WP3
Membrane Based Technologies

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Partners:
• NTNU Norway (WP-Leader)
  • Sintef M&C Norway
  • TNO. The Netherlands
    • TIPS, Russia
    • CNRS, France
    • EDF, France
  • CSIRO, Australia

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Membrane based technologies

Task 3.1 Hybrid membrane development (NTNU, SINTEF, TNO) - OBJECTIVES
• Develop high flux mixed matrix membrane based on incorporation of nanoparticles in polymer.
  ➢ Target: CO$_2$ permeance of 2.5 m$^3$(STP)/ m$^2$ h bar, selectivity CO$_2$/N$_2$ above 100.
  ➢ Membrane fabrication and study on transport phenomena.

Task 3.2 Supported ionic liquid membranes (SILM) (NTNU, TIPS) - OBJECTIVES
• Develop contained supported ionic liquid ceramic membranes (CILM)
  ➢ Target: CO$_2$ permeance above 4 m$^3$(STP)/ m$^2$ h bar, selectivity CO$_2$/N$_2$ above 100
• Develop nanoporous polymer/ILs membranes
  ➢ Target: CO$_2$ permeance 12-15 m$^3$(STP)/ m$^2$ h bar, selectivity CO$_2$/N$_2$ = 20-30
• Temperature stability >100°C.

Task 3.3 Process modelling and simulation (CNRS, EDF, NTNU) - OBJECTIVES
• Develop membrane module simulation model for nanocomposite and SILM membranes.
  ➢ Evaluate the energy requirement & membrane area for different set of operating conditions
• Develop concepts for utilizing the membranes in a post-combustion process.
Task 3.1: Hybrid Membrane Development

Objectives

- Develop a high flux mixed matrix membrane based on incorporation of functionalized SiO-particles and nano TiO2-particles in a polymer.
  - Target: CO₂ permeance of 2.5 m³(STP)/ m² h bar
    selectivity CO₂/N₂ above 100.
  - Membrane fabrication and study on transport phenomena.

Research Activities

- Study of the transport mechanism and role of the nano-sized particles.
- Tailoring nanoparticles to tune the desired membrane properties such as selectivity and flux.
  - Nanosized particles prepared and characterized (SINTEF & TNO)
  - Hybrid membranes prepared and performance tested at NTNU
- Optimization in different iteration steps for the hybrid membrane.

Expected outcome

- Hybrid membranes with targeted performance
- Dedicated permeability model based on experimental flux data over a wide range of operating conditions
Task 3.1 Hybrid membrane development

Status on Work

1. Study of the transport mechanism and role of the nano-sized particles: (report delivered)

2. The mechanism of gas transport in Facilitated Transport Membranes (FTM) most complicated The total transport flux is the sum of both the Fickian diffusion and the carrier mediated diffusion.

Hence: The gas stream has to be humid for the facilitated transport to take place

→ CO₂ reacts and forms bicarbonate (fast reaction) and is released again as CO₂ on permeate side

→ The functionalized SiO₂-particles (HAPS) must not be protonised in order to promote facilitated transport (hence pH must be high)

3. Two types of hybrid membranes will be tested:

HAPS embedded in PVA (facilitated transport)

TiO₂ nanoparticles in PVA (Maxwell adapted transport)

(PVA is hydrophilic by nature and has good film forming properties)
Task 3.1 Hybrid Membrane Development

Status on Work

At NTNU-Sintef: Facilitated transport: Initial focus is on reproducing good results obtained

- New PVA-HAPS-1 membrane samples are manufactured
  - PPO-supported PVA/HAPS asymmetric membrane
  - PSf-supported PVA/HAPS asymmetric membrane
    (PPO = Hollow fibers; PSf = flat sheets)

Results to date

- First permeance measurements using PPO HF support, indicated CO$_2$ no success in facilitated transport

Conclusion

- The various parameters and variables which may influence the preparation of these membranes containing the functionalized nanoparticles are currently being systematically investigated
- Aim is to establish a reproducible manufacturing, and prepare a somewhat larger module for flux evaluation providing task 3.3 and WP4 with the required input
Task 3.1: Hybrid Membrane Development

Status on Work

Ongoing Research Activities at TNO

- Synthesis of Nano-TiO2 particles seems successful (first indication d < 20 nm)
- Well soluble/dispersible in water
- Study on interaction between PVA and nano-TiO2 to indicates physical network is formed (see figure). More solid-like behaviour at low deformation and more liquid-like behaviour at high deformation.
- Factors affecting interaction under study.

Further:

- Nanoparticles will be sent to NTNU to be prepared as hybrid membranes; embedded in PVA on PSf flat sheet support
- Performance will be measured with and without humid gas
Task 3.2 Ionic Liquid Membranes

Objectives

- Develop contained supported ionic liquid membranes (CILM)
  - Target: $\text{CO}_2$ permeance above $4 \text{ m}^3(\text{STP})/\text{ m}^2 \text{ h bar}$, selectivity $\text{CO}_2/\text{N}_2$ above 100
- Develop nanoporous polymer/ILs membranes
  - Target: $\text{CO}_2$ permeance $12-15 \text{ m}^3(\text{STP})/\text{ m}^2 \text{ h bar}$, selectivity $\text{CO}_2/\text{N}_2 = 20-30$
- Temperature stability $>100^\circ\text{C}$.

Research activities

- Selection, synthesis & evaluation of ILs for $\text{CO}_2$ facilitated transport membranes (NTNU).
- Selection and synthesis of high free volume polymers and advanced porous ceramic membranes (TIPS, NTNU).
- SILMs preparation, with focus on polymeric thin film composite support (TIPS).
- SILMs preparation, with focus on ceramic supports (NTNU).
- Separation performance testing (NTNU).
### Task 3.2 Ionic Liquid Membranes

**Status on Work at NTNU – screening; OK 😊**

<table>
<thead>
<tr>
<th>ILs</th>
<th>T&lt;sub&gt;d&lt;/sub&gt; °C</th>
<th>Types of absorption</th>
<th>CO&lt;sub&gt;2&lt;/sub&gt; absorption capacity</th>
<th>Conditions bar/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim][PF&lt;sub&gt;6&lt;/sub&gt;]</td>
<td>622.15</td>
<td>physisorption</td>
<td>0.295 g/mol CO&lt;sub&gt;2&lt;/sub&gt;/IL</td>
<td>15.79/60</td>
</tr>
<tr>
<td>[C&lt;sub&gt;8&lt;/sub&gt;mim][PF&lt;sub&gt;6&lt;/sub&gt;]</td>
<td>647.15</td>
<td>physisorption</td>
<td>0.330 g/mol CO&lt;sub&gt;2&lt;/sub&gt;/IL</td>
<td>17.38/60</td>
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<td>243</td>
<td>physisorption</td>
<td>0.224 g/mol CO&lt;sub&gt;2&lt;/sub&gt;/IL</td>
<td>15.61/60</td>
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<tr>
<td>[bmim][Tf&lt;sub&gt;2&lt;/sub&gt;N]</td>
<td></td>
<td>physisorption</td>
<td>0.213 g/mol CO&lt;sub&gt;2&lt;/sub&gt;/IL</td>
<td>13.64/60</td>
</tr>
<tr>
<td>[TETA]L</td>
<td>——</td>
<td>chemisorption</td>
<td>0.944 g/mol CO&lt;sub&gt;2&lt;/sub&gt;/IL</td>
<td>/110</td>
</tr>
<tr>
<td>[aP&lt;sub&gt;4443&lt;/sub&gt;][Ala]-SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>283</td>
<td>chemisorption</td>
<td>~1.0 mol CO&lt;sub&gt;2&lt;/sub&gt;/IL</td>
<td>/25</td>
</tr>
<tr>
<td>[aP&lt;sub&gt;4443&lt;/sub&gt;][Gly]-SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>281</td>
<td>chemisorption</td>
<td>~1.0 mol CO&lt;sub&gt;2&lt;/sub&gt;/IL</td>
<td>/25</td>
</tr>
<tr>
<td>[P&lt;sub&gt;66614&lt;/sub&gt;][Im]</td>
<td>252</td>
<td>chemisorption</td>
<td>1.0 mol CO&lt;sub&gt;2&lt;/sub&gt;/IL</td>
<td>/23</td>
</tr>
<tr>
<td>[Li(DOBA)][Tf&lt;sub&gt;2&lt;/sub&gt;N]</td>
<td>319</td>
<td>chemisorption</td>
<td>0.71 g/mol CO&lt;sub&gt;2&lt;/sub&gt;/g IL</td>
<td>/100</td>
</tr>
</tbody>
</table>

**Common anions in ILs**

- BF<sub>4</sub>⁻, BF<sub>3</sub>CH<sub>3</sub>⁻, BF<sub>3</sub>CF<sub>3</sub>⁻, PF<sub>6</sub>⁻
- C(CN)<sub>3</sub>⁻, N(CN)<sub>2</sub>⁻, B(CN)<sub>4</sub>⁻, NO<sub>3</sub>⁻
- SO<sub>3</sub>CF<sub>3</sub>⁻, N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>⁻, N(FSO<sub>2</sub>)<sub>2</sub>⁻
Task 3.2 Ionic Liquid Membranes
Status on Work at NTNU – synthesis and character.; OK 😊

- **Polyamine-based ILs**

  Triethylene tetramine

  Lactic acid

  Trifluoroacetic acid

  [TETA]L  [TETA][Tfa]

- **Amino acid ILs**

  Structures of the cation and anions of AAIsLs
Task 3.2 Ionic Liquid Membranes
Status on Work at NTNU – evaluation of synthesized IL; OK 😊

- **CO₂ sorption**

![Diagram showing CO₂ sorption](image1)

*Fig. 2* Absorption of CO₂ in [TETA]L with pure CO₂ at different temperatures: ■ 110 °C, ● 120 °C, ▲ 130 °C.


- **Thermal stability**

![Diagram showing thermal stability](image2)

Universal V4.3A TA Instruments

Objectives
• Develop nanoporous polymer/ILs membranes
  ➢ Target: CO$_2$ permeance 12-15 m$^3$(STP)/ m$^2$ h bar, selectivity CO$_2$/N$_2$ = 20-30
• Temperature stability >100°C.

Research activities at TIPS
✓ The two samples of high free volume glassy polymer - poly[1-trimethylsilyl-1-propyne] (PTMSP) were synthesized.
✓ Two ionic liquids (ILs) based on imidazolium cation with high solubility selectivity for gas pair CO$_2$/N$_2$ were selected.
✓ Three methods of incorporation of selected ILs into the PTMSP dense membranes were developed: modification by swelling in IL/EtOH mixture, bulky hydrophilization by X-linked PEI and IL incorporation, surface hydrophilization by chemical etching and IL incorporation.
Task3.2 Supported Ionic Liquid Membranes
Status on Work at TIPS – the Concept

<table>
<thead>
<tr>
<th>Imidazolium-based IL (EmimDCA)</th>
<th>Nanoporous glassy polymers (PTMSP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ High CO₂/N₂ selectivity – 50</td>
<td>✓ Extra high CO₂ permeability</td>
</tr>
<tr>
<td>✓ Low vapor pressure</td>
<td>coefficient 29000 Barrer</td>
</tr>
<tr>
<td>✓ High thermal stability</td>
<td>✓ High thermal stability</td>
</tr>
<tr>
<td>✓ High tunability</td>
<td>✓ High film-forming ability</td>
</tr>
<tr>
<td>✓ Relatively high CO₂ solubility</td>
<td></td>
</tr>
</tbody>
</table>

Hybrid PTMSP/EmimDCA membrane material with improved CO₂/N₂ selectivity


The two samples of high free volume glassy polymer - poly[1-trimethylsilyl-1-propyne] (PTMSP) were synthesized.

Two ionic liquids (ILs) based on imidazolium cation with high solubility selectivity (50 – 80) for gas pair CO₂/N₂ were selected.

Three methods of incorporation of selected ILs into the PTMSP dense membranes were developed: modification by swelling in IL/EtOH mixture, bulky hydrophilization and IL incorporation, surface hydrophilization and IL incorporation.
## Task3.2  Supported Ionic Liquid Membranes
### Status on Work at TIPS

#### Gas permeation results

<table>
<thead>
<tr>
<th>Membrane</th>
<th>CO$_2$ permeance, l(STP)/m$^2$h bar</th>
<th>N$_2$ permeance, l(STP)/m$^2$h bar</th>
<th>CO$_2$/N$_2$ selectivity</th>
<th>Membrane thickness, μm</th>
<th>Gas pressure, bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMSP unmodified</td>
<td>2700</td>
<td>670</td>
<td>4</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2900</td>
<td>770</td>
<td>3.8</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>PTMSP / IL</td>
<td>6.8</td>
<td>0.43</td>
<td>16</td>
<td>42</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>20.7</td>
<td>0.42</td>
<td>47</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Bulky modified PTMSP + IL</td>
<td>110</td>
<td>8</td>
<td>14</td>
<td>25</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>8</td>
<td>15</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Surface modified PTMSP + IL</td>
<td>240</td>
<td>20</td>
<td>12</td>
<td>45</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>18</td>
<td>13</td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>
## Task 3.2  Supported Ionic Liquid Membranes
Status on Work at TIPS

### PTMSP modified by swelling in alcohol/IL

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Sorption, vol.%</th>
<th>CO₂ permeance, l(STP)/m² h bar</th>
<th>N₂ permeance, l(STP)/m² h bar</th>
<th>CO₂/N₂ selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMSP unmodified</td>
<td>-</td>
<td>2900</td>
<td>770</td>
<td>3.8</td>
</tr>
<tr>
<td>PTMSP + (1% EmimDCA in EtOH)</td>
<td>0.2</td>
<td>2930</td>
<td>660</td>
<td>4.4</td>
</tr>
<tr>
<td>PTMSP + (5% EmimDCA in EtOH)</td>
<td>3.1</td>
<td>1060</td>
<td>230</td>
<td>4.6</td>
</tr>
</tbody>
</table>

- Relatively low CO₂ permeance loss and gradual increase during incorporation of IL in PTMSP
- Optimization of swelling method is in progress
Task 3.3 Process modelling and simulations

Objectives

- Develop membrane module simulation model for nanocomposite and SILM membranes.
  - Evaluate the energy requirement & membrane area for different set of operating conditions
- Develop concepts for utilizing the membranes in a post-combustion process.

Research Activities

- Development of permeability models based on the experimental results obtained in tasks 3.1 and 3.2:
  - Analysis of the mass transfer characteristics (constant or variable permeability, coupling phenomena, role of temperature)
  - Modelling of the mass transfer performances for the different compounds through a general permeability relationship.
- Parametric simulation study of the performances for the two types of membranes
  - Review of the different modelling approaches
  - Influence of feed mixture composition (i.e. CO2 content)
  - Parametric study for a target CO2 purity and capture ratio
  - Analysis of the energy (pressure ratio) / membrane area trade-off
- Modelling framework in a process simulation environment with energy integration aspects
Task 3.3 Process Modelling and simulations
Status on Work at CNRS

Objectives
• Develop membrane module simulation model for hybrid membranes.
  ➢ Model mass transfer with a reaction diffusion mechanism
  ➢ Enquire about possible disturbances of process modelling (temperature, water impact, competing reaction...)
  ➢ Evaluate the impact of inlet conditions variations

• Develop concepts for utilizing the membranes in a post-combustion process (Aspen Plus software)
Task 3.3 Process Modelling and simulations
Status on Work at CNRS

- Two transport mechanisms:
  - Sorption diffusion for N2 compound
  - Reaction diffusion for CO2 compound

- Main reversible chemical reaction:

\[ CO_2 + H_2O \overset{+NH_2}{\rightleftharpoons} HCO_3^- + H^+ \]

- Water in the feed flow is a requirement

- Competing reactions between amine fixed sites and CO2 occur
Task 3.3 Process Modelling and simulations
Status on Work at CNRS

- Two Transport mechanisms but only one equation:

\[
J_A = -D_A \frac{dC_A}{dx} = \frac{D_A}{dx} (C_{A,f} - C_{A,p}) + \frac{D_{AC}}{dx} (C_{AC,f} - C_{AC,p})
\]

- Important parameters:
  - \( K \) (equilibrium constant of the reaction) depends on temperature
  - \( C_T \) (Total carrier concentration) depends on nanoparticles volume fraction (5, 10, 25 wt%)
  - Carrier diffusion coefficient is considered as constant
Task 3.3 Process Modelling and simulations
Status on Work at CNRS

• Membranes in a post-combustion process:
  ➢ Aspen Plus software

[Diagram of a membrane unit with labels for retentate and permeate flow]
Task 3.3 Process Modelling and simulations
Status on Work at CNRS

• Variation of the Input conditions:
  ➢ Temperature
  ➢ Pressure in the upside part of the membrane
  ➢ Pressure in the downside part of the membrane
  ➢ CO2 volume fraction in the feed flow

• Membrane area estimation

• Energy requirement evaluation (compressor, expender, vacuum pumping)

• Technical economical estimation (in collaboration with EDF)
Task 3.3 Process Modeling and simulations
Status on Work at NTNU

**NTNU will contribute with:**

- Details on the facilitated transport model for the functionalized nanocomposite hybrid membranes.
- Providing experimental data to check the model at given conditions.
- Compare the simulation results with their own in-house model, and discuss the impact of inlet conditions variations.
- Contribute in discussions with respect to utilizing the hybrid membranes in a post-combustion process.