Advanced CO$_2$ Separation Using Molecular Gates

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Outline

1. CO₂ Separation Membrane for IGCC
2. CO₂ Molecular Gate Function for CO₂/H₂ separation
3. Dendrimer for Possible Molecular Gate
4. Dendrimer Hybrid Membrane
5. Next Generation of CO₂ Molecular Gate in GCEP research
6. Concluding Remarks
# CO₂ Capture Methods for CCS

## 1. CO₂ Sources
- **Fossil Fuel**
- **Bio-Mass**

## 2. CO₂ Capture (Chemical Research Group in RITE)

<table>
<thead>
<tr>
<th>Method</th>
<th>CO₂ Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>CO₂ &lt; 2%</td>
</tr>
<tr>
<td></td>
<td>CO₂ &gt; 99%</td>
</tr>
<tr>
<td>Membrane</td>
<td>CO₂ &gt; 95%</td>
</tr>
<tr>
<td>Adsorption</td>
<td>CO₂ &lt; 2%</td>
</tr>
</tbody>
</table>

- **Absorber**
  - Absorbent
  - Novel process
  - Waste heat utilization
- **Regenerator**
- **Polymer**
- **Zeolite**
- **Carbon**
- **Nanocomposite material**

**Zeolite, Mesoporous silica**

**Plant analysis for the decreasing energy and cost**

## 3. Storage (CO₂ Storage Group in RITE)
- **Geological**
- **Utilization**
- **Ocean**
### Driving Force in PCPP and IGCC

<table>
<thead>
<tr>
<th>Gas source</th>
<th>Pulverized Coal Power Plant</th>
<th>IGCC with WGS reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total press. in Feed</td>
<td>101 kPa</td>
<td>4000 kPa</td>
</tr>
<tr>
<td>CO₂ Conc./ %</td>
<td>14 %</td>
<td>40 %</td>
</tr>
<tr>
<td>Total press. in Permeate</td>
<td>10 kPa Vacuum</td>
<td>101 kPa</td>
</tr>
<tr>
<td>Difference of CO₂ partial press. (initial)</td>
<td>8.9 kPa</td>
<td>1,470 kPa</td>
</tr>
</tbody>
</table>

Driving force of CO₂ permeation more than 150 times
### Cost Estimation of CO₂ Membrane Separation from IGCC

<table>
<thead>
<tr>
<th>CO₂ Source</th>
<th>Gas Pres.</th>
<th>CO₂ Comp.</th>
<th>Membrane Performance (Target in RITE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGCC w/ WGS</td>
<td>4 MPa</td>
<td>CO₂:40% H₂, H₂O</td>
<td>αCO₂/H₂: 30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂ Permeance: 1x10⁻⁹ (m³ m⁻² s⁻¹ Pa⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 Stages</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ref. Absorption</th>
<th>Gas Pres.</th>
<th>Gas Comp.</th>
<th>Membrane Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine solution (MDEA-Flash)</td>
<td>4 MPa</td>
<td>Amine solution (MDEA-Flash)</td>
<td></td>
</tr>
<tr>
<td>Phys Absorption</td>
<td>4 MPa</td>
<td>Phys Absorption</td>
<td></td>
</tr>
<tr>
<td>Amine solution (KS solution)</td>
<td>0.1 MPa</td>
<td>Amine solution (KS solution)</td>
<td></td>
</tr>
</tbody>
</table>

* Duration period: Facility: 15 years, Membrane: 5 years
  Membrane Skid Cost: 50,000 JPY/m²
What is an ideal membrane for CO$_2$/H$_2$ separation?

A hint may exist in a towel balloon.

Dry Towel

Wet Towel
Concept of CO$_2$ Molecular Gate for CO$_2$/H$_2$ Separation

Excellent CO$_2$ selectivity
Dendrimer Membrane:
A CO$_2$ Selective Molecular Gate

Polyamidoamine (PAMAM) dendrimer

CO$_2$/N$_2$ separation:
J. Am. Chem. Soc. 2000, 122, 7594-7595
Design of Dendrimer's Chemical Structure for better CO$_2$/H$_2$ separation

Original Polyamidoamine (PAMAM) dendrimer

Newly Synthesized

Hydroxyl Polyamidoamine (PAMAM) dendrimer
CO$_2$/H$_2$ Permeability & Selectivity of Dendrimers

3OH-PAMAM dendrimer

$P_{CO_2} = 7.8 \times 10^{-12}$ [m$^3$(STP) m$^{-2}$ s$^{-1}$ kPa$^{-1}$], $\alpha_{CO_2/H_2} = 1,000$ (at 80RH%)

- Feed: (CO$_2$/H$_2$=5/95) at 25 °C, Dendrimer was supported in porous substrate
- Isobaric test condition
H₂ Blockage by CO₂ in Dendrimer

H₂ Permeability
Pure gas > Mixed-gas
(CO₂: 5 %)

CO₂ blocks H₂ permeation

Mixed-gas | 5%CO₂ | Pure gas
---|---|---
4OH | ▲ | ■
Possible Model of \(H_2\) Perm. Blockage

- Carbamate Formation
- Pseudo-cross-linkage
- \(H_2\) permeation blockage
Dendrimer Hybrid Membrane for CO₂ Capture from Pressurized Gas Stream

O-OH-PAMAM dendrimer

UV Curing

PEGDMA

TMPTMA
CO₂/H₂ Separation Properties of Dendrimer Hybrid Membrane at Elevated Pres.

PAMAM/PEGDMA/TMPTMA, Feed : 100 mL/min, Sweep: 20 ml/min, T = 313 K, R.H. = 80%
CO₂/H₂ Separation Properties of Various Dendrimer Hybrid Membranes

Film Thickness: 500 μm
CO₂ partial press.: 6 bar at 313 K

Temperature Dependence of Membrane Performance

[Graph showing temperature dependence of membrane performance with CO$_2$/H$_2$ selectivity and CO$_2$ permeance plotted against temperature.]

CO$_2$/H$_2$ Selectivity

CO$_2$ Permeance / m$^3$(STP)/(m$^2$ s Pa)

- 25 ºC
- 40 ºC
- 55 ºC

Thickness: 500 µm

PAMAM/ PEGDMA/ TMPTMA
Development of Membrane Module

Now fabricating dendrimer membrane modules with membrane module makers

Dendrimer/Polymeric matrix: Dendrimer Hybrid
Current Generation:
High CO$_2$/H$_2$ selectivity
at various CO$_2$ partial pressure
from atmospheric to elevated pressure
at high relative humidity such as 80 %RH or more
→ Required no dehumidifying process

Next Generation:
Should be adapted over a wide range of relative humidity
GCEP’s Challenge
**CO₂ permeation Model of Current Dendrimer Hybrid Membrane**

[Diagram showing the process of CO₂ permeation through a hybrid membrane with steps labeled as Gas Feed, Sorption, Diffusion, and Desorption.]
Sc-CO$_2$ Structure Directing Method for Next Generation Membrane

Inject Sc-CO$_2$

Remove Sc-CO$_2$

Pre-formed Solid Membrane

Amino moiety

CO$_2$

carbamate formation

Ion Hopping Channel
Set-up for Sc-CO$_2$ Structure Directing Method

Membrane under Sc-CO$_2$

Pressure: 10 MPa
Temperature: 20-60°C
Membrane application for CO\textsubscript{2} capture from a pressurized gas stream is promising way of reducing CO\textsubscript{2} capture cost and energy.

- Molecular gate membrane (MGM) is proposed for high CO\textsubscript{2} selectivity over H\textsubscript{2}.
- Dendrimer membrane has good CO\textsubscript{2} separation performance over a wide range of CO\textsubscript{2} partial pressure and highly humidified feed gas.
- Next generation MGMs that work well in a wide range of humidity in a feed gas and have higher selectivity are now under development in GCEP project.
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GHGT-11

- 11th International Conference on Greenhouse Gas Control Technologies -

November 2012 - Kyoto will welcome experts in greenhouse gas control technologies from across the world!


2. Venue : Kyoto International Conference Center, Japan

3. Organizers : RITE & IEAGHG

4. Estimated Number of Attendees: 1,600

5. Themes of Technical Sessions
   (at GHGT-10, Sep. 2010, Amsterdam, the Netherlands)
   - Capture, Utilisation, Storage,
   - Integrated, Demonstrations,
   - Policy, Negative Emissions, Legal,
   - Public Perception
Thank you for your attention!

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