Transformational Membranes for Pre-combustion Carbon Capture

Winston Ho / Yang Han

William G. Lowrie Department of Chemical & Biomolecular Engineering
Department of Materials Science and Engineering
The Ohio State University

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Project Objective

- Develop a cost-effective design and fabrication process for a novel transformational membrane and its membrane modules that capture CO$_2$ from coal-derived syngas
  - 95% CO$_2$ Purity
  - >99% H$_2$ Recovery
  - COE 30% Less than Baseline Approaches
2-Budget Period Project

• BP1: 10/01/2018 – 03/31/2020
  – Laboratory-scale membrane synthesis, characterization and transport performance studies
  – High-level preliminary techno-economic analysis

• BP2: 04/01/2020 – 09/30/2021
  – Laboratory-scale membrane synthesis, characterization and transport performance studies to continue
  – Fabrication, characterization and transport performance studies of scale-up membrane (14” wide by 20’ long)
  – Fabrication, performance and stability testing of spiral-wound membrane modules
  – Update techno-economic analysis performed in BP 1

• Integrated program with fundamental studies, applied research, synthesis, characterization and transport studies, and high-level techno-economic analysis
Funding and Performance Dates

• **Total Budget:** 10/01/2018 – 09/30/2021
  **DOE:** $799,988; **OSU:** $199,998 (20% cost share)

• **BP1:** 10/01/2018 – 03/31/2020
  **DOE:** $386,694; **OSU:** $96,674

• **BP2:** 04/01/2020 – 09/30/2021
  **DOE:** $413,294; **OSU:** $103,324
Technical Background: Proposed Process

• Proposed membrane process does not require significant syngas cooling (compared to competition)
Location of Proposed Technology in IGCC Plant

Air Separation

Gasifier & Quench

Heat Recovery

Particulate Removal

Water Gas Shift

Syngas Expander

Sulfur Recovery

Membrane

H₂S Removal

CO₂ Compression

Sulfur

CO₂ to Storage

O₂

N₂

Vent

Coal

Slag

Air

O₂

N₂

Vent

Flue Gas

Water

H₂ as Fuel Gas

H₂ as Fuel Gas
Selective Amine Polymer Layer / Polymer Support

Simplicity of Membrane for Low Cost

Selective amine polymer layer (~15 µm, dense layer)

Polymer support (~20 µm, Ø ~10 nm)

Nonwoven fabric backing (~100 µm)
Amine Polymer Layer Contains Mobile and Fixed Carriers: Facilitated Transport

Feed Side

Permeate Side

Facilitated Transport

Mobile Carrier

CO₂

Mobile Carrier

CO₂

Mobile Carrier

CO₂

Physical Solution-Diffusion

Non-Reacting Gas: H₂

H₂
Tunable Amine-CO$_2$ Chemistry

- Reaction of CO$_2$ with Unhindered Amines

\[
\text{CO}_2 + \text{R–NH}_2 \rightleftharpoons \text{R–NH}_2^+–\text{COO}^- \\
\text{R–NH}_2^+–\text{COO}^- + \text{R–NH}_2 \rightleftharpoons \text{R–NH–COO}^- + \text{R–NH}_3^+ \\
\text{Overall:} \\
\text{CO}_2 + 2 \text{R–NH}_2 \rightleftharpoons \text{R–NH–COO}^- + \text{R–NH}_3^+
\]

- Reaction of CO$_2$ with Hindered Amines

\[
\text{CO}_2 + \text{R}_1–\text{NH–R}_2 \rightleftharpoons \text{R}_1\text{R}_2–\text{NH}^+–\text{COO}^- \\
\text{R}_1\text{R}_2–\text{NH}^+–\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{R}_1\text{R}_2–\text{NH}_2^+ + \text{HCO}_3^- \\
\text{Overall: Can double the CO}_2\text{ capacity} \\
\text{CO}_2 + \text{R}_1–\text{NH–R}_2 + \text{H}_2\text{O} \rightleftharpoons \text{R}_1\text{R}_2–\text{NH}_2^+ + \text{HCO}_3^-
\]
Facilitated Transport vs. Solution-Diffusion Mechanism

• CO$_2$ Facilitated Transport Flux: Very High
  – CO$_2$-amine reaction enhances CO$_2$ flux

• H$_2$ Flux: Very Low
  – H$_2$ does not react with amine
  – H$_2$ transport follows conventional physical solution-diffusion mechanism, which is very slow
Membrane Performances

CO$_2$/H$_2$ selectivity vs. CO$_2$ permeance (GPU)

Enhanced Physical Solubility
Enhanced Chemical Solubility

BP1Q1
BP1Q2
BP1Q3

Continued Performance Improvement
Membrane Performances

Simulated Syngas at 107°C and 31.7 bar

![Graph showing CO₂ permeance (GPU) and CO₂/H₂ selectivity as a function of feed CO₂ partial pressure (bar) for different membranes.](image)
Effect of Carrier Saturation Phenomenon on Performance

Graph showing:
- Feed CO₂ partial pressure
- CO₂ permeance
- CO₂/H₂ selectivity

Membrane BP1Q3
Feeding inlet

Membrane M6
Retentate outlet

Normalized distance from feed inlet
Effect of CO$_2$ Permeance on Cost of Electricity Increase

- COE increase
- Membrane area

COE increase of BP1Q1
COE increase of BP1Q2
COE increase of BP1Q3

CO$_2$ permeance (GPU)

Membrane area (x10$^4$ m$^2$)

Cost of Electricity Increase (%)

CO$_2$ permeance (GPU)
Membranes Synthesized with Tuned H$_2$S/CO$_2$ Selectivities

![Graph showing H$_2$S/CO$_2$ selectivity against feed CO$_2$ partial pressure (bar). Two membranes are compared: Membrane M6 and Membrane BP1Q3. Membrane M6 shows a significant increase in selectivity with increasing feed CO$_2$ partial pressure, while Membrane BP1Q3 remains relatively constant.]
Effect of H$_2$S/CO$_2$ Selectivity on H$_2$S Concentration in H$_2$ Product

< 6 ppm H$_2$S for BP1Q3
Plans for Future Testing/Development

• Remaining BP1
  – Increase CO₂ Sorption at High Pressure
  – Enhance Membrane Mechanical Properties
  – Preliminary Techno-Economic Analysis

• BP2
  – Membrane Scale-up and Characterization
    + Continuous roll-to-roll fabrication (14” wide by 20’ long)
  – Prototype SW Module Fabrication
    + Fabricate 9 prototype SW modules (800 cm² each)
    + 200-h stability test with simulated syngas
  – Final Techno-Economic Analysis
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