MODELLING OF ADSORPTION BASED CO_2 CAPTURE PROCESSES FOR LARGE-SCALE APPLICATIONS

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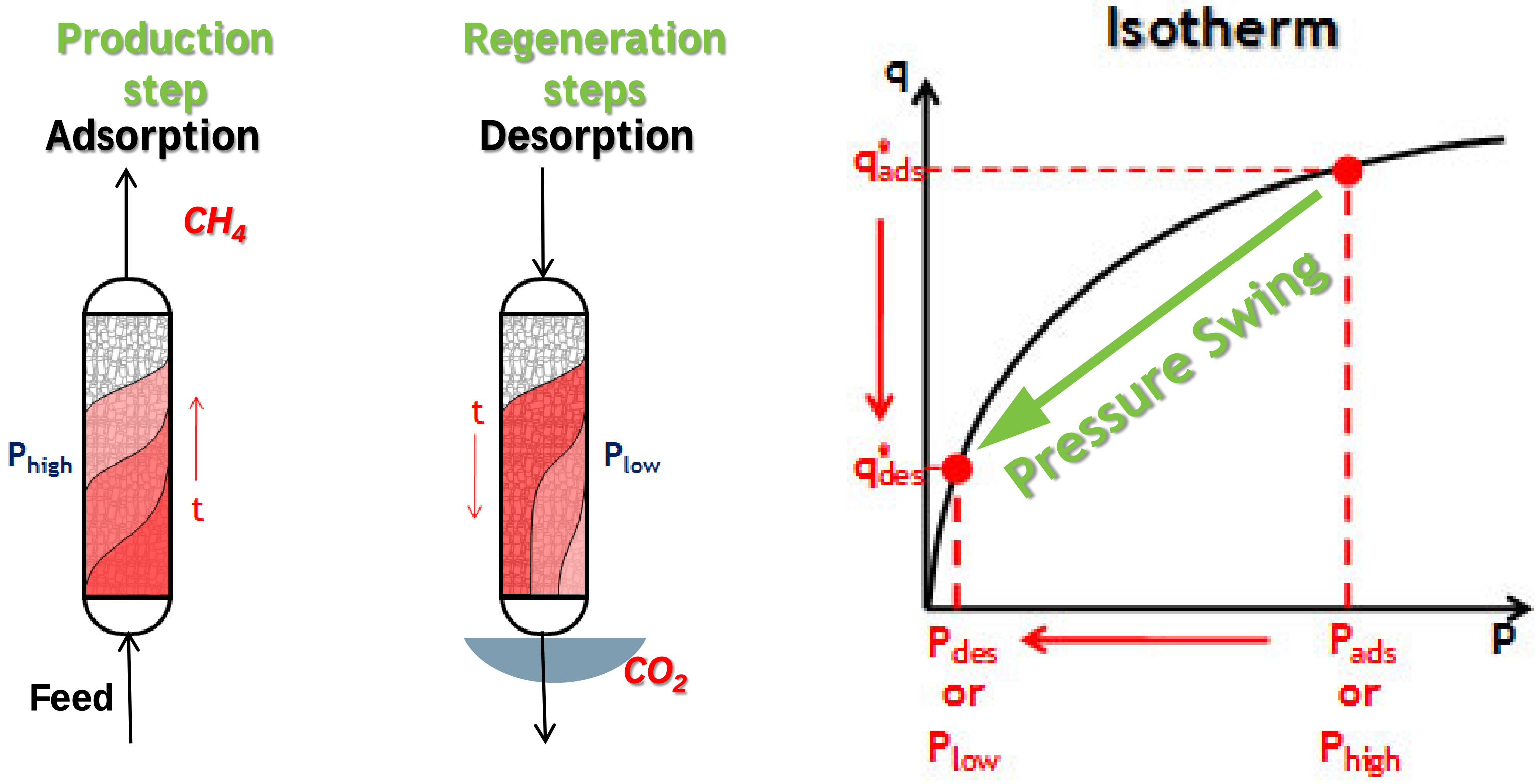
Adsorption & adsorption processes

- 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.

Example: the PSA operation



Before CO_2 break through the adsorbent bed, the feed step is stopped and column is regenerated by lowering the pressure.

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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

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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>
<tr><td>1</td><td colspan="3">ADSORPTION</td><td>EQ1</td><td>CD</td><td>EQ2</td><td>CD</td><td>PU</td><td>EQ2</td><td>EQ1</td><td colspan="2">RE</td></tr>
<tr><td>2</td><td>CD</td><td>PU</td><td>EQ2</td><td>EQ1</td><td colspan="2">RE</td><td colspan="3">ADSORPTION</td><td>EQ1</td><td>CD</td><td>EQ2</td></tr>
<tr><td>3</td><td>EQ1</td><td>CD</td><td>EQ2</td><td>CD</td><td>PU</td><td>EQ2</td><td>EQ1</td><td colspan="2">RE</td><td colspan="3">ADSORPTION</td></tr>
<tr><td>4</td><td>EQ1</td><td colspan="2">RE</td><td colspan="3">ADSORPTION</td><td>EQ1</td><td>CD</td><td>EQ2</td><td>CD</td><td>PU</td><td>EQ2</td></tr>
</table>

The mathematical model for the column

System of partial differential equations

Material balances

Gas phase: $$\frac{\partial}{\partial z}\left(\varepsilon D_{ax} C_{g,T} \frac{\partial y_i}{\partial z}\right) - \frac{\partial}{\partial z}\left(u_0 C_{g,i}\right) - \varepsilon \frac{\partial C_{g,i}}{\partial t} - (1-\varepsilon) a_p k_f \left(C_{g,i} - C_{s,i}\right) = 0$$

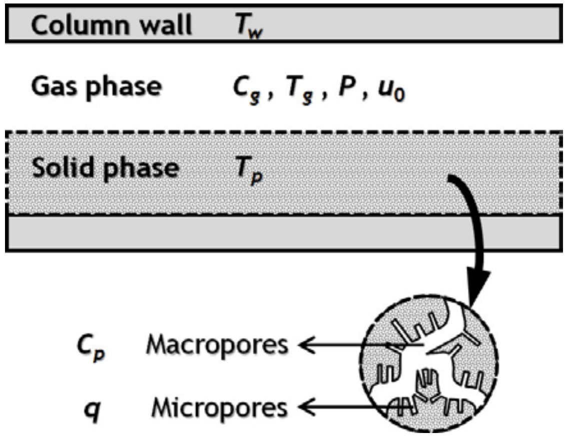
Solid phase:

Macropore $$\frac{\partial \langle C_{m,i}\rangle}{\partial t} = \frac{\Omega_m D_{p,i}}{R_p^2}\left(C_{s,i} - \langle C_{m,i}\rangle\right) - \frac{\rho_p}{\varepsilon_p}\frac{\partial \langle \bar{q}_i\rangle}{\partial t}$$

Micropore $$\frac{\partial \bar{q}_i}{\partial t} = \frac{\Omega_c D_{c,i}}{r_c^2}\left(q_i^* - \bar{q}_i\right)$$

Momentum balance

Ergun Equation: $$-\frac{\partial P}{\partial z} = \frac{150\mu(1-\varepsilon)^2}{\varepsilon^3 d_p^2} u_0 + \frac{1.75(1-\varepsilon)\rho_g}{\varepsilon^3 d_p}\left|u_0\right| u_0$$



Energy balances

Gas phase: $$\frac{\partial}{\partial z}\left(\lambda \frac{\partial T_g}{\partial z}\right) - u_0 G_{g,T} C_p \frac{\partial T_g}{\partial z} + \varepsilon R_g T_g \frac{\partial G_{g,T}}{\partial t} - (1-\varepsilon) a_p h_f \left(T_g - T_p\right) - \frac{4 h_w}{d_{wi}}\left(T_g - T_w\right) - \varepsilon C_{g,T} C_v \frac{\partial T_g}{\partial t} = 0$$

Solid phase: $$(1-\varepsilon)\left[\varepsilon_p \sum_{i=1}^{n} C_{m,i} C_{v,i} + \rho_p \sum_{i=1}^{n} \langle \bar{q}_i \rangle C_{v,ads,i} + \rho_p \hat{C}_{p,s}\right]\frac{\partial T_p}{\partial t} = (1-\varepsilon)\varepsilon_p R_g T_p \frac{\partial C_{m,T}}{\partial t} + \rho_b \sum_{i=1}^{n} (-\Delta H)_i \frac{\partial \langle \bar{q}_i \rangle}{\partial t} + (1-\varepsilon) a_p h_f \left(T_g - T_p\right)$$

Column wall: $$\rho_w \hat{C}_{p,w} \frac{\partial T_w}{\partial t} = \alpha_w h_w \left(T_g - T_w\right) - \alpha_{w\ell} U \left(T_w - T_\infty\right) \qquad \alpha_w = d_{wi} / \left[e\left(d_{wi} + e\right)\right] \qquad \alpha_{w\ell} = 1 / \left[\left(d_{wi} + e\right) \ln\left(\left(d_{wi} + e\right)/d_{wi}\right)\right]$$

Linked by the isotherm equation and the gas phase equation of state.

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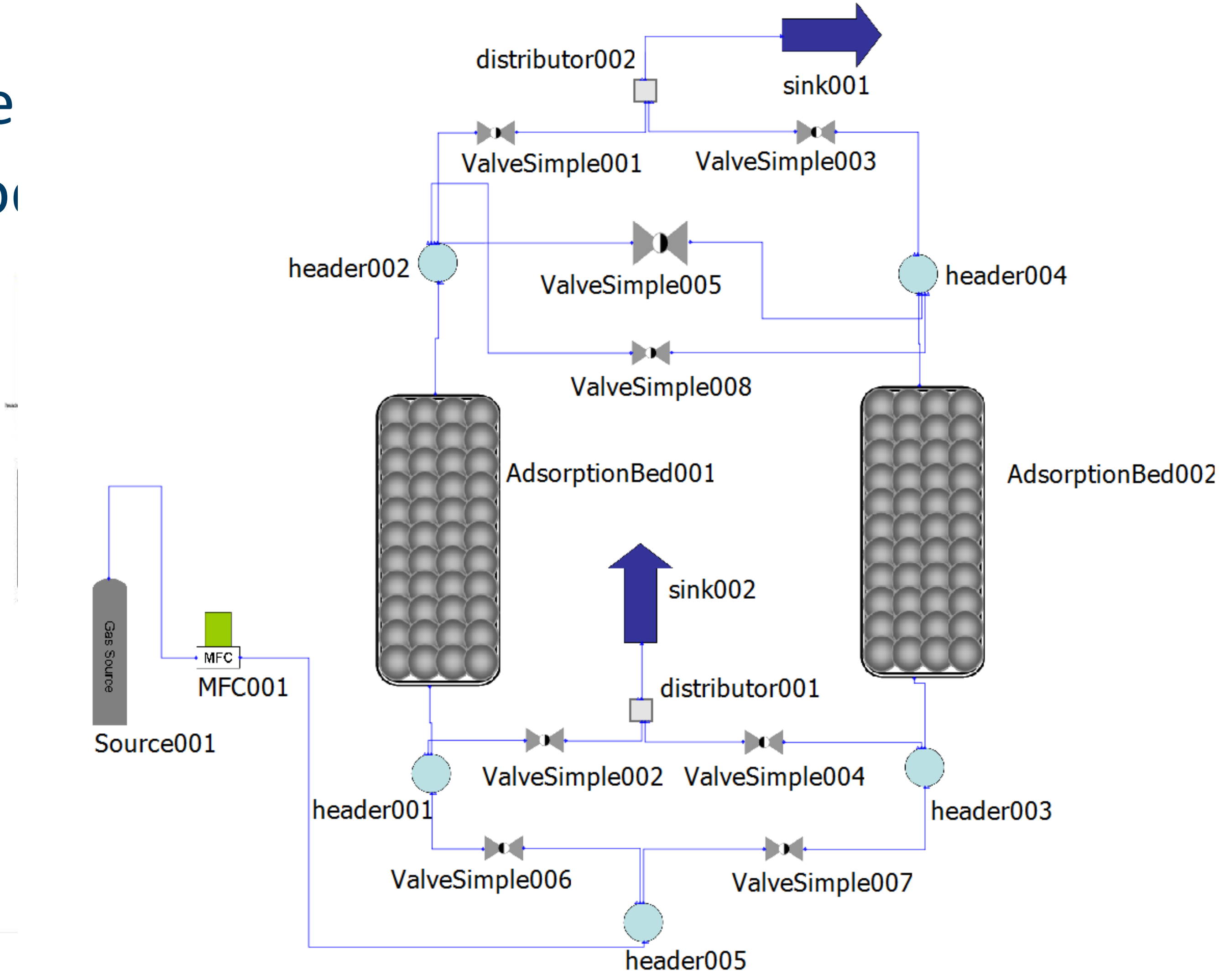
For the model you need…

- 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 e   'op code where
  units can be mo(



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Calendar of operation. Remember high-school?

C1	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓
C2	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓
C3	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓
C4	Pu ↓	E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓
C5	Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓		
C6	B ↓		Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓
C7	R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑	
C8	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑
C9	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑
C10	D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑					
C11	FEED ↑		D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑			
C12	FEED ↑				D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	

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.

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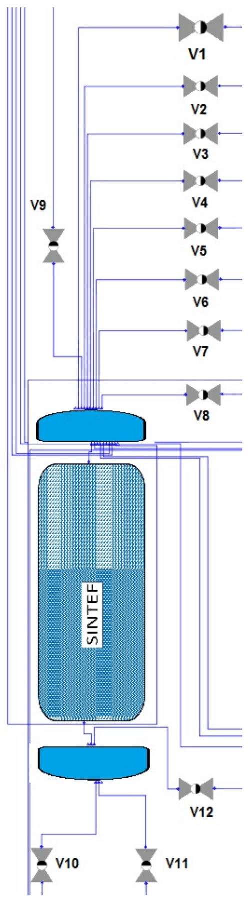
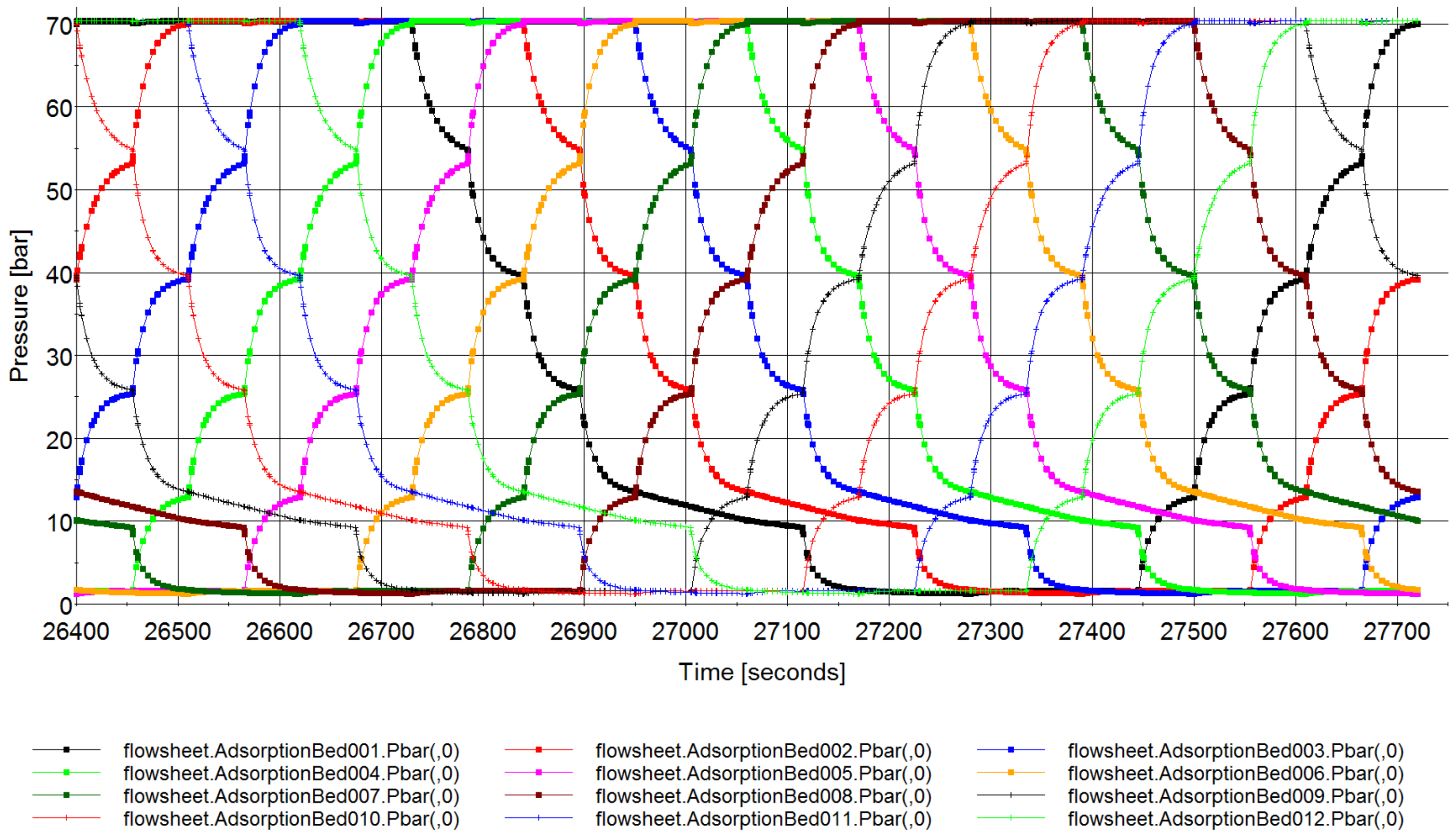
Pressure swing in each column



Column connections for multi-column PSA modelling.



Each simulation took 2 days…

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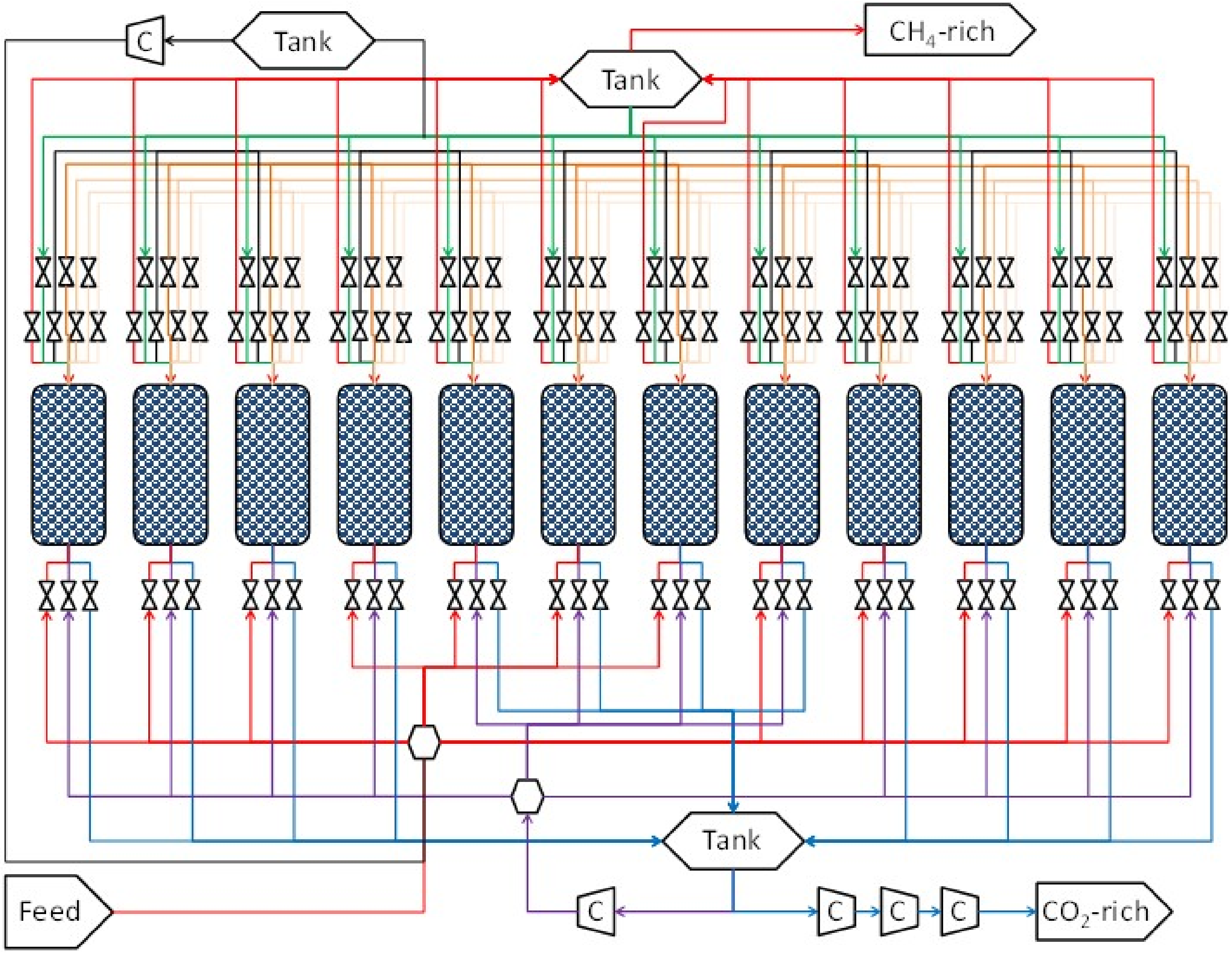
Example I: PSA for CO_2 removal from natural gas

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Blog

New IEAGHG report: CO_2 capture in natural gas production by adsorption

Written by Jasmin Kemper on 02 March 2017. Posted in CO_2 capture

CO_2 capture from natural gas (NG) can be done by several technologies, e.g. solvent scrubbing, membranes, adsorption or cryogenic processes. The future demand in NG might trigger development of NG fields with high CO_2 partial pressure, for which pressure swing adsorption (PSA) processes could be more suitable than the other options. Besides, PSA processes have the potential to reduce energy consumption and costs. Hence, there is a requirement to evaluate the feasibility of PSA processes for CO_2 capture from NG at high pressures.

The aim of this work was to evaluate PSA processes for removal of CO_2 from NG at high pressure. For this, the study performed a techno-economic comparison of PSA with an amine based solvent process and identified candidate materials for the PSA process. Researchers from SINTEF Chemistry & Materials and SINTEF Energy Research have carried out this study for IEAGHG.

The key messages from the report are:

- An iterative pathway was applied to find a PSA cycle design with maximum CO_2 purity. The final design consists of a 12-column multi-feed cycle with around 85% CO_2 purity and is the first reported design for the separation of CO_2 and CH_4 at a pressure of 70 bar and flowrates of 500 000 Sm³/h.
- The final PSA design has about 50% higher costs of CO_2 removal (including CO_2 conditioning, transport and storage) and NG sweetening than the reference amine process. However, the process is not yet optimised, so there is ample room for improvement.
- Data availability for suitable adsorbent materials is severely limited. This study used a carbon molecular sieve (CMS) and identified other materials worthwhile of further investigation, such as certain zeolites, titanosilicates, metal organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs) and honeycomb monoliths.
- A combined approach of material and process optimisation could significantly reduce the cost of the proposed PSA design, potentially even below the cost for the reference case of amine scrubbing.
- Improving the feasibility of the PSA process for CO_2 capture from NG requires more work in several areas. This includes optimisation of the PSA cycle to minimise NG losses, investigation of novel cycle concepts (e.g. hybrid of single and dual PSA), evaluation of advanced adsorption materials and data for suitable adsorbents at high pressure. This is basic research and modelling work that should be taken up by related research groups from academia and industry.

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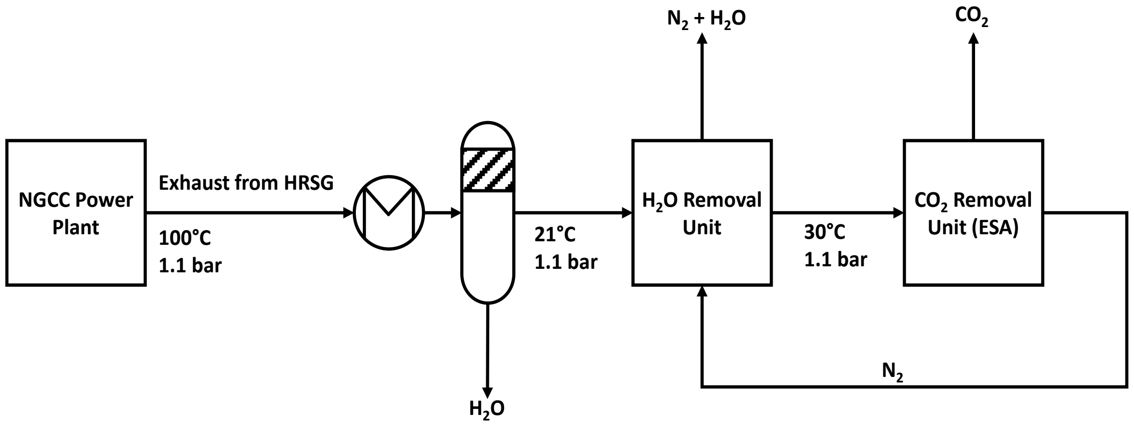
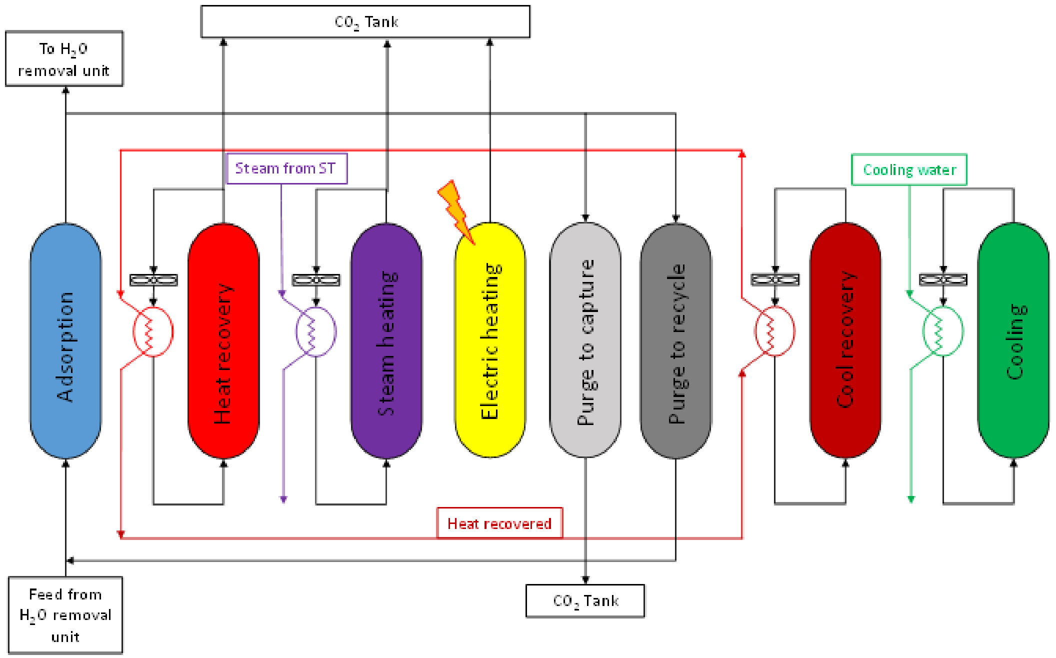
Example II: ESA for CO_2 removal NGCC

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





Main results	
Carbon Capture ratio	92.14
CO_2 purity	95.04
Electric duty for the fans [MJ_{el}/kg_{CO2}]	1.43
Heat duty means steam bleeding @150°C [MJ_{th}/kg_{CO2}]	0.71
Heat duty means electricity [MJ_{el}/kg_{CO2}]	1.30
Heat recovered [MJ_{th}/kg_{CO2}]	2.90

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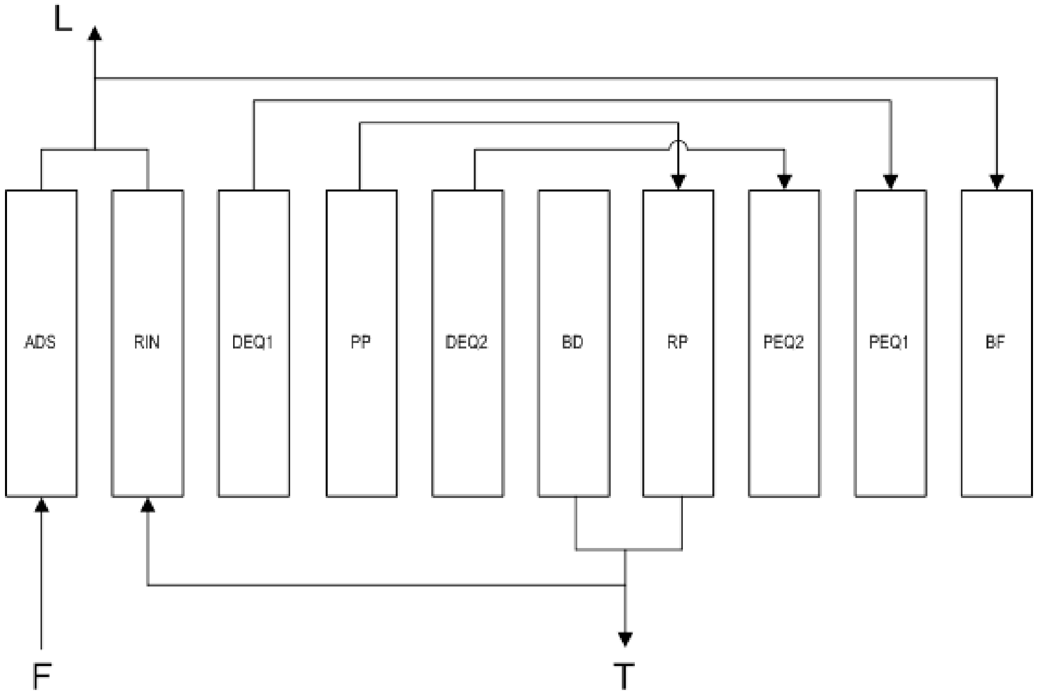
Example III: Pre-combustion

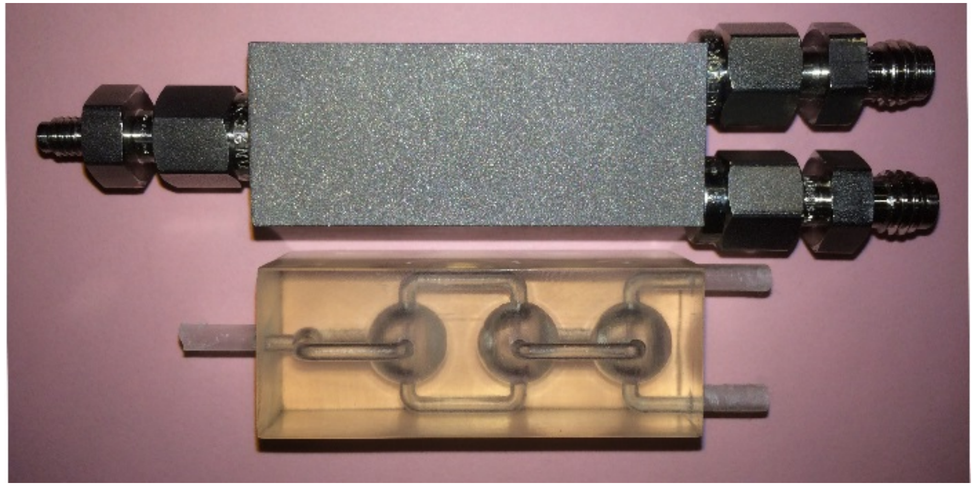
- We have a new material here that we believe that can make a difference.
  - UTSA-16 is good for removing CO_2 and also to remove CO so it can make the control of the PSA easier. A pre-layer for water will still be necessary like with materials used today.

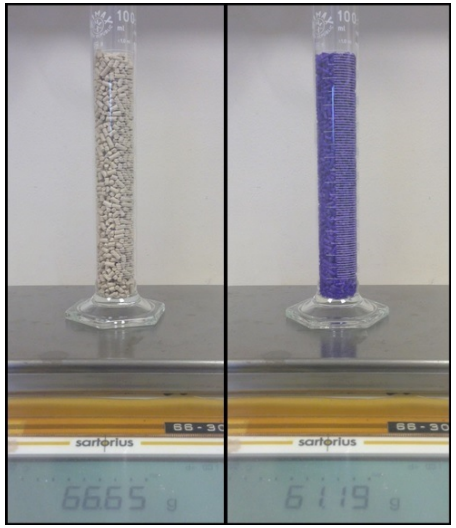


Simulation	u_F, m s^{-1}	t_{RIN}, s	$^aP_{DEQ1}$, bar	$^aP_{DEQ2}$, bar	Pur., %	Rec., %	Productivity, mol_{H2} kg^{-1} h^{-1}
1	0.0529	0	9.16	3.21	99.9902	80.3	3.71
2	0.0462	65	8.50	2.89	99.9947	94.8	2.78
3	0.0398	95	8.37	2.80	99.9980	96.7	2.03
4	0.0460	60	8.61	2.96	99.9991	93.0	2.80

SINTERCAP project

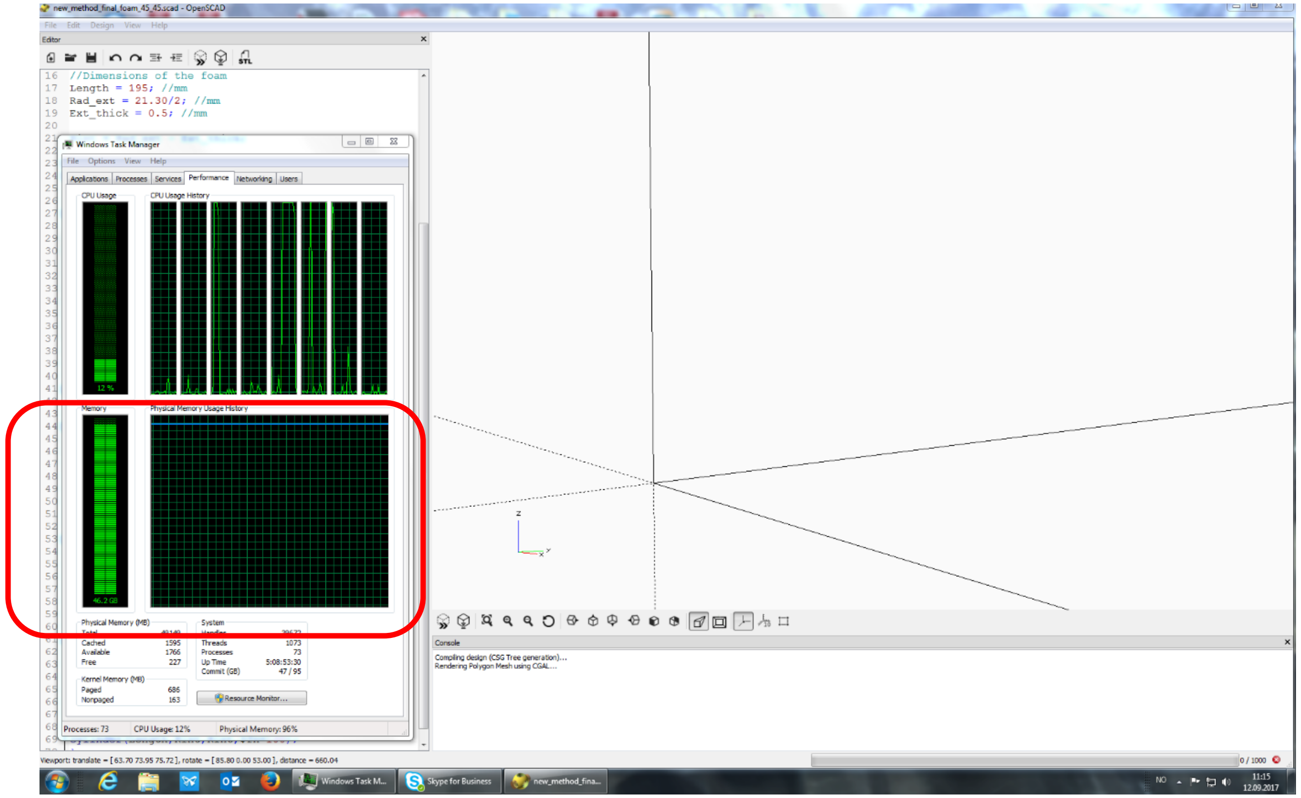
- We have started exploring a new dimension: utilization of 3D printing technology.
- First steps were in 3D printed reactors for continuous synthesis of materials.





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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Conclusions

- Adsorption processes could be more popular if they were tought 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 sucess.
  - 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
  - "Advanced Materials and Electric Swing Adsorption Process for CO_2 capture", 2013-2016, FP7. www.sintef.no/matesa
  - "CO_2 Capture in Natural Gas Production by Adsorption Processes for CO_2 Storage, EOR and EGR". 2015-2016, IEAGHG
  - SINTERCAP: Shaping of advanced materials for CO_2 capture processes. NFR, Norway through the CLIMIT program: project 233818.

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