Energy Efficient GO-PEEK Hybrid Membrane Process for Post-combustion CO$_2$ Capture

DOE Contract No. DE-FE0026383

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CO$_2$ Capture Technology Project Review Meeting  
August 21 - 25, 2017, Pittsburgh, PA
Process description

GO for bulk/partial CO₂ removal

1. Flue gas
2. Blower
3. Filter

GO membrane (conventional process)

4. GO membrane
5. Vacuum pump
6. Condenser
7. Treated flue gas to stack (1.3 (vol.)% CO₂, 0.5 psi)

CO₂ enriched permeate

8. PEEK HFMC to further capture CO₂

9. Flash regenerator
10. Surge tank
11. Plant’s low pressure steam
12. HFMC
13. CO₂ captured (95% purity of CO₂)

PEEK membrane absorber

H₂O to surge tank

CO₂/SO₂ selectivity through GO membrane will be tested in the current program:

- **Case 1**: SO₂ permeates through the membrane, a caustic scrubber is needed before the GO membrane.
- **Case 2**: SO₂ stays in the retentate, scrubber unneeded; HFMC can handle 150 ppmv SO₂ (DE-FE-0004787)

GO = graphene oxide
GO-PEEK project overview

- **Performance period**: Oct. 1, 2015 – Sep. 30, 2018
- **Funding**: $1,999,995 from DOE; $500,000 cost share
- **Objectives**: Develop a hybrid membrane process combining a graphene oxide (GO) gas separation membrane configuration unit and a PEEK hollow fiber membrane contactor (HFMC) unit to capture ≥90% of the CO\(_2\) from flue gases with 95% CO\(_2\) purity at a cost of electricity 30% less than the baseline CO\(_2\) capture approach

**Team:**

<table>
<thead>
<tr>
<th>Member</th>
<th>Roles</th>
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<tbody>
<tr>
<td>gti</td>
<td>• Project management and planning</td>
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<td>• Quality control and CO(_2) capture performance tests</td>
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<tr>
<td>University of South Carolina</td>
<td>• GO membrane development</td>
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<td>Air Liquide</td>
<td>• PEEK membrane development</td>
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<tr>
<td>Trimeric Corporation</td>
<td>• High-level technical &amp; economic feasibility study</td>
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</table>
GO membrane technology based on our pioneering work published in *Science* (2013, 342 (6154) 95)

**Ultrathin, Molecular-Sieving Graphene Oxide Membranes for Selective Hydrogen Separation**
Hang Li et al.
*Science* 342, 95 (2013);
DOI: 10.1126/science.1236686

- **Contribution of the paper:**
  - Structural defects on GO flakes can be controlled as transport pathway for selective gas separations

Single-layered GO flake prepared as thin as 1 nm
Singular PEEK HFMC technology currently at pilot scale development stage (DE-FE0012829)

Membrane contactor: high surface area device that facilitates mass transfer
Singular PEEK HFMC technology currently at pilot scale development stage (DE-FE0012829)

Membrane contactor: high surface area device that facilitates mass transfer

Commercial-sized modules
Singular PEEK HFMC technology currently at pilot scale development stage (DE-FE0012829)

Membrane contactor: high surface area device that facilitates mass transfer

Commercial-sized modules

NCCC PSTU system (0.5 MW_e)

GTI HFMC system (0.5 MW_e)

Plant constructed and installed at NCCC
Singular PEEK HFMC technology currently at pilot scale development stage (DE-FE0012829)

Membrane contactor: high surface area device that facilitates mass transfer

Commercial-sized modules

NCCC testing results indicate DOE’s technical target can be achieved

**CO₂ removal rate:**

- **CO₂ purity:** > 98.6% CO₂

Plant constructed and installed at NCCC

GTI HFMC system (0.5 MWₑ)

NCCC PSTU system (0.5 MWₑ)
GO-PEEK technical goals

GO-PEEK hybrid process

GO membranes

- CO$_2$ permeance $\geq$ 1,000 GPU
- CO$_2$/N$_2$ selectivity $\geq$ 90

PEEK membranes

- Intrinsic CO$_2$ permeance $\geq$ 3,000 GPU
- CO$_2$ mass transfer coefficient $\geq$ 3 (sec)$^{-1}$

Capture 45% CO$_2$

Separate and capture $\geq$ 90% CO$_2$ from a simulated flue gas with 95% CO$_2$ purity

GPU = Gas Permeation Unit
Progress on PEEK Membranes

\[
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\text{C} \\
\text{O} \\
\text{O}
\end{array}\right)_{n}
\]

A

B
Under the current program, we are developing PEEK fibers with intrinsic CO$_2$ permeance of 3,000 GPU.

\[ 1 \text{ GPU} = 1 \times 10^6 \text{ cm}^3 \text{(STP)/cm}^2 \cdot \text{s} \cdot \text{cmHg} \]
Eight types of fibers were investigated

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fiber OD (Micron)</th>
<th>Fiber ID (Micron)</th>
<th>CO₂ permeance* (GPU)</th>
</tr>
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<tbody>
<tr>
<td>78-33-3A</td>
<td>582</td>
<td>350</td>
<td>2,300</td>
</tr>
<tr>
<td>78-33-3B</td>
<td>582</td>
<td>350</td>
<td>2,500</td>
</tr>
<tr>
<td>78-118-3A</td>
<td>569</td>
<td>358</td>
<td>2,300</td>
</tr>
<tr>
<td>78-118-3B</td>
<td>569</td>
<td>358</td>
<td>2,800</td>
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<tr>
<td>78-117-5A</td>
<td>569</td>
<td>353</td>
<td>3,400</td>
</tr>
<tr>
<td>78-117-5B</td>
<td>569</td>
<td>353</td>
<td>3,400</td>
</tr>
<tr>
<td>78-117-5C</td>
<td>569</td>
<td>353</td>
<td>3,700</td>
</tr>
<tr>
<td>78-117-5D</td>
<td>569</td>
<td>353</td>
<td>3,800</td>
</tr>
</tbody>
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Temperature: 25°C, feed pressure: ~ 5 psig
2-inch module 2PG819 containing 78-117-5C fibers (CO\textsubscript{2} permeance of 3,700 GPU)

Module 2PG819
23-25°C
10 psig feed pressure
PEEK membrane module effective in capturing CO$_2$ from low CO$_2$-concentration feeds in membrane contactor

Goal of mass transfer coefficient $> 3$ (sec)$^{-1}$ achieved
Progress on GO Membranes

GO: single-atomic layered, oxidized graphene
Procedure developed for coating GO-based membrane on hollow fiber (HF) support

Coating procedure:
1. Valves A and B are open, GO dispersion flows continuously in hollow fiber
2. Vacuum filtration is conducted for a controlled time; and
3. Valves A and B are closed; coated fiber stays under vacuum for a controlled time
GO membrane (thickness: ~9 nm) supported on polyethersulfone (PES) hollow fiber
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Coated fiber sealed in a mini-module for gas permeation testing

Permeation testing unit

Water bubbler and knockout vessel
Initial GO membrane performance under simulated flue gas condition

- CO$_2$ permeance of 100 GPU and selectivity of 49 obtained for a humidified 15%/85% CO$_2$/N$_2$ mixture
Challenge: GO membrane performance needs significant improvement

Li et al., ACS Appl. Mater. Interfaces. 7, 5528 (2015)

Kim et al., Science 342, 91 (2013)

Our membrane at early stage

Our target


Approaches to improve $\text{CO}_2$ permeance

- Create more structural defects on GO flake by $\text{HNO}_3$ etching

- Reduce GO flake lateral size by ultra-sonication
Approach to improve CO$_2$/N$_2$ selectivity: fill the space between GO layers with CO$_2$-philic agent

- CO$_2$-philic agent enables facilitated transport mechanism to separate CO$_2$ from N$_2$

0.7-1.1 nm
Approach to improve CO$_2$/N$_2$ selectivity: fill the space between GO layers with CO$_2$-philic agent

- CO$_2$-philic agent enables facilitated transport mechanism to separate CO$_2$ from N$_2$

CO$_2$-philic agent example: piperazine (PZ)
Cross-sectional SEM of the PZ filled GO membrane
XPS and FTIR analysis confirmed the crosslinking of PZ with GO sheets

XPS

FTIR

C-N bonds
GO-based membranes separation performance

Feed: 15% CO₂/85%N₂ with saturated water vapor
Permeate: with sweep gas

\[ \Delta E_p = 40.6 \text{ kJ/mol} \]
Facilitated transport mechanism

- 0.7-1.1 nm
Facilitated transport mechanism

\[ 2\text{CO}_2 + 2\text{RR'}\text{NH} + \text{H}_2\text{O} \rightleftharpoons \text{RR'}\text{NCOOH} + \text{RR'}\text{NH}_2^+ + \text{HCO}_3^- \]

\[ \text{CO}_2 + \text{RR'}\text{R''N} + \text{H}_2\text{O} \rightleftharpoons \text{RR'}\text{R''NH}^+ + \text{HCO}_3^- \]

0.7-1.1 nm
Facilitated transport mechanism

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\[\text{CO}_2 + \text{RR''R''N} + \text{H}_2\text{O} \rightleftharpoons \text{RR''R''NH}^+ + \text{HCO}_3^-\]
Comparison to other CO$_2$/N$_2$ separation membranes

Note: Polymer data points (red): 100 nm membrane thickness assumed

Comparison to other CO$_2$/N$_2$ separation membranes

2. Merkel, et al., Ibid.
3. Venna, Ibid.

Note: Polymer data points (red): 100 nm membrane thickness assumed

Comparison to other CO\textsubscript{2}/N\textsubscript{2} separation membranes

Our GO membranes: \( P_{\text{CO}_2} \): 1000 GPU, \( \alpha_{\text{CO}_2/\text{N}_2} \): 680 (tested at 80°C with sweep gas)

2. Merkel, et al., Ibid.
3. Venna, Ibid.

\( \alpha \) (CO\textsubscript{2}/N\textsubscript{2})

1000

100

10

1

\( \text{CO}_2 \) permeance (GPU)

1. OSU composite membranes

2. MTR Polaris advanced (lab scale) membranes

3. NETL MOF mixed matrix membranes

4. GE composite hollow fiber membranes

Note: Polymer data points (red): 100 nm membrane thickness assumed

Future work overview/roadmap

GO Membrane Development

Task 6.0 (RPI) – Further GO optimization

Task 7.0 (GTI) – Performance stability testing of GO membranes using simulated flue gases

Task 9.1 (RPI) – GO membrane support for integrated testing

PEEK Membrane Development

Task 8.0 (GTI) – Modification of an existing HFMC apparatus to GO-PEEK system

Task 10.0 (GTI) – CO$_2$ capture testing using integrated GO-PEEK hybrid system

Task 11.0 (Trimeric) – High-level techno-economic feasibility study

Integrated GO-PEEK Hybrid System

Task 9.2 (ALaS) – PEEK membrane support for integrated testing
After the current project, steps can be taken to further reduce cost for GO-based membranes

- New process design
- Increase CO$_2$ permeance for GO membrane
- Advanced manufacture process to lower membrane costs

Hollow fiber configuration

module can be used in bench scale
After the current project, steps can be taken to further reduce cost for GO-based membranes

- New process design
- Increase CO$_2$ permeance for GO membrane
- Advanced manufacture process to lower membrane costs

Hollow fiber configuration

Flat sheet membranes to be used in spiral wound configuration

module can be used in bench scale
Summary

- We are developing a transformational hybrid process for CO$_2$ capture combining a conventional gas membrane unit and a HFMC unit.

- **The 3$^{rd}$ Generation PEEK fiber** developed to date:
  - Fibers with intrinsic CO$_2$ permeance $>3,000$ GPU at 25°C.
  - Membrane module effective in capturing CO$_2$ from low CO$_2$-concentration feeds with aMDEA solvent.

- **GO membrane** developed to date:
  - CO$_2$ permeance $>1,000$ GPU and $\alpha_{CO_2/N_2}>600$ obtained at 80°C for a humidified CO$_2$/N$_2$ mixture.
  - Superior performance to GO-based membranes reported in the literature.

- Future work will focused on further GO membrane development, integrated testing and TEA.
Acknowledgements

- Financial and technical support

- DOE NETL José Figueroa and Lynn Brickett
- Dr. Yu Group
  - Fanglei Zhou
  - Huynh Ngoc Tien
  - Jarvis Chen
  - Mahdi Fathizadeh