Novel CO$_2$-Selective Membranes for CO$_2$ Capture from <1% CO$_2$ Sources

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Project Objective

• Develop a novel cost-effective membrane and design of membrane modules that capture CO₂ from <1% CO₂ sources
  • 90% CO₂ Capture
  • 95% CO₂ Purity
3-Budget Period Project

• **BP1: 03/01/2016 – 02/28/2017**
  - Conduct laboratory-scale membrane synthesis, characterization and transport performance studies
  - Carry out high-level preliminary techno-economic analysis

• **BP2: 03/01/2017 – 02/28/2018**
  - Continue laboratory-scale membrane synthesis, characterization and transport performance studies
  - Fabricate larger lab size membrane (~ 6” by 6”)
  - Fabricate, evaluate and down-select from plate-and-frame and spiral-wound membrane modules
  - Update techno-economic analysis performed in BP 1

• **BP3: 03/01/2018 – 02/28/2019**
  - Fabricate 3 laboratory membrane modules
  - Test modules with <1% CO₂ simulated gas mixture
  - Update techno-economic analysis

• Integrated program with fundamental studies, applied research, synthesis, characterization and transport studies, and high-level techno-economic analysis
Project Organization and Roles

Ohio State University
- Technical lead
- Concept development and execution
- Novel membrane synthesis/characterization
- Laboratory-size membrane scale-up
- Process design considerations
- Cost calculations

Winston Ho

DOE NETL
Project Manager
José Figueroa

TriSep Corporation
- Consult on membrane scale-up/module fabrication
  Peter Knappe

Gradient Technology
- Consult on system and cost analyses
  Steve Schmit

AEP
- Consult on plant integration and demonstration considerations
  Matt Usher
Funding and Performance Dates

• **Total Budget:** 03/01/2016 – 02/28/2019  
  **DOE:** $1,248,278; **OSU:** $372,864 (23% cost share)

• **BP1:** 03/01/2016 – 02/28/2017  
  **DOE:** $407,616; **OSU:** $121,756

• **BP2:** 03/01/2017 – 02/28/2018  
  **DOE:** $419,628; **OSU:** $125,344

• **BP3:** 03/01/2018 – 02/28/2019  
  **DOE:** $421,034; **OSU:** $125,764
Process Proposed for CO₂ Capture from <1% CO₂ Sources

- Proposed membrane process does not require cryogenic distillation (compared to competition)
Location of Proposed Technology in Coal-fired Power Plant

- **Pulverized Coal Boiler**
  - Primary Air Fans
  - Secondary Air Fans
  - Feed Water
  - Coal Feed
  - Bottom Ash

- **Steam to Turbine**
  - Induced Draft Fans
  - Baghouse

- **Primary CO₂ Capture System**
  - <1% CO₂ Feed Gas
  - >95% CO₂ Treated Gas

- **Membrane Module 1**
  - Membrane Module 2

- **Vacuum Pump 1**
  - Vacuum Pump 2

- **Compressor**
  - 152 bar
  - >95% CO₂
Selective Amine Polymer Layer / Polymer Support

Simplicity of Membrane for Low Cost

Selective amine polymer layer (180 nm, dense layer)

Polymer support (~30 μm, Ø ~70 nm)

Nonwoven fabric backing (~120 μm)
Selective Amine Polymer Layer / Polymer Support

- Selective Amine Polymer Layer
  - Facilitated transport of CO₂ via reaction with amine
    $$\text{CO}_2 + \text{R-NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{R-NH}_3^+ + \text{HCO}_3^-$$
  - Facilitated transport = flux augmentation via reaction
  - High CO₂ permeance and CO₂/N₂ selectivity
BP1 – 5-Month Accomplishments

• Improved 14”-wide PES Polymer Support Fabricated with Continuous Machine
  – Economical substrate for lab membrane synthesis

• Composite Membrane Synthesized in Lab
  – Elucidated carrier saturation phenomenon
  – 940 GPU with 150 CO$_2$/N$_2$ selectivity obtained at 57°C from lab test using 1% CO$_2$ concentration feed gas
  + 770 GPU with 140 CO$_2$/N$_2$ selectivity obtained using 20% CO$_2$ concentration feed gas due to carrier saturation phenomenon

• High-Level Techno-economic Analysis Showed Capture Cost of ~$310/tonne CO$_2$ (in 2011 $)
  – ~22% increase in COE

• 2 PCT (Patent Cooperation Treaty) Applications Filed for New Membrane Composition and Process
Affordable Fabrication of PES Support

Continuous Membrane Fabrication Machine at OSU
Successful Continuous Fabrication of Affordable PES Support Demonstrated in DE-FE0007632

- Manufacturer could not supply PES needed for scale-up
- PES synthesized/developed at OSU to resolve supply issue
- PES technology being transferred to a membrane company

2500 feet fabricated
Successful Continuous Fabrication of Affordable PES Support

SEM Analysis of 14-inch PES Support

Ave. pore size = 43.7 nm, Porosity = 13.1%

• Optimal pore size identified to reduce penetration for improving membrane performance
Composite Membrane Synthesized
Selective Amine Polymer Layer on PES Support

Selective layer = 165 nm
Amine Polymer Layer Contains Mobile and Fixed Carriers: Facilitated Transport

Feed Side

Permeate Side

Facilitated Transport

Physical Solution-Diffusion

Non-Reacting Gas: \( N_2 \)
Facilitated Transport vs. Solution-Diffusion Mechanism

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

- **N$_2$ Flux: Very Low**
  - N$_2$ does not react with amine
  - N$_2$ transport follows conventional physical solution-diffusion mechanism, which is very slow
Carrier Saturation Phenomenon

- **CO₂ Flux Increases as Pressure Increases until Carrier Saturation Occurs**
  
  \[ \Delta p = p_f - p_p \text{ or Feed CO}_2 \text{ concentration} \]

- **At Carrier Saturation, i.e., High CO₂ Pressure**
  - CO₂ at high pressure reacts with all carriers incorporated in the membrane
  - CO₂ flux reaches maximum and does not increase with pressure any further
Carrier Saturation Phenomenon (cont’d)

• At Carrier Saturation (High CO₂ Pressure), i.e., Maximum, But Constant CO₂ Flux ( j )
  - CO₂ permeance reduces as pressure increases
  - That is: CO₂ permeance increases as pressure reduces

\[ \Delta p = p_f - p_p \text{ or Feed CO₂ concentration} \]

\[ \text{CO₂ Permeance} = \frac{j}{\Delta p} \]

• At Low CO₂ Pressure, i.e., Less CO₂ Molecules
  - More free carriers available for reaction with CO₂
    + Greater CO₂ facilitation and then higher CO₂ permeance
  - CO₂ permeance increases as pressure reduces
Carrier Saturation Phenomenon Data

CO₂ Permeance (GPU) vs. CO₂ Concentration (%)

CO₂/N₂ Selectivity

- CO₂ Permeance decreases sharply with increasing CO₂ Concentration.
- CO₂/N₂ Selectivity remains relatively constant across the concentration range shown.
High-Level Techno-Economic Calculations

• **Basis: Membrane Results at 57°C**
  - 940 GPU & 150 Selectivity for 1% CO₂ concentration feed gas
  - 770 GPU & 140 Selectivity for 20% CO₂ concentration feed gas
  - Include Membrane Module Installation Cost and 20% Process Contingency
  - In 2011 dollar: NETL Case 12 of *Updated Costs (June 2011 Basis) for Selected Bituminous Baseline Cases*

• **Calculated Cost Results**
  - 32.1 tonne/h of CO₂ captured from 1% CO₂ source
  - $112 million bare equipment cost
    - Membrane 25%, blowers and vacuum pumps 61%, others 14%
  - 1.82 ¢/kWh (1.29 ¢/kWh capital cost, 0.23 ¢/kWh fixed cost, 0.26 ¢/kWh variable cost, and 0.04 ¢/kWh T&S cost)
    - COE = 8.09 ¢/kWh for 550 MW supercritical pulverized coal power plant
  - $311/tonne capture cost ($18.2/MWh × 550 MW/(32.1 tonne/h))
  - 22.4% Increase in COE (1.82/8.09 = 22.4%)
Plans for Future Testing/Development

• Remaining BP1
  – Continue laboratory-scale membrane synthesis, characterization & transport performance studies in BP1
  – Complete carrier saturation phenomenon study
  – Update high-level preliminary techno-economic analysis

• BP2
  – Continue laboratory-scale membrane synthesis and characterization for performance improvement
  – Fabricate larger lab-size membrane (~ 6” by 6”)
  – Fabricate, evaluate and down-select from plate-and-frame and spiral-wound membrane modules
  – Update techno-economic analysis performed in BP 1

• BP3
  – Fabricate 3 laboratory membrane modules
  – Test modules with <1% CO₂ simulated gas mixture
  – Update techno-economic analysis
Acknowledgments

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