Membranes and post-combustion carbon dioxide capture

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Nancy, Lorraine, France
**Membrane team LRGP (EMSP) Current research projects on CCS**

**Membrane contactors for intensified absorption processes:**
- High flux dense skin composite fibers (ANR Cicadi)
- Pilot membrane contactor design and test (FP7 CESAR)
- Membrane contactor for chilled ammonia process (ANR Amélie)
- Pilot absorption unit for gas boiler plants (ANR Energicapt)
- Optimization of solvent/gas absorption processes (with EDF)

**Membrane gas separations:**
- Material synthesis Mixed Matrix Membranes (ACI Carbomem)
- Membrane characterization (mass transfer, separation performances)
- Process modelling (M3Pro software)

**Hybrid processes:**
- Oxygen enriched air combustion / membrane capture (Cocase ICEEL)
- Membrane concentration / cryogenic condensation (with EDF)
Prospective & breakthrough approaches

Liquid membranes (TIPS Russia)

Impregnated particles (MESR)

Electrical swing adsorption (ACI Procap)

Cyclic membrane gas separations (ICEEL)
Outline

i) Introduction

ii) Single stage parametric sensitivity

iii) Multistage approaches

iv) Hybrid process:

   - Coal power plant
   - Gas turbine

v) Conclusion
Introduction
Membranes: a potential 2nd generation carbon capture process

Membranes & carbon capture strategies

<table>
<thead>
<tr>
<th>Carbon capture strategy</th>
<th>Target mixture</th>
<th>Conditions</th>
<th>First generation separation process</th>
<th>Possible breakthrough membrane process</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxycombustion</strong></td>
<td>O₂/N₂</td>
<td>P atmospheric</td>
<td>Cryogeny</td>
<td>Ion Transfer Membranes (ITM)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T ambient</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Precombustion</strong></td>
<td>CO₂/H₂</td>
<td>P up to 80 Bar</td>
<td>Gas-liquid absorption in physical solvent</td>
<td>Membrane reactor</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T 300 – 500 C</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Postcombustion</strong></td>
<td>CO₂/N₂</td>
<td>P atmospheric</td>
<td>Gas-liquid absorption in chemical solvent (MEA)</td>
<td>Membrane gas separation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T 100 – 250 C</td>
<td></td>
<td></td>
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</tbody>
</table>
A classical single stage gas permeation modelling framework

Permeability of A ≡ \( P_A = D_A S_A \)

where \( D_A \) = diffusion coefficient

\( S_A \) = solubility coefficient

Selectivity

\[
\alpha_{A/B} = \left( \frac{P_A}{P_B} \right) = \left( \frac{S_A}{S_B} \right) \left( \frac{D_A}{D_B} \right)
\]
Membrane separation & CCS: a simplified overview

- Feed composition \( x \)
  - Capture ratio \( R \)
  - Purity \( y \)
- Operating Conditions \((P, T)\)
- Feed flow rate vs outlet performances
  - Selectivity
  - Challenge
  - \( \alpha \)
  - Energy cost
    - OPEX
    - CAPEX
    - Overall Capture Cost
    - Energy cost
      - \( \text{GJ}_\text{th}/\text{ton} \)
      - Productivity
      - Maximal flux
      - Membrane cost
        - \( €/m^2 \)
## Materials performances for post-combustion carbon capture

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Material and/or carrier</th>
<th>$\text{CO}_2/\text{N}_2$ selectivity</th>
<th>$\text{CO}_2$ permeability (Barrer) or permeance (GPU)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas separation membrane (dense polymers)</strong></td>
<td>PEO-PBT</td>
<td>70</td>
<td>120 Barrer</td>
</tr>
<tr>
<td></td>
<td>PEG/Peback®</td>
<td>47</td>
<td>151 Barrer</td>
</tr>
<tr>
<td></td>
<td>PEG-DME/ Peback®</td>
<td>43</td>
<td>600 Barrer</td>
</tr>
<tr>
<td></td>
<td>PEGDA/PEGMEA Polaris™</td>
<td>41</td>
<td>570 Barrer</td>
</tr>
<tr>
<td></td>
<td>Polaris™</td>
<td>50</td>
<td>1000 GPU</td>
</tr>
<tr>
<td><strong>Fixed Site Carrier Membrane (FSCM)</strong></td>
<td>PAAM-PVA / PS</td>
<td>80</td>
<td>24 GPU</td>
</tr>
<tr>
<td></td>
<td>PVAm/PVA</td>
<td>145</td>
<td>212 GPU</td>
</tr>
<tr>
<td></td>
<td>PEI / PVA</td>
<td>230</td>
<td>1 GPU</td>
</tr>
<tr>
<td></td>
<td>PDMA/PS</td>
<td>53</td>
<td>30 GPU</td>
</tr>
<tr>
<td></td>
<td>PDMAMA</td>
<td>80</td>
<td>5 GPU</td>
</tr>
<tr>
<td><strong>Liquid Membrane (LM)</strong></td>
<td>PVAm-PVA/PS</td>
<td>90</td>
<td>22 GPU</td>
</tr>
<tr>
<td></td>
<td>PVAm/PVA</td>
<td>90</td>
<td>15 GPU</td>
</tr>
<tr>
<td></td>
<td>Amines/PVA</td>
<td>500</td>
<td>250 GPU</td>
</tr>
<tr>
<td></td>
<td>Carbonic anhydrase</td>
<td>250</td>
<td>80 GPU</td>
</tr>
<tr>
<td></td>
<td>Amines / PVA</td>
<td>493</td>
<td>693 Barrer</td>
</tr>
</tbody>
</table>
**Single stage simulations: Process alternatives**

Feed compression with ERS on the retentate

\[ Q_{in} \ x_{in} \ P_{in}=1\text{bar} \rightarrow \text{Compressor} \rightarrow P_{upstream} \rightarrow \text{Membrane} \rightarrow P_{downstream} \rightarrow \text{Expander} \rightarrow Q_{R} \ x_{R} \]

\[ E=E_{C}-E_{T} \]

Permeate vacuum pumping

\[ Q_{in} \ x_{in} \ P_{in}=1\text{bar} \rightarrow \text{Vacuum pump} \rightarrow \text{Membrane} \rightarrow P_{upstream} \rightarrow P_{downstream} \rightarrow \text{Expander} \rightarrow Q_{R} \ x_{R} \]

\[ E \]

\[ Q_{P} \ y \ P_{out}=1\text{bar} \]

Permeate CO₂ rich stream
The feed compression / vacuum pumping dilemma

Energy requirement (GJ/ton of recovered CO$_2$)

Recovery ratio, $R$

$x_{in}=0.3$

$y=0.9$

$\alpha=100$

Membrane Surface area [$\times 10^3$ m$^2$/kg CO$_2$.s$^{-1}$]
Parametric study of a single stage gas permeation module
Strong parametric sensitivity on feed composition
Tackling the capture ratio / purity challenge

Energy requirement (GJ/ton CO₂) vs. Recovery ratio, R

- Standard MEA absorption process
- y = 0.4, 0.5, 0.6, 0.7, 0.8, 0.85
- α = 50
- x_{in} = 0.15

A tentative process selection map

![Graph showing process selection map with various process options and CO₂ mole fraction.]
Multistage gas permeation modules for carbon capture
First two stages membrane gas separation process

- CO$_2$ recovery 80%, CO$_2$ purity 90%
- Energy requirement 50-75% of combustion energy of coal (MEA 47-79%)

**Multistaged membrane gas separation processes: overview**

<table>
<thead>
<tr>
<th>Module type</th>
<th>Operating conditions</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two stage with recycle</td>
<td>Compression (21.4 Bar)</td>
<td>Herzog et al. (1991)</td>
</tr>
<tr>
<td>Two stage with expander</td>
<td>Compression (54 Bar)</td>
<td>Van der Sluis et al. (1992)</td>
</tr>
<tr>
<td>Two stage with recycle</td>
<td>Compression (1.5 Bar) and vacuum (80 mBar)</td>
<td>Ho et al. (2008)</td>
</tr>
<tr>
<td>Multistage with or without recycle</td>
<td>Compression (10 bar), vacuum (0.03 Bar)</td>
<td>Zhao et al. (2009)</td>
</tr>
<tr>
<td>Two stage with recycle</td>
<td>Compression (3 Bar) and vacuum (0.2 Bar)</td>
<td>Merkel et al. (2009)</td>
</tr>
<tr>
<td>Two stage with or without sweep</td>
<td>Compression (2-5 Bar) or vacuum (25-125 mBar)</td>
<td>Hussain et al. (2010)</td>
</tr>
</tbody>
</table>
MTR novel 2 stage membrane flowsheet for post-combustion CCS application

Hybrid processes with membrane modules for carbon capture
A membrane / absorption hybrid process is (probably) not relevant.
Hybrid process: Membrane preconcentration + cryogeny

Cryogenic CO$_2$ capture is not efficient for low CO$_2$ content

Cryogenic CO$_2$ capture can be very efficient for high CO$_2$ content

Inlet CO$_2$ mole fraction (x')

E cryogenic unit (GJ/ton of recovered CO$_2$)

<table>
<thead>
<tr>
<th>Q$_{in}$</th>
<th>X$_{in}$</th>
<th>P$_{in}$=1bar</th>
<th>Retentate</th>
</tr>
</thead>
<tbody>
<tr>
<td>E$_M$</td>
<td></td>
<td></td>
<td>E$_C$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Q$_{out}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>P$_{out}$=110bar</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>T=30°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>X'</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>P'=1bar</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>X$_{out}$&gt;90%</td>
</tr>
</tbody>
</table>

Incondensable outlet
Cryogenic separation: simulation

Three-stage compression with intercoolers (Aspen software)

\[ P'_{\text{out}} = 1 \text{ bar} \]
\[ x'_{\text{CO}_2} \]
\[ x_{\text{out}} > 98\% \]
\[ P_{\text{out}} = 110\text{ bar} \]

<table>
<thead>
<tr>
<th>CO\textsubscript{2} capture ratio</th>
<th>&gt;0.95</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2} purity (x_{\text{out}})</td>
<td>&gt;0.98</td>
</tr>
</tbody>
</table>

Pump isentropic efficiency : 0.8

Compressor isentropic efficiency : 0.85
The hybrid process significantly decreases the energy requirement compared to the standalone cryogenic separation and MEA absorption.

Hybrid process: Membrane / OEA / FGR on Gas turbine

There is a substantial benefit from increasing the inlet CO$_2$ content: flue gas recirculation and/or combustion in oxygen enhanced air (OEA)
Improved energy efficiency  Selectivity helps

Integrated approach: Performances

![Graph showing the overall energy requirement (GJ/ton CO₂ vs. heat exchanger efficiency) for different configurations and heat exchanger efficiencies.]

- **Reference gas turbine cycle (config. A), α=50**
- **Reference gas turbine cycle (config. A), α=100**
- **Reference gas turbine cycle (config. A), α=200**
- **Config.B, α=50**
- **Config.B, α=100**
- **Config.B, α=200**

**Legend:**
- Blue filled circle: α=50
- Blue open circle: α=100
- Blue triangle: α=200
- Red filled circle: Config.B, α=50
- Red open circle: Config.B, α=100
- Red triangle: Config.B, α=200
Conclusion
Membranes processes and post combustion CCS: utopy or opportunity?

- Membranes processes offer a large variety of potential applications in a CCS framework (separation, concentration, polishing)

- Very large number of publications on materials, few on process, very few on technico-economical studies. The interest of selective vs permeable materials remains controversial

- Investigations are mostly limited to model mixtures and at laboratory scale

- Crucial need for studies on real flue gases (dust, water, SOx, O$_2$), ideally at pilot scale

- Hybrid and/or integrated processes should be more systematically investigated
Skid footprint is 24’ x 7’
250,000 scfd flue gas slipstream
Captures 1 ton CO₂/day

The APS Cholla power plant
1 ton/day field test pilot unit
Thank you for your attention!

Eric.Favre@univ-lorraine.fr
Air Liquide DOE project

Project DE-FE004278
Unconventional approach: Reverse selective membranes

$CO_2$ selective membrane

$N_2$ selective membrane

Hybrid process: Impact on energy efficiency

Membrane Gas Separation: Applications & Market

Market size: 150 MUS$/y (Baker, 2002)

- Nitrogen from air: 50%
- Hydrogen recovery: 13%
- Carbon dioxide - natural gas: 20%
- Vapour separations: 17%
Ashkelon desalination plant

- 40,000 spiral-wound RO modules
- 1.5 million m² membrane area

- Total energy use is 56 MW.
- Plant produces 100 million m³/yr of water.