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Acidic gas removing from biogas by adsorption: study for assessing the performances of Metal-Organic Frameworks

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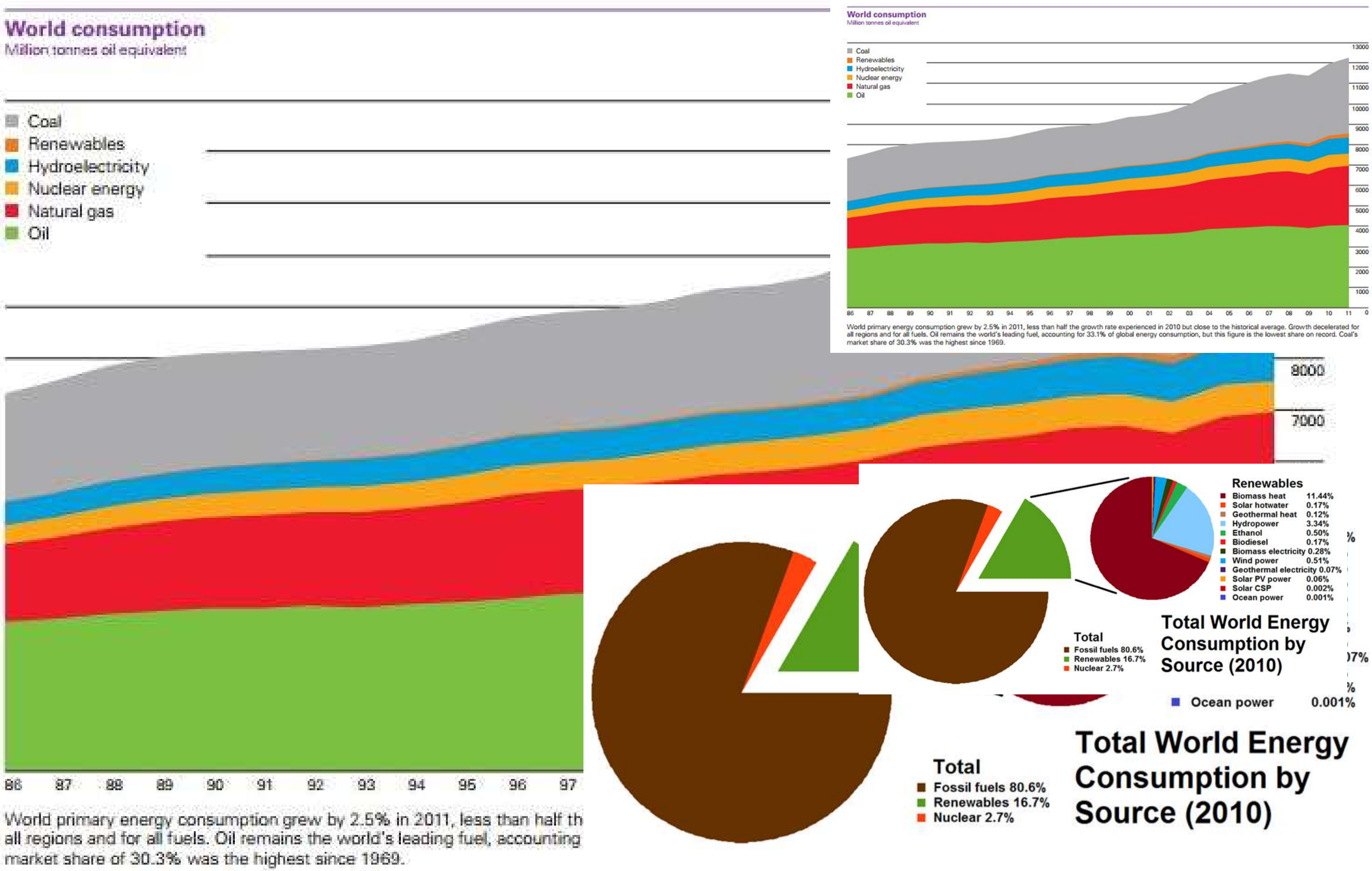
POLYTECH MONS

- Increase in global energy production



- Biogas production
  - Wastewater treatment plant
  - Landfills
  - Industrial organic waste
  - Organic waste digesters

Compound	Minimum	Maximum
CH_4	40	75
CO_2	15	60
H_2O	5	10
H_2S	0.005	2
Siloxanes	0	0.02
VOV	traces	0.6
NH_3	traces	1
O_2	0	1
CO	traces	0.6
N_2	0	2

→ Wide variety of compositions (% vol)

CO_2 : Decrease of the calorific value

H_2S : Toxicity Corrosion Formation of SO_x

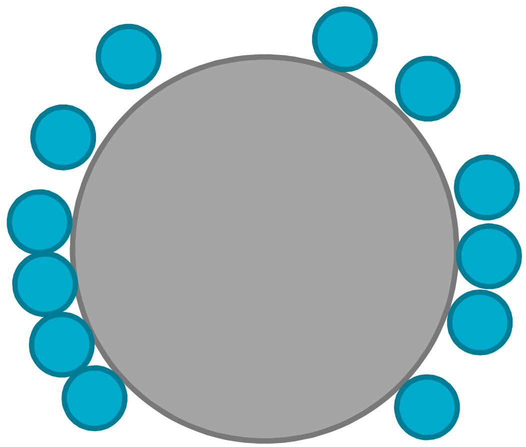
→ Maximum allowable concentrations before injection into the distribution network

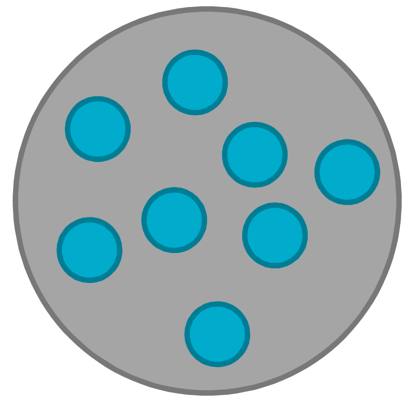
CO_2 : 2.5 % (molar basis)

H_2S : 5 mgS Nm^{-3} (≈ 3.5 ppm)

→ Separation and purification techniques

- **Ad**sorption (≠ **Ab**sorption)



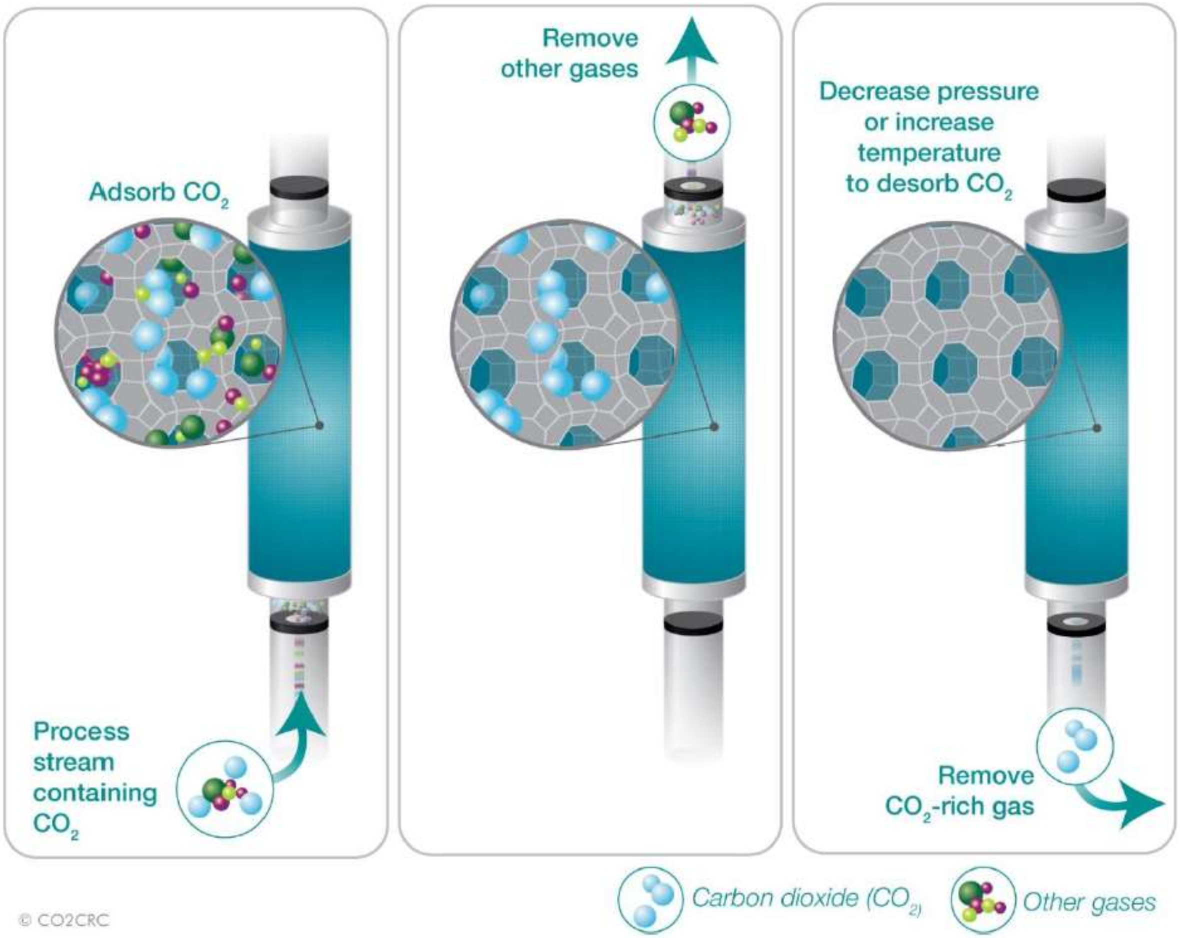


Force field on the surface of a solid

➔ passage of a molecule from a fluid phase (gas or liquid) to an adsorbed phase: fixation on the surface of the solid

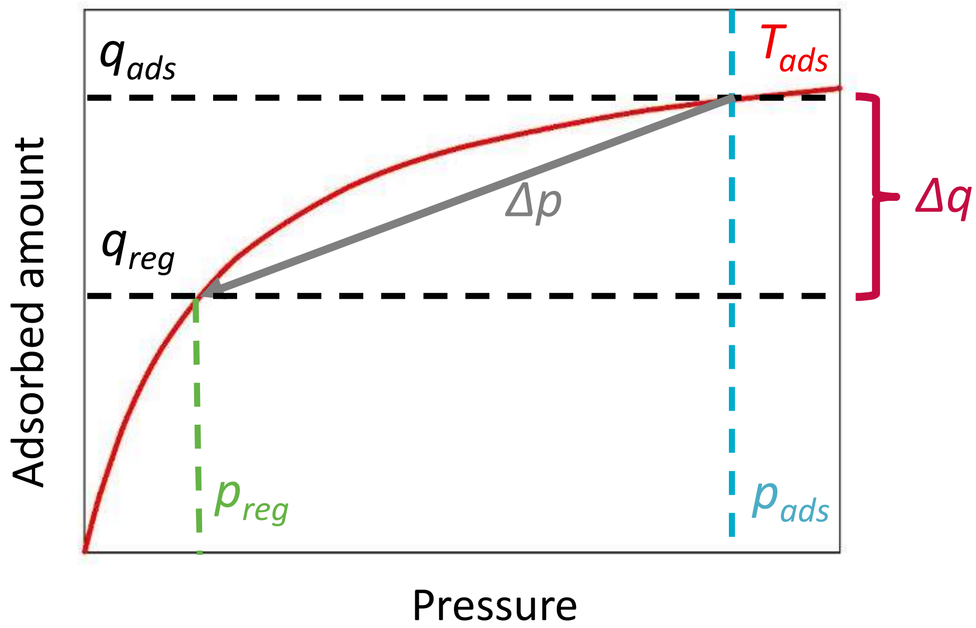
- Adsorbent
  - Specific surface area (several thousand m2 g-1)
  - Porous volume (cm3 g-1)
  - Pore size (from a few Å to a few nm)

Adsorption Principe



- Adsorption processes
  - Joint elimination of both compounds
  - Concentrations below limits
  - Low regeneration costs

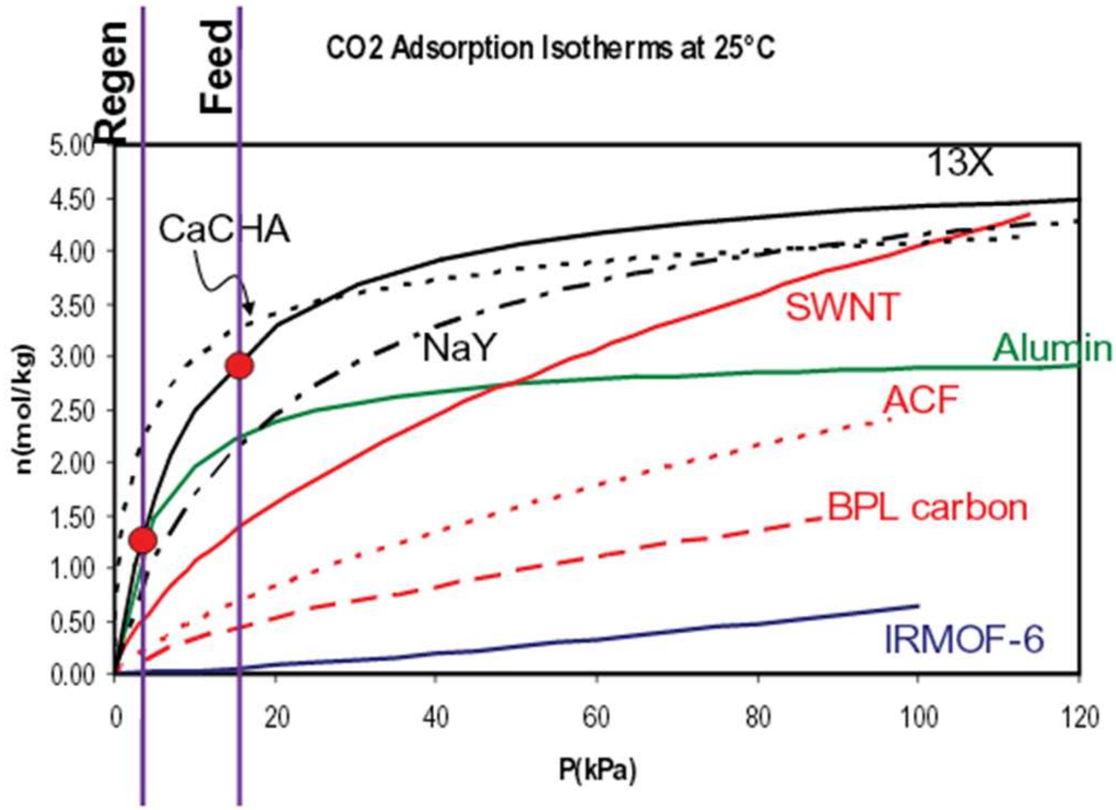
- Regeneration
  - Decrease of pressure
  - Working capacity (Δq)



- PSA
  - Pressure Swing Adsorption
  - Large amount of CO_2
  - Fast cycles

→ Study of porous hybrid solids (numerous types and stability against H_2S

- Key challenge: The selection of a optimal adsorbent with the required
  - ✓ Adsorption capacity

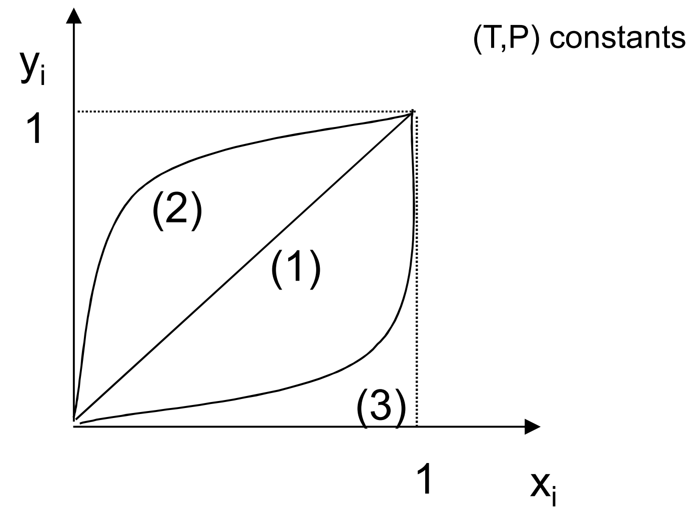


Paul A. Webley, Monash University

Selectivity

$$S_{CO2/N2} = \frac{x_{CO2}}{x_{N2}} \frac{y_{N2}}{y_{CO2}}$$

Difference of enthalpies : $\Delta H_{ads,\,CO2} - \Delta H_{ads,\,N2}$



- Other challenges
  - ✓ Chemical stability (water)
  - ✓ Synthesis : environmentally friendly
  - ✓ Scale up and shaping
  - ✓ Price
  - ✓ ….

- Evaluate new materials for biogas purification

  - Screening : Porous Hybrid Solids Resistant to H_2S and Possessing Attractive Properties :

    - working capacity (pure isotherm measurements)
    - selectivity (equilibrium simulations in mixtures)

    → selection criteria

  - Selection: PSA process simulations and performance evaluation :

    - Purity of CH_4 (%)
    - Recovery of CH_4 (%)
    - Productivity of the PSA

    → thermodynamic data

    → kinetic data (development of a measurement system)

Context

Porous hybrid solids

Screening of adsorbents

Thermodynamic study

Evaluation of adsorbents for PSA processes

PSA process simulations

Thermodynamic data

Kinetic data

Results

Conclusions et perspectives

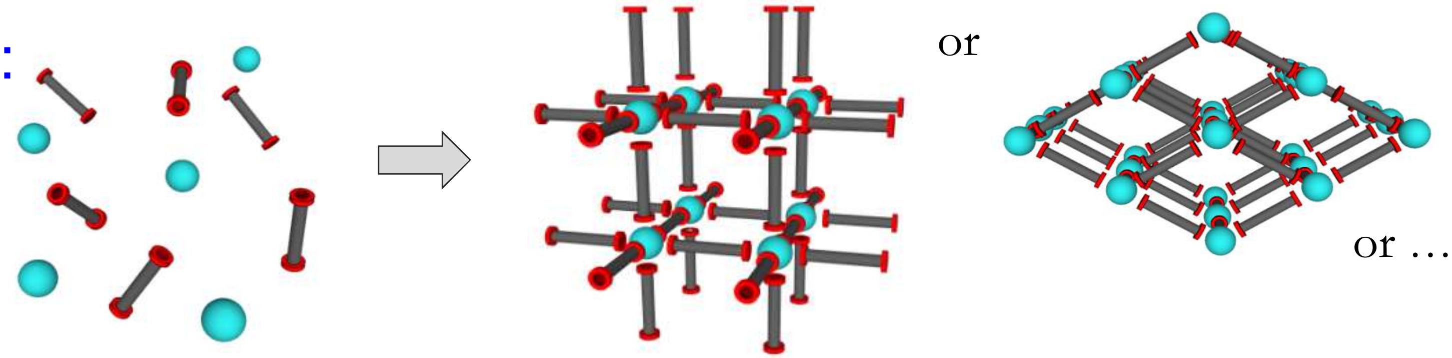
Metal Organic Framework

Hybride solids:

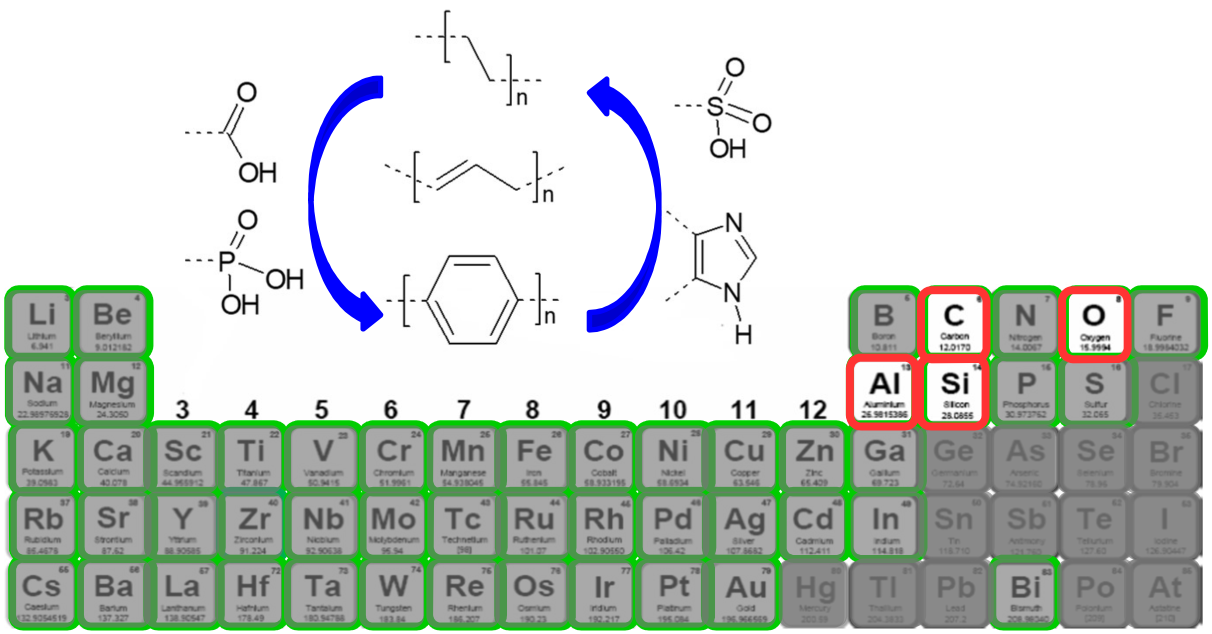
Metal ions

or clusters

+ Ligands



→ Multifunctional Solids



SBU (secondary building unit)→Building blocks 6.2 - 16.5 Å

- 1D networks

8.5 Å ↕

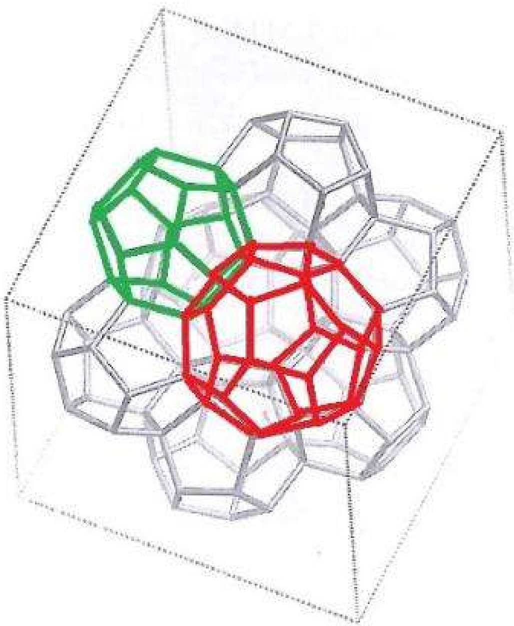
- 3D Crystal lattices

6.3 - 12.3 Å *

8 - 11 Å *

*http://commons.wikimedia.org/User:Cdang (GFDL Licence)

- Superstructures



25 Å

29 Å

- Materials studied (resistant to H_2S)

MIL : Matériaux de l'Institut Lavoisier (Versailles, France)

UiO : Universitetet i Oslo (Oslo, Norvège)

CAU : Chistian-Albrechts-Universität (Kiel, Allemagne)

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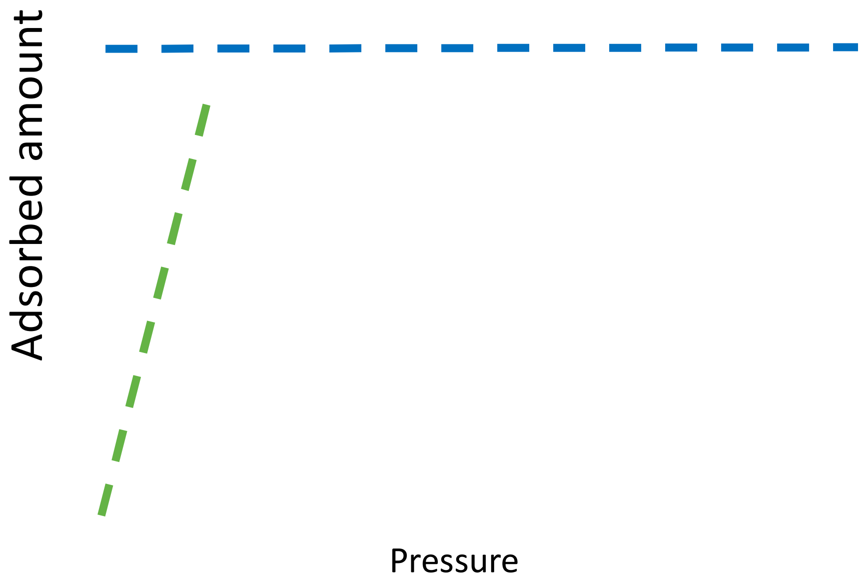
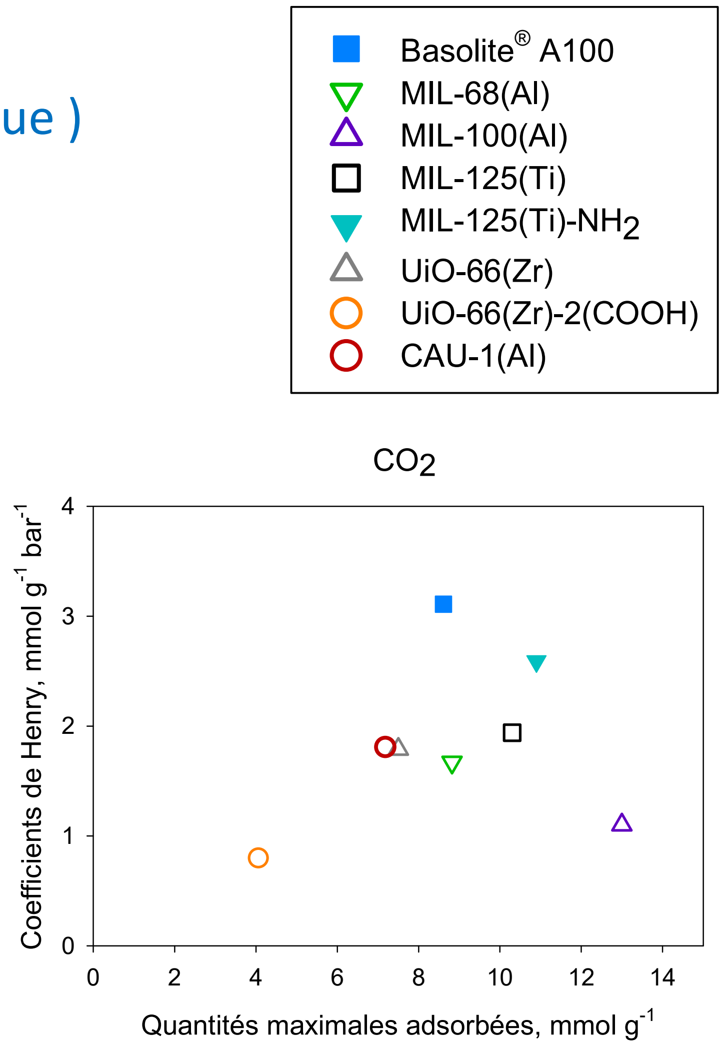
- Pure isotherm measurement at 30°C

Henry Coefficient (slope at the origin)

Maximum amount adsorbed (plateau value)





- Selection criteria

$$\alpha = (\Delta q_i/\Delta q_{CH_4})\left(S_{i/CH_4}^{prod}\right)^2/\left(S_{i/CH_4}^{purge}\right)$$

$$\Delta q = q_{ads} - q_{reg}$$

$$S_{i/CH_4} = \frac{x_i}{x_{CH_4}} \Big/ \frac{y_i}{y_{CH_4}}$$

Adsorbed amount

Pressure

Selection criteria

$$\alpha = (\Delta q_i/\Delta q_{CH_4})\left(S_{i/CH_4}^{prod}\right)^2/\left(S_{i/CH_4}^{purge}\right)$$

$$\Delta q = q_{ads} - q_{reg}$$

$$S_{i/CH_4} = \frac{x_i}{x_{CH_4}} \Big/ \frac{y_i}{y_{CH_4}}$$

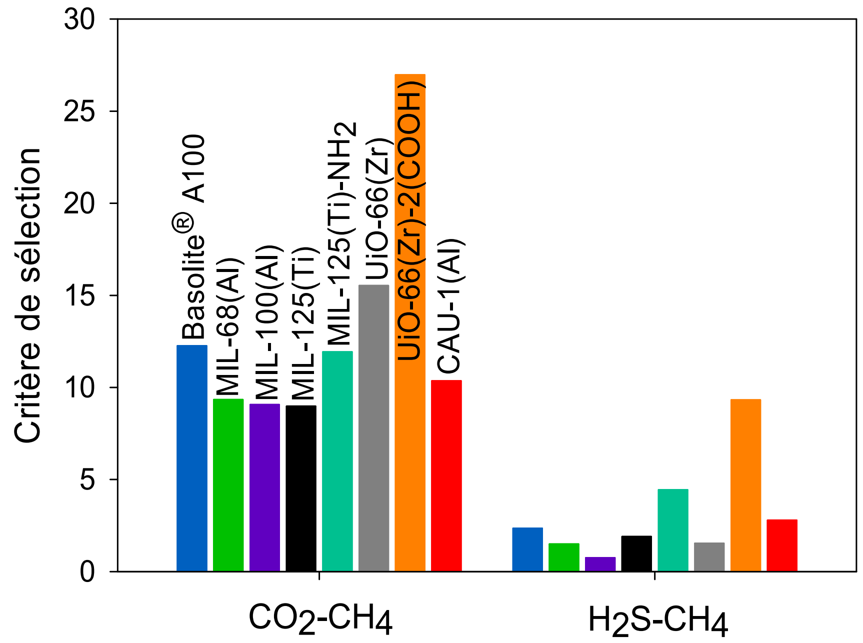
Pressure (bar)		Molar fraction	
Production	**Purge**	**$CO_2 - CH_4$**	**$H_2S - CH_4$**
4	1	0.4 – 0.6	0.005 – 0.995

➔ Selection for shaping :

- UiO-66(Zr)-2(COOH)
- MIL-125(Ti)-NH_2
- Basolite® A100

Comparaison with

Benchmark zeolite 13X



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- Simple PSA process based on Skarstrom cycle
- 2 columns in opposite step

  Continuous production

- 4 steps

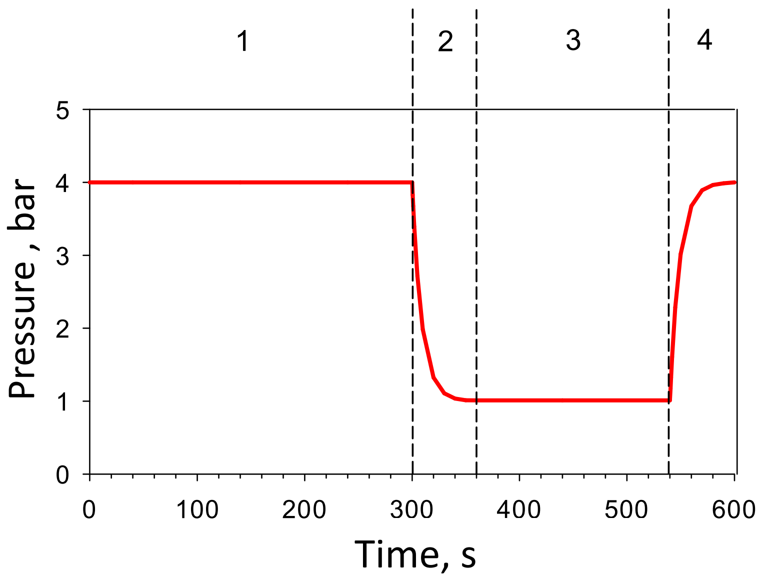
  1 : Production (4 bar) : 300 s

  2 : Depressurisation (4 → 1 bar) : 60 s

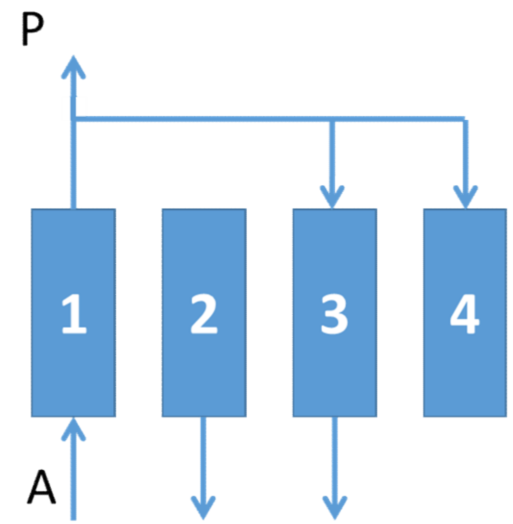
  3 : Purge (1 bar) : 180 s

  4 : Pressurisation (1 → 4 bar) : 60 s

- Purge flow rate / production flow rate
  12.5 - 18.75 - 25 - 37.5 %
- Operating conditions



- Performance



Purity of CH_4 (%) :

$$\bar{y}_{CH4}(-) = \frac{Flow\ rate\ of produced\ CH_4}{Total\ produced flowrate}$$

Recovery of CH_4 (%)

$$R_{CH_4}(\%) = \frac{produced\ CH_4 - purged\ CH_4\ - pressurized\ CH_4}{CH_4\ feed} * 100$$

Productivity of the PSA :

$$P_{CH_4}(mol\ h^{-1} liter^{-1}) = \frac{produced\ CH_4 - purged\ CH_4\ - pressurized\ CH_4}{velocity\ \ x\ total\ time}$$

Kinetic model

- **Simulations with Aspen Adsorption v9.0®**
- **Mass balances:** including axial dispersion, convection flow, accumulation in the fluid and sources

$$-D_{z,i}\frac{\partial^2 C_i}{\partial z^2}+\frac{\partial (uC_i)}{\partial z}+\frac{\partial C_i}{\partial t}+\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\rho_p\frac{\partial \overline{q_i}}{\partial t}=0$$

- **Diffusive phenomena:** **Linear Driving Force (LDF)** approximation:

$$\frac{\partial \overline{q_i}}{\partial t}=K_{LDF,i}(q_i^*-\overline{q_i})$$

- **Momentum balances:** based on the Ergun equation

$$-\frac{\partial p}{\partial z}=150\,u\frac{(1-\varepsilon_b)\mu_g}{\varepsilon_b^3 d_p^2}+1.75\,u^2\frac{(1-\varepsilon_b)\rho_g}{\varepsilon_b^3 d_p}$$

- **Energy balances:** performed on gas phase, solid phase and wall

Solid phase: $\rho_p c_{p,s}\frac{\partial T_s}{\partial t}=h_f a_s\left(T_g-T_s\right)+\sum_{i=1}^{n}(-\Delta H_i)\frac{\partial \overline{q_i}}{\partial t}$

Thermodynamic model

- **Isosteric heats of adsorption:** calculated using the Clausius-Clapeyron equation on our experimental isotherm curves

$$\frac{\mathrm{Q}}{RT^2} = -\left(\frac{\partial \ln P}{\partial T}\right)_{q_i}$$

- **Toth – extended**: fit of the experimental pure component isotherms

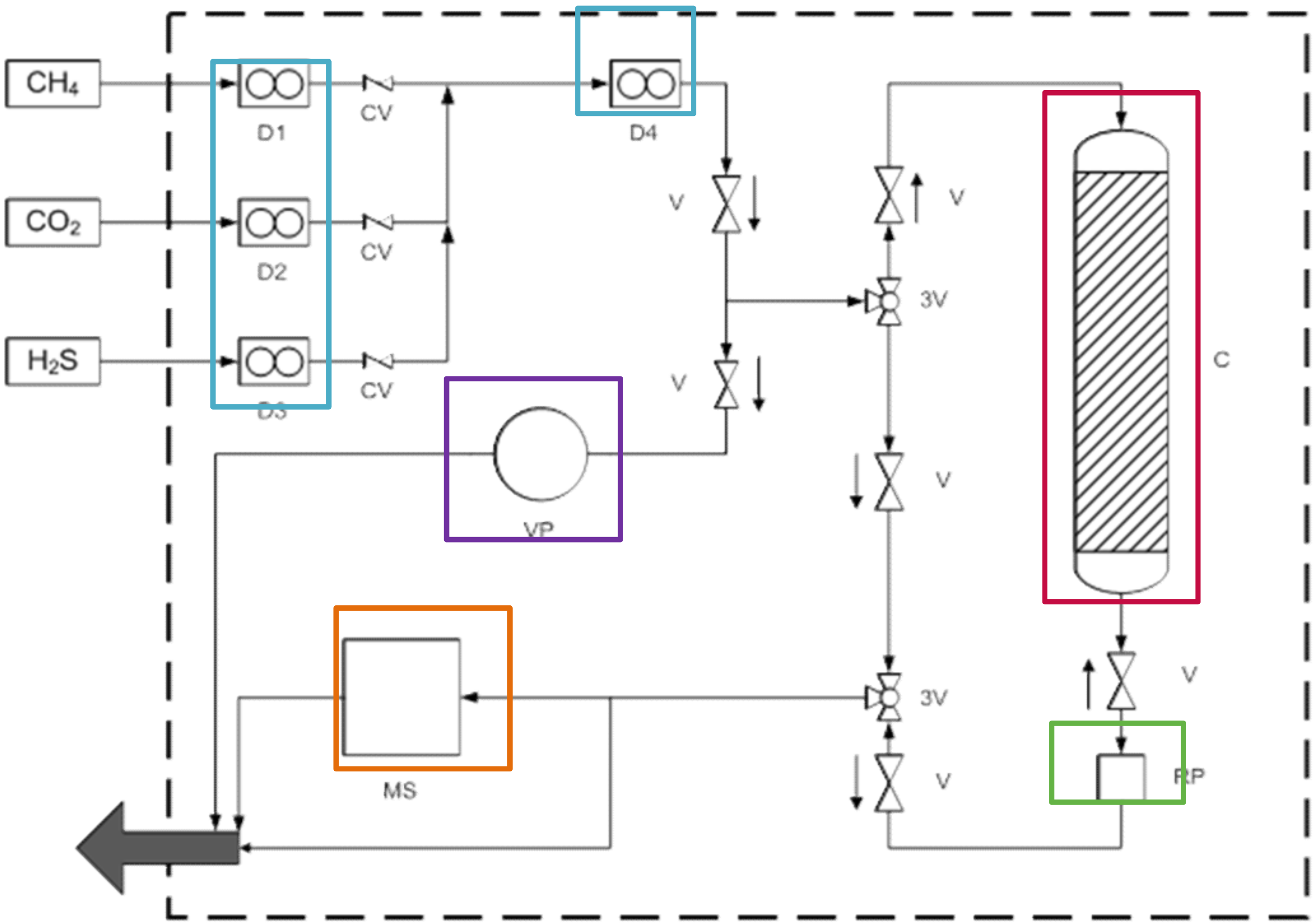
$$q_i = q_{sat,i} \cdot \frac{b_{0,i} \exp\left(\frac{-\Delta H_{0,i}}{RT}\right) p_i}{\left[1 + \left(b_{0,i} p_i\right)^{\frac{1}{t_i}}\right]^{\frac{1}{t_i}}}$$

- ***IAS Theory***: multi-components mixtures prediction : working capacity & selectivity

$$p y_i \phi_i = f_i^0(\pi) \gamma_i x_i \quad (constant\ T)$$ (Myers and Prausnitz, 1965)

=1 ∀i

- **Breakthrough curves (homemade pilot unit) :**



Column (C) : 50 x 2.17 cm

Flowmeters (D1-4)

Pressure regulation (PR)

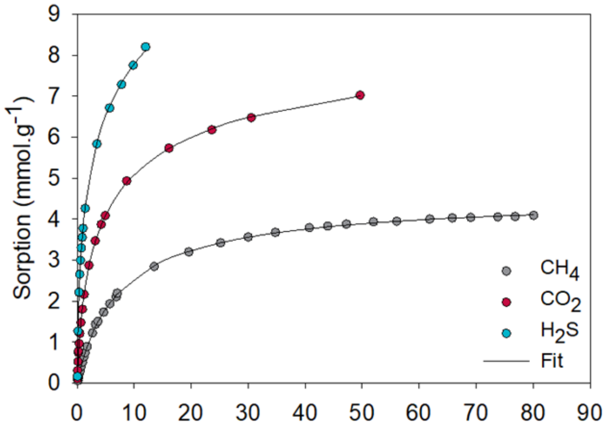
Mass spectrometer (MS)

Turbo vaccum pump (VP)

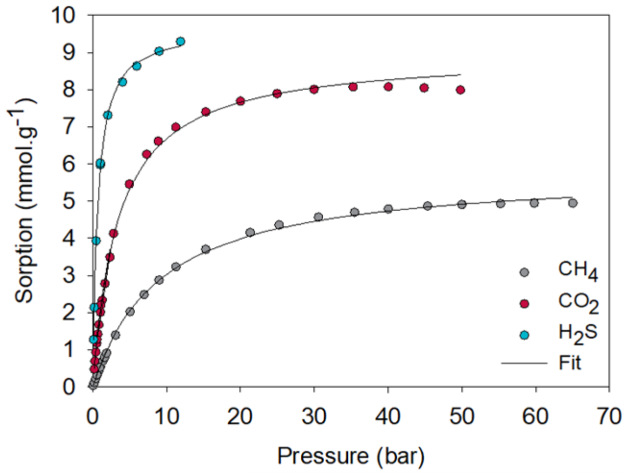
Valves (V)

3-ways valves (3V)

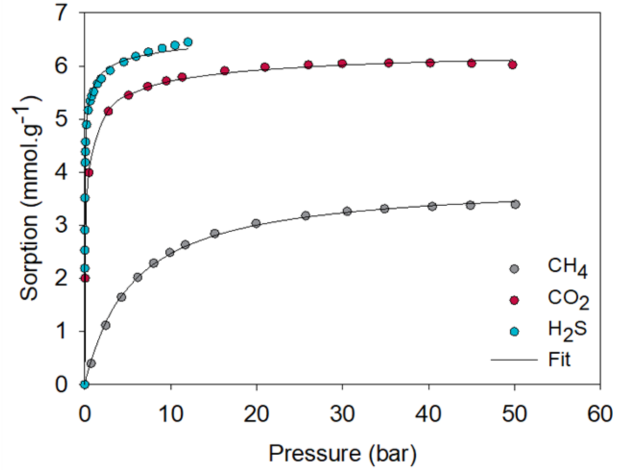
Basolite® A100

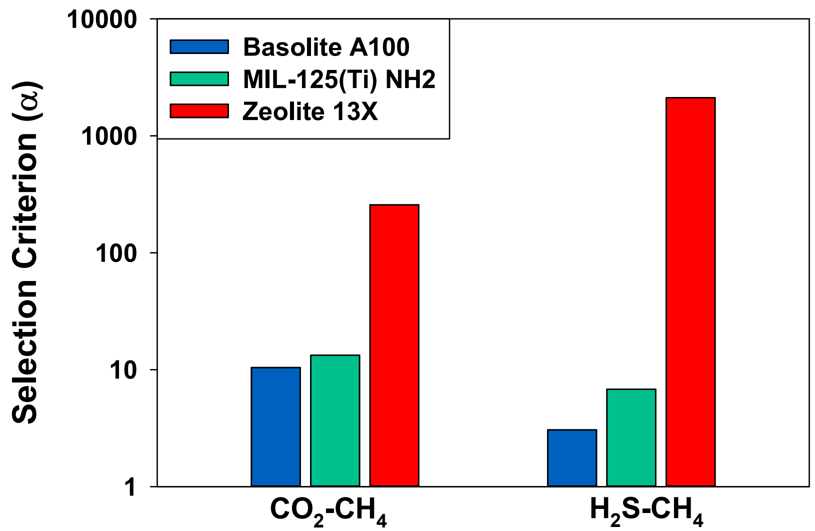


MIL-125(Ti)-NH_2



Zeolite 13X





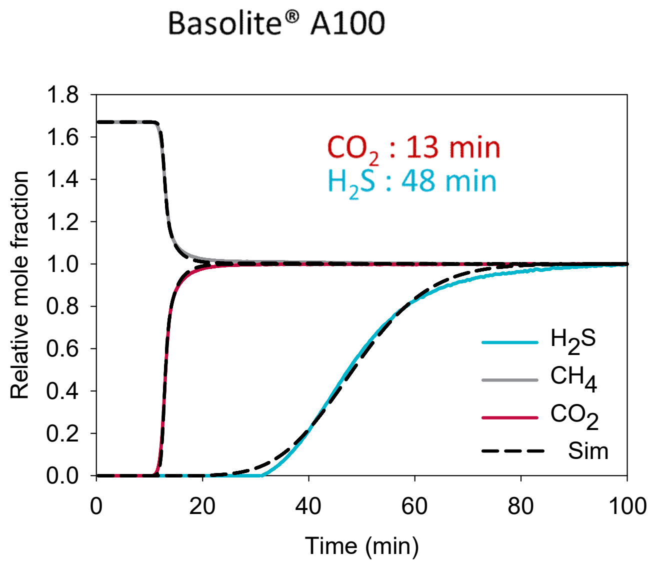
Thermodynamic criteria

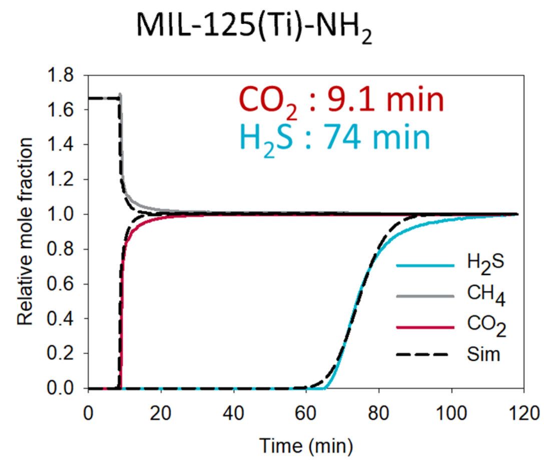
CO_2/CH_4:

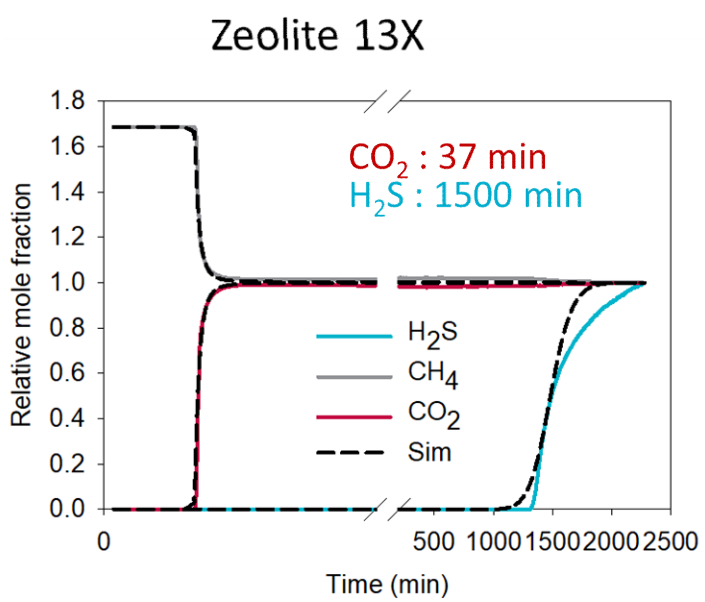
Zeolite 13X>>Basolite® A100 ≃ MIL-125(Ti)-NH_2

H_2S/CH_4:

Zeolite 13X>>> MIL-125(Ti)-NH_2 > Basolite® A100







Kinetic criteria

Good separation for all samples

k_{LDF}: MIL-125(Ti)-NH_2 > Basolite® A100 >> Zeolite 13X

Simulation fits well the measured data (CO_2 and CH_4)

Tails can be observed for H_2S

Flowrate purge/prod.	Basolite® A100	MIL-125(Ti)-NH_2	Zeolite 13X
Purity of CH_4 produced (% mol)			
37.5 %	99.99	> 99.999	94.62
25 %	99.76	> 99.999	83.72
18.75 %	98.74	> 99.999	79.95
12.5 %	94.52	98.58	75.62
Recovery of CH_4 (%)			
37.5 %	15.3	26.8	54.6
25 %	29.1	40.1	68.6
18.75 %	36.0	46.7	74.3
12.5 %	40.6	53.9	79.3
Productivity in CH_4 (mol l^{-1} h^{-1})			
37.5 %	0.56	0.96	1.96
25 %	1.05	1.45	2.46
18.75 %	1.29	1.68	2.67
12.5 %	1.46	1.94	2.84

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Conclusions et perspectives

- Biogas purification by the means of hybrid porous solids can be performed
- Methodology including thermodynamic and dynamic measurements, we demonstrate the feasibility of ternary separation (elimination of acidic gases: CO_2 and H_2S) with pure CH_4 production.
- In terms of PSA performances, MIL-125 (Ti)-NH_2 shows very promising results, outperforming the 13X zeolite ones which presents the higher thermodynamic selection criterion.
- The thermodynamic selection criterion appears insufficient to correctly select to best adsorbent. In next steps, we interest in optimization of PSA (additional columns and additional steps) to increase the recovery and productivity.

Acknowledgments

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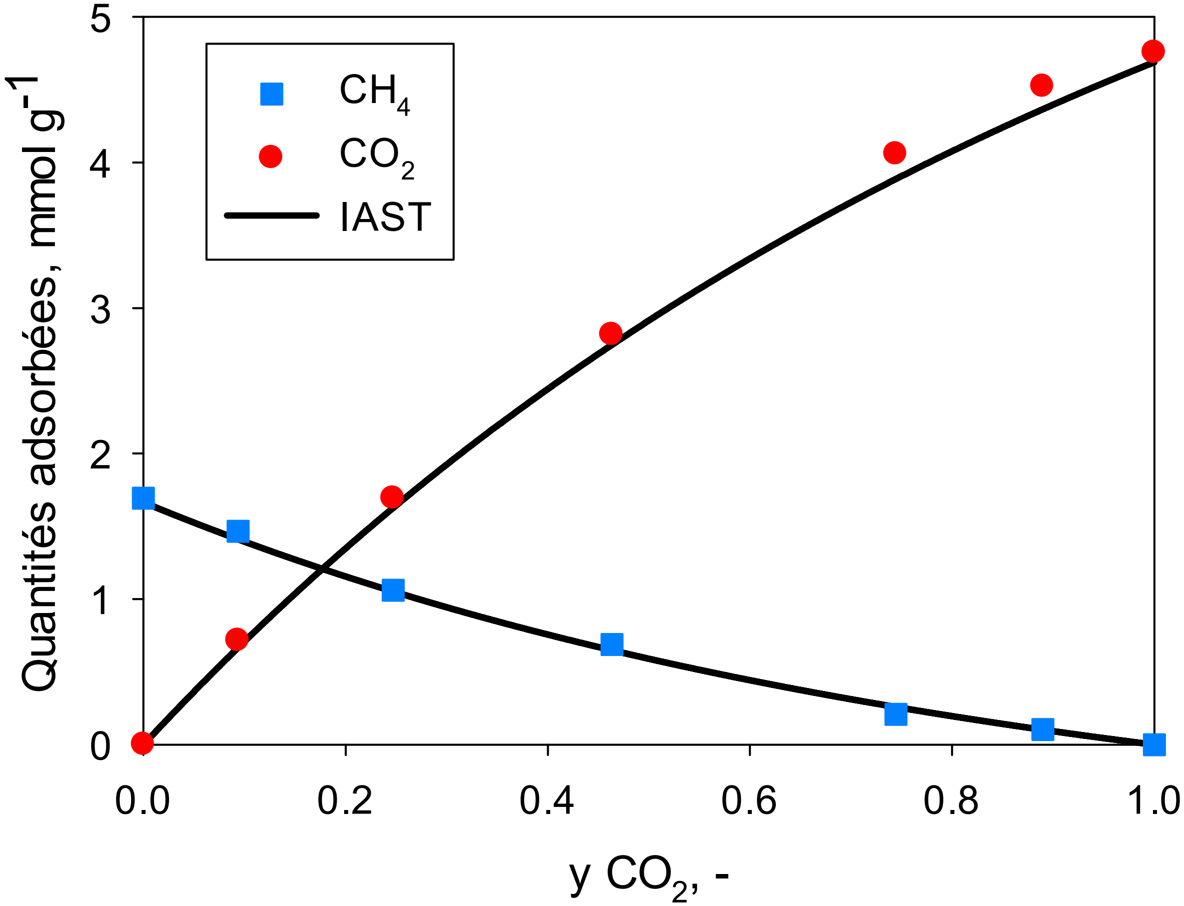
Modélisation IAST sur MIL-125(Ti)-NH_2 (4 bar, 303 K)



Modélisation

Bilans de matière partiels, total et bilans d'énergies

Dispersion longitudinale — Accumulation dans la phase gazeuse

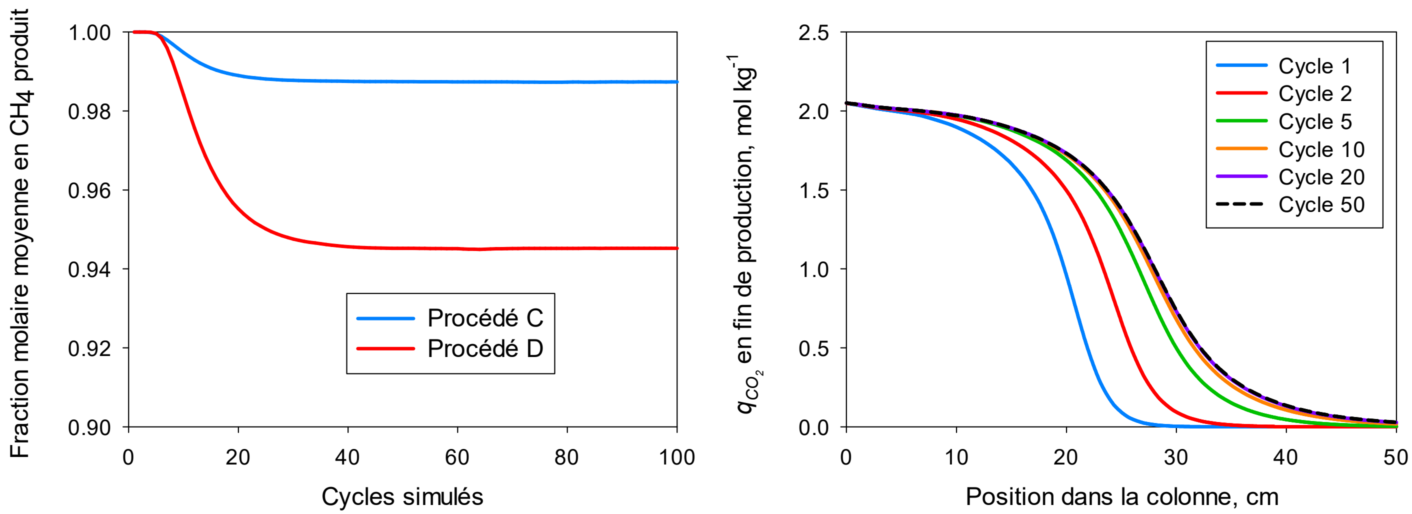
$$\underbrace{-D_{L,i}\frac{\partial^2 c_i}{\partial z^2}}_{\text{Dispersion longitudinale}} + \underbrace{\frac{\partial (v c_i)}{\partial z}}_{\text{Convection forcée du fluide}} + \underbrace{\frac{\partial c_i}{\partial t}}_{\text{Accumulation dans la phase gazeuse}} + \underbrace{\left(\frac{1-\ \varepsilon_e}{\varepsilon_e}\right)\rho_p\frac{\partial q_i}{\partial t}}_{\text{Accumulation dans la phase solide}} = 0$$

Convection forcée du fluide — Accumulation dans la phase solide

- les gradients de concentration, vitesse et températures sont négligés dans la direction radiale (modèle 1D) ;
- les propriétés de l'adsorbant et de la paroi de la colonne sont considérées comme constantes (masse volumique, capacité calorifique…) ;
- les différents coefficients et les propriétés du fluide dans la colonne sont considérés égaux à ceux calculés à l'entrée de celle-ci ;
- les composés adsorbés sont négligés dans les bilans énergétiques ;

Mise en régime des procédés

Fraction molaire en CH_4 produit et quantités adsorbées de CO_2 en fin d'étape de production (Basolite® A100)



Phase de saturation de la colonne

Le modèle atteint une valeur de régime avec un nombre de cycles raisonnables

→ Comparaison des performances des adsorbants