MODELLING OF ADSORPTION BASED CO$_2$ CAPTURE PROCESSES FOR LARGE-SCALE APPLICATIONS

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Adsorption & adsorption processes

- Adsorption: spontaneous phenomenon of attraction that a molecule from a fluid phase experiences when it is close to the surface of a solid, named adsorbent.
Desorption processes

• PSA: Pressure Swing Adsorption. Regenerated by lowering the pressure.
• VPSA: same as PSA but using a vacuum pump.
• TSA: Temperature Swing Adsorption. Regenerates by heating the adsorbent.
• ESA: Electric Swing Adsorption: same as TSA using electricity.
• SMB: Simulated Moving Bed. Displaces one component with other.
• Moving beds: sends the adsorbent to other process "compartments" where T and or P can be changed.
Before CO₂ break through the adsorbent bed, the feed step is stopped and column is regenerated by lowering the pressure.
Rationale for modelling

• Get a good model for a "column" where the process will happen.
  • Column is the closed environment where we can define a unitary process
Rationale for modelling II

- When your 1-column model works you are half-way. You need to do the proper cycling and get the number of columns.

<table>
<thead>
<tr>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>CD</td>
<td>PU</td>
<td>EQ2</td>
<td>EQ1</td>
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<tr>
<td>3</td>
<td>EQ1</td>
<td>CD</td>
<td>EQ2</td>
<td>CD</td>
</tr>
<tr>
<td>4</td>
<td>EQ1</td>
<td>RE</td>
<td>ADSORPTION</td>
<td>EQ1</td>
</tr>
</tbody>
</table>

ADSORPTION

RE
The mathematical model for the column

System of partial differential equations

Material balances

Gas phase:
\[
\frac{\partial}{\partial z} \left( \epsilon D_{\text{w}} C_{\text{g},\text{r}} \frac{\partial y_{\text{r}}}{\partial z} \right) - \frac{\partial}{\partial z} \left( u_0 C_{\text{g},\text{r}} \right) - \epsilon \frac{\partial C_{\text{g},\text{r}}}{\partial t} - (1 - \epsilon) \alpha_{\text{p},k_j} (C_{\text{g},j} - C_{\text{g},r}) = 0
\]

Solid phase:
\[
\text{Macropore: } \frac{\partial (C_{m,i,j})}{\partial t} = \frac{\Omega_m D_{\text{p},i,j} (C_{i,j} - (C_{m,i,j}) - \rho_{\text{p},i,j} \frac{\partial q_i}{\partial t})}{\epsilon_{i,j}} \\
\text{Micropore: } \frac{\partial q_i}{\partial t} = \frac{\Omega_m D_{\text{p},i,j}}{r_{\text{p},i,j}} (q_i^* - q_i)
\]

Momentum balance

Ergun Equation:
\[
-\frac{\partial P}{\partial z} = 150 \mu (1 - \epsilon)^2 \frac{u_0^3}{\epsilon^3 d_p} - \frac{1.75(1 - \epsilon) \rho_0}{\epsilon^3 d_p} |u_0| |u_0|
\]

Energy balances

Gas phase:
\[
\frac{\partial}{\partial z} \left( \lambda \frac{\partial T_{\text{g}}}{\partial z} \right) - u_0 G_{\text{g},r} C_{\text{p}} \frac{\partial T_{\text{g}}}{\partial z} + \epsilon R_s T_{\text{g}} \frac{\partial G_{\text{g},r}}{\partial t} - (1 - \epsilon) \alpha_{\text{p},h_j} (T_g - T_p) - \frac{4 h_w}{d_{\text{w},i}} (T_g - T_w) - \epsilon C_{\text{g},r} C_v \frac{\partial T_{\text{g}}}{\partial t} = 0
\]

Solid phase:
\[
(1 - \epsilon) \left[ \epsilon_p \sum_{i=1}^{n} C_{m,i,j} + \rho_p \sum_{i=1}^{n} (\bar{q}_i) C_{v,ad,i} + \rho_p \hat{C}_{m,p,i,j} \right] \frac{\partial T_{\text{p}}}{\partial t} = (1 - \epsilon) \epsilon_p R_s T_p \frac{\partial C_{m,p}}{\partial t} + \rho_p \sum_{i=1}^{n} (\Delta H) \frac{\partial (\bar{q}_i)}{\partial t} + (1 - \epsilon) \alpha_{\text{p},h_j} (T_g - T_p)
\]

Column wall:
\[
\rho_w \frac{\partial T_{\text{w}}}{\partial t} = \alpha_w \left( T_g - T_w \right) - \alpha_w U(T_w - T_c) \\
\alpha_w = d_{\text{w},i} / [\epsilon (d_{\text{w},i} + e)] \\
\alpha_w = 1 / [(d_{\text{w},i} + e) \ln((d_{\text{w},i} + e) / d_{\text{w},i})]
\]

Linked by the isotherm equation and the gas phase equation of state.
For the model you need...

- Adsorption isotherms: at all P and T (try to avoid extrapolation)
- Some equation to predict real behavior: might not work in real life.
- Diffusion coefficients
- Heat capacity
- Dispersion, many properties of the adsorbent, etc
- The beauty of large-scale processes: they are adiabatic so we need less heat transfer parameters.
  - Bad part of large-scale processes: they are adiabatic so is a big job to take out heat (fast).
Software for modelling: alternatives

- I don't see the equations anymore: we've built a drag-and-drop code where units can be modelled together.
Calendar of operation. Remember high-school?

Multi-feed 12-column scheme. Four pressure equalizations, provide purge, rinse with heavy gas, counter-current blowdown, purge and one counter-current final pressurization with light product.
Pressure swing in each column

Each simulation took 2 days...
Example I: PSA for CO$_2$ removal from natural gas
Example II: ESA for CO₂ removal NGCC

- We did this work within MATESA project. Main difficulty is modelling hybrid sources of energy: heat produced by electricity and hot gas.

<table>
<thead>
<tr>
<th>Main results</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Capture ratio</td>
<td>92.14</td>
</tr>
<tr>
<td>CO₂ purity</td>
<td>95.04</td>
</tr>
<tr>
<td>Electric duty for the fans [MJₐ/kgCO₂]</td>
<td>1.43</td>
</tr>
<tr>
<td>Heat duty means steam bleeding @150°C [MJₐ/kgCO₂]</td>
<td>0.71</td>
</tr>
<tr>
<td>Heat duty means electricity [MJₐ/kgCO₂]</td>
<td>1.30</td>
</tr>
<tr>
<td>Heat recovered [MJₐ/kgCO₂]</td>
<td>2.90</td>
</tr>
</tbody>
</table>
Example III: Pre-combustion

- We have a new material here that we believe that can make a difference.
- UTSA-16 is good for removing CO\textsubscript{2} and also to remove CO so it can make the control of the PSA easier. A pre-layer for water will still be necessary like with materials used today.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>$u_F$, m s\textsuperscript{-1}</th>
<th>$t_{RIN}$, s</th>
<th>$P_{DEQ1}$, bar</th>
<th>$P_{DEQ2}$, bar</th>
<th>Pur., %</th>
<th>Rec., %</th>
<th>Productivity, mol H\textsubscript{2} kg\textsuperscript{-1} h\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0529</td>
<td>0</td>
<td>9.16</td>
<td>3.21</td>
<td>99.9902</td>
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<tr>
<td>2</td>
<td>0.0462</td>
<td>65</td>
<td>8.50</td>
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<tr>
<td>3</td>
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<td>95</td>
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<td>4</td>
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<td>60</td>
<td>8.61</td>
<td>2.96</td>
<td>99.9991</td>
<td>93.0</td>
<td>2.80</td>
</tr>
</tbody>
</table>
SINTERCAP project

• We have started exploring a new dimension: utilization of 3D printing technology.

• First steps were in 3D printed reactors for continuous synthesis of materials.
Next steps: 3D modelling in adsorption processes

- We will soon start 3D-CAPS project (ACT) and CARMOF (H2020).
- New challenges are coming...
  - RAM memory flyes away...

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**SINTEF**
Conclusions

• Adsorption processes could be more popular if they were taught at university level.

• There is a lot about the process itself and not just the material.

• They generally result in larger footprint but lower consumption.

• Everything that helps in making them faster helps. Moving beds and monoliths can be a major success.
  • If monoliths can be 3D printed it might be even better.
Acknowledgments

• All the colleagues at University of Porto, SINTEF and other partner institutions in joint projects.

• Projects:
  • “New Challenges in Adsorption Technologies”, 2005-2008, FCT, Portugal
  • "CO₂ Capture in Natural Gas Production by Adsorption Processes for CO₂ Storage, EOR and EGR". 2015-2016, IEAGHG
  • SINTERCAP: Shaping of advanced materials for CO₂ capture processes. NFR, Norway through the CLIMIT program: project 233818.
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