CO_2 CAPTURE FROM POST-COMBUSTION FLUE GAS USING VPSA PROCESS WITH ZEOLITE 13X

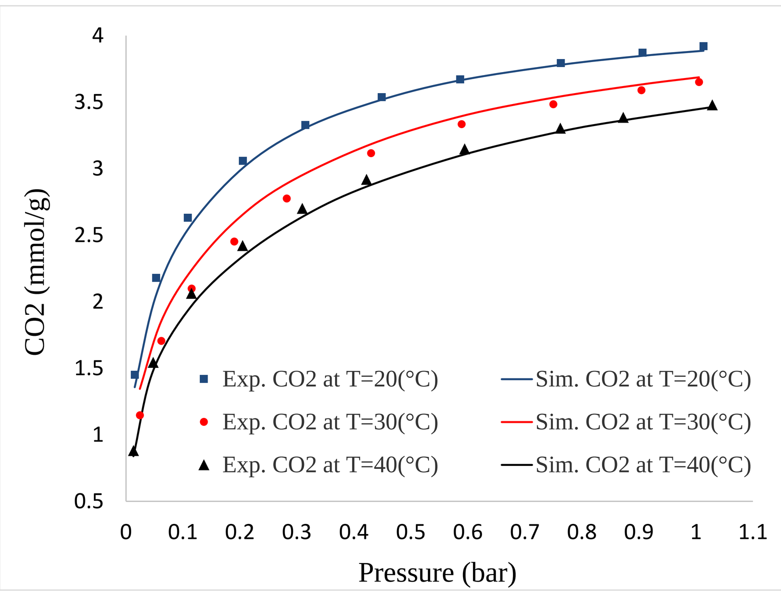
Haidar Al-Awaad[1]*, Guy De Weireld[1]
[1]Thermodynamic & Mathematical Physics Unit, Faculty of Engineering, University of Mons,7000 Mons, Belgium
*Corresponding Author: haidar.al-awaad@student.umons.ac.be

INTRODUCTION:

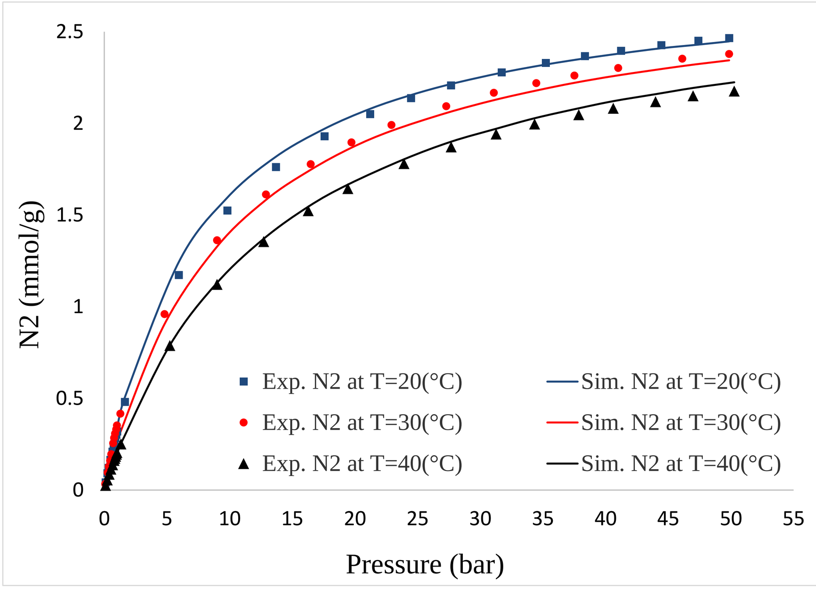
For several years, the reduction of anthropogenic CO_2 emissions from industries has become one of the most crucial issues to combat global warming. Shifting towards a low-carbon economy needs cost-effective novel carbon capture utilization or sequestration (CCUS) solutions. The current benchmark technique, the absorption amine-based process, suffers from high energy penalties due to solvent regeneration and high environmental impact. So, the adsorption process is widely considered as a promising alternative. However, the performances of adsorbents have not been fully evaluated in real industrial conditions. In this context, this study focuses on the determination of Zeolite 13X performances in the Vacuum Pressure Swing Adsorption (VPSA) process to capture CO_2 from flue gases in post-combustion conditions.

ADSORPTION ISOTHERMS MEASUREMENTS & MODELING:

CO_2 adsorption isotherms



N_2 adsorption isotherms



Dual-Site Langmuir Model

$$q_i^* = q_{sb}\frac{b_i P_i}{1+b_i P_i} + q_{sd}\frac{d_i P_i}{1+d_i P_i}$$

Heat of Adsorption

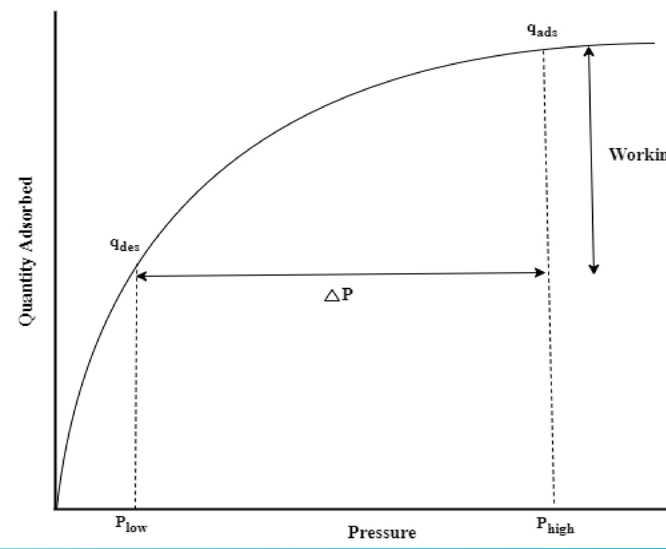
- Clausius-Clapeyron equation:

$$\Delta H_{isos} = -R * \left[\frac{\ln p}{1/T}\right]_{q_i}$$

ΔH_i (kJ/mol)	
CO_2	N_2
-40.5	-22.2

Working Capacity:

Working Capacity (W.C.)= $\Delta q(CO_2) = q(CO_2)_{Adsorption} - q(CO_2)_{Desorption}$
- At 1.1 bar adsorption pressure, 0.1 bar desorption pressure, and a temperature of 30°C: **W.C**=1.47 mmol/g



CO_2 Selectivity:

$$S_{CO_2/N_2} = \frac{X_{CO_2}/X_{N_2}}{Y_{CO_2}/Y_{N_2}}$$

- Using IAST theory, at 1.1 bar and temperatures :
  - ✓ At 20°C→ Selectivity = 557
  - ✓ At 30°C→ Selectivity = 460
  - ✓ At 40°C→ Selectivity = 393

BREAKTHROUGH CURVES MEASUREMENTS & MODELING:

- Measurement temperature (25 °C).
- Experimental breakthrough curves were modelled in Aspen Adsorption©.
- The column has only one vertical adsorbent layer within the bed.
- The Redlich-Kwong-Soave equation of state determines gas phase properties.
- Mass balance assumption is described by convection only.

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

$D_{z,i}$ is the axial diffusion coefficient (m²/s), y_i is the molar fraction in the gas phase, z is the axial position in the column (m), υ is the interstitial velocity (m/s), t is the time (s), ε_b is the bulk porosity, ρ_p is the adsorbent density (kg/m³).

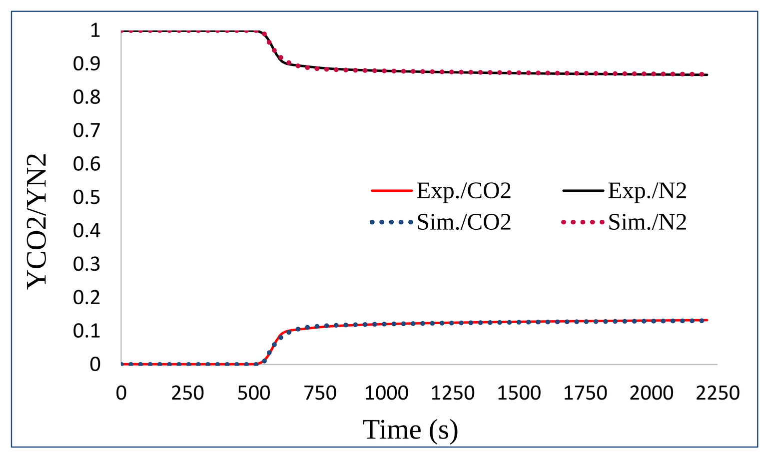
- The axial dispersed plug flow model describes the flow in the bed.
- Pressure Drop: Ergun Equation.
- Linear driving force with a constant coefficient is used for the mass transfer resistance.
- Energy balance: non-isothermal with gas and solid conduction.
- Upper difference scheme UDS1 used with (100 nodes) as a discretization method.

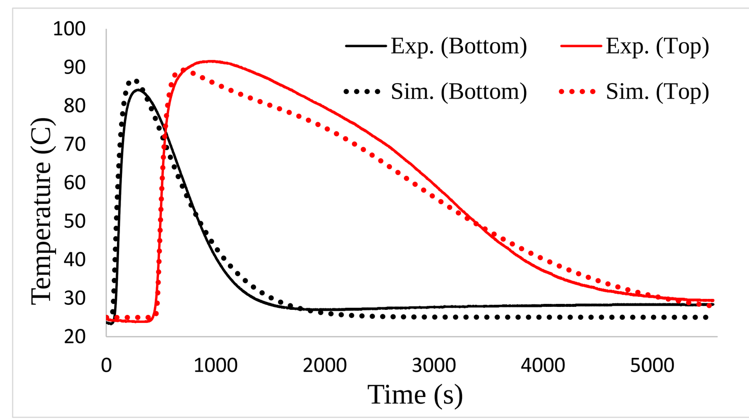
Parameters	Zeolite 13X
Height of the adsorbent layer (cm)	30
Diameter of the column (cm)	7.01
Flowrate (Nm³/h)	1.04
CO_2 Molar fraction in the feed (%)	14.99
Bed volume (cm³)	1157.25
Mass of the adsorbent (g)	800.2

$$\frac{\partial q_i}{\partial t} = k_{LDF}(q_i^* - q_i)$$

k_{LDF} (CO_2) [s⁻¹]	0.0143
k_{LDF} (N_2) [s⁻¹]	0.0021

✓ Adsorbent Thermal Conductivity= 0.12 (W/(m.K))



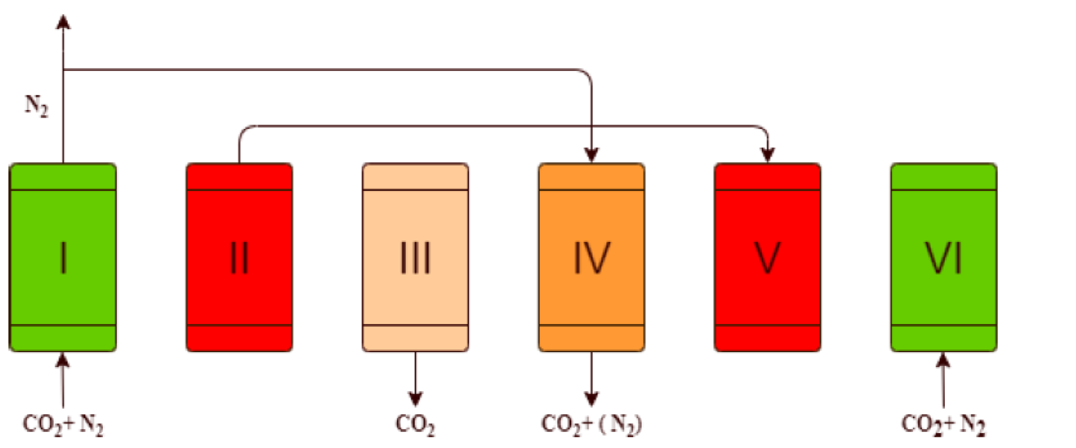


CYCLES STUDIED AND RESULTS:

Targets of the capture process:

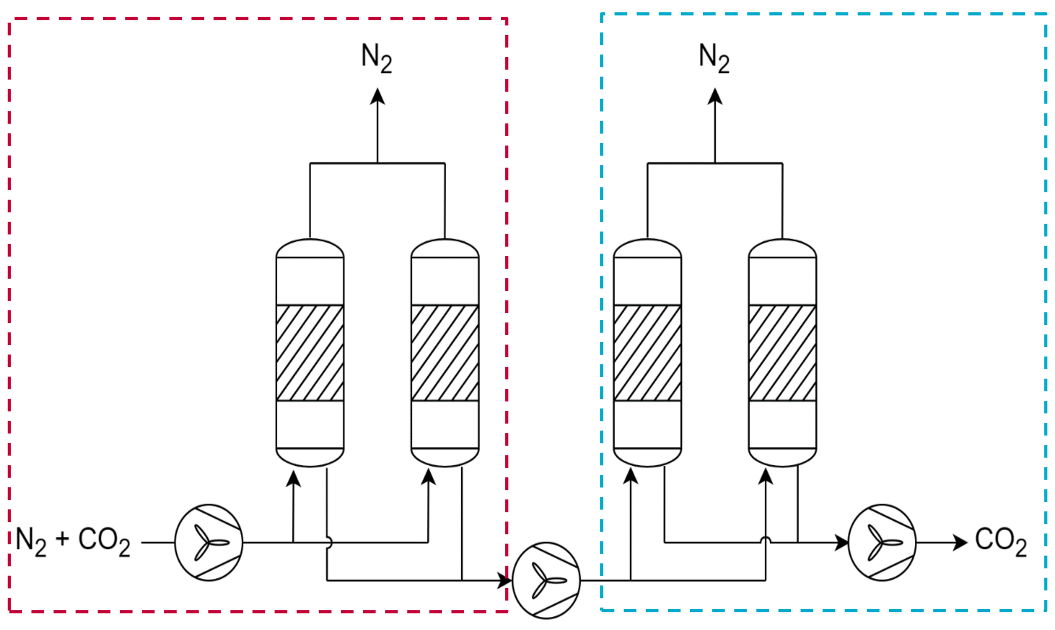
- Recovery > 90% $\left(\frac{n_{CO_2}\text{ in product}}{n_{CO_2}\text{ in feed}}\right)$
- Purity > 95% (y_{CO_2} in the product)

Objective: Designing a Two-Unit (two columns in each unit) VPSA process and using the Skarstrom Cycle to reach high purity and recovery level.

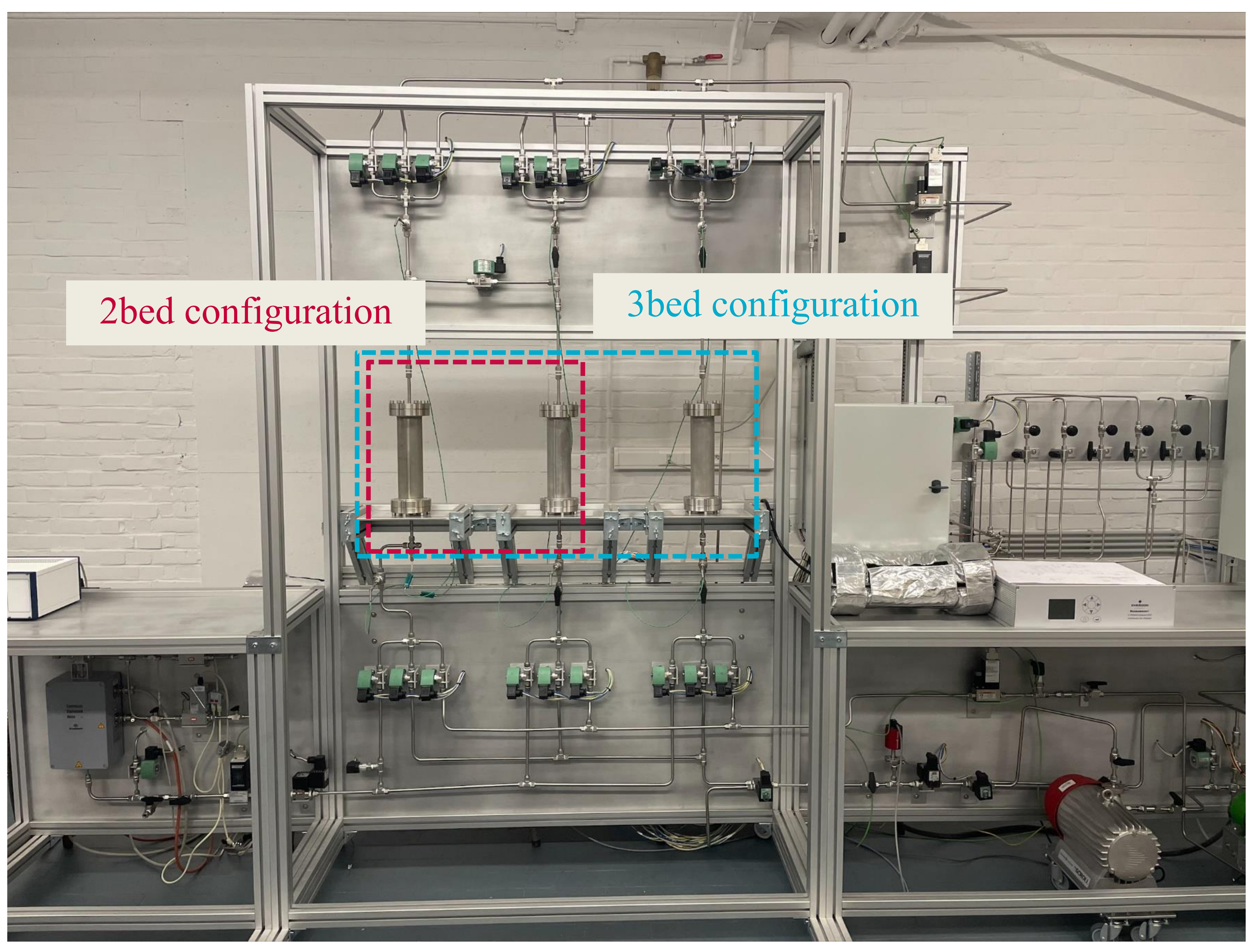


Bed 1	Adsorption		Equalization	Blowdown		purge	Equalization	Pressurization
Bed 2	Blowdown	purge	Equalization	Pressurization	Adsorption		Equalization	Blowdown

Two-Unit/ 5-Step



- The target of the two successive units of two beds:
  - Unit 1: High recovery (>95%) and purity of 40-60%.
  - Unit 2: Increase the purity to >95%.



Operating Conditions	Unit 1	Unit 2
Feed flowrate (Nm³/h)	1	0.259
Feed flowrate (kmol/h)	0.0446	0.0115
Feed pressure (bar)	1.46	1.1-1.5
Vacuum pressure (bar)	0.1	0.1
CO_2 in feed (%)	15	55.34
Adsorption time (s)	40-140	300-450
Purge time (s)	20-120	50-150
Purge flowrate (Nm³/h)	0.1-0.3	0.05-0.15
Temperature (°C)	25	25

Results:

✓ 18 runs for the first unit were tested in the VPSA pilot using the range of the operation conditions according to the design of the experiment to find the best one.

✓ One of the runs of the first unit resulted in a purity of 55.34% and a recovery of 95.38%, The run reluts have been used as a feed for the second unit.

	Unit 1	Unit 2	Overall
CO_2 Recovery [%]	95.38	95.89	**91.46**
CO_2 Purity[%]	55.34	89.03	**89.03**

* A purity target of > 95% was not reached, only the recovery target of > 90 %.

✓ Another run obtained from the first unit VPSA-pilot experiment resulted in a purity of 53.66% and a recovery of 97.86%, The run reluts have been used as a feed for the second unit by simulation the process in Aspen adsorption software.

✓ The vacuum pressure has been decreased to 0.05 bar instead of 0.1 bar to improve the process's overall performance.

✓ The feed pressure of the second unit has been fixed at 1.1 bar.

✓ The second unit operated with an adsorption time of 310 s, purge time of 20 s, and purge flow rate of 0.02 Nm³/h.

	Unit 1	Unit 2	Overall
CO_2 Recovery [%]	97.86	92.94	**90.95**
CO_2 Purity[%]	53.66	95.08	**95.08**

* The efficient carbon capture unit targets of a purity > 95% and a recovery > 90 % have been reached with this cycle.

CONCLUSIONS

- CO_2/N_2 isotherms are measured using a homemade gravimetric apparatus.
- Pure gas isotherms and breakthrough data are employed to estimate the adsorption parameters used in the process simulation.
- Low performances were noticed using only a two-bed VPSA with 15% CO_2 in the feed.
- Only one target is reached (recovery) of the efficient capture unit using the run of purity 55.34% and recovery 95.34% as a feed to the second VPSA unit.
- Using other run results of purity 53.66% and recovery of 97.86% as a feed to the second VPSA unit alongside decreasing the vacuum pressure to 0.05 bar allowed to reach the targets of an efficient carbon capture unit.
- The next step will be the optimization of the tow-unit simultaneously and testing the performance of another adsorbent (MOF) in the VPSA pilot.

This project has received fundings from the European Union's Horizon 2020 research and innovation programme under grant agreement Nº 831975 (MOF4AIR)