New Amine-Based Membranes for Post- and Pre-Combustion CO$_2$ Capture

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Outline

• Post-Combustion CO$_2$ Capture
  – Flue Gas in Coal- and/or Natural Gas-fired Power Plants

• Pre-Combustion CO$_2$ Capture
  – Coal- and/or Natural Gas-derived Syngas
  – Integrated Gasification Combined Cycle (IGCC)
Post-Combustion CO$_2$ Capture

Introduction

- Coal-fired power plants
  - 40% of global CO$_2$ emission
  - Remain as major energy supply

- Membranes for CO$_2$ capture from flue gas
  - System compactness
  - Energy efficiency
  - Operational simplicity
  - Kinetic ability to overcome thermodynamic solubility limitation
CO₂ Capture from Flue Gas

• Flue Gas
  - Low pressure: 1 atm
  - Low CO₂ concentration: ~ 6 – 14%

• Low Driving Force

• Single-Stage Membrane Process Cannot Achieve DOE Targets
  - 90% capture with ≥95% CO₂ concentration
  - ≤$40/tonne CO₂ captured (in 2007 dollar)
Amine-Containing Polymer Membrane Structure

Simplicity of Membrane for Low Cost

- Amine layer
- Porous PES or PSf
- Non-woven fabric
Amine Polymer Layer Contains Mobile and Fixed Carriers: Facilitated Transport

Feed Side

Permeate Side

Facilitated Transport

Physical Solution-Diffusion

Non-Reacting Gas: $N_2$
Amine-Containing Carriers

- **Fixed-Site Carrier**
  
  ![Chemical Structure](PNVF-co-VAm)

- **Mobile Carriers**
  
  - PZ-Gly
  
  ![Chemical Structure](PZ-Gly)
  
  - PZEA-Gly
  
  ![Chemical Structure](PZEA-Gly)
  
  - PZEA-Sar
  
  ![Chemical Structure](PZEA-Sar)
High CO₂ Permeability/Selectivity Achieved

Membrane Scale-up: Continuous Roll-to-Roll Fabrication Machine at OSU
Composite Membrane Synthesized
Selective Amine Polymer Layer on PES Support

Selective layer = 165 nm
Effects of Temperature and Permeate Vacuum

4 atm Feed Pressure

Membrane dehydrated

Reverse reaction resistance

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

Vacuum pressure (atm)
Spiral-Wound Module Fabrication

Element Rolling Machine

Spiral-Wound Membrane Element

Membrane Module

Salim et al., *JMS*, 556, 126 (2018)
Scale-up of SW Modules

![Graph showing scale-up of SW Modules](image)

- **Membrane area (cm²)**
- **CO₂ permeance (GPU)**
- **CO₂/N₂ selectivity**

Legend:
- ■ Permeance with BP2 membrane
- ▲ Permeance with BP1 membrane
- ● Selectivity with BP2 membrane
- △ Selectivity with BP1 membrane

Temperatures and permeance/ selectivity values indicated at 57°C and 67°C.
Good SW Module Stability Obtained

- Simulated Flue Gas: 17.1% CO₂, 68.5% N₂, 7.4% H₂O, 7% O₂, 3 ppm SO₂
- Simulated Residual Flue Gas: 1% CO₂, 84.6% N₂, 7.4% H₂O, 7% O₂, 3 ppm SO₂

- 67°C, 4 atm Feed
- 14,000 cm² Membrane Area

CO₂/N₂ selectivity

CO₂ permeance (GPU)
Good SW Module Stability at NCCC

14,000 cm² Membrane Area

- 1 atm Feed
  - 0.2 atm Vacuum
  - 57°C
- 4 atm Feed
  - 0.3 atm Vacuum
  - 67°C

Onset of FG Shutdown Reducing CO₂%
Cumulatively 500-h test
Low FG Flow
FG Shutdown
Process Proposed for CO$_2$ Capture from Flue Gas in Coal-Fired Power Plants

- **Retentate Recycle – No Air Sweep Needed**
  - No need to modify combustion air system of existing power plant
  - Capital cost of retrofitting the existing ductwork is avoided
  - Avoiding reduced O$_2$ content encountered in CO$_2$ laden air
  - Boiler efficiency is not affected

- **Proposed Membrane Process**
  - Does not require cryogenic distillation (compared to competition)
SO₂ Polishing & Membrane Process

- Absorption into 20 wt% NaOH Solution
  - Polishing step based on NETL baseline document
    • Estimated to be ~ $4.3/tonne CO₂ (in 2007 $, 6.5% COE increase)
    • Non-plugging, low-differential-pressure, spray baffle scrubber
    • High efficiencies (>95%)
Techno-Economic Calculations for Flue Gas
(In 2011 dollar)

• **Basis: Membrane Results at 67°C**
  - 1911 GPU & 256 Selectivity for 1% CO₂ concentration feed gas
  - 1450 GPU & 185 Selectivity for 20% CO₂ conc. 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**
  - 490.6 tonne/h of CO₂ captured from flue gas
  - $378 million bare equipment cost
    - Membrane 45%, blowers and vacuum pumps 45%, others 10%
  - 3.72 ¢/kWh (2.81 ¢/kWh capital cost, 0.40 ¢/kWh fixed cost, 0.51 ¢/kWh variable cost)
    - COE = 8.09 ¢/kWh for 550 MW supercritical pulverized coal power plant
  - $41.7/tonne capture cost ($37.2/MWh × 550 MW/(490.6 tonne/h))
  - 46.0% Increase in COE (3.72/8.09 = 46.0%)
Lower Capture Cost for 70% CO₂ Recovery

In 2011 dollar

Capture cost ($/tonne) vs. CO₂ recovery (%)

- 1450 GPU
- 2700 GPU
- 4000 GPU
Pre-Combustion CO$_2$ Capture: Proposed Process

- Proposed membrane process does not require significant syngas cooling (compared to competition)

54.1 bar, 31% CO$_2$

31.7 bar

50 bar

H$_2$S Removal (Selexol)

>95% CO$_2$

31.7 bar

4% CO$_2$

<10 ppm H$_2$S

Clean Syngas to Combustion Turbine

153 bar
Composite Membranes Synthesized

Membrane M1

Membrane M2

Membrane M3

PZEA-Sar

PZEA-AIBA

PEGDME
Membrane Performances

Simulated Syngas at 107°C and 31.7 bar
Effect of Carrier Saturation Phenomenon on Performance

![Graph showing the effect of carrier saturation on performance]

- CO₂ partial pressure
- CO₂ permeance
- CO₂/H₂ selectivity

Feed CO₂ partial pressure (bar)

Membrane 3
Membrane 2

Feed inlet
Retentate outlet

35%
Effects of Membrane Allocation on Membrane Area and H\textsubscript{2} Recovery

35%
Effect of CO$_2$ Permeance on Cost of Electricity Increase

COE increase of current Membranes 2 and 3
Membranes Synthesized with Tuned $\text{H}_2\text{S}/\text{CO}_2$ Selectivities
Effect of $\text{H}_2\text{S}/\text{CO}_2$ Selectivity on $\text{H}_2\text{S}$ Concentration in Retentate
Summary

• Post-Combustion CO$_2$ Capture from Flue Gas
  – Composite membranes synthesized in lab
    + 1450 GPU with 185 selectivity at 67°C
  – Membrane scaled up successfully
  – Membrane modules fabricated & scaled up successfully
  – Modules tested at NCCC performed similarly to those in OSU lab
    + Good module stability demonstrated with actual flue gas
  – Scale-up membrane / modules promising for meeting DOE cost target of $40/tonne CO$_2$ (in 2007 $) for 2025

• Pre-Combustion CO$_2$ Capture from Syngas
  – Composite membranes synthesized in lab
    + 206 GPU with 103 selectivity at 107°C and 12.5 bar CO$_2$
  – CO$_2$ capture process proposed for 107°C and 31.7 bar
  – 6 ppm H$_2$S in H$_2$ product achievable
  – TEA shows 15.66% increase in COE
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Decreasing Emissions Preserves Environment