Functional materials for the separation of carbon dioxide from flue gas, natural- and biogas streams

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Content
- overview on different methods
- requirements for different processes
- opportunities for tuning separation properties
- polymeric materials with functionalities
- porous materials
- hybrid materials
- conclusion

CO₂ capture - comparison of methods

- technology domain is strongly increasing in ad- and absorption processes
- Germany/UK is leading in number of patents for membrane processes
- in many cases materials are not clearly specified

CO₂ reduction in flue gas, natural gas streams and biogas applications

- in total 30 giga tons/y of carbon dioxide are emitted in the atmosphere
- around 40-50% is produced by coal burning power plants
- around 170 bio. m³ of natural gas per year are set free or burned on oil platforms

ICEPE, 2011, June 20-22, Frankfurt, C.Staudt
**CO₂ removal from natural gas, biogas and flue gas**

**natural gas**
- 70-90% CH₄
- < 10% CO₂ (much higher in EOR processes)
- < 6% higher hydrocarbons
- up to 15% hydrogen sulfide
- 1-10% nitrogen

**biogas**
- 40-75% CH₄
- 25-55% CO₂
- 0-10% water vapor
- 0-10% nitrogen
- 0-1% hydrogen sulfide

**flue gas**
- up to 15% CO₂ in coal burning power plant
- carbon black

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**CO₂ separations using membranes**

**natural gas/biogas**
- CO₂/CH₄
- high pressure, H₂S (plasticization!)
- moderate temperature

**flue gas**
- CO₂/N₂
- low pressure (low driving force)
- high temperature (stability)

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**High performance polymers**

<table>
<thead>
<tr>
<th>Polymer structure</th>
<th>Tₘ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>285</td>
</tr>
<tr>
<td></td>
<td>342</td>
</tr>
<tr>
<td></td>
<td>377</td>
</tr>
</tbody>
</table>

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**Solution-diffusion properties of materials**

<table>
<thead>
<tr>
<th>gas</th>
<th>CO₂</th>
<th>N₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>kinetic diameter (Å)</td>
<td>3.3</td>
<td>3.64</td>
<td>3.8</td>
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</tbody>
</table>

**P = S · D**

**αₘ = \frac{P_A}{P_B} = \frac{S_A}{S_B} \cdot \frac{D_A}{D_B}**

- diffusion coefficient (N₂) is 1.3 to 5 times higher compared to CH₄
- solubility coefficient N₂ is 2-3 times lower compared to CH₄
- permselectivity CO₂/N₂ > CO₂/CH₄ for rubbery polymers but in most cases lower for glassy polymers
Permeabilities (barrer) for different commercially applied gas separation materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>$P(\text{CO}_2)$</th>
<th>$P(\text{N}_2)$</th>
<th>$P(\text{CH}_4)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marimid</td>
<td>![Structure]</td>
<td>6.50</td>
<td>0.25</td>
<td>0.19</td>
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<tr>
<td>Kapton</td>
<td>![Structure]</td>
<td>1.24</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>PA4</td>
<td>![Structure]</td>
<td>1.20</td>
<td>--</td>
<td>0.02</td>
</tr>
</tbody>
</table>

- selectivity $\text{CO}_2/\text{CH}_4$ 30-60
- selectivity $\text{CO}_2/\text{N}_2$ < 30

Robeson upper bond diagram for natural gas separation

Only few materials can "beat" the upper bond

Influence of operating temperature

- Significant loss in selectivity is expected at operating temperatures above 120°C

How to improve the separation characteristics

- Use materials which can act as molecular sieves
- Polymer backbones with strong polar groups (PEG)
- Materials with fixed carrier sites (PVAM)
MOF/PI phase inversion

Mixed gas results show selectivity increase with increasing MOF loading
Permeability can be also improved
PSU additive is not helpful

Plasticization phenomena in MOF/PI

- Loss in selectivity with increasing CO₂ content in feed
- Plasticization of the polymer matrix (no cross-linking)

Carbon molecular sieve membranes

- Highly porous structure
- Functional groups and cross-links are still present
- High temperature and plasticization resistant
Carbon molecular sieve membranes

- extremely high permeability
- only for CO₂/CH₄ high very selectivity

PVAm coating of polysulfone hollow fibers

- selectivity improvement

Final remarks

- high temperature stability and plasticization resistance is necessary
- commercially available gas separation polymers are useful as “basic membrane materials”
- functionalisation for improving CO₂ solubility
- cross-linking in order to prevent plasticization
- MOFs might help to improve selectivity/permeability
- mixed matrix membranes might be also interesting

- a lot of chemistry has to be done in order to develop new materials