Simulations on Lab Scale CO_2 Capture Vacuum Pressure Swing Adsorption Pilot Unit using MOF

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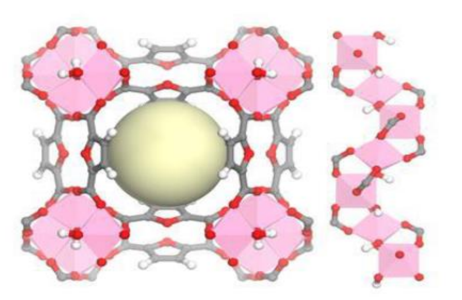
Introduction

Nowadays, power plants and carbon-intensive industries (cement, steel, limestone or (petro)chemical, … plants) are responsible for almost 50% of anthropogenic CO_2 emissions to the atmosphere (37 $GTCO_2$ in 2018 [1]) that mainly contributes to global warming. Since two decades, CO_2 capture techniques were investigated to envisage CO_2 storage and more recently CO_2 reuse. Beside the mature absorption-regeneration technologies using amine solvents but having an impact on the environment, adsorption processes are a promising capture technique thanks to improvement of process design and development of new materials. Among these materials, MOFs appears as very promising materials for both gas separation and purification. However, the performances of these hybrid materials in carbon capture technologies have not been fully evaluated and fine-tuning is still needed for adsorption processes at large scale in real industrial conditions. In this work, the performances of MIL-160(Al) (selected after screening in the begin of the project) for CO_2 capture from flue gases with lab-scale Vacuum Pressure Swing Adsorption (VPSA) processes was evaluated by simulation. These results will later be experimentally validated on a 3-column VPSA lab-scale pilot to confirm the influence of the parameters and allow the use of these results for the optimization of an industrial unit.

Adsorption isotherms and breakthrough curve measurements

MIL-160 (Al) [2] [3]



Powder
Formula: $Al(OH)[C_4H_2O-(CO_2)_2]$
Pore diameter: 5 Å
S_{BET}: 1150 m²/g
Pore volume: 0.479 cm³/g

Shaped
Synthesized in batch of 200g
Binder used: 3%PVB
Beads of 2mm

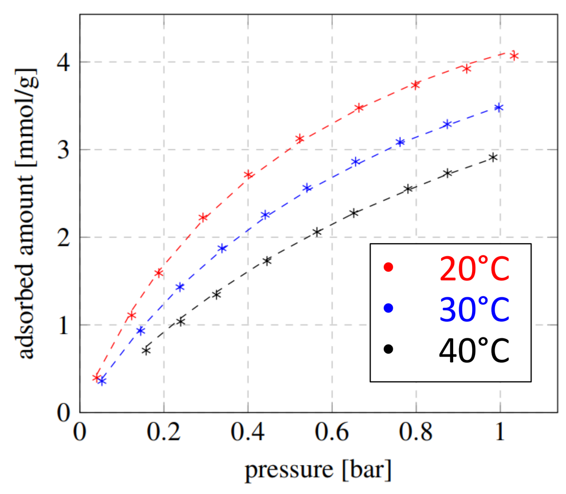
Adsorption isotherm measurements and modelling

Measurement of CO_2 and N_2 adsorption isotherms by gravimetric method at 20°C, 30°C, 40°C (Rubotherm).

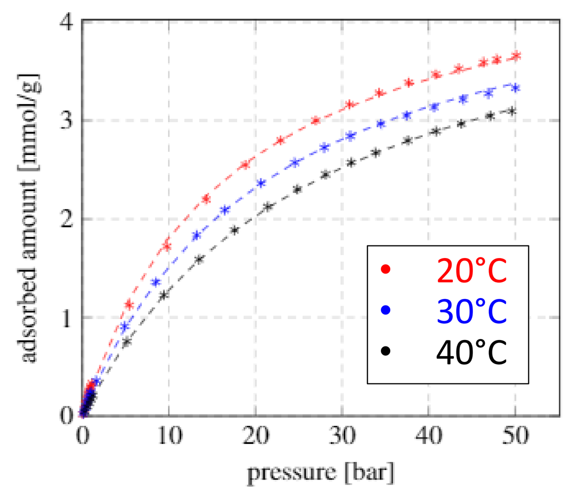
Fitting of the data by a Langmuir model with nonlinear least-squares solver in Matlab©.

Parameters	CO_2	N_2
$q_s[mmol/g]$	6.33±0.15	4.85±0.05
$b_0\ [bar^{-1}]$	$1.28\times 10^{-5} \pm 4.42\times 10^{-6}$	$1.89\times 10^{-5} \pm 4.49\times 10^{-6}$
$\Delta H\ [kJ/(mol.K)]$	240.5±7.7	163.3±5.1

CO_2 adsorption isotherms



N_2 adsorption isotherms



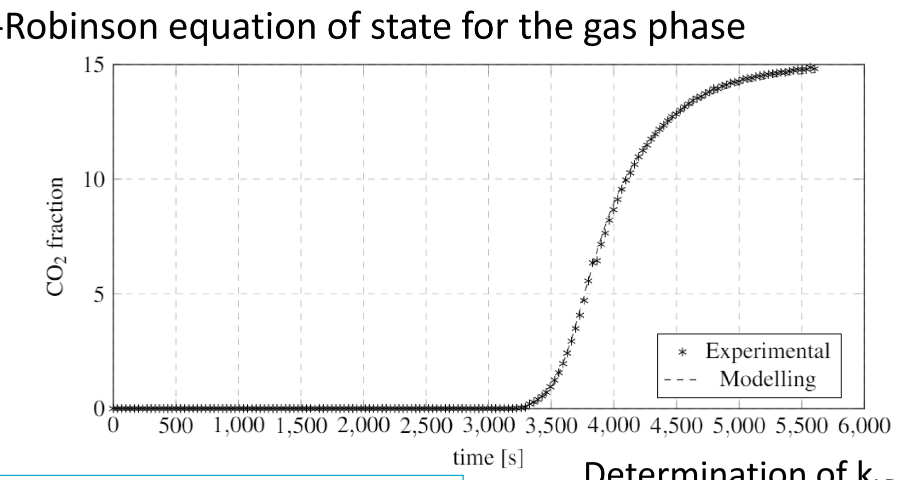
Langmuir Model

$$q = q_s \frac{b_0 \exp\left(\frac{\Delta H}{RT}\right) p}{1 + b_0 \exp\left(\frac{\Delta H}{RT}\right) p}$$

Breakthrough curve measurements and modelling

Modelling of the experimental breakthrough curve on Aspen Adsorption

- Ideal Adsorbed Solution [4] model for co-adsorption prediction
- Linear driving force for adsorption kinetic $\left(\frac{\partial q_i}{\partial t} = k_{LDF,i}[q_i^* - q_i]\right)$
- 1D discretization of the bed
- Non-isothermal bed with double jacket for cooling
- Peng-Robinson equation of state for the gas phase



Length of column (m)	0.5
Diameter of column (m)	0.0217
Flowrate (NL/h)	11.9
CO_2 molar fraction in feed (%)	14.95
Volume (cm³)	184.8
Mass of adsorbent (g)	95.17

Determination of k_{LDF} and λ by least-squares minimization

k_{LDF} (CO_2) [s^{-1}]	0.175
k_{LDF} (N_2) [s^{-1}]	0.017
Adsorbent thermal conductivity [W/(m.K)]	0.74

Cycles studied and results

Objective: simulate in Aspen Adsorption© a future lab scale VPSA pilot and study several operating parameters with the help of a design of experiments on three different cycles.

Targets of the capture process:

- Recovery > 90% $\left(\frac{n_{CO_2}\ in\ product}{n_{CO_2} in\ feed}\right)$
- Purity > 95% (y_{CO_2} $of\ product$)
- Energy consumption < 2.3 kJ/kg_{CO_2}

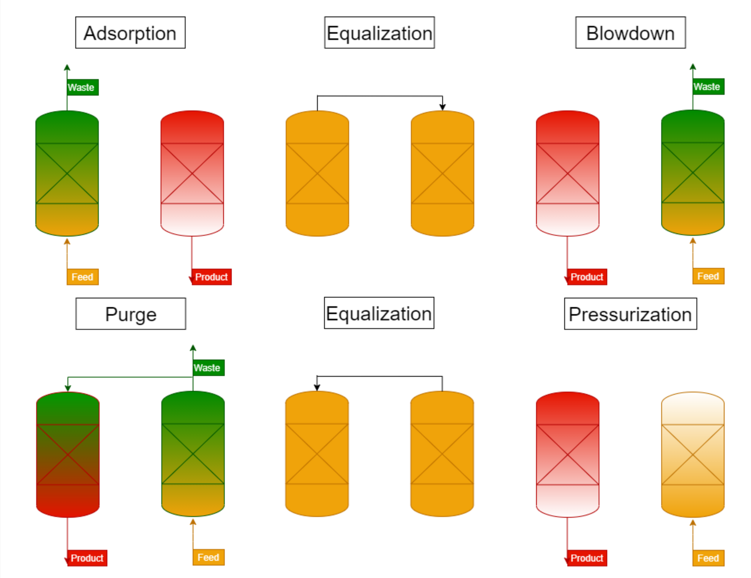
Length of column (m)	0.3
Diameter of column (m)	0.0701
Flowrate (Nm³/h)	1
CO_2 molar fraction in feed (%)	15
Volume (cm³)	1157.25
Temperature (°C)	25

Model assumptions:

- Same assumptions as for the breakthrough curve
- Ideal work for compressor and vacuum pump

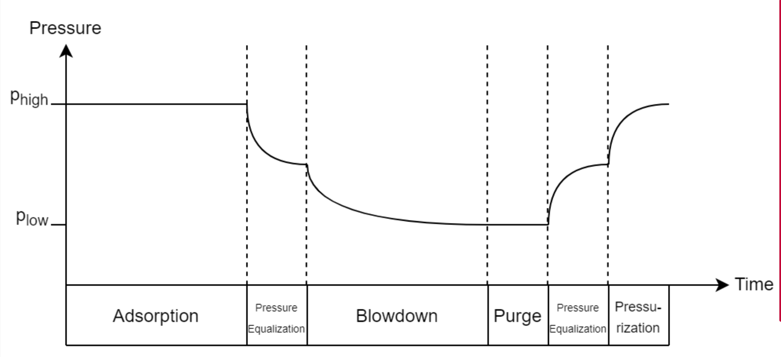
$$W_{ideal} = RT_1 \frac{\gamma}{\gamma - 1}\left(\left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right)$$

2-bed 4-step VPSA [5]



Skarstrom cycle with pressure equalization step.

→ Two successive units to reach the targets



Parameters studied:

- Adsorption pressure [1.1 – 1.5 bar]
- Blowdown pressure [0.1 – 0.4 bar]
- Adsorption time [40-200 s]
- Purge flowrate [5-60 $\%_{feed}$]
- Purge time [5-80 % t_{feed}]

Results

First case: Adsorption at 1.1 bar and blowdown at 0.1 bar.

	Unit 1	Unit 2	Total
Recovery [%]	95.9	96.7	92.8
Purity [%]	57.7	91.4	91.4
Energy [kJ/kg CO_2]	343.5	194.7	538.2

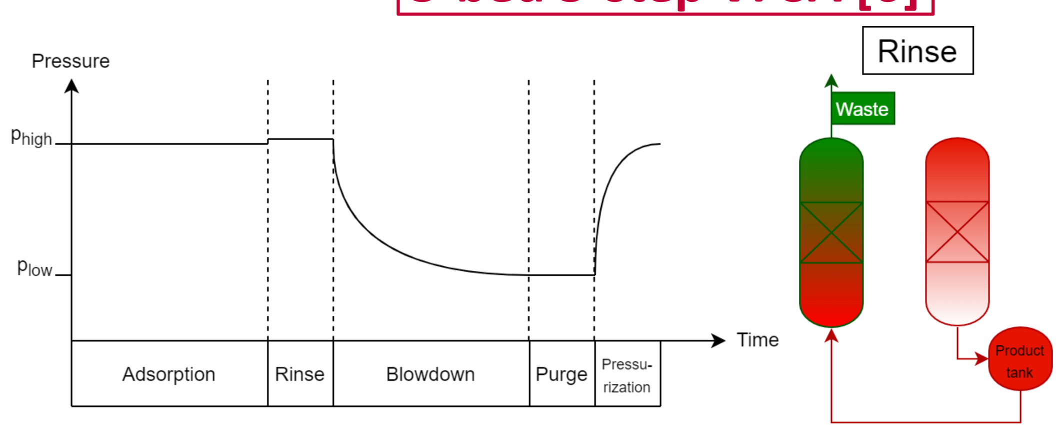
	Unit 1	Unit 2
Adsorption time [s]	75	300
Purge flowrate [Nm³/h]	0.25	0.012
Purge time [s]	7.5	15

Second case: Adsorption and blowdown pressure can be higher.

	Unit 1	Unit 2	Total
Recovery [%]	96.2	94.3	90.7
Purity [%]	61.8	94.7	94.7
Energy [kJ/kg CO_2]	451	215.1	666.1

	Unit 1	Unit 2
high pressure [bar]	1.5	1.5
low pressure [bar]	0.1	0.1
Adsorption time [s]	110	430
Purge flowrate [Nm³/h]	0.05	0.012
Purge time [s]	5.5	21.5

3-bed 5-step VPSA [6]



Cycle with 3 beds in order to reach the targets with a single capture unit.

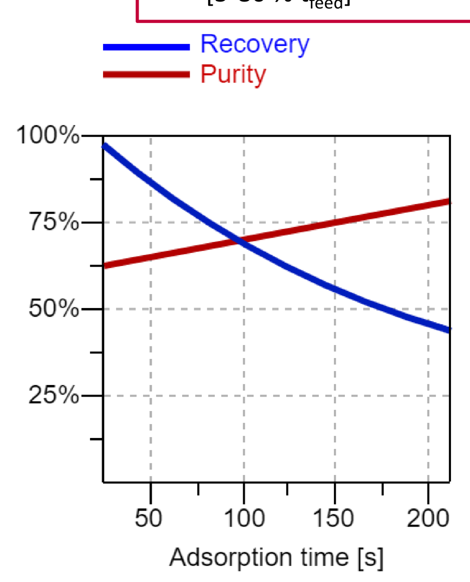
- No more equalization step
- Rinse step to increase the purity before blowdown

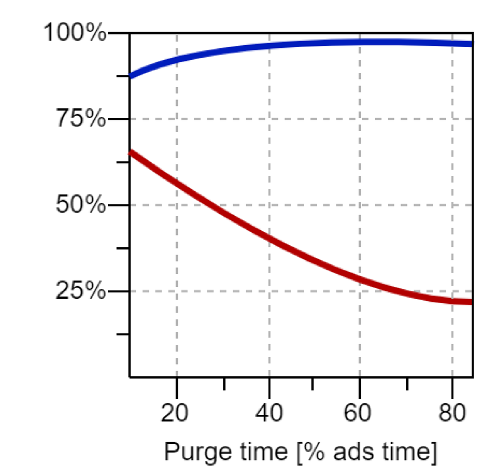
Parameters studied:

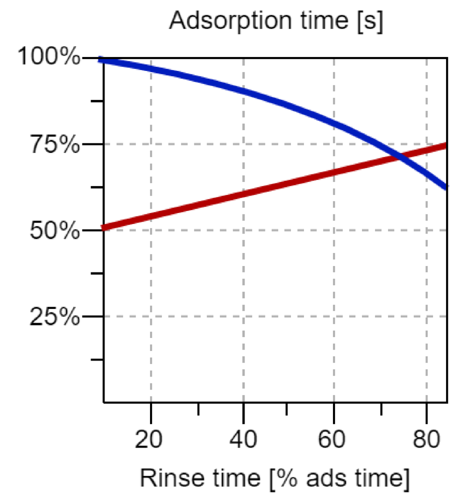
- Adsorption pressure [1.1 – 1.5 bar]
- Blowdown pressure [0.1 – 0.4 bar]
- Adsorption time [40 – 200s]
- Purge flowrate [5-60 $\%_{feed}$]
- Purge time [5-80 % t_{feed}]
- Rinse flowrate [5-60 $\%_{feed}$]
- Rinse time [5-80 % t_{feed}]

Results

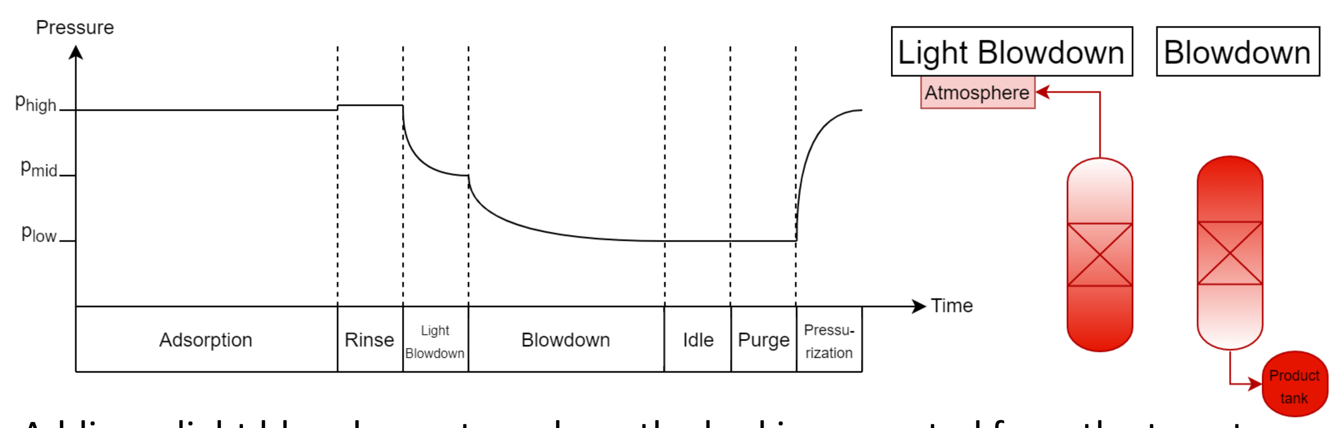
Recovery [%]	95.9
Purity [%]	64.2
Energy [kJ/kg CO_2]	605.5
Adsorption pressure [bar]	1.1
Blowdown pressure [bar]	0.1
Adsorption time [s]	40
Purge flowrate [Nm³/h]	0.05
Purge time [s]	2
Rinse flowrate [Nm³/h]	0.6
Rinse time [s]	16







3-bed 7-step VPSA [7]



Adding a light blowdown step where the bed is evacuated from the top at an intermediate pressure and not stocked in the product tank in order to improve the purity. Idle step is used to synchronize the three beds.

	Setting 1	Setting 2
Recovery [%]	92.9	94.8
Purity [%]	81.7	66.4
Energy [kJ/kg CO_2]	619	419.7
Adsorption pressure [bar]	1.1	1.5
Blowdown pressure [bar]	0.1	0.1
Midle pressure [bar]	0.5	0.6
Adsorption time [s]	50	90
Purge flowrate [Nm³/h]	0.05	0.15
Purge time [s]	7.5	13.5
Rinse flowrate [Nm³/h]	0.6	0.1
Rinse time [s]	30	13.5
Ligth Blowdown time [s]	7.5	54

Parameters studied:

- Adsorption pressure [1.1 – 1.5 bar]
- Blowdown pressure [0.1 – 0.4 bar]
- Ligth Blowdown pressure [0.2 – 0.6]
- Adsorption time [40 – 200s]
- Purge flowrate [5-60 $\%_{feed}$]
- Purge time [5-80 % t_{feed}]
- Rinse flowrate [5-60 $\%_{feed}$]
- Rinse time [5-80 % t_{feed}]
- Light Blowdown time [5-80 % t_{feed}]

The separation of the blowdown into two stages allow to increase the purity of the CO_2 stream without impacting the recovery. The results obtained show that this cycle can approach the targets of recovery and purity (setting 1) or can be used as a first unit for a two-stage VPSA capture process (setting 2). Performances of this cycle can be increased by studying more parameters such as flowrate or L/D ratio.

Conclusions

In this work, the adsorption performance of MIL-160(Al) was determined by measuring and modelling the adsorption isotherms and breakthrough curves. The modelling results represent the experimental data well and have been used to model a future lab scale CO_2 VPSA pilot capture unit in Aspen Adsorption. 3 cycles were studied by design of experiments to find the operating parameters that would reach the targets of purity and recovery while minimizing the energy required. The two-column cycle allows targets to be approached using two successive units. The main problem is to have very high CAPEX compared to a 3-column cycle. The 3-bed, 5-step cycle does not achieve the objectives. High purity is difficult to achieve while keeping recovery and energy consumption acceptable. The 3-bed, 7-stage cycle is promising for approaching the targets without drastically increasing energy consumption. The objectives could be achieved by further studying certain parameters and other variants of the cycle to find the best possible configuration for CO_2 capture.

References

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