Membrane-assisted CO$_2$ liquefaction

David Berstad, Rahul Anantharaman (SINTEF Energy Research)
Peter van Os, Frank Vercauteren (TNO)
Basic system layout, membrane-assisted CO₂ liquefaction process

Neither sub-technology is particularly optimal for post-combustion capture in stand-alone application. By combining the technologies, both can operate in their optimal separation ranges.
Motivation for combining membrane separation and CO₂ liquefaction

- The CO₂ concentration after a membrane stage can be configured to be typically 60–70 vol%.
- These conditions are close to typical oxyfuel flue gas conditions, and can thus be obtained with an "end-of-pipe" solution, without retrofitting a plant to oxy-combustion.
- CO₂ liquefaction expected to be a better 2nd-stage option than another membrane stage:
  - Superior scaling of liquefaction capacity
  - Superior purity of captured CO₂
  - Energy efficiency likely to be superior
- The density of captured CO₂ in liquid form is 600–3000 higher than in gaseous from at vacuum or atmospheric pressure!
Pros and cons about membrane-assisted CO\textsubscript{2} liquefaction

**Pros:**

- Performance of membranes improves dramatically with increased CO\textsubscript{2} concentration in flue gases
- No need for handling large inventories of chemicals and disposal of degradation products
- No need for large auxiliary steam generation plants → Mostly grid power is needed
- Prospect for low investment cost for CO\textsubscript{2} capture
- Potential for very competitive per-unit cost [€/ton CO\textsubscript{2} captured] at optimal CO\textsubscript{2} capture ratio

**Cons:**

- Generally lower optimal CO\textsubscript{2} capture ratio than solvents and sorbents
- Scaleability: Generally limited size of each membrane module
  - Membrane unit scales linearly
  - NB: This is not an issue for the CO\textsubscript{2} liquefaction part of the process
- Membranes are not yet mature technology for post-combustion CO\textsubscript{2} capture, but already shown to be mature in other demanding industries (e.g. natural gas upgrading)
Membrane separation of flue gas – Process principle

Partial pressure differences for CO₂, N₂, O₂ etc. between feed and permeate is the principal driving force of permeation of the difference gas components.

The membrane's ability to favour CO₂ over the other gas components is the membrane selectivity.

The selectivity of CO₂ over e.g. N₂ for membranes appropriate for post-combustion capture are typically from approximately 50 up to a few 100s.

The result is an increased CO₂ concentration on the other side of the membrane.
Membrane separation of flue gas – Pressure levels

Max theoretical enrichment of CO₂ through membrane:

\[
\frac{\text{CO}_2 \text{ permeate concentration}}{\text{CO}_2 \text{ retentate concentration}} \leq \frac{p_{\text{feed}}}{p_{\text{perm}}}
\]

Example: CO₂ enrichment from 15 vol% to 75 vol%:

\[
\frac{p_{\text{feed}}}{p_{\text{perm}}} \geq \frac{75 \text{ vol}\%}{15 \text{ vol}\%} = 5
\]

The actual \( p_{\text{feed}}/p_{\text{perm}} \) pressure ratio must be even higher than this number, due to practicalities.
Membrane separation of flue gas – Pressure levels

- A membrane process will have typically a moderate flue gas pressure on the feed side and a moderate vacuum level on the permeate side
- Membrane pressure ratio \( \frac{p_{\text{feed}}}{p_{\text{perm}}} \) must be high to allow high enrichment of \( \text{CO}_2 \)
  - Can be promoted by having vacuum on the permeate side, i.e. \( p_{\text{perm}} < 1 \text{ atm} \)
- Membrane pressure difference \( p_{\text{feed}} - p_{\text{perm}} \) must be relatively high to allow high flux through the membrane and thus reduce the overall membrane area requirement
  - Can be promoted by raising the feed pressure \( p_{\text{feed}} \) by using a blower/compressor
- There are, however, several trade-offs to consider:
  - Vacuum pumping power requirement + volume flow increase significantly at low vacuum levels
  - Feed gas compression is very power-demanding to the vast volume flows
  - Too high membrane pressure difference promotes flux of other components than \( \text{CO}_2 \) and therefore counteracts the desired \( \text{CO}_2 \) enrichment effect
Single-stage membrane process

Optimal CO$_2$ capture rate$^a$: $\approx 30\%$

Two-stage membrane process with recycle loop

Optimal CO$_2$ capture rate$^{a,b}$: ≈ 40–60%

$^b$ Internal optimisation analyses
Hybrid membrane-assisted CO₂ liquefaction process
2-stage membrane CO$_2$ separation process

Optimal CO$_2$ capture rate: ≈ 40–60 %

Membrane-assisted CO$_2$ liquefaction process

Optimal CO$_2$ capture rate: CEMCAP research task
Liquefaction process for CO$_2$ purification

Simplified process layout

<table>
<thead>
<tr>
<th>Separator</th>
<th>Pressure level</th>
<th>Temp. level</th>
<th>CO$_2$ purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main</td>
<td>30–40 bar</td>
<td>-53°C to -55°C</td>
<td>95–96 %</td>
</tr>
<tr>
<td>Purification</td>
<td>6–10 bar</td>
<td>-53°C to -56°C</td>
<td>99.5–99.9 %</td>
</tr>
</tbody>
</table>

CO$_2$ purity at -50°C (phase equilibrium)$^a$

> Westman et al. Vapor–liquid equilibrium data for the carbon dioxide and nitrogen (CO$_2$ + N$_2$) system at the temperatures 223, 270, 298 and 303 K and pressures up to 18 MPa. Fluid Phase Equilibria 409, 207–241.
Principal layout of combined membrane and liquefaction capture process
Ongoing and further work

- Modelling and simulation of full-scale process configurations
  - Includes in-house model for membrane unit
  - Foundation for the techno-economic analysis in CEMCAP
  - Determine optimal CO₂ capture ratio and specific cost and energy requirement

- Bench-scale testing of (pre-)commercial membrane material
  - Verify selectivity and flux appropriateness for CO₂ capture

- Laboratory pilot testing of the CO₂ liquefaction and purification unit
  - Test facility under commissioning
  - Capacity: Approximately 10 ton CO₂ per day
  - Experimental verification of CO₂ separation ratio and product purity
  - Comparison with theoretically obtainable performance

→ Determine techno-economically optimum full-scale layout and KPIs
→ Propose layout of a scaled-up, on-site pilot plant
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