasification syngas at temperatures of 400-550°C and pressures of 20-30 atm:

- Bench-scale zeolite membrane reactor: 21 zeolite membrane tubes of 3.5 ID, 5.7 OD and 25-cm long (active)
- A system producing H₂ at rate of about 2 kg/day, equivalent to a 2 kWₜₐₜ IGCC power plant
General Approach to Scaling up WGS-ZMR

Single-tube zeolite membrane reactor: study WGS up to 30 atm by experiments and modeling

Intermediate-scale zeolite membrane reactor: 3-7 tube membrane module for WGS reaction

Bench-scale zeolite membrane reactor: 21 tube membrane module for WGS reaction at UK-CBTL

Zeolite membrane reactor in IGCC with CO₂ capture - process design and techno-economic analysis
Progress and Accomplishments

- Modeling and Analysis of WGS in Bench-Scale Zeolite Membrane Modules (Task 10.0)
- Fabrication of Large Quality Tubule Supports (Task 11.0)
- Preparation of Large Quantity MFI Zeolite Tubule Membranes for Bench-Scale Module (Task 12.0)
- Design and Fabrication of Bench-Scale Zeolite Membrane Housing (Task 13.0)
- Building Bench-Scale Zeolite Membrane Reactors (Task 14.0)
- Testing WGS Reaction in Bench-Scale Membrane Reactor (Task 15.0)
- Process Design, Techno-Economic and EH&S Analyses (Task 16.0)
Task 10: Modeling and Analysis of WGS in Bench-Scale Zeolite Membrane Modules

Research target for ZMR performance

**Feed stream**

- syngas mixture

**Permeate stream**

- H₂ recovery:
  \[ R_{H_2} = \frac{F_{H_2, \text{perm}}}{F_{H_2, \text{reten}} + F_{H_2, \text{perm}}} > 92\% \]

- H₂ purity:
  \[ G_{H_2} = \frac{F_{H_2, \text{perm}}}{F_{\text{total, perm}}} \]

**Retentate stream**

- CO₂ capture:
  \[ R_{CO_2} = \frac{F_{CO_2, \text{reten}}}{F_{CO_2, \text{reten}} + F_{CO_2, \text{perm}}} > 90\% \]

- CO₂ purity:
  \[ G_{CO_2} = \frac{F_{CO_2, \text{reten}}}{F_{\text{total, reten}}} > 95\% \]

**CO conversion:**

\[ X_{CO} = \frac{F_{CO, \text{feed}} - F_{CO, \text{reten}} - F_{CO, \text{perm}}}{F_{CO, \text{feed}}} > 99\% \]
**Figure 1.** Profile of CO conversion and gas flow rates in zeolite membrane reactor and fixed-bed reactor.

- **(1) Simulated gas**
  - Purity, $G_{H_2} > 84\%$
  - $G_{CO_2} > 99\%$
  - $X_{CO,FBR} < 92\%$
  - $X_{CO,ZMR} > 99\%$

- **(2) Air-blown gasifier syngas**
  - $G_{H_2} > 78\%$
  - $G_{CO_2} < 16\%$
  - $X_{CO,FBR} < 85\%$
  - $X_{CO,ZMR} > 99\%$

- **(3) O_2-blown gasifier syngas**
  - $G_{H_2} > 84\%$
  - $G_{CO_2} > 92\%$
  - $X_{CO,FBR} < 82\%$
  - $X_{CO,ZMR} > 99\%$
• CO conversion: 87.2% → 97.0%.

• Pre-reactor effect: equilibrium conversion a higher H₂ partial pressure for but a lower CO partial pressure.

• Catalyst packing UC: 30%
Simulation: 50%

Figure 2. Profile of CO conversion and gas flow rates in a zeolite membrane reactor with/without a pre-reactor at 450°C. Pressure: 30 bar; Steam/CO mole ratio: 3.0.
Effect of H₂/CO₂ selectivity (GHSV: 14446.5 h⁻¹)

- PR enhances the CO conversion but less enhancement in the CO₂ capture and H₂ purity.
- Increasing GHSVs improves the CO₂ capture ratio significantly.

Effect of GHSV (H₂/CO₂ Selectivity: 10)

Temperature profile (GHSV: 5417.5 h⁻¹)

Inlet temperature: 450°C; Pressure: 30 bar; Steam/CO mole ratio: 3.0.
## Task 11: Fabrication of a Large Quantity of Tubular Supports

### Tubular Substrate Supply

Over 250 tubular substrates of various types and formulations have been prepared.

<table>
<thead>
<tr>
<th>UC-#</th>
<th>Batch-#</th>
<th>Date shipped</th>
<th>Items</th>
<th>Qty.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>B5</td>
<td>MPT-4</td>
<td>8/29/2017</td>
<td>1</td>
<td>10</td>
<td>96% Alumina body, 5.7x3.5mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on both open ends.</td>
</tr>
<tr>
<td>B6</td>
<td>MPT-5</td>
<td>9/6/2017</td>
<td>1</td>
<td>4</td>
<td>99.9% Alumina body, 5.7x3.5mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on both open ends. (These are test pieces for 99.9% Alumina body.)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>4</td>
<td>96% Alumina body, 5.7x1.9mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on both open ends. (These are thick-wall substrates.)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>3</td>
<td>96% Alumina body, 5.7x3.5mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on the sealed end, 25cm glass on the open end.(For A2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>9</td>
<td>99.9% Alumina body, 5.7x3.5mm(ODxID), 10cm, outside coated 0.05 µm, NO glass end seal. (These are test pieces for 99.9% Alumina body.)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>6</td>
<td>96% Alumina body, 5.7x1.9mm(ODxID), 10cm, outside coated 0.05 µm, NO glass end seal. (These are thick-wall substrates.)</td>
</tr>
<tr>
<td>B7</td>
<td>MPT-6</td>
<td>9/21/2017</td>
<td>1</td>
<td>11</td>
<td>96% Alumina body, 5.7x1.9mm(ODxID), 10cm, outside coated 0.05 µm, NO glass end seal. (thick-wall substrate)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>12</td>
<td>96% Alumina body, 5.7x1.9mm(ODxID), 10cm, outside coated 0.05 µm, 5cm glass glaze on both open ends. (thick-wall substrate)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>10</td>
<td>96% Alumina body, 5.7x3.5mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on both open ends. (thick-wall substrate)</td>
</tr>
<tr>
<td>B8</td>
<td>MPT-7</td>
<td>10/17/2017</td>
<td>1</td>
<td>38</td>
<td>96% Alumina body, 5.7x2.9mm(ODxID), 10cm, outside coated 0.05 µm, NO glass end seal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>10</td>
<td>96% Alumina body, 5.7x2.9mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on both open ends</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>9</td>
<td>96% Alumina body, 5.7x2.9mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on the open and tipped end</td>
</tr>
<tr>
<td>B9</td>
<td>MPT-8</td>
<td>12/7/2017</td>
<td>1</td>
<td>21</td>
<td>96% Alumina body, 5.7x2.9mm(ODxID), 35cm, outside coated 0.05 µm (25cm long), 5cm glass glaze on tipped end, 5cm glass glaze on open end.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>5</td>
<td>96% Alumina body, 5.7x3.5mm(ODxID), 35cm, outside coated 0.05 µm (5cm long), 5cm glass glaze on tipped end, 25cm glass glaze on open end.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>5</td>
<td>96% Alumina body, 5.7x3.5mm(ODxID), 35cm, outside coated 0.05 µm (10cm long), 5cm glass glaze on tipped end, 20cm glass glaze on open end.</td>
</tr>
<tr>
<td>B10</td>
<td>MPT-9</td>
<td>1/9/2018</td>
<td>1</td>
<td>18</td>
<td>96% Alumina body, 5.7x2.9mm(ODxID), 35cm, outside coated 0.05 µm (25cm long), 5cm glass glaze on tipped end, 5cm glass glaze on open end.</td>
</tr>
<tr>
<td>B11</td>
<td>MPT-10</td>
<td>3/8/2018</td>
<td>1</td>
<td>4</td>
<td>99-3070, 5.7x3.5mm (ODxID), 3x10in, 1x7in, no top layer/glass glaze</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>1</td>
<td>99-115, 5.7x3.5mm (ODxID), 1x5in, no top layer/glass glaze</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>1</td>
<td>99-114, 5.7x3.5mm (ODxID), 1x5in, no top layer/glass glaze</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>23</td>
<td>96%, 5.7x2.9mm (ODxID), 35cm, 5cm glass glaze on the tipped &amp; open ends</td>
</tr>
<tr>
<td>B12</td>
<td>MPT-11</td>
<td>3/22/2018</td>
<td>1</td>
<td>2</td>
<td>99-3070, 5.7x3.5mm (ODxID), 35cm long, no glass end seal</td>
</tr>
<tr>
<td>B13</td>
<td>MPT-12</td>
<td>5/17/2018</td>
<td>1</td>
<td>3</td>
<td>99-3070, 5.7x3.5mm (ODxID), 2x6.5in, 1x7.5in, no top layer/glass glaze, fired at 1650°C</td>
</tr>
<tr>
<td>B14</td>
<td>MPT-13</td>
<td>6/14/2018</td>
<td>1</td>
<td>5</td>
<td>96%-body, 5.7x2.9mm (ODxID), 35cm long, outside coated 0.05 µm, 5cm glass glaze on the open &amp; tipped ends</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>1</td>
<td>96%-body, 5.7x2.9mm (ODxID), 35cm long, outside coated 0.05 µm (10cm), 5cm glass glaze on the tipped end, 20cm glass on the open end</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>2</td>
<td>96%-body, 5.7x3.5mm (ODxID), 35cm long, outside coated 0.05 µm (10cm), 5cm glass glaze on the tipped end, 20cm glass on the open end</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>1</td>
<td>96%-body, 5.7x2.9mm (ODxID), 35cm long, outside coated 0.05 µm (5cm), 5cm glass glaze on the tipped end, 25cm glass on the open end</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>2</td>
<td>96%-body, 5.7x3.5mm (ODxID), 35cm long, outside coated 0.05 µm (5cm), 5cm glass glaze on the tipped end, 25cm glass on the open end</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>15</td>
<td>96%-body, 5.7x3.5mm (ODxID), 35cm long, outside coated 0.05 µm (25cm), 5cm glass glaze on two open ends</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7</td>
<td>200</td>
<td>200 grams MPT-114-99% powders, for discs</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6/14/2018 ASU</td>
<td>1 200 grams MPT-114-99% powders, for discs (Shipped to Lie Meng, ASU)</td>
<td></td>
</tr>
<tr>
<td>B15</td>
<td>MPT-14</td>
<td>7/2/2018</td>
<td>1</td>
<td>23</td>
<td>96%-body, 5.7x3.5mm (ODxID), 35cm long, outside coated 0.05 µm, 5cm glass glaze on the open &amp; tipped ends</td>
</tr>
</tbody>
</table>

Total = 258
Task 12: Preparation of Large Quantity Zeolite Membranes for Bench-Scale Module

Alumina leaching in the synthesis of MFI zeolite membranes

(a) MPT disk  (b) A-16 SG disk

microscope digital images

XRD patterns

A-16 SG: 100%  MPT: 0%
A-16 SG: 75%  MPT: 25%
A-16 SG: 50%  MPT: 50%
A-16 SG: 25%  MPT: 75%
A-16 SG: 0%  MPT: 100%

Bi-layer
in-situ crystallization at 180°C, 3 hours using 0.055 SiO₂: 0.0058 NaOH: 0.017 TPAOH: 0.92 H₂O

High Al content was found in the MFI zeolite formed in the synthesis of zeolite membranes supported by disks pressed with MPT powder.

Figure 4. Al/Si ratio in powders collected at the bottom of autoclaves for in-situ synthesis of MFI zeolite membranes supported by varied disks.
Task 12: Preparation of Large Quantity Zeolite Membranes for Bench-Scale Module

Quality of modified tubular MFI zeolite membranes

- Crystal size: 600 nm
- Layer thickness: 5-8 μm
- Excellent surface coverage
- 75% membrane reproducibility

**Knudsen factor ~ 4.7**

**H₂/CO₂ separation selectivity**

**H₂ permeance (mol/(Pa·m²·s))**

- 1
- 2
- 3
Task 13: Design and Fabrication of Bench-Scale Zeolite Membrane Module Housing
On-going work: design of bench-scale membrane module

Module material: SS316

21-Tubule Membrane Bundles
- Bench scale testing
- H₂ production rate > 30 L/min
- Mesh number > 1,000,000

Zeolite Membrane Reactor
Pending to be optimized
- Module configuration
- Catalyst loading
- Operation conditions
Task 14: Building Bench-Scale Zeolite Membrane Reactors
Fabrication and evaluation of WGS catalyst for bench-scale WGS reaction

**Kinetic model for the Co-Mo catalyst in the high-temperature WGS**

**Reaction pathway of WGS over Co-Mo catalysts**

Sulfidation (pre-treatment):

\[ \text{MoO}_3 + 2\text{H}_2\text{S} + \text{H}_2 \rightarrow \text{MoS}_2 + 3\text{H}_2\text{O} \]

WGS:

- **R1:** \( \text{MoS}_2 + \text{H}_2\text{O} \rightarrow \text{MoSO} + \text{H}_2\text{S} \)
- **R2:** \( \text{MoSO} + \text{CO} \rightarrow \text{MoS} + \text{CO}_2 \)
- **R3:** \( \text{MoS} + \text{H}_2\text{S} \rightarrow \text{MoS}_2 + \text{H}_2 \)

The power-law model

\[ r_{CO} = k_0 \exp\left( \frac{-E_a}{RT} \right) P_{CO}^{a} P_{H_2O}^{b} P_{CO_2}^{c} P_{H_2}^{d} (1 - \beta) \]

\[ \beta = \frac{1}{K} \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \]

SSK-10 catalyst (Co-Mo-Mg(AlO_2)_2)
Determination of power-law model reaction orders

Log-log plots for the effect of CO, H₂O, CO₂, and H₂ partial pressure on reaction rates over Co-Mo catalyst.

\[
r_{CO} = 1.58 \times 10^{-4} \exp\left(\frac{-37.99}{RT}\right) P_{CO}^{0.50} P_{H₂O}^{0.32} P_{CO₂}^{-0.12} P_{H₂}^{-0.11} (1 - \frac{1}{K P_{CO} P_{H₂O}})
\]
Task 14: Building Bench-Scale Zeolite Membrane Reactors
Assembling and Testing Bench Scale Zeolite Membrane Reactor

**Thermal Stability Testing of Mock 21-tube Membrane Bundle**

*Testing Conditions:* $T = 450^\circ C; P = 300$ to $350$ psig

---

**21-Tube Candle Filter Bundle**
- Ceramic Tube Sheet
- Ceramic/Glass Potting

**Bundle Leak Rate during Challenge Testing**

*No leak development in the three major components was observed in nearly 3,500 hours of challenge testing.*

---

**Impermeable Ceramic Tip**

---

**Bubble test seal. Tighten packing.**

---

**Repack graphite seal.**

---

**High Temperature Test Housing**

---

**Chart:**
- Leak Rate, N2 [GPU]
- Time [hours]
**Fabrication and Performance Testing of a 3-tube Zeolite Membrane Bundle**

**3-Tube Candle Filter Bundle (ID: K3-3)**

- **Impermeable Ceramic Tip**
- **Zeolite Membrane Layer**
- **Ceramic Tube Sheet and Ceramic/Glass Potting**

**Single-gas permeation at 200°C**

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube 70B</td>
<td>1.449</td>
<td>0.811</td>
</tr>
<tr>
<td>Tube 70C</td>
<td>1.336</td>
<td>0.711</td>
</tr>
<tr>
<td>Tube 71C</td>
<td>1.422</td>
<td>0.742</td>
</tr>
<tr>
<td>Tube average</td>
<td>1.400</td>
<td>0.755</td>
</tr>
<tr>
<td>3-tube bundle</td>
<td>1.310</td>
<td>0.707</td>
</tr>
</tbody>
</table>
Task 14: Building Bench-Scale Zeolite Membrane Reactors
Modification and Installation of Bench-Scale Reactor Test Skid

Front View: Oven Chamber with Membrane Test Module and a 3” x 85-tube Membrane Bundle for Perspective

Back View: Major Bench Scale Reactor Test Skid Subsystems
- Pressure Control Panel
- Mass Flow Meter Enclosure
- Reject and Permeate Liquid Knockout Pots
- Steam Injection Subsystem
- Water Sampling Subsystem
- 3” x 85-tube Membrane Bundle

Power Distribution Skid
- Oven Controls
Conclusions

- Mathematical models of WGS-ZMR and Reaction kinetics of WGS catalysts established.
- 25-cm long CCD-modified zeolite membranes scaled up on alumina substrates.
- Multiple-tube ZMRs assembled and evaluated, and test skid for bench-scale test modified.

Acknowledgement

Thank You!