CO_2 CAPTURE IN NATURAL GAS PRODUCTION USING ADSORPTION PROCESSES

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Target

Decarbonize the production of natural gas. CO_2 contained in the natural gas can be captured and permanently stored or used for enhanced oil recovery (EOR).

Location of the site and gas composition is very different and thus the conclusions of which is the best technology should be taken case-by-case.

Objective

Evaluate adsorption technologies for CO_2 removal from natural gas, mainly oriented to EOR applications. This application is **NOT COMMERCIAL YET**.

H_2 purification (Linde)

CO_2 and N_2 rejection (molecular gate)

Gas dehydration	Helium purification	H_2S removal
Biogas upgrading	Medicinal oxygen	CO_2 recycle
Air separation	OBOGS	...and more

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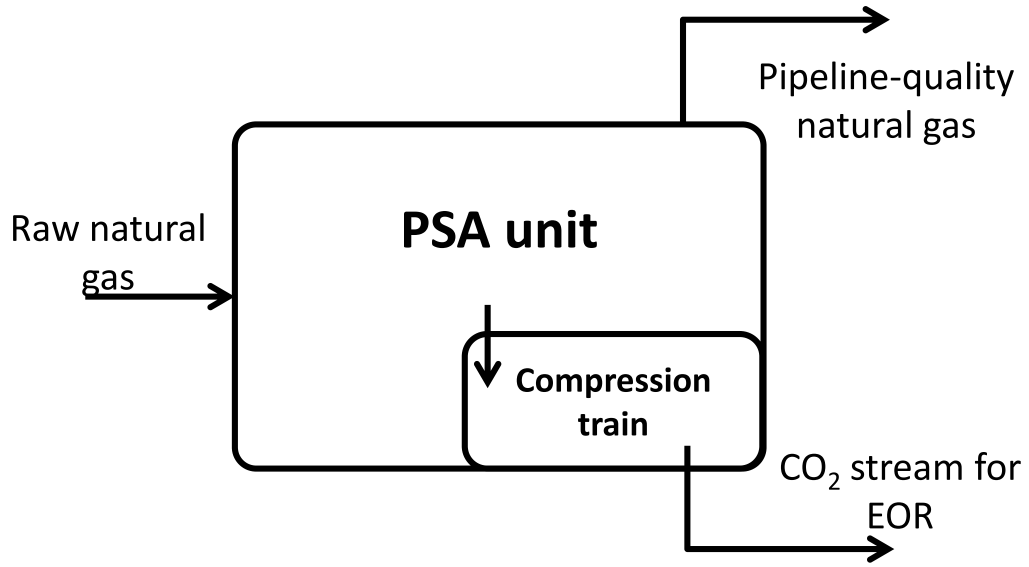
Technology & boundaries definition

SINTEF collected data and some experience in A Green Sea project. We have used similar conditions as in that project for this study.

We have considered costs for CO_2 removal and also for compression. It was set as mandatory to produce pipeline-quality NG and "high purity" CO_2.



Property	Value
Temperature [K]	313
Pressure [bar]	70
Flowrate [Nm³/h]	500,000
y_{CH4}	0.8300
y_{C2H6}	0.070
y_{CO2}	0.1000

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Technology challenges

Pressure of 70 bar is not common in PSA technology. Combined with high flow and low CO_2 content it can be problematic. But is doable. (Pearl GTL in Qatar is an example).

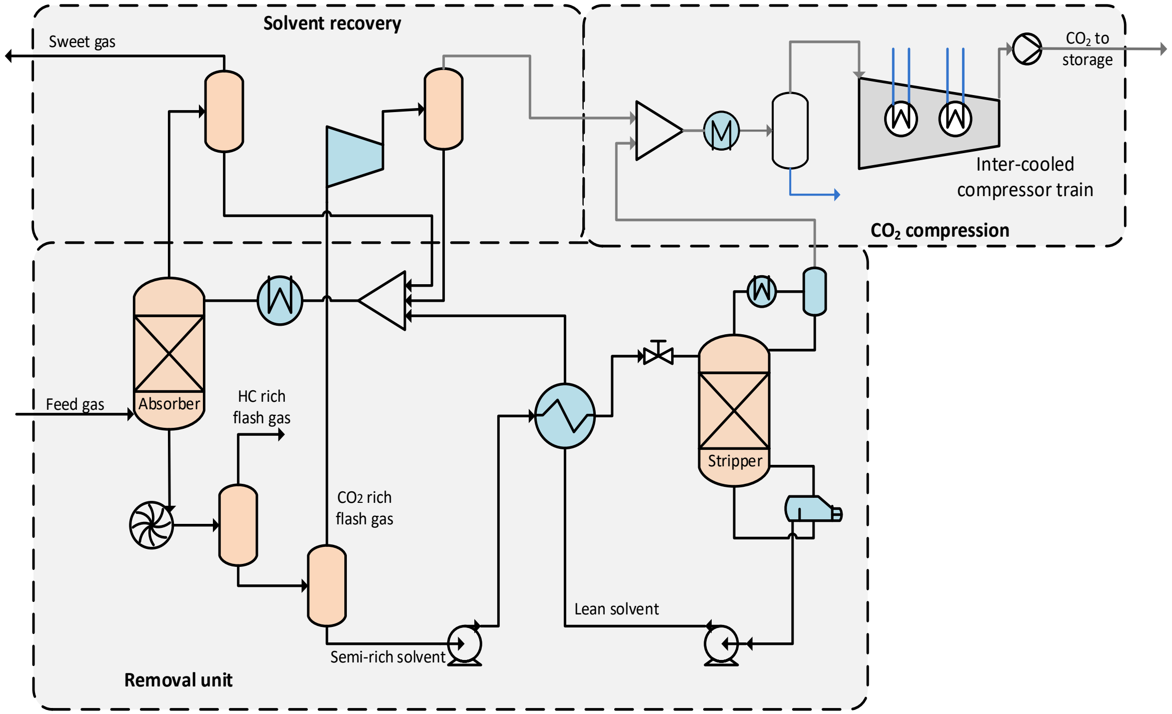
Footprint can be an issue…

http://www.gasification-syngas.org/uploads/eventLibrary/51BEYS.pdf

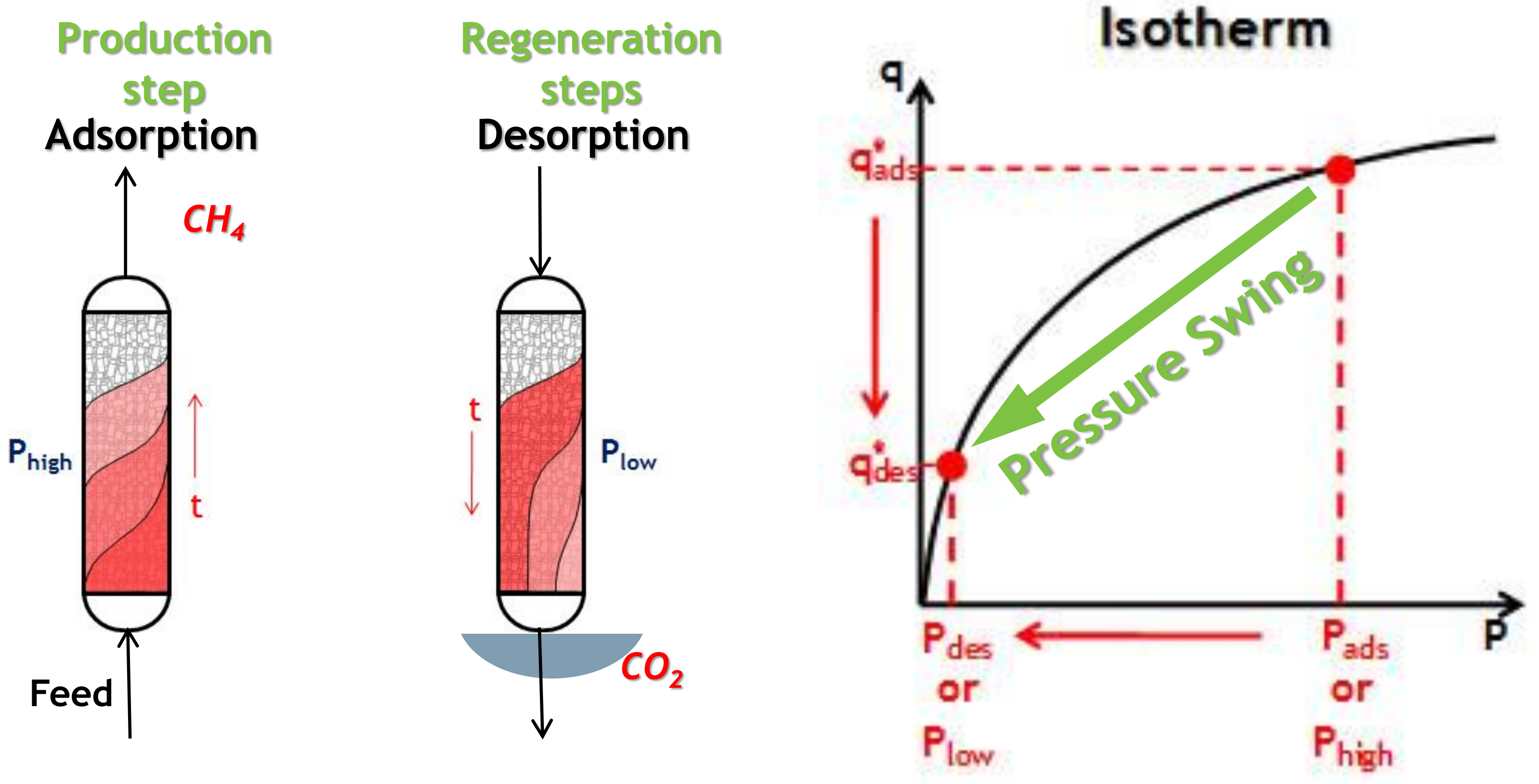
Benchmark case: amine scrubbing

Steady state and commercial process. Lots of available data…

This process is certainly mature (and efficient).



The PSA operation



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

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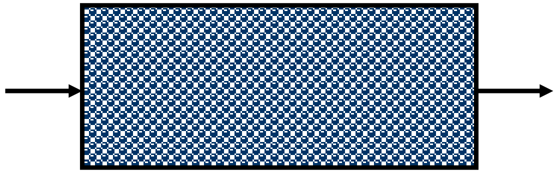
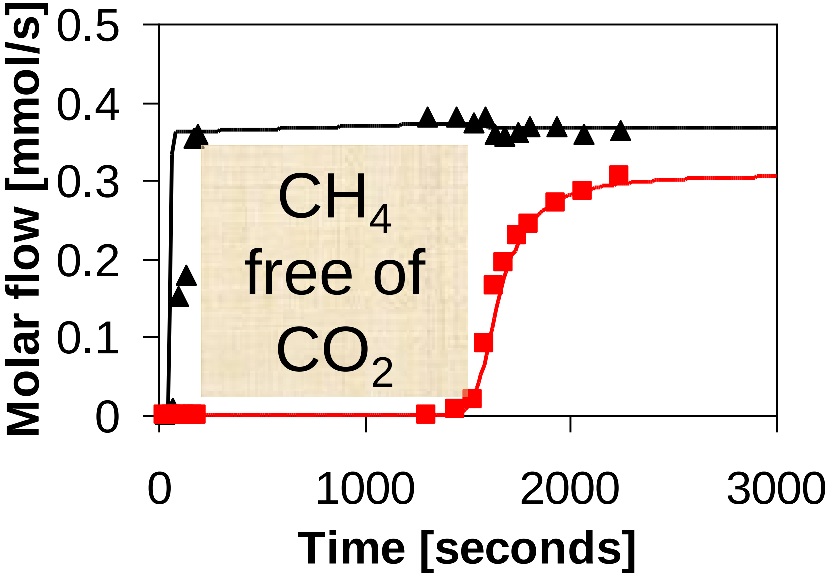
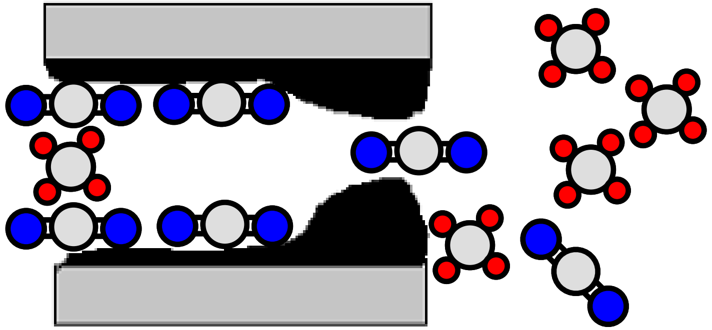
How does this PSA works?



Fixed-bed packed with extrudates of Carbon Molecular Sieve CMS-3K.





CH_4: 3.8 Å; CO_2: 3.4 Å

Adsorption is ”automatic”. Our job is to make desorption look simpler.

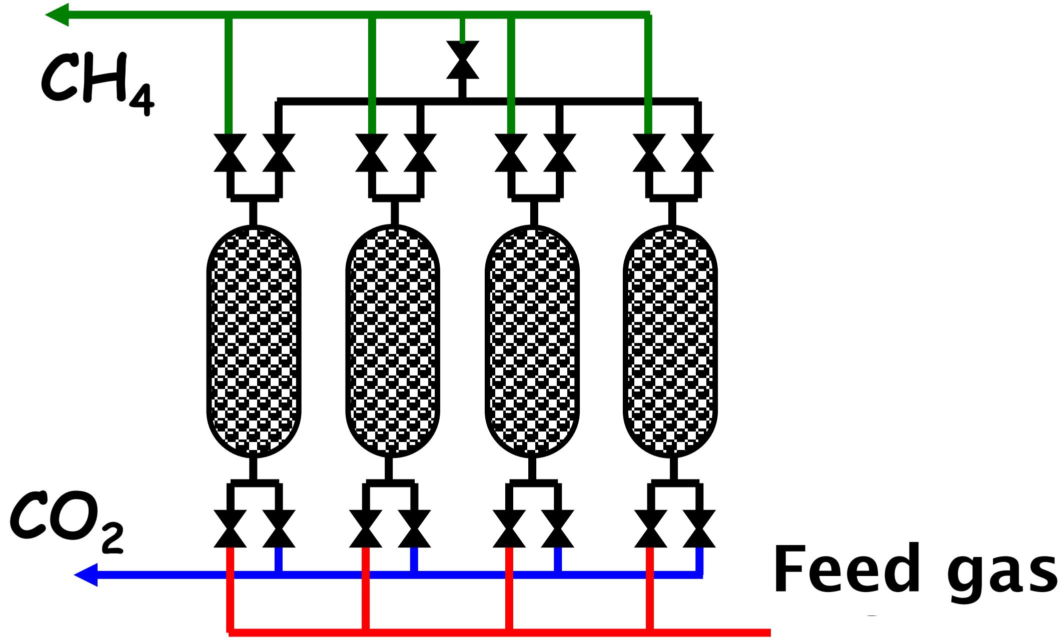
Continuous operation

EQ1: Pressure equalization

CD: Provide purge step

RE: Repressurization

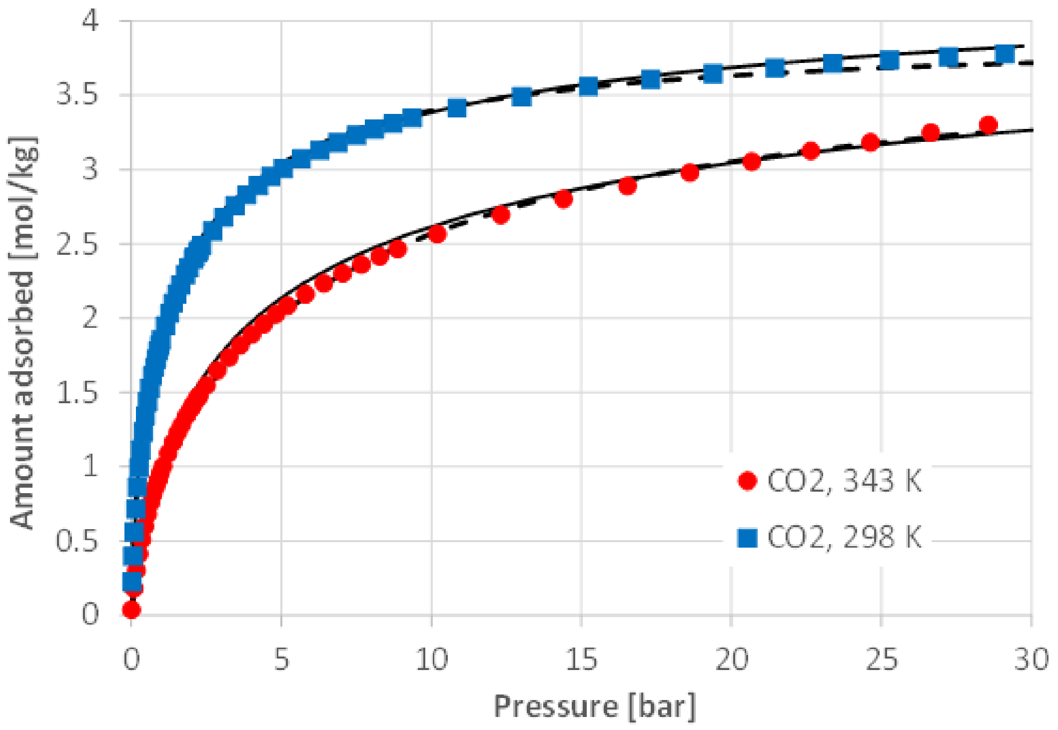
PU: Purge with light gas

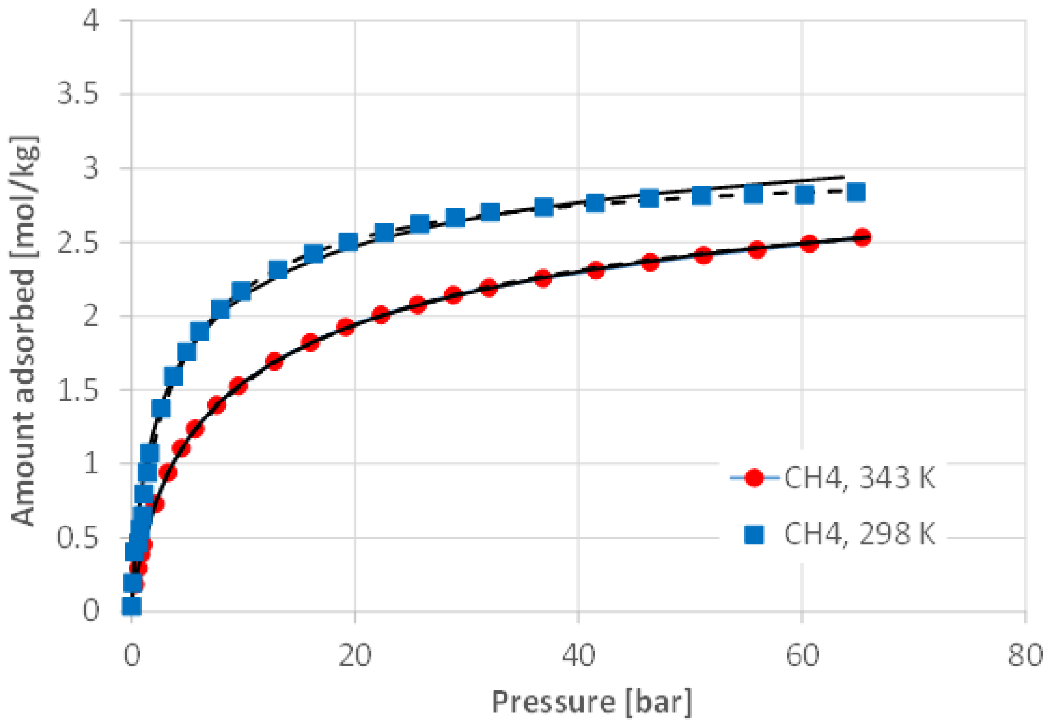


1	ADSORPTION			EQ1	CD	EQ2	CD	PU	EQ2	EQ1	RE	
2	CD	PU	EQ2	EQ1	RE		ADSORPTION			EQ1	CD	EQ2
3	EQ1	CD	EQ2	CD	PU	EQ2	EQ1	RE		ADSORPTION		
4	EQ1	RE		ADSORPTION			EQ1	CD	EQ2	CD	PU	EQ2

Collect some data... isotherms

Material: carbon molecular sieve. Data published in Chem. Eng. Sci., 2017, 164, 148-157.





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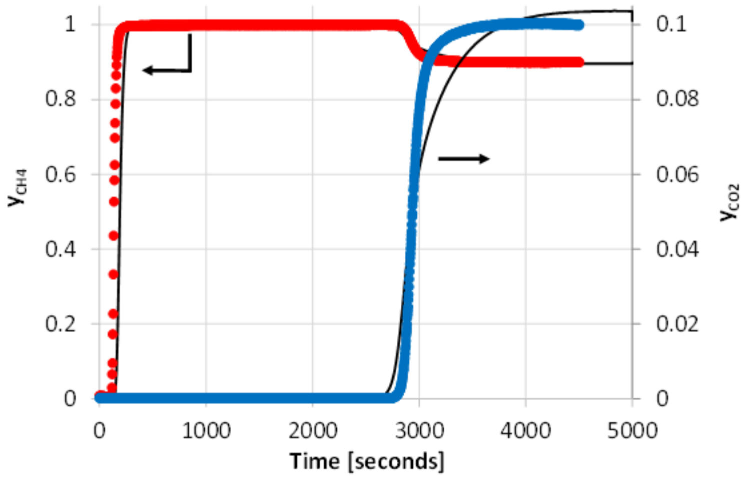
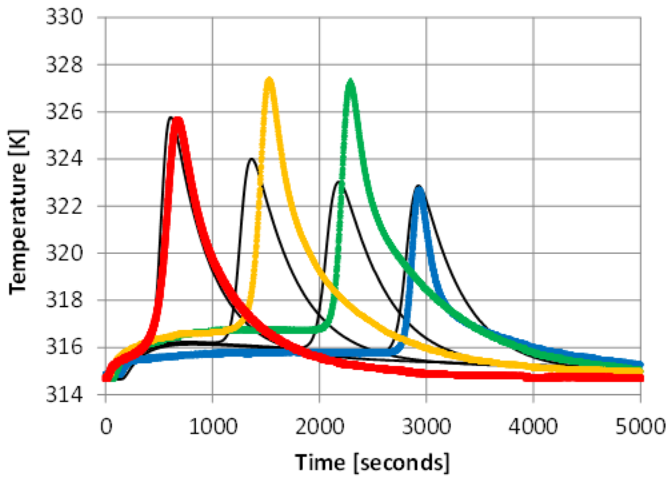
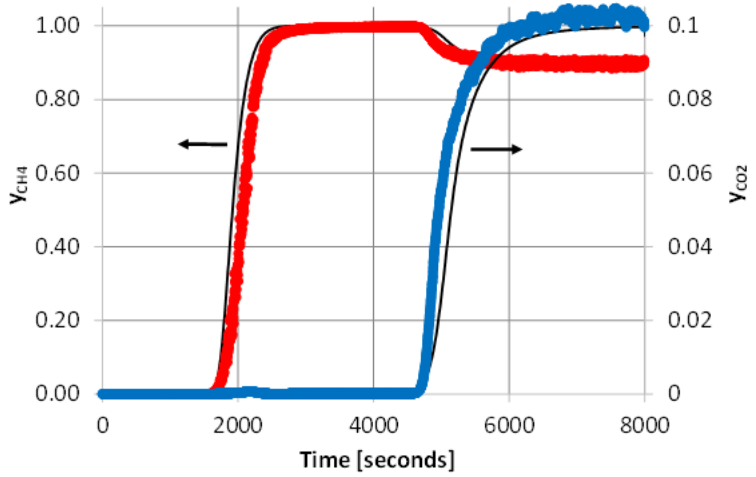
Breakthrough curves: first time at 70 bar.

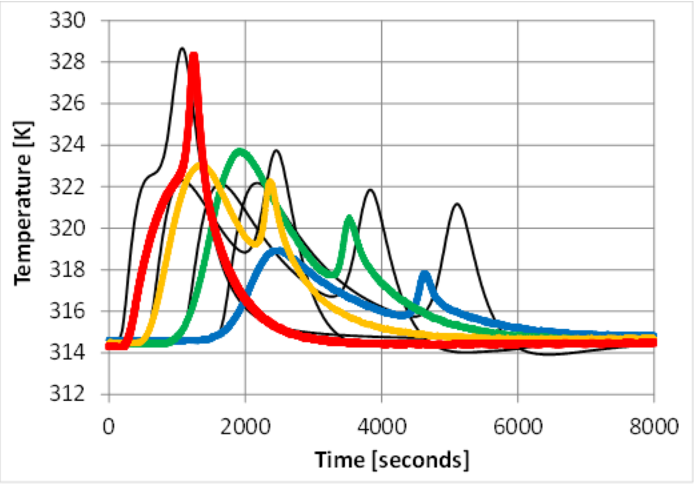
5 bar





70 bar





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MATHEMATICAL MODEL

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

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

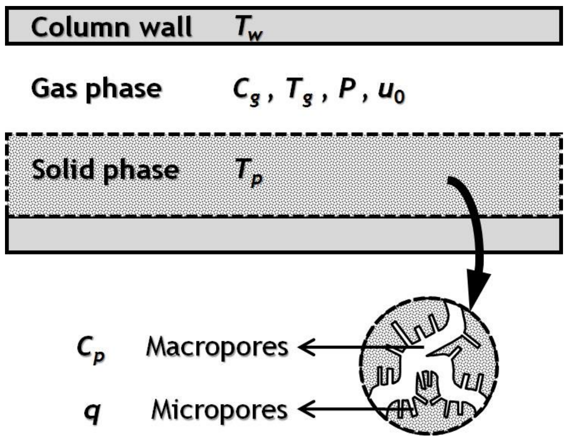
Micropore

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

Momentum balance

Ergun Equation:

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



Ribeiro AM, Grande CA, Lopes FVS, Loureiro JM, Rodrigues AE. Chemical Engineering Science 2008;63:5258-5273.

Energy balances

Gas phase:

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

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:

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

Adsorption isotherm model

Virial isotherm

$$P = \frac{q}{K_H}\exp\left(\frac{2}{S}Aq + \frac{3}{2S^2}Bq^2 + \ldots\right) \qquad A = \sum_{m=0}^{\infty}\frac{A_m}{T^m} \qquad B = \sum_{m=0}^{\infty}\frac{B_m}{T^m}$$

Virial extended isotherm

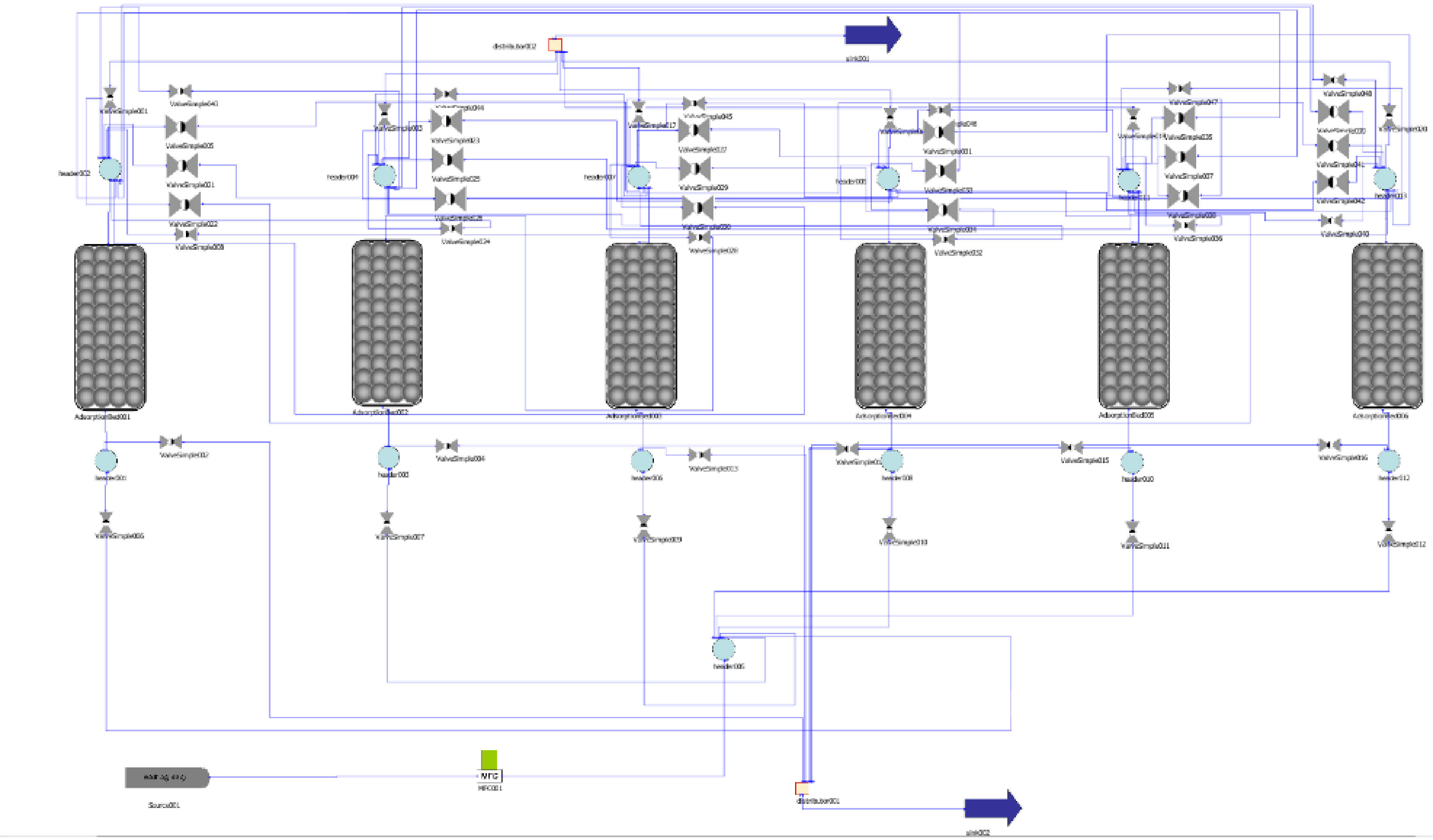
$$P_i = \frac{q_i}{K_{Hi}}\exp\left(\frac{2}{S}\sum_{j=1}^{N}A_{ij}\,q_j + \frac{3}{2S^2}\sum_{j=1}^{N}\sum_{k=1}^{N}B_{ijk}\,q_j q_k\right) \qquad A_{ij} = \frac{\left(A_i + A_j\right)}{2} \qquad B_{ijk} = \frac{\left(B_i + B_j + B_k\right)}{3}$$

Van't Hoff equation

$$K_H = K_\infty\exp\left(\frac{-\Delta H}{R_g T}\right)$$

From equations to the world…

Good results were obtained with a 12-column PSA. So you can see valves, I show a 6-column



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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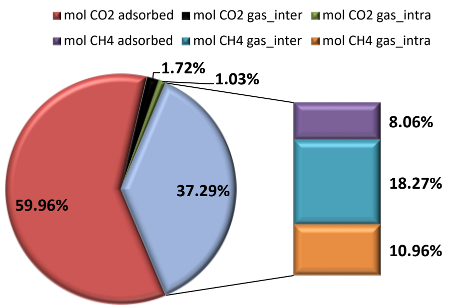
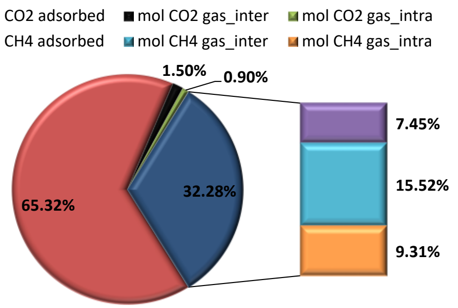
Why we need so many steps?

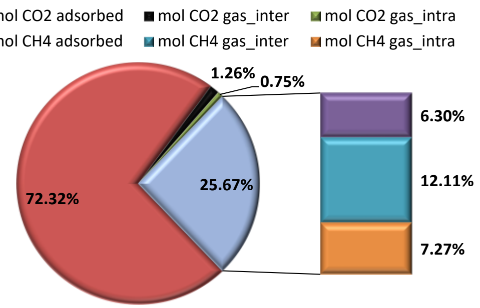
End of first step



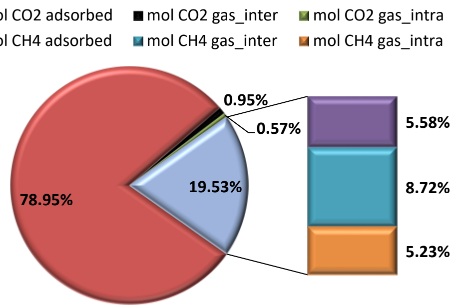
End of first depress



End of second depress



End of third depress



Simple accountability: Even assuming that almost no methane and ethane adsorbs, there is 90% of hydrocarbons in the gas phase (at 70 bar) at the end of the feed step. We need several depressurization steps to remove this gas. By doing this, we are also making the recovery higher.

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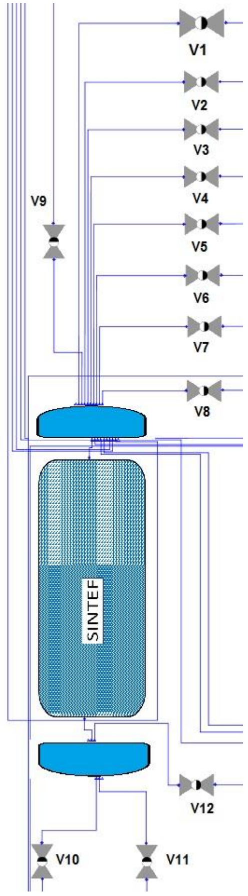
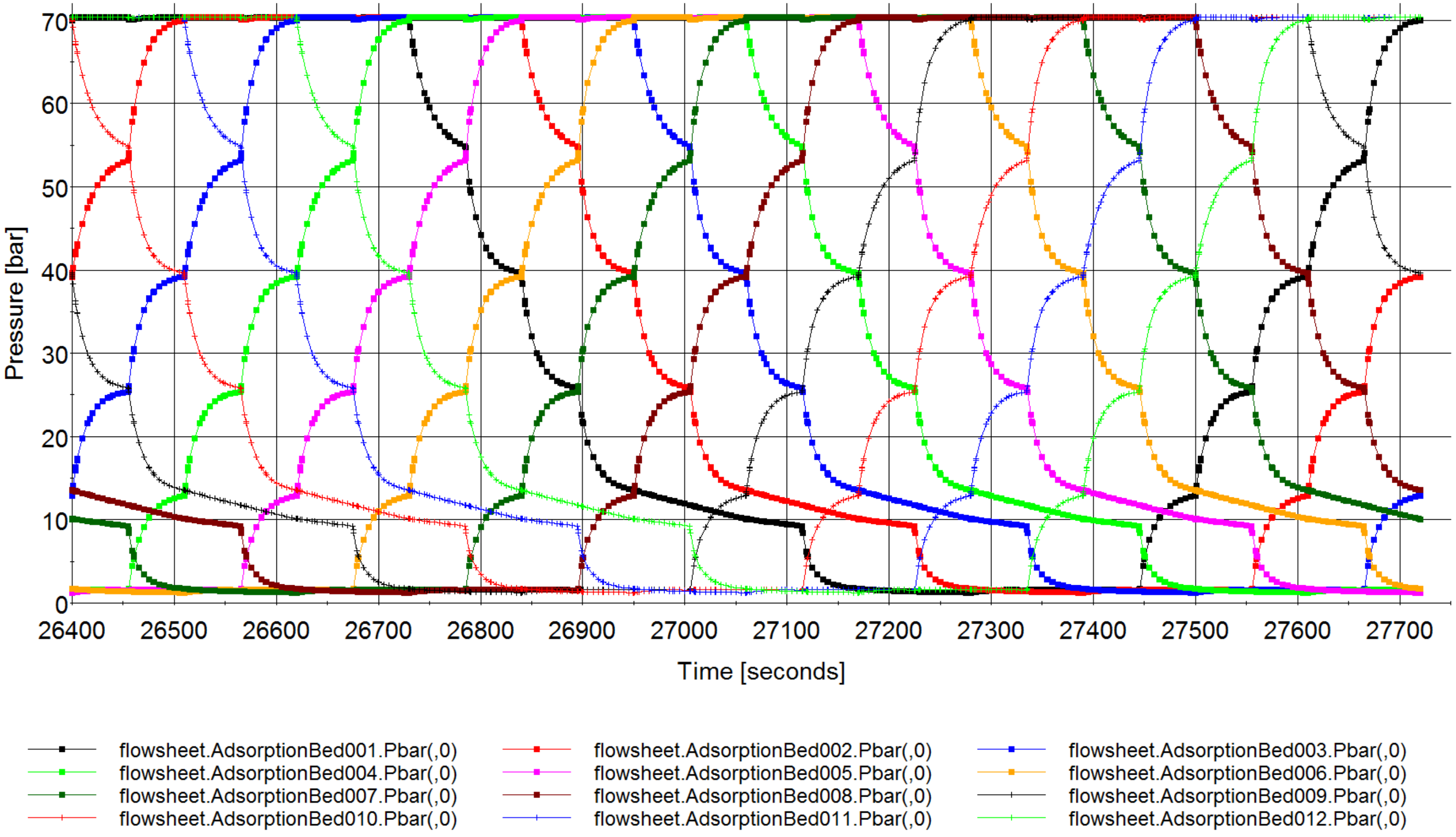
Pressure swing in each column



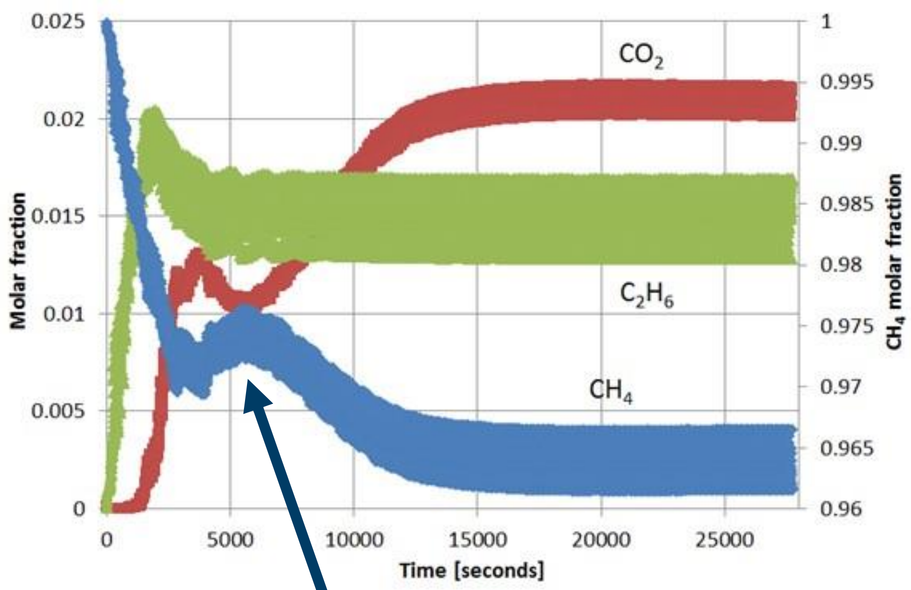
Column connections for multi-column PSA modelling.



Each simulation took 2 days…

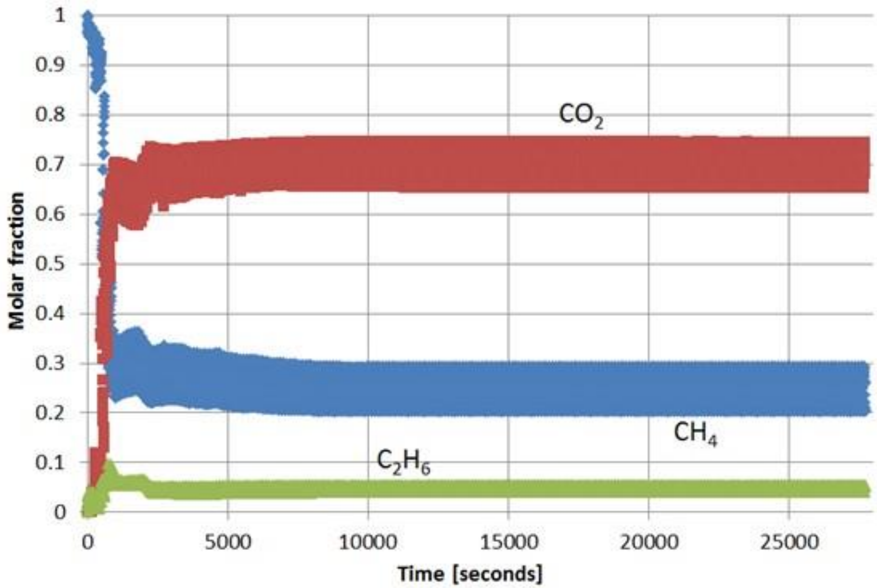
Pressure swing in each column

"light" product

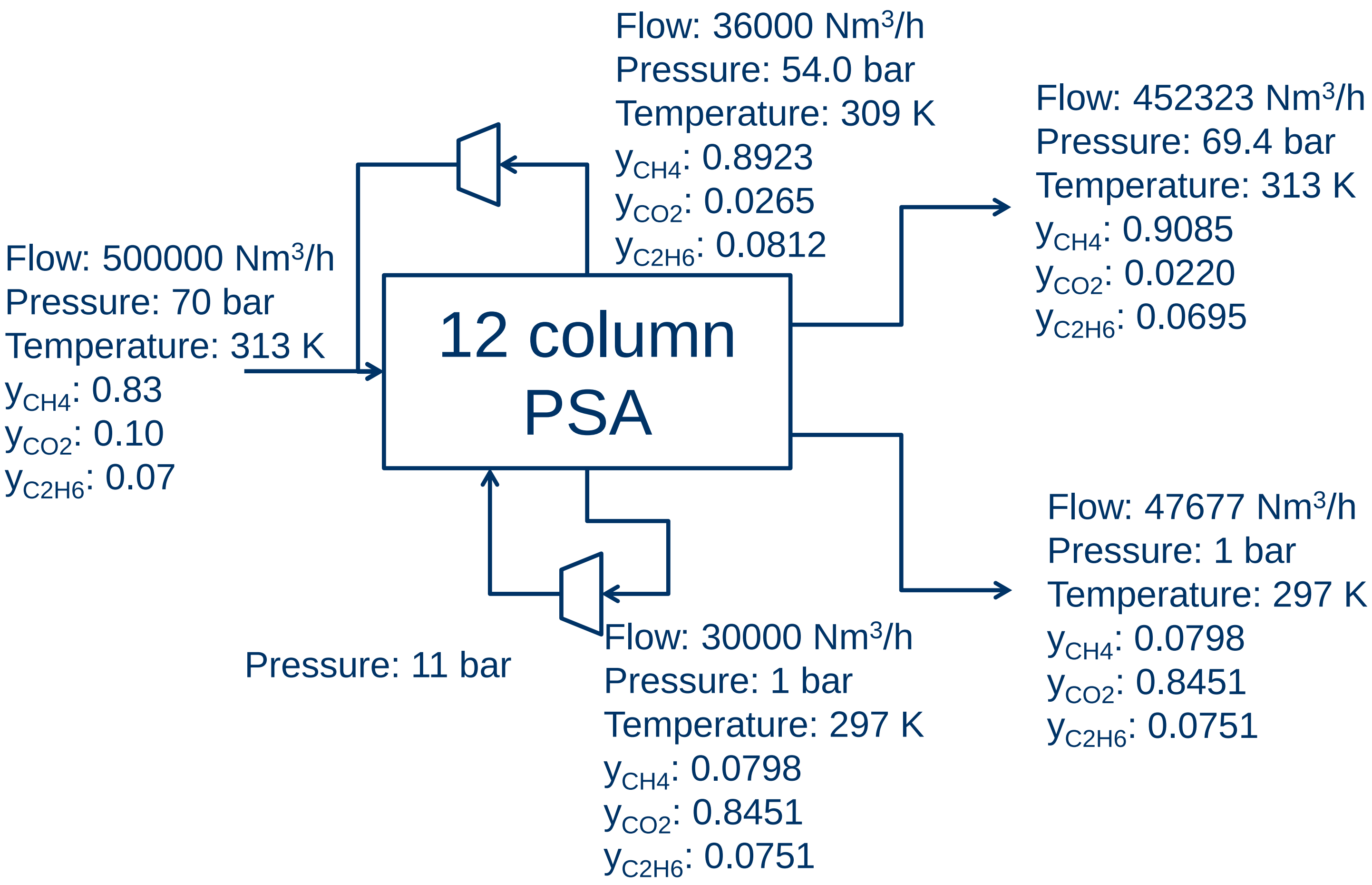


Typical "jump" from adiabatic processes

"heavy" product



The mass balance of the unit.



Note that CO_2 purity is not very high…

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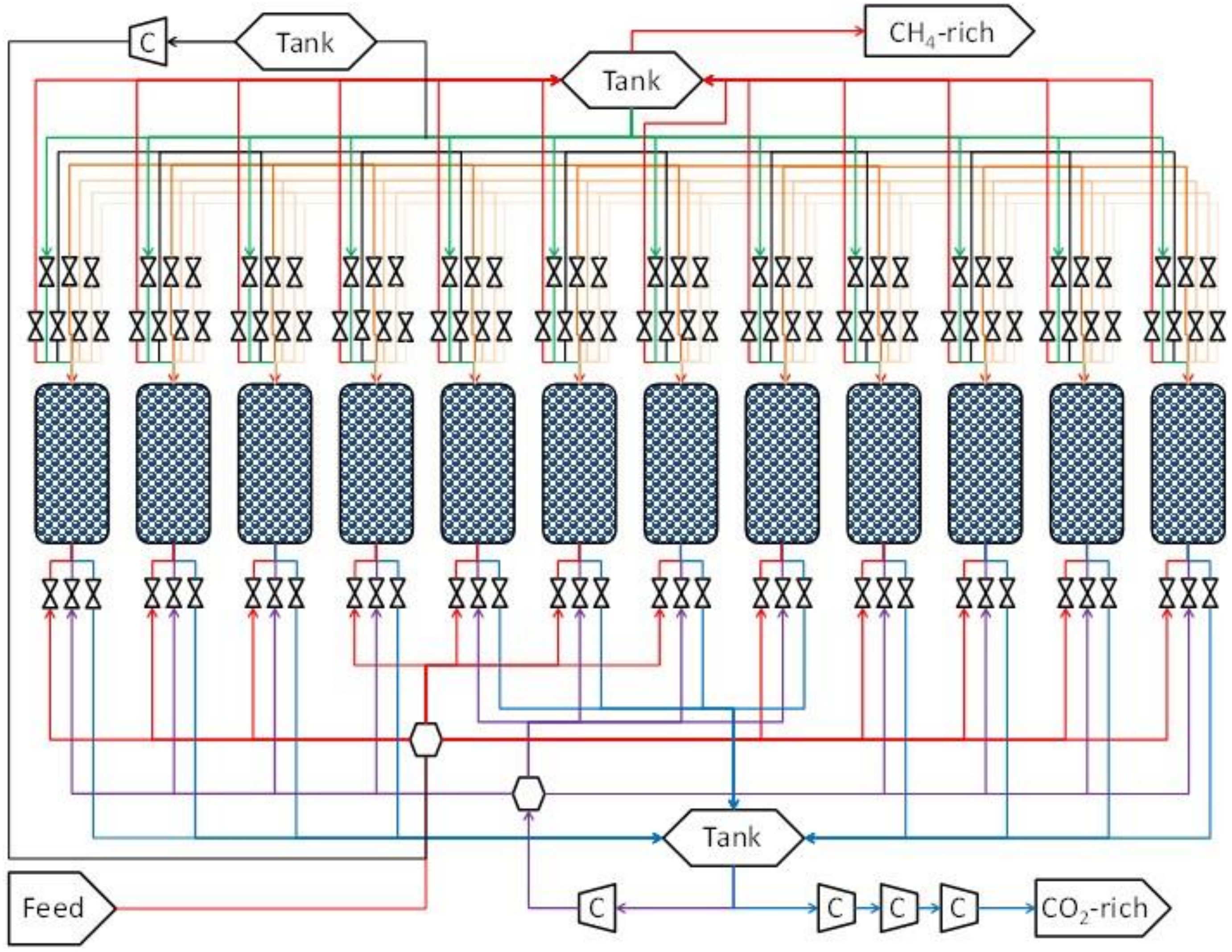
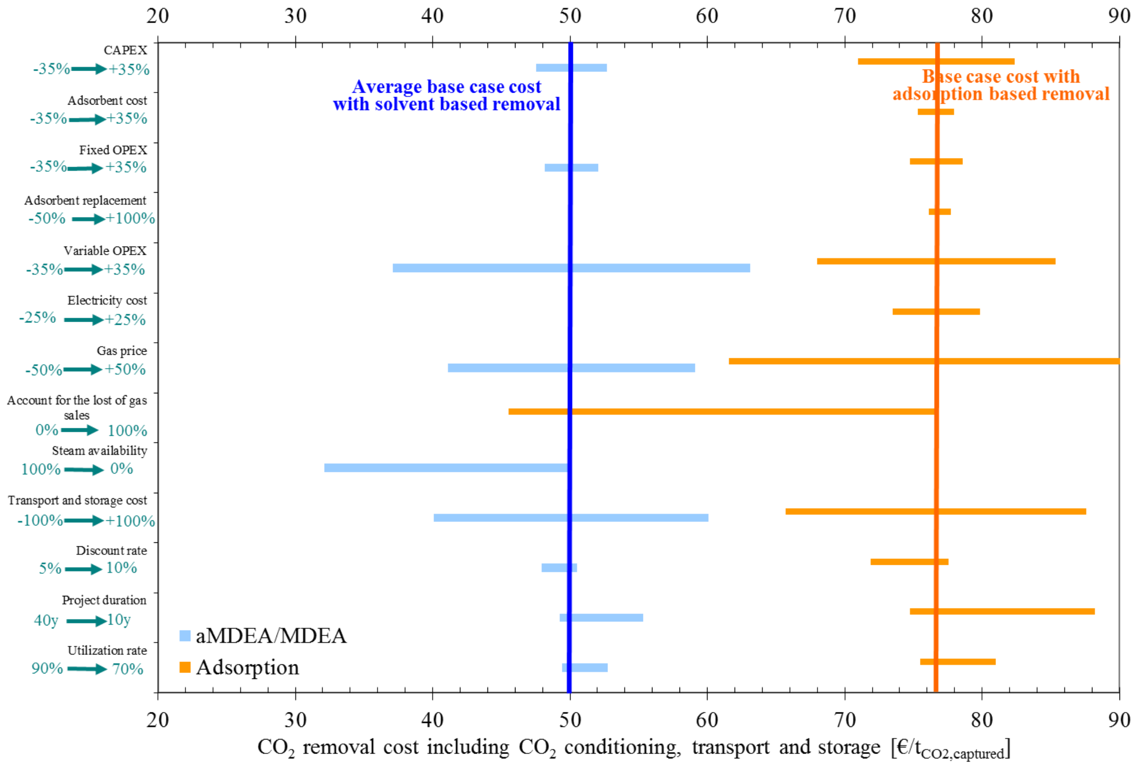
How does the PSA looks like?



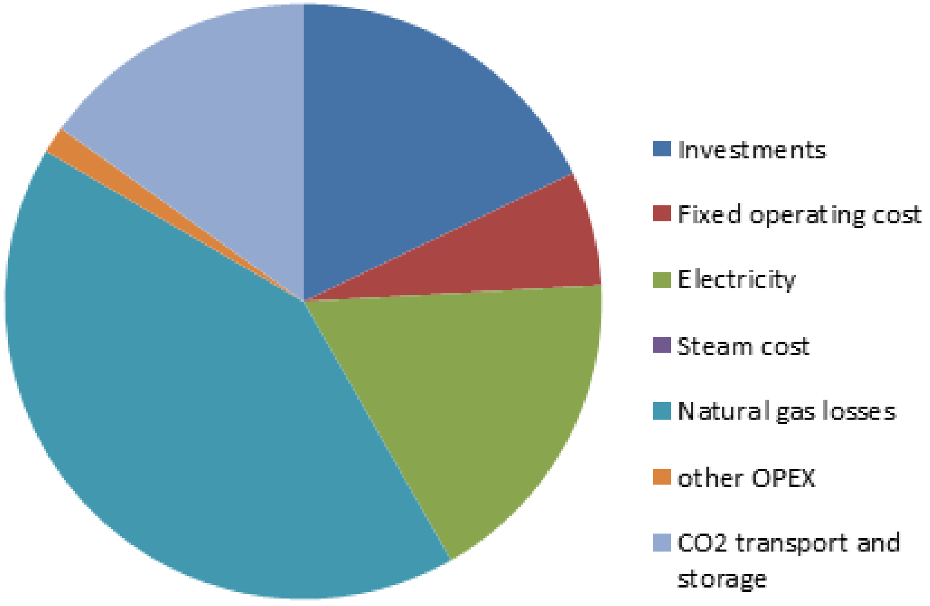
There are many valves.

The footprint of the unit will not allow utilization off-shore. Optimization of this part is reuired.

The truth is … expensive but we might go there



Sensitivity analyses on the CO_2 removal cost.



Break-down of the total discounted cost of the PSA unit.

The largest contribution to the cost is losses with CO_2 that can be improved by tuning process engineering.

Conclusions

Using gPROMS software, we have designed a PSA unit that can simultaneously produce high-purity CO_2 from natural gas and pipeline-quality natural gas.

Additional work in the cycle scheduling is required to improve the purity of CO_2. By reducing the amount of hydrocarbons lost in the CO_2, the economics will improve.

Using honeycomb monoliths we can drastically change the size of the unit. Most we have like 40% of the time spent in pressure equalization that can be reduced. By doing so, thermal effects will be more important.

The comparison between PSA and other techniques will probably be more positive if higher concentrations of CO_2 are used.

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The full report is now available!

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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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Acknowledgments

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