PSA SIMPLIFICATION FOR BIOGAS UPGRADING IN FARMS

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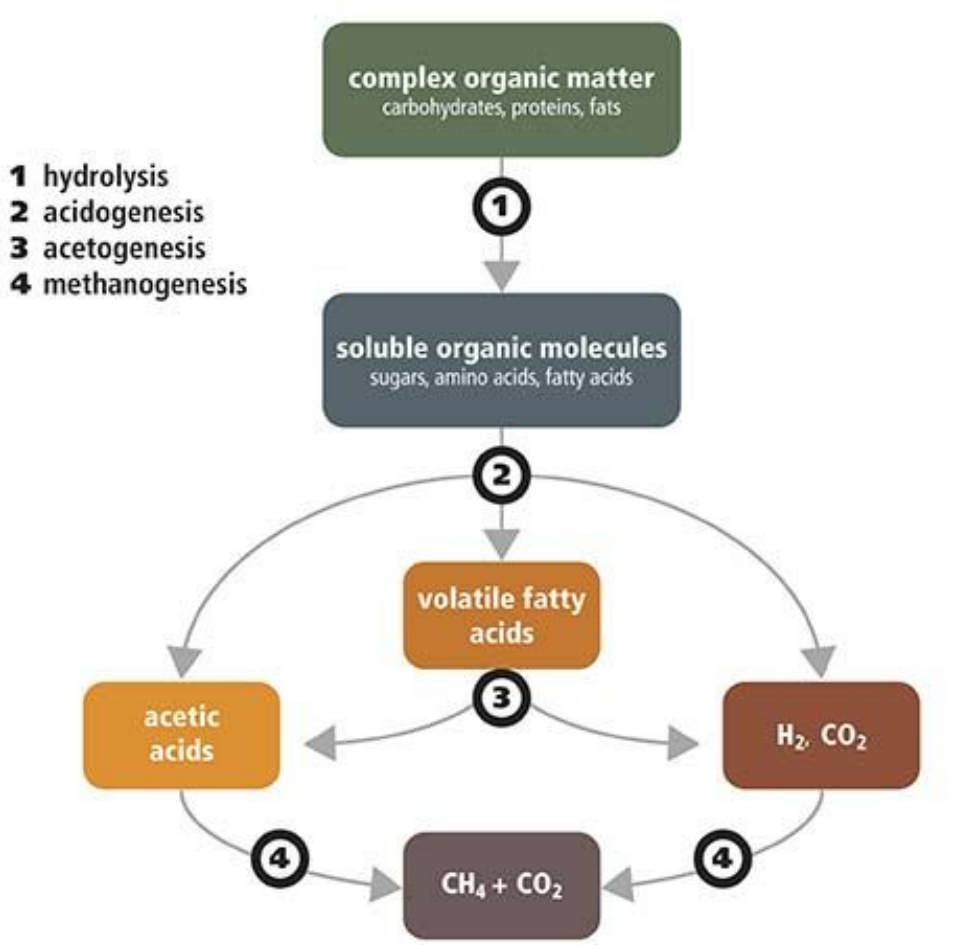
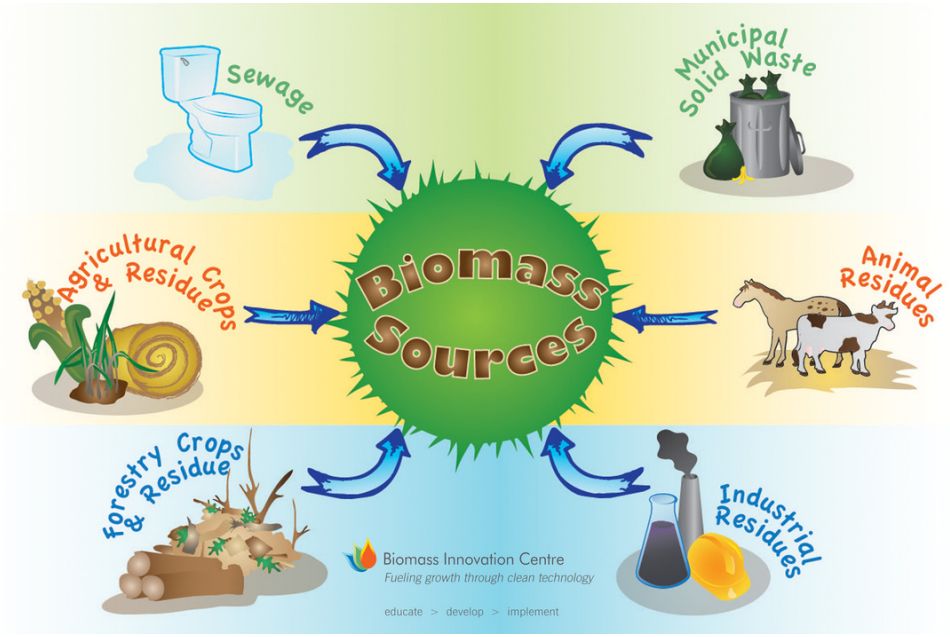
What is biogas?



Biological sources in presence of the right bacteria and lack of oxygen can produce methane (and CO_2 as by-product)



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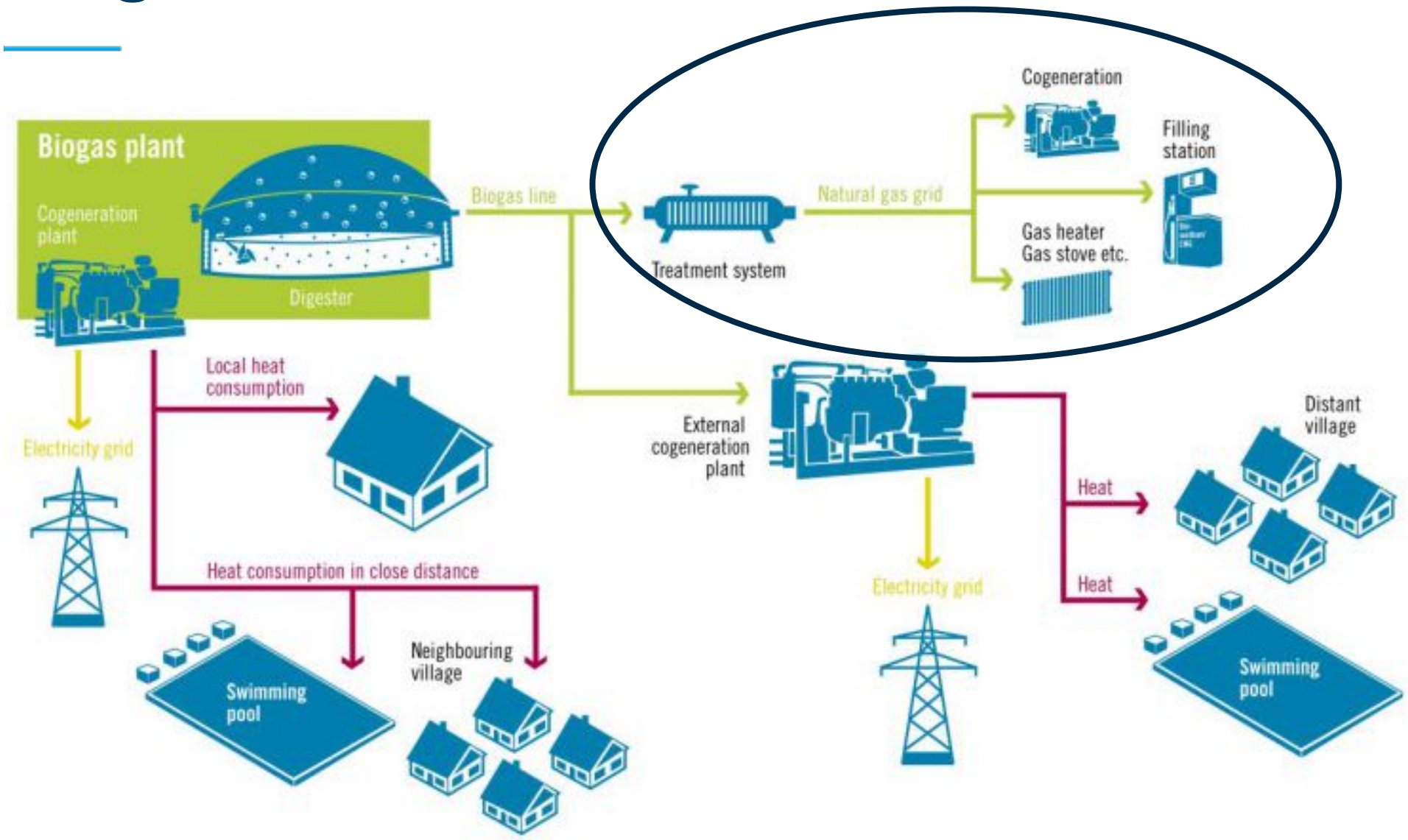
Biogas uses



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Biogas as a fuel

Basically all the existing fleets running on natural gas can be adapted at zero cost to use biogas.

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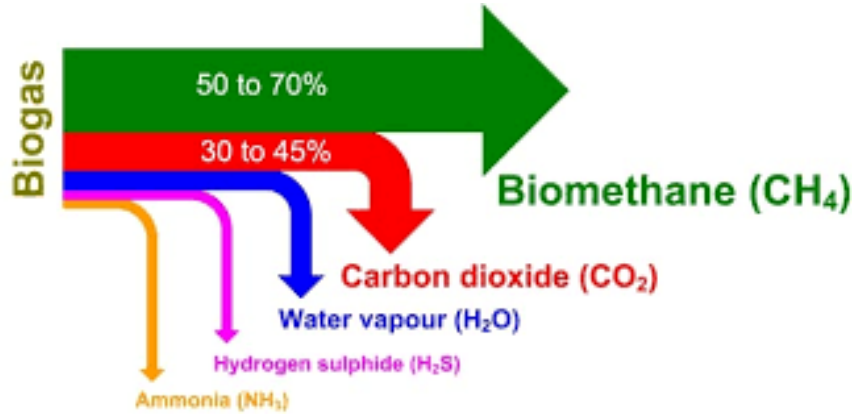
Why biogas needs upgrading?

Component	Agricultural waste	Landfills	Industrial waste
Methane CH_4	50–80	50–80	50–70
Carbon dioxide CO_2	30–50	20–50	30–50
Hydrogen sulphide H_2S	0.70	0.10	0.80
Hydrogen H_2	0–2	0–5	0–2
Nitrogen N_2	0–1	0–3	0–1
Oxygen O_2	0–1	0–1	0–1
Carbon monoxide CO	0–1	0–1	0–1
Ammonia NH_3	Traces	Traces	Traces
Siloxanes	Traces	Traces	Traces
Water H_2O	Saturation	Saturation	Saturation



Minimum bio-methane purity ranges from >97% to > 98.5%, depending on country legislation

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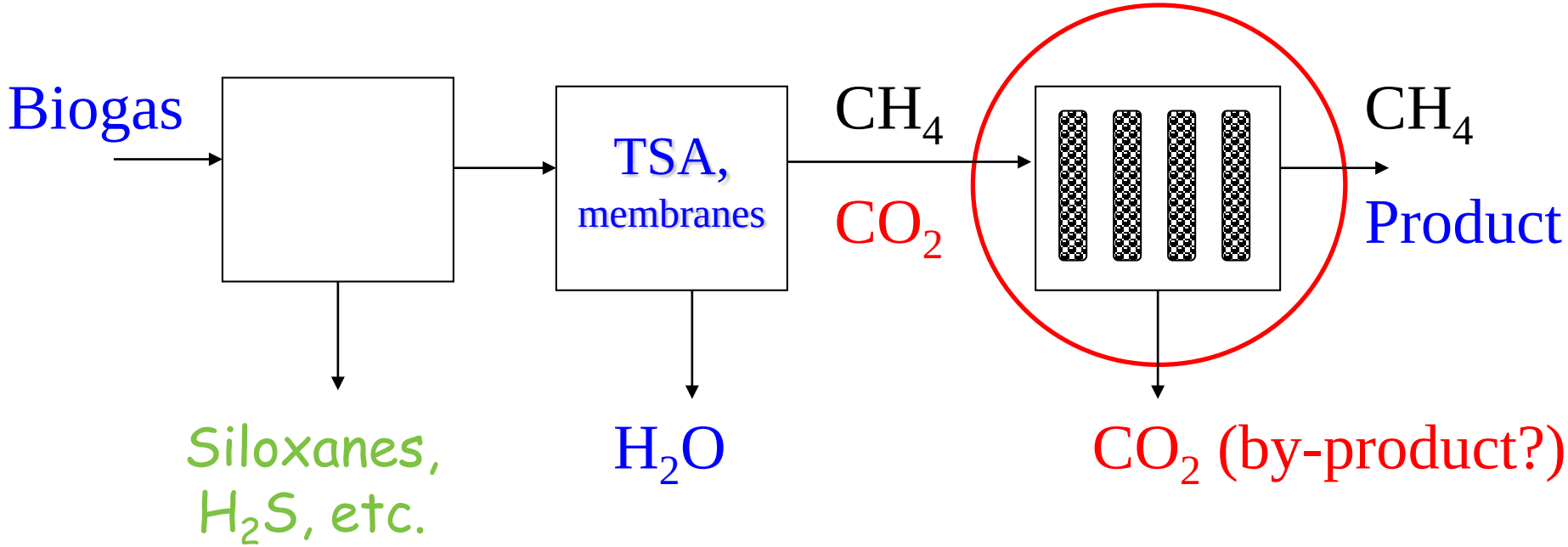
Biogas "upgrading"

The scheme is to obtain bio-methane for fuel or grid injection: we need to remove CO_2 to increase calorific power / m^3.



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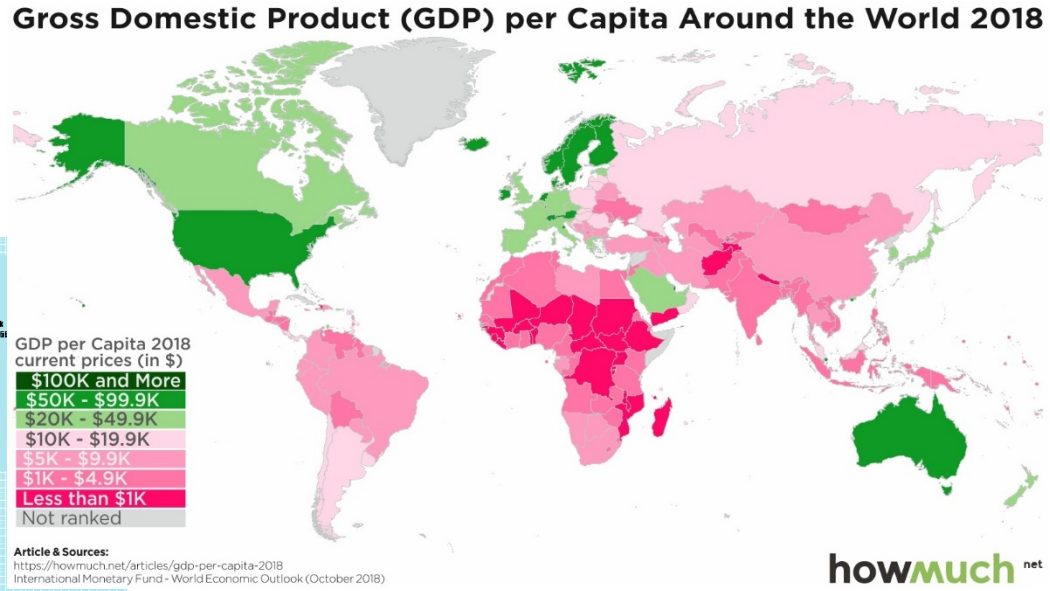
Example

One "traditional" plant

Upgrading module

But to make a global impact…



How do we implement bio-methane in low GDP countries?

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Economy / savings is a serious push up

One biogas plant

"Fitting" upgrading module

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Why fitting?

There is no standard size of upgrading unit for this plant

Even if done with same design principles, this farmer will most probably not be able to pay for it.

First choice: adsorbent

CMS

Zeolite

This is the most used commercial adsorbent for biogas upgrading

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First choice: adsorbent

Chemical Engineering Science 164 (2017) 148–157

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Separation of CO_2/CH_4 using carbon molecular sieve (CMS) at low and high pressure

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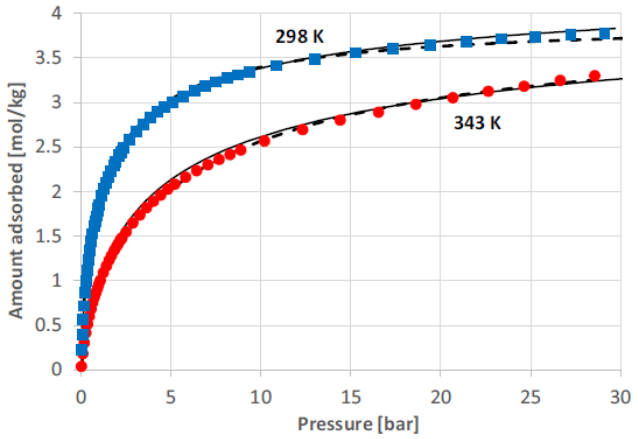

Fig. 2. Adsorption equilibrium of carbon dioxide at 298 and 343 K on CMS KP 407. Solid lines represent the fitting from MSL and dashed lines from DSL.

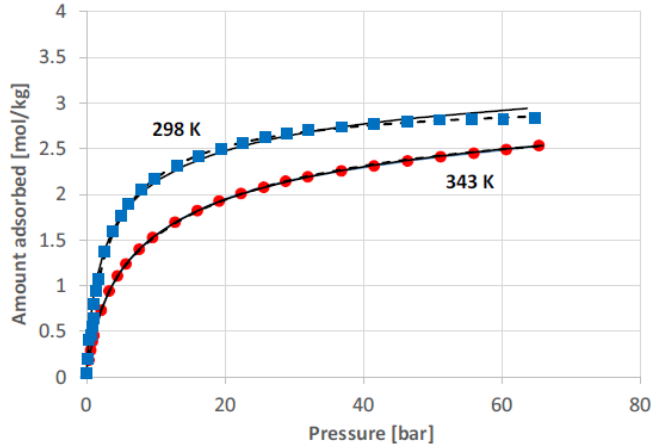

Fig. 3. Adsorption equilibrium of methane at 298 and 343 K on CMS KP 407. Solid lines represent the fitting from MSL and dashed lines from DSL.

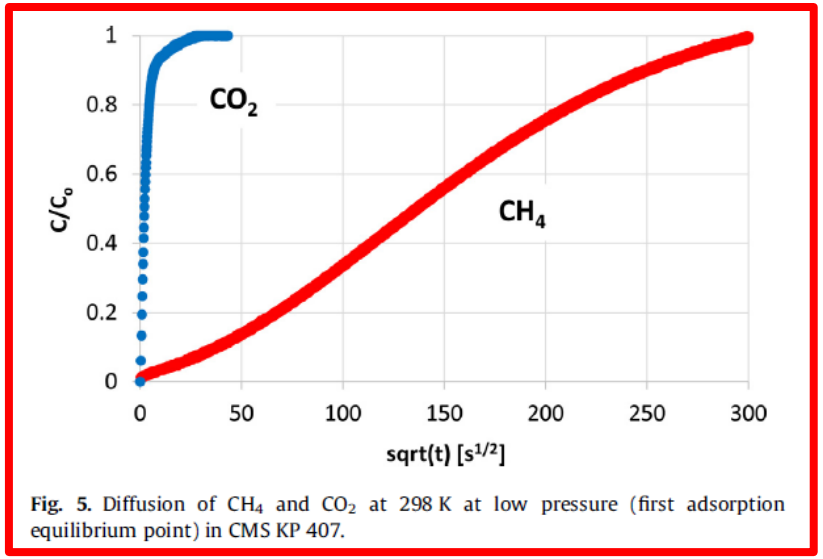

Fig. 5. Diffusion of CH_4 and CO_2 at 298 K at low pressure (first adsorption equilibrium point) in CMS KP 407.

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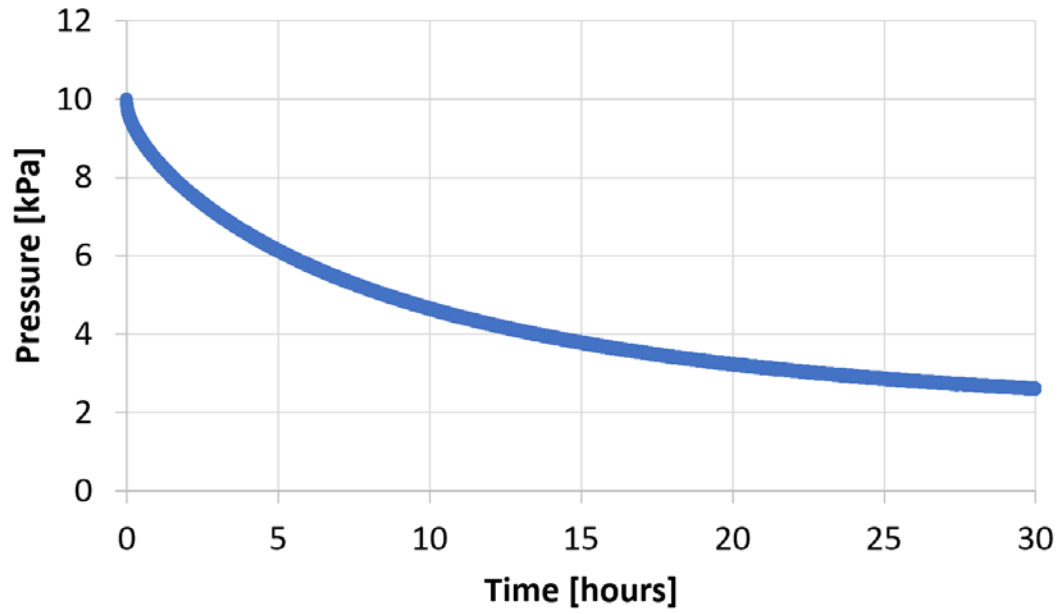
Measurements are problematic

- Each point takes 2 days to reach equilibrium. The isotherm takes 1 month.
  - Any small leak might be understood as adsorption.
  - If adsorption takes long, desorption takes much longer.



Equilibrium value : 2.1 kPa.

The "equilibrium criterion" is to keep the pressure within a certain interval of Y kPa for a given time of X seconds.
When we move to higher pressures, the Y interval is given by the error of the pressure transducer. Is this enough?

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Dynamic performance

- 4-column PSA unit from 0.1 – 70 bars (two pressure zones), 25-300 C and dry gases. Around 200 ml of adsorbent per column.

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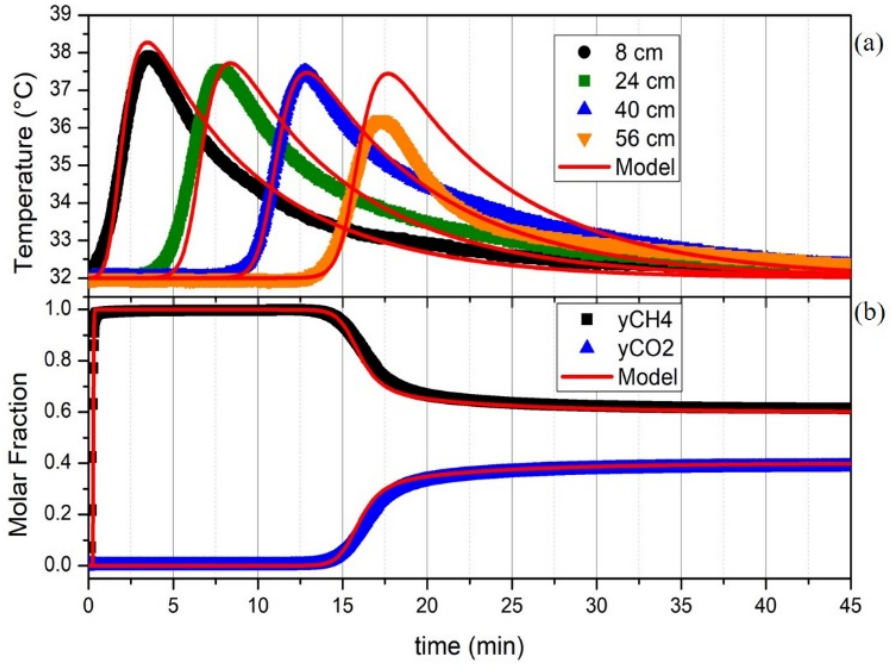
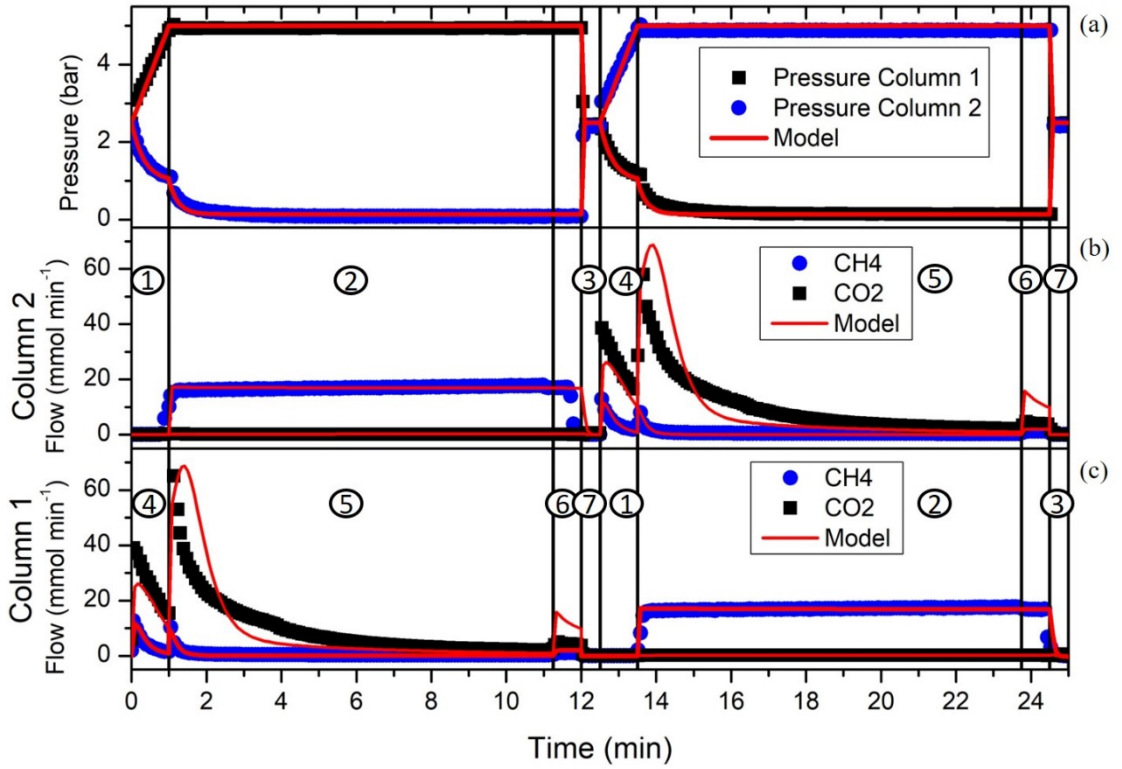
Breakthrough examples



Total pressure: 0.25 bar
NO DILUTION!



2-column cycle performance

Ind. Eng. Chem. Res., 2018, 57, 8057-8067

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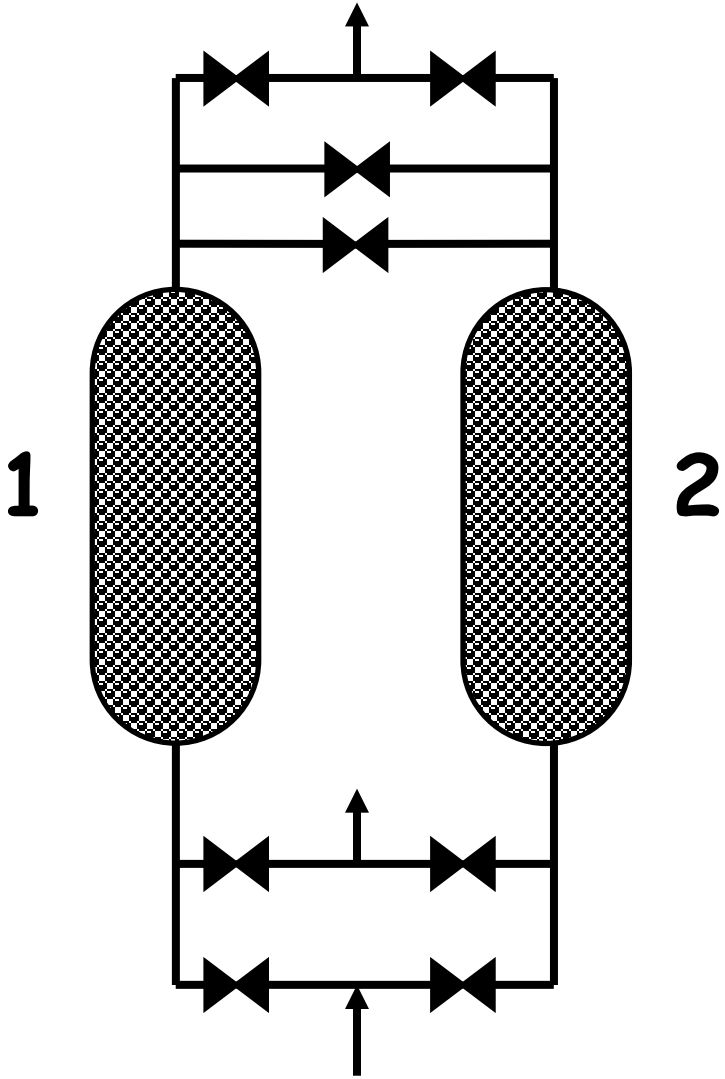
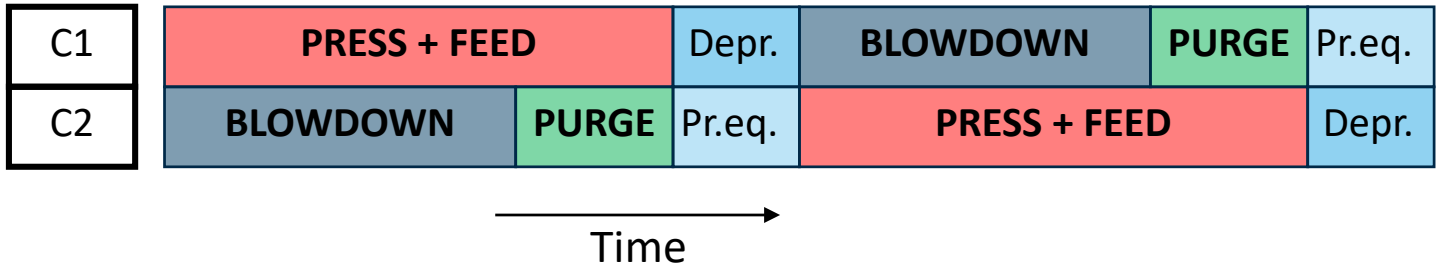
Second choice: the process (rarely a choice)



With this arrangement the cycle is not continuous.
We spend the same time using the adsorbent and regenerating it.
Recover almost all methane will be impossible.



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Rationale to define a cycle

- The feed should be continuous.
- Gas velocity cannot be high to avoid particle crushing

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

- There is no theoretical solution to tell which PSA cycle is optimal

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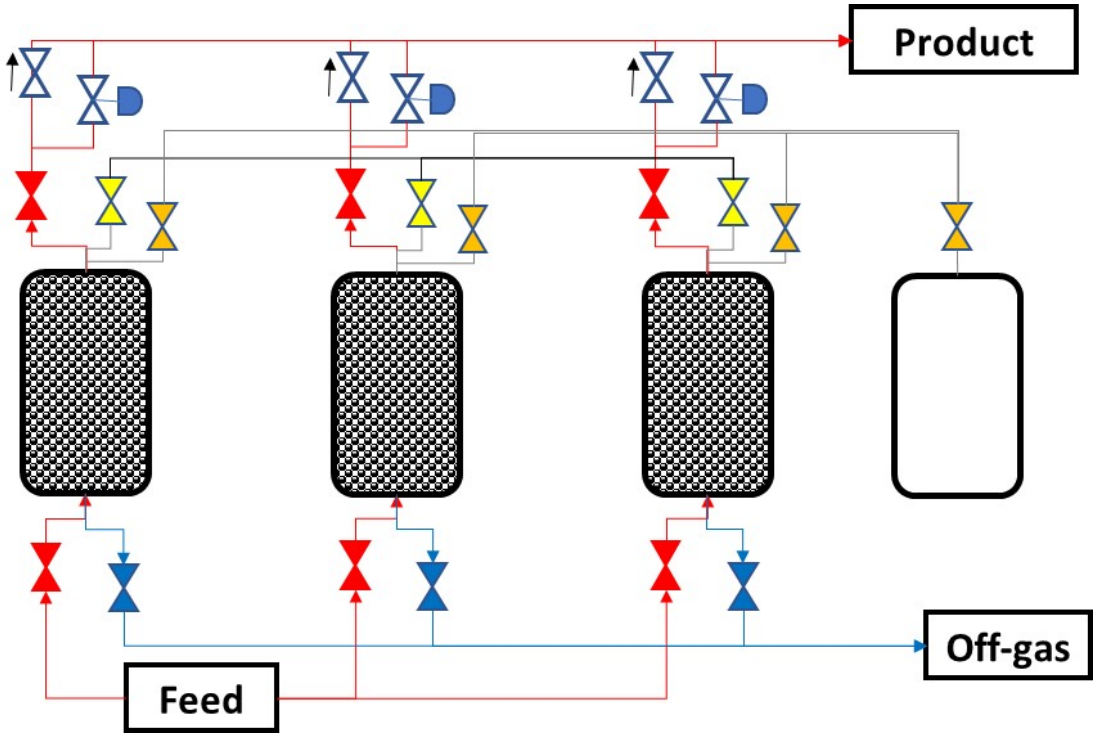
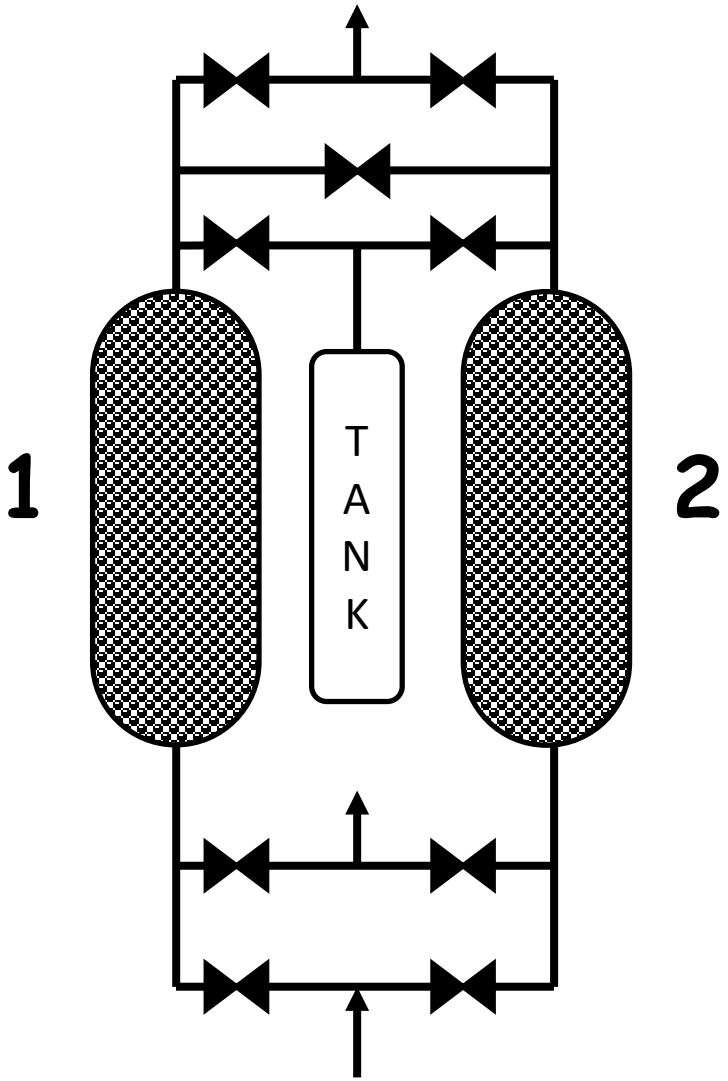
One possible configuration



With this arrangement the cycle is continuous.
We use the time only 1/3 of the cycle time.
We used more valves and more equipment.
Very little methane slip.

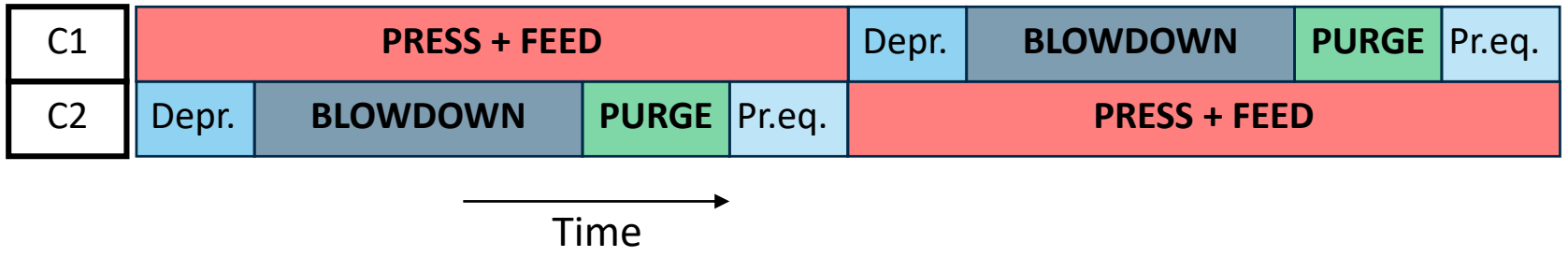
Col. 1	FEED								D1	D2	BLOW								E2	E1	Pr	
Col. 2	B		E2	E1	Pr				FEED								D1	D2	BLOW			
Col. 3	D1	D2	BLOW									E2	E1	Pr	FEED							
Tank	T1			T1				T1					T1				T1			T1		

"Something in the middle" and simpler



With this arrangement the cycle is continuous!

Feed time is equal to regeneration and conditioning of the column (more efficient). Tank allow us pressure equalization and eventual purge. Possible low methane slip. Much less equipment!



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MATHEMATICAL MODEL

System of partial differential equations

Material balances

Gas phase:

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

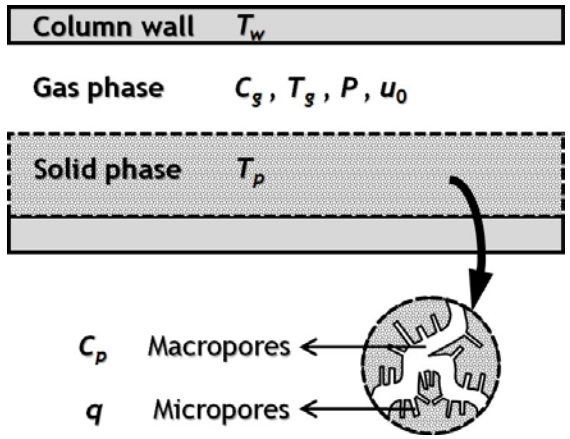
Solid phase:

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

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



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

Momentum balance

Ergun Equation:

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

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:

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

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

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

Van't Hoff equation

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

Water?

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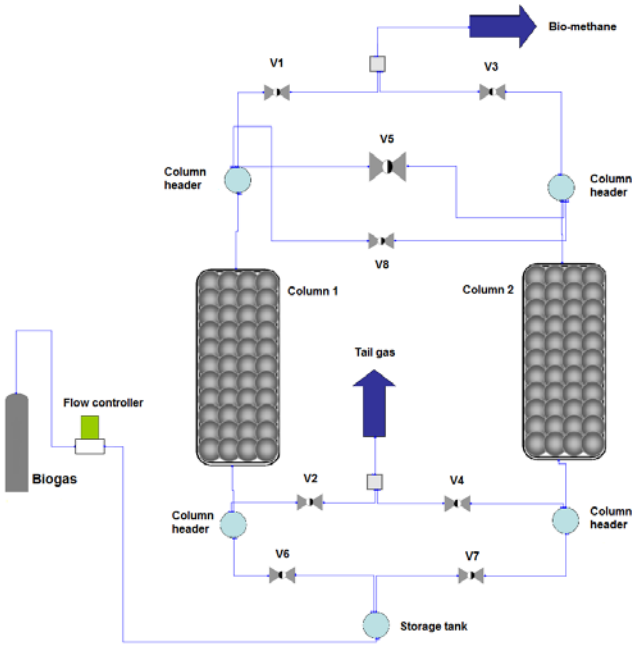
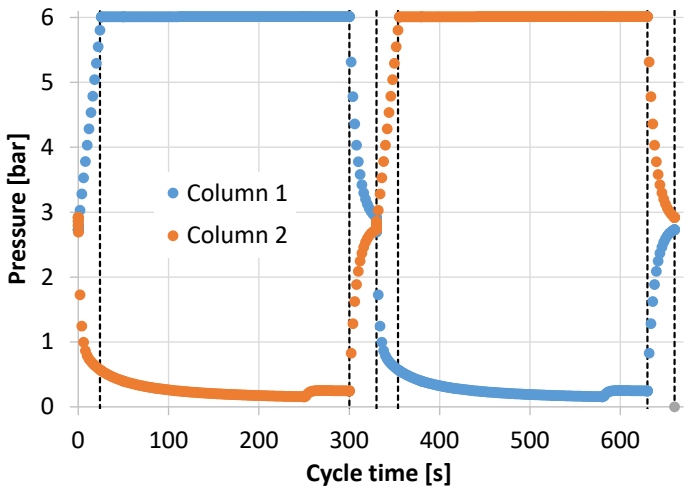
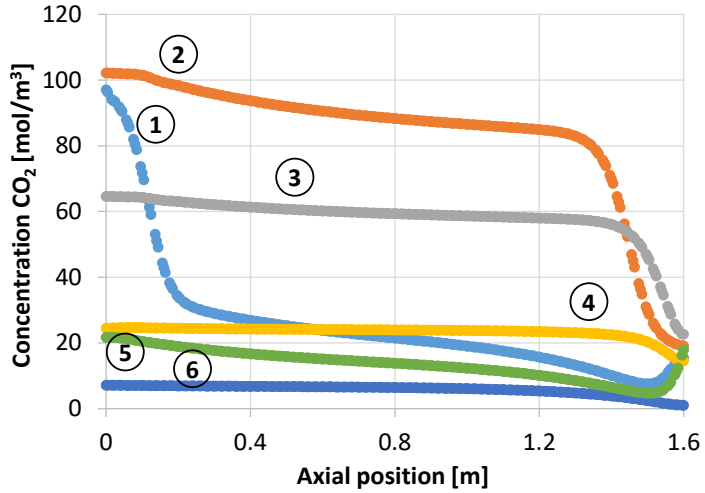
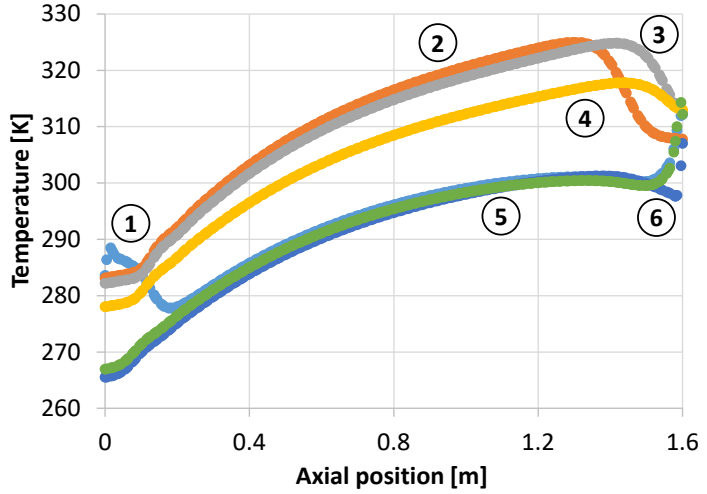
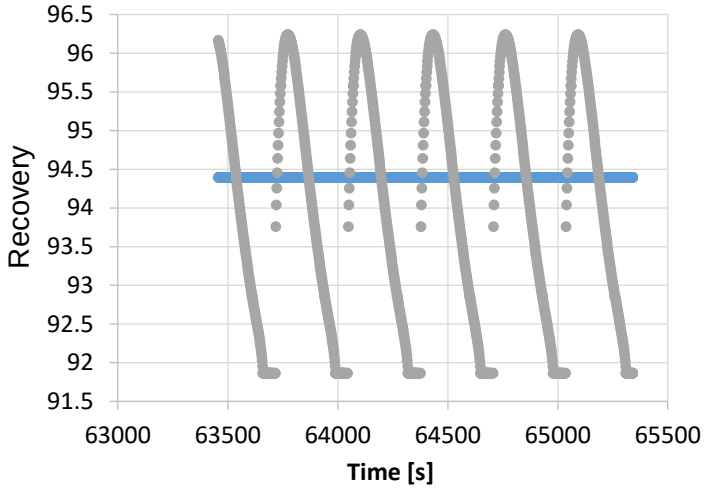
What happens inside the column?











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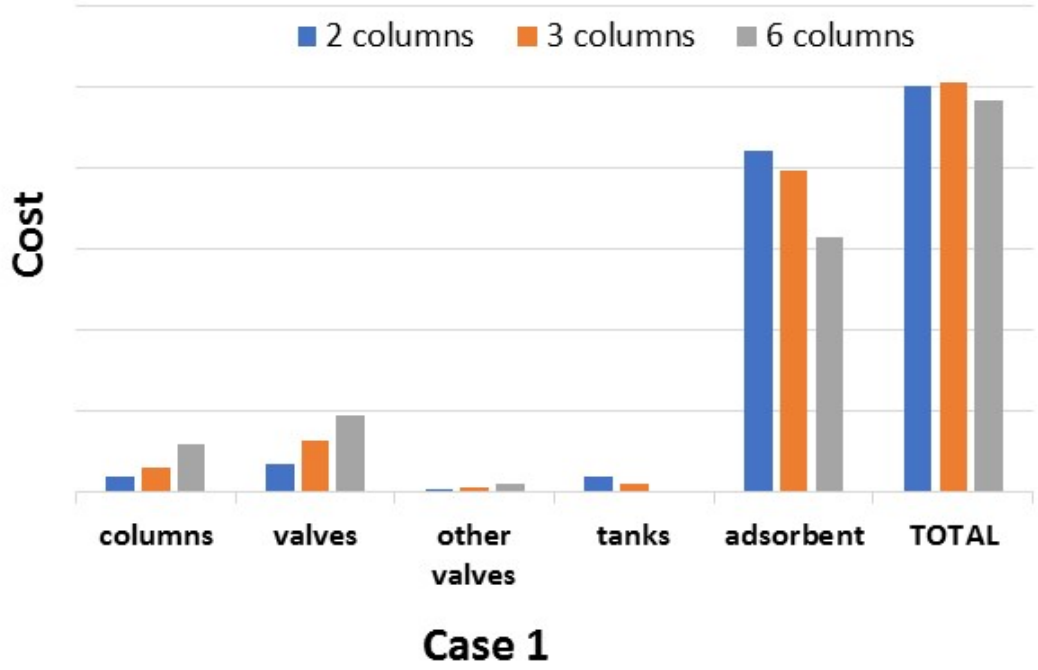
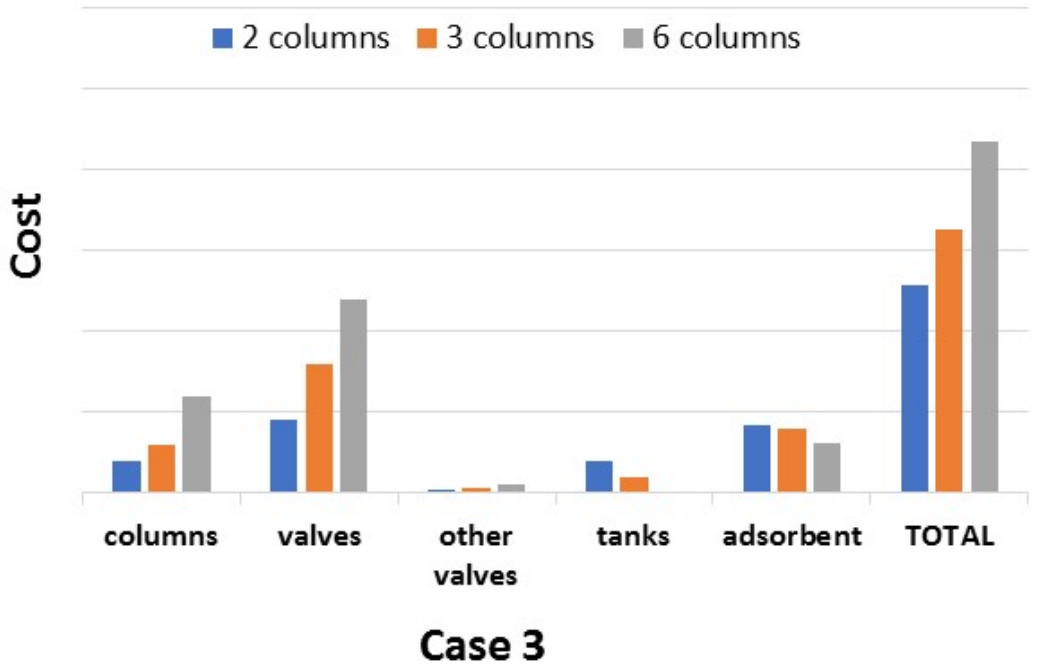
Process selection: all produce >98% CH_4.

PSA configuration	2-column + tank	3-column + tank	6-column
Superficial gas velocity [m/s]	0.13	0.20	**0.25**
Total adsorbent weight [kg]	420.9	396.5	**315.7**
Cost scenarios	Case 1	Case 2	**Case 3**
Cost of adsorbent [€/kg]	5*commercial	3*commercial	**commercial**
Cost of automatic valves [€/unit]	commercial	0.75*commercial	**5*commercial**
Cost of valves [€/unit]	commercial	commercial	**commercial**
Cost of columns [€/unit]	**commercial**	**commercial**	**2*commercial**

Cost cases





Probably not good for our farmer.

For large sources it means that cheaper materials can push cost down!

Better scenario for our farmer.

Perhaps unrealistic for larger sources

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Conclusions

- For small-scale biogas upgrading by PSA, new design principles should be used focusing on economy
- For large sources of biogas, improvements on the adsorbent might have larger impacts than improvement of process design.
- Whatever we do for small-scale PSA units, we need good and cheap valves.

Acknowledgments

This work was partly funded by the Innovation Fund Denmark (IFD) under File No. 5157-00008B, HiGradeGas (www.higradegas.eu). R. L. S. C. thank to CAPES (Coordination for the Improvement of Higher Education Personnel) the financial support.

Perfection is achieved, not when there is nothing more to add, but when there is nothing else to take away. (Saint Exupéry).

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Technology for a better society