Cascaded Membrane Processes for Post-Combustion CO₂ Capture

Li Zhao, Ernst Riensche, Michael Weber, Detlef Stolten

5. Juli 2011 | IEK-3, Forschungszentrum Jülich, Germany
Outline

1. Why CO$_2$/N$_2$ gas separation membrane for post-combustion?
2. Why not a single-stage membrane?
3. Membrane cascade concepts
4. Water removal
5. Pressure losses in membrane modules
6. Concluding remarks
Why $\text{CO}_2/\text{N}_2$ Gas Separation Membrane for Post-combustion?

Main flue gas components: $\text{N}_2$, $\text{CO}_2$, $\text{H}_2\text{O}$, $\text{O}_2$, $\text{Ar}$

Advantages:

• Potentially low environmental impact;
• Use as add-on equipment with a few changes on power plants;
How a Single-stage Membrane Works?

Operating conditions
- pressure
- temperature
- feed gas flow rate
- CO₂ concentration

Membrane
- selectivity, permeability
- area

Separation performance
- CO₂ purity
- CO₂ separation degree
**Driving Force**

\[ \Delta p_{CO_2} = p_{\text{feed}} \cdot x_f, CO_2 - p_{\text{permeate}} \cdot y_p, CO_2 \]

**CO\textsubscript{2} partial pressure difference**

\[ \Delta p_{CO_2} = \text{Flow rate of the flue gas } 830 \text{ Nm}^3/\text{s} \]

**Membrane area**

**Degree of CO\textsubscript{2} separation**

**CO\textsubscript{2} purity**

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4/22
Why not a Single-stage Membrane?

600 MW North Rhine-Westphalia (NRW) reference power plant of 45.9% net efficiency
Ideal flue gas: 14 mol% CO₂, 86 mol% N₂
Membrane CO₂ permance: 3 Nm³/m²hbar

<table>
<thead>
<tr>
<th>Permeate vacuum [mbar]</th>
<th>Degree of CO₂ separation [%]</th>
<th>CO₂ purity [mol%]</th>
<th>CO₂/N₂ permselectivity</th>
<th>Δη [%-Ponints]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>50</td>
<td>95</td>
<td>200</td>
<td>-3,4</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>95</td>
<td>3750</td>
<td>-2,8</td>
</tr>
<tr>
<td>100</td>
<td>70</td>
<td>95</td>
<td>No solution</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>90</td>
<td>95</td>
<td>No solution</td>
<td>-</td>
</tr>
</tbody>
</table>
Optimization of a Membrane Cascade


2-stage

3-stage

4 variants for each cascade
Using compressor or vacuum pump for each membrane

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Criteria for the Evaluation

Specifications

- CO₂ purity
- Degree of CO₂ separation

Criteria for the Evaluation

- Energy demand
- Capture cost
- Specific energy
- Membrane area
- CO₂ purity
- Degree of CO₂ separation
Cascade Concepts

Lowest energy consumption
(70% degree of CO₂ separation)

A higher energy demand, distinctly decreased membrane area

Membrane CO₂ permeance: 3 Nm³/m²hbar; CO₂/N₂ selectivity: 50 (HZG)
Simulation Results

600 MW North Rhine-Westphalia (NRW) reference power plant of 45.9% net efficiency
Ideal flue gas: 14 mol% CO$_2$, 86 mol% N$_2$
Membrane CO$_2$ permance: 3 Nm$^3$/m$^2$hbar, CO$_2$/N$_2$ selectivity: 50 (HZG, Germany)
Short Summary for ideal flue gas

• For 50% and 70% degree of CO$_2$ separation cascade A (w/o feed flue gas compression) has energetic advantage against MEA absorption;

• For 90% degree of CO$_2$ separation cascade A has a slight energetic disadvantage, while cascade B (feed flue gas compression) is on the MEA absorption level.

• For all separation degrees cascade A needs much more membrane area than cascade B.
## Water Removal

### Ideal flue gas

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>14 mol%</td>
</tr>
<tr>
<td>N₂</td>
<td>86 mol%</td>
</tr>
</tbody>
</table>

### Real flue gas *

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>13.5 mol%</td>
</tr>
<tr>
<td>N₂</td>
<td>70.1 mol%</td>
</tr>
<tr>
<td>O₂</td>
<td>3.7 mol%</td>
</tr>
<tr>
<td>H₂O</td>
<td>11.9 mol%</td>
</tr>
<tr>
<td>Ar</td>
<td>0.8 mol%</td>
</tr>
<tr>
<td>SOₓ</td>
<td>200 mg/Nm³</td>
</tr>
<tr>
<td>NOₓ</td>
<td>200 mg/Nm³</td>
</tr>
</tbody>
</table>

### Purity requirements for pipeline

- CO₂ > 95 mol%
- No free water, < 500 ppm
- Limited non-condensable gas (N₂, Ar, H₂, NOₓ and CH₄), < 4 mol%
- Limited contaminants (SO₂, H₂S, O₂)

* Hard coal combustion, 50°C after FGD

- For post-combustion using membrane capture method, water removal is the other important topic in addition to CO₂ separation.

[Hagdoorn 2007]
Measures for Dewatering (Cascade A)

Dewatering procedures:
- Using dehydration membrane prior to CO$_2$ separation
- Combing with inter- and aftercooling for each compression stage
- Remaining water removed by desiccant
Dehydration Membranes

Area of interest

Single component permeabilities and selectivities at 25°C

Schematic illustration

Hollow fiber membrane module

19 composite hollow fibers

Feed

Retentate

Dehydrated flue gas activity < 1

Vacuum

PVC tube filled with resin

Array of 20 modules

Saturated flue gas activity = 1

K. Nijmeijer, 10th Jülicher Werkstoffsyposium, 2007
Case Studies

600 MW North Rhine-Westphalia (NRW) reference power plant of 45.9% net efficiency

The energy consumption for driving the water pump and for the regeneration of the desiccant medium are neglected.

Membrane CO$_2$ permance: 3 Nm$^3$/m$^2$hbar

### Quasi real flue gas *

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>13.5</td>
</tr>
<tr>
<td>N$_2$</td>
<td>70.1</td>
</tr>
<tr>
<td>O$_2$</td>
<td>3.7</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>11.9</td>
</tr>
<tr>
<td>Ar</td>
<td>0.8</td>
</tr>
</tbody>
</table>

* Hard coal combustion, 50°C after FGD

### Selectivity

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$/N$_2$</td>
<td>50</td>
</tr>
<tr>
<td>N$_2$/N$_2$</td>
<td>1</td>
</tr>
<tr>
<td>O$_2$/N$_2$</td>
<td>2</td>
</tr>
<tr>
<td>H$_2$O/N$_2$</td>
<td>10$^5$</td>
</tr>
<tr>
<td>Ar/N$_2$</td>
<td>2</td>
</tr>
</tbody>
</table>
Simulation Results

Cascade A, 70% degree of CO₂ separation

<table>
<thead>
<tr>
<th>Water removal prior to CO₂ separation</th>
<th>Separation degree</th>
<th>Membrane area [10⁶ m²]</th>
<th>Specific energy for capture [kWhₑ/t₈CO₂]</th>
<th>Specific energy for compression [kWhₑ/t₈CO₂]</th>
<th>Efficiency loss [%-pts]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar ideal flue gas</td>
<td>70</td>
<td>2.39</td>
<td>151</td>
<td>105</td>
<td>6.4</td>
</tr>
<tr>
<td>Ideal flue gas</td>
<td>68</td>
<td>2.39</td>
<td>181</td>
<td>110</td>
<td>7.9</td>
</tr>
<tr>
<td>Ideal flue gas</td>
<td>67</td>
<td>2.39</td>
<td>198</td>
<td>110</td>
<td>8.4</td>
</tr>
<tr>
<td>Ideal flue gas</td>
<td>66</td>
<td>2.39</td>
<td>212</td>
<td>110</td>
<td>8.9</td>
</tr>
</tbody>
</table>

More water in flue gas, more energy consumption for CO₂ separation.
### Gas compositions

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas</td>
<td></td>
<td>1.05</td>
<td>70499</td>
<td>13.5</td>
<td>70.1</td>
<td>3.7</td>
<td>0.8</td>
<td>11.9</td>
</tr>
<tr>
<td>1</td>
<td>1/3</td>
<td>1.05</td>
<td>68147</td>
<td>14.0</td>
<td>72.70</td>
<td>3.83</td>
<td>0.82</td>
<td>8.64</td>
</tr>
<tr>
<td></td>
<td>2/3</td>
<td>1.05</td>
<td>65624</td>
<td>14.54</td>
<td>75.49</td>
<td>3.98</td>
<td>0.86</td>
<td>5.13</td>
</tr>
<tr>
<td>2</td>
<td>1/3</td>
<td>1</td>
<td>8364</td>
<td>90.06</td>
<td>3.57</td>
<td>0.71</td>
<td>0.04</td>
<td>5.63</td>
</tr>
<tr>
<td></td>
<td>2/3</td>
<td>1</td>
<td>8293</td>
<td>89.99</td>
<td>3.61</td>
<td>0.72</td>
<td>0.04</td>
<td>5.64</td>
</tr>
<tr>
<td>3</td>
<td>1/3</td>
<td>110</td>
<td>7897</td>
<td>95.38</td>
<td>3.78</td>
<td>0.75</td>
<td>0.04</td>
<td>500 ppm</td>
</tr>
<tr>
<td></td>
<td>2/3</td>
<td>110</td>
<td>7830</td>
<td>95.32</td>
<td>3.82</td>
<td>0.76</td>
<td>0.04</td>
<td>500 ppm</td>
</tr>
</tbody>
</table>
Short Summary for quasi real flue gas

- **Water removal** is an important procedure of membrane separation process for post-combustion capture.

- **Water in flue gas increases energy demand** for post-combustion CO₂ capture using gas separation membranes.

- **Water content** in the flue gas shows a **positive sweep gas effect for CO₂ separation membrane**.
Pressure Losses in Membrane Modules

Hollow Fiber Module [Hoting 2007].

Structure and function of a hollow fiber module

- Feed
- Retentate
- Potting material
- Permeate
- Hollow fibers / capillaries
- Self-supporting fibers or capillaries

<table>
<thead>
<tr>
<th>Category</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>tubular</td>
<td>&gt; 5 mm</td>
</tr>
<tr>
<td>capillary</td>
<td>0.5 .. 5 mm</td>
</tr>
<tr>
<td>hollow fiber</td>
<td>&lt; 0.5 mm</td>
</tr>
</tbody>
</table>

Spiral-Wound Module [NETL-2]

Envelope Module [Beeskow 2007].

Structure and Function of an Envelope Module

1. Feed streams into the membrane module.
2. Feed enters through the single membrane stacks.
3. Feed is separated into permeate and retentate.
4. Permeate leaves the module via the permeate pipe.

Source:
Influence on the Energy Demand

<table>
<thead>
<tr>
<th>Case</th>
<th>Δp Feed</th>
<th>Δp Permeate</th>
<th>Compensation of Δp</th>
<th>Spec. energy demand kWh_{e}/t_{CO2-sep}</th>
<th>Δη %-points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>50 mbar</td>
<td>---</td>
<td>Blower 1.05-1.10 bar</td>
<td>10.5</td>
<td>-0.26</td>
</tr>
<tr>
<td>Case 2</td>
<td>---</td>
<td>50 mbar</td>
<td>Vacuum pump 50-100 mbar</td>
<td>31.5</td>
<td>-0.79</td>
</tr>
</tbody>
</table>

The extra energy demand shows how it is important to avoid pressure loss in membrane module design.
Concluding remarks

- **For ideal flue gas**
  - For 50% and 70% degree of CO$_2$ separation the **cascade without feed flue gas compression** has energetic energy advantage against MEA absorption;
  - For 90% degree of CO$_2$ separation the **cascade with feed flue gas compression** is on the MEA absorption level of the specific energy.
  - For all separation degrees the cascade without feed flue gas compression needs much **more membrane area**.

- **Water in flue gas increases the energy demand**, but sweep effect allows to reach a higher degree of CO$_2$-separation. Detailed investigations are needed.

- **Pressure losses** on the feed side as well as on the permeate side must be taken into account for **membrane module design**.
Thank you for your attention!