IMPLEMENTATION OF VPSA TECHNOLOGY TO SEPARATE CO_2 FROM FLUE GASES USING METAL-ORGANIC FRAMEWORK (MOF)

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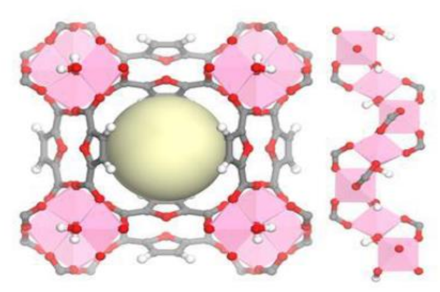
INTRODUCTION

CO_2 emissions from large stationary sources like power plants and energy-intensive industries (cement, chemicals, steel,..) have been identified as major global warming and climate change sources. Roughly, over 60 % of global warming effects are relevant to carbon dioxide emissions into the atmosphere [1]. In this study, an adsorption process (VPSA-vacuum pressure swing adsorption) using electricity from renewable sources was proposed and implemented for the reduction of CO_2 industrial emissions. The VPSA technology seems to effectively separate CO_2 from flue gases with relatively low energy consumption, flexible operation conditions, low operation cost, and low environmental impacts compared to absorption/regeneration technology using amine (3800-4000 kJ/kgCO_2). Al-MOF MIL-160 [Al (OH)(O_2C-C_4H_2O-CO_2)] was selected as an adsorbent because it exhibited: good working capacity, good selectivity to capture CO_2 from post-combustion conditions, green synthesis, water stability, and the possibility of scaling-up and shaping [2]. Hence, a two-stage (the first one to increase the concentration, the second one for purification) VPSA process composed of two columns in each stage was designed. A five-step Skarstrom cycle including a pressure equalization step in each stage was employed, and the impacts of various operation parameters were studied. The overall process performance of the two-stage VPSA process resulted in a CO2 purity of 95.01% and a CO_2 recovery of 90.04% with a productivity of 0.1165 gCO_2/g ads.h. The total energy consumptions were 993 kJ/kgCO_2. The simulation results are well conformed with the requirements of the U.S. Department of Energy (DOE).

ADSORPTION ISOTHERMS AND BREAKTHROUGH CURVE MEASUREMENTS

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



- Aluminum Carboxylate: [Al (OH)(O_2C-C_4H_2O-CO_2)]
- Pore size is 4 to 6 Å.
- S_{BET} = 1010 m²/g.
- Binder 3% of PVB (wet granulation).
- Diameter of pellets [mm] : 1.4 – 2.5.

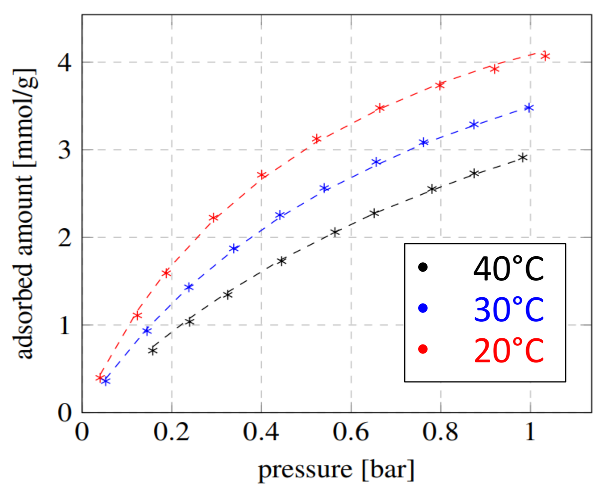
- Working capacity at 30 °C and 1.1 bar=0.87 mmol/g .
- Selectivity for CO_2 at 30 °C and 1.1 =33.

Adsorption Isotherms Measurements and Modelings

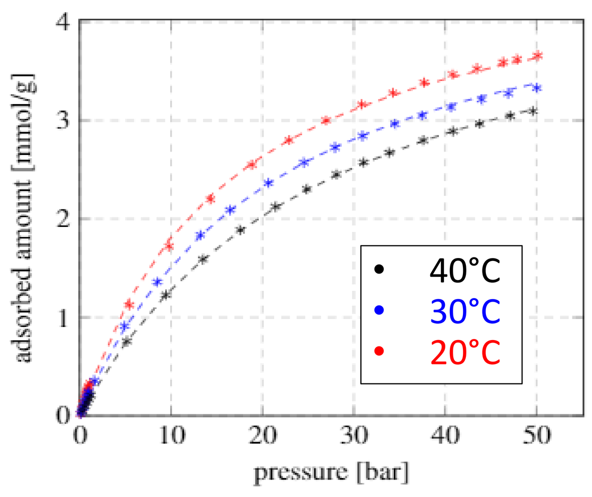
- Measurement of CO_2 and N_2 isotherms at 20,30,40°C by gravimetric method (Rubotherm).
- For CO_2 up to 1 bar and up to 50 bar for N_2 .
- Adsorption isotherms of CO_2 and N_2 are fitted in Matlab software (least square curve fitting) using the Langmuir model.
- R^2 =0.99.

Parameters	CO_2	N_2
$q_s.b_0 [mmol/g.bar^{-1}]$	4.72E-05	1.51E-04
$\Delta H/R(K)$	3607.5	2169.6
$b_0\ [bar^{-1}]$	8.03E-06	3.37E-05

CO_2 adsorption isotherms



N_2 adsorption isotherms



Langmuir Model

$$q_i^* = q_{s,i}\frac{b_{o,i}e^{-\Delta H_i/RT}P_i}{1+b_{o,i}e^{-\Delta H_i/RT}P_i}$$

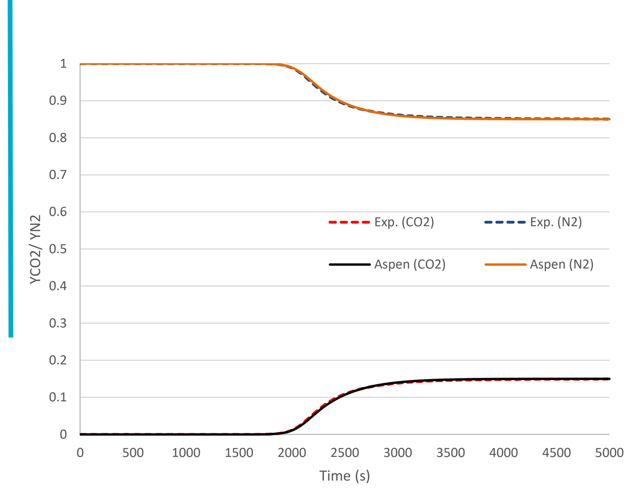
Breakthrough Curve Measurement and k_{LDF} Estimation

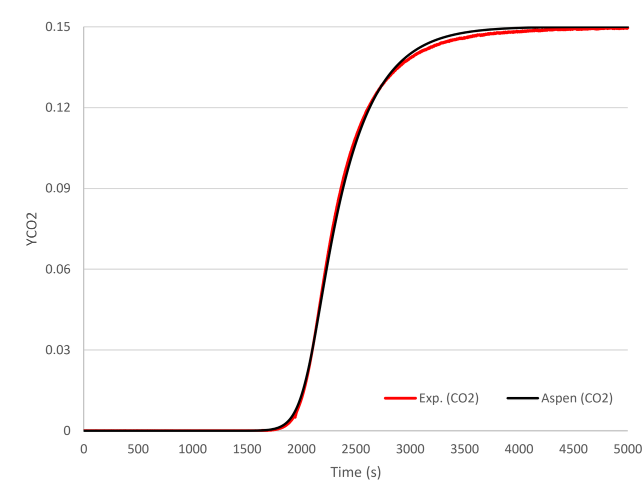
- Breakthrough curve measurements have been performed employing a homemade pilot adsorption unit.
- Linear driving force for adsorption kinetic $\left(\frac{\partial q_i}{\partial t} = k_{LDF,i}[q_i^* - q_i]\right)$

Length of adsorbent layer (m)	0.36
Diameter of column (m)	0.0217
Flowrate (NL/min)	0.1915
CO_2 molar fraction in feed (%)	14.92
Volume (cm³)	130.21
Mass of adsorbent (g)	56

Determination of k_{LDF} by least-squares minimization.

k_{LDF} (CO_2) [s^{-1}]	0.335
k_{LDF} (N_2) [s^{-1}]	0.031





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)
- Energy consumption < 2.3 kJ/kg$_{CO_2}$

VPSA process will be in a cyclic order because the beds will be alternated between adsorption and desorption, whereas one bed will be in an adsorption stage, and the other bed will be in a desorption stage. In the adsorption stage, at relatively high pressure, the solid adsorbent in the bed will selectively adsorb the CO_2 from the binary gas mixture, while N_2 which is less strongly adsorbed will be removed from the top of the column.

Assumptions:

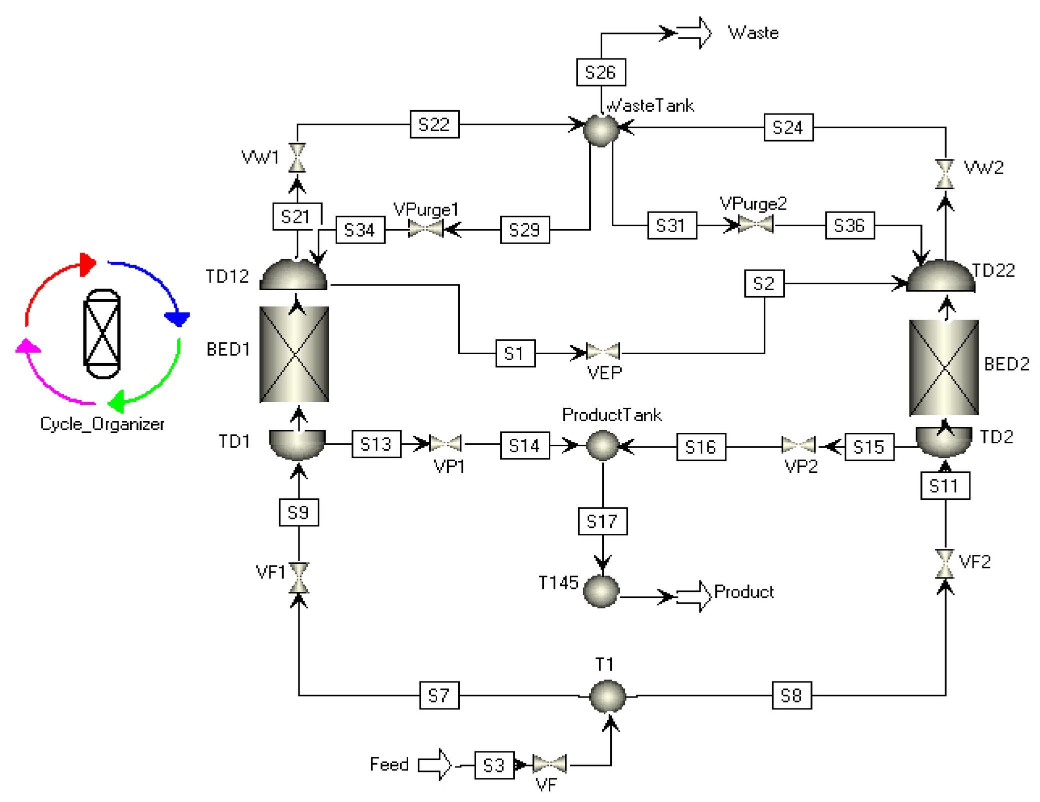
- The column has only one vertical adsorbent layer within the bed with the same packed adsorbent of MIL-160 (Al).
- Upwind differencing scheme 1 (UDS1) with 20 nodes has been selected as the discretization method.
- Gas phase properties determined by Peng Robinson equation of state.
- Adsorption equilibrium isotherms predicted by Langmuir Model.
- Mass balance: convection flow, accumulation in the gas phase and into the pores.
- Energy balance: non-isothermal with gas and solid conduction.
- Pressure Drop: Ergun Equation.

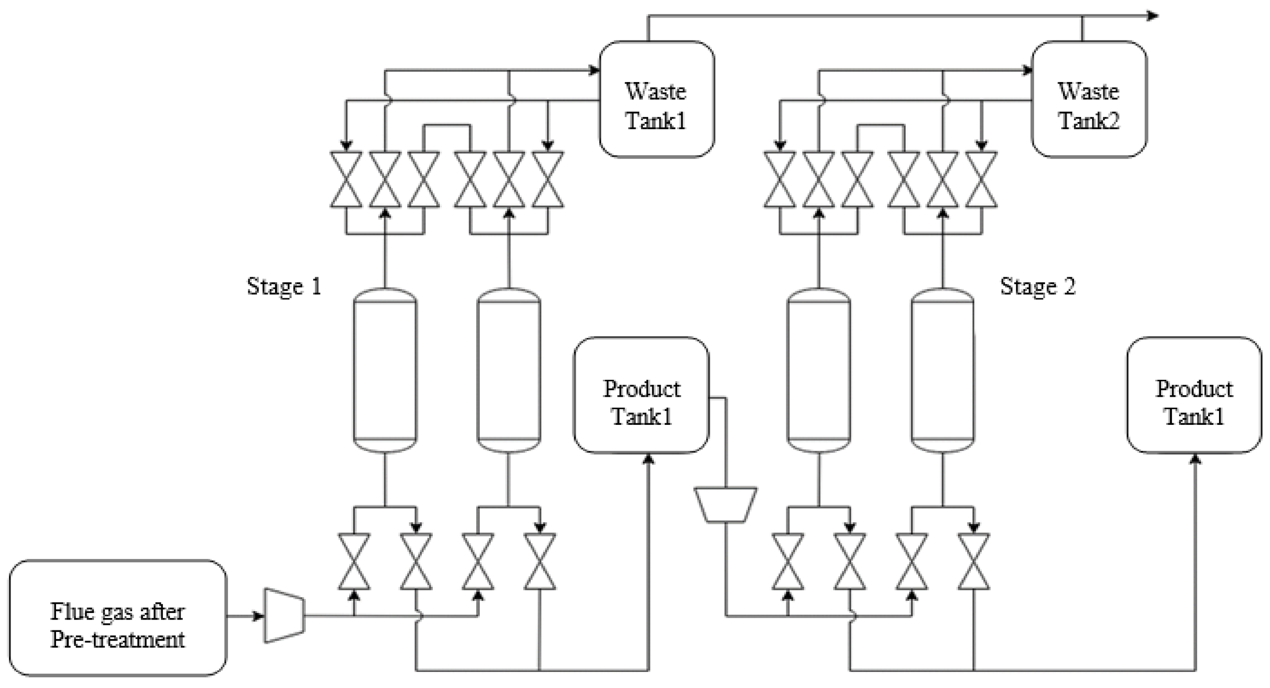
$$\frac{\partial p}{\partial z} = -\left(\frac{1.5*10^{-3}(1-\varepsilon_b)^2}{(2r_p\psi)^2\varepsilon_b^3}\mu_g u + 1.75*10^{-5}\frac{(1-\varepsilon_b)}{2r_p\psi\,\varepsilon_b^3}M\rho_g u^2\right)$$

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)	30

Objective: Designing a Two-stage (two columns in each stage) VPSA process and Using Skarstrom Cycle to reach high purity and recovery with less energy consumption.

Bed 1	Adsorption.		Equalization	Blowdown		Purge	Equalization	Pressurization
Bed 2	Blowdown	Purge	Equalization	Pressurization	Adsorption.		Equalization	Blowdown





Heat of adsorption

$$H_{isos} = -R\left(\frac{\partial \ln p}{\partial(1/T)}\right)_{n\ ads}$$

ΔH_{ads} (kJ/mol)	CO_2	N_2
	- 31.59	-19.12

$$E\left(\frac{kJ}{kg_{CO_2}}\right) = \frac{\int_0^{t_{press.+ads.}} P_{comp}dt + \int_0^{t_{blowdown+purge}} P_{Vac}dt}{\int_0^{t_{blowdown+purge}} Q_{prod}y_{CO_2}dt} / M.W_{CO_2}$$

$$P_{Comp} = \frac{\gamma}{\gamma-1}RT\left[\left(\frac{p_{feed}}{p_{atm}}\right)^{\frac{\gamma-1}{\gamma}}-1\right]Q_{feed}$$

$$P_{Vac} = \frac{\gamma}{\gamma-1}RT\left[\left(\frac{p_{atm}}{p_{blow}}\right)^{\frac{\gamma-1}{\gamma}}-1\right]Q_{product}$$

The operation conditions of the first stage (front) VPSA process are as below:

- Adsorption Time: 70 s.
- Purge Time: 30 s.
- Purge to feed ratio: 10%.
- Feed Flowrate: 1 Nm³/h [0.0446 Kmol/h], Y CO_2 =0.15.
- Feed Pressure= 1.1 bar.
- Vacuum Pressure= 0.1 bar.

For the second stage (tail), the operation conditions are as below:

- Adsorption Time: 407-557 s.
- Purge Time: 40-70 s.
- Purge to feed ratio: 5-30%.
- Feed Pressure= 1.6 bar.
- Vacuum Pressure=0.1 bar.
- Flowrate Q2=Q1* Y CO_2 *R/P.
- Flowrate= 0.0116 kmol/h.
- Y CO_2 =0.5565.

Results:

	Stage 1	Stage 2	Overall
CO_2 Recovery [%]	97.24	92.60	**90.04**
CO_2 Purity[%]	55.65	95.01	**95.01**
Energy [kJ/kg CO_2]	606	387	**993**
Productivity (gCO_2/ g ads.h)	0.229	0.233	**0.1165**

CONCLUSIONS

The equilibrium adsorption isotherms of CO_2 and N_2 on MIL-160 (Al) were measured successfully using a RUBOTHERM magnetic suspension balance and it was found that CO_2 exhibited a much stronger adsorption capacity than nitrogen. The adsorption isotherms of CO_2 and N_2 on MIL-160 (Al) were well-fitted by a Langmuir model with R^2 (coefficient of determination) equal to 0.99. The breakthrough measurements have been done using in situ pilot and the global mass transfer linear driving force coefficients for both CO_2 and N_2 have been estimated through the minimization of the differences between the observed and predicted breakthrough data. Aspen adsorption software version 11 was successfully used to design the VPSA process flowsheet. Two-stage VPSA process consisting of two columns in each stage was designed using the Adsim library in the software. The simulation results were well conformed to the U.S. Department of Energy (DOE) requirements in terms of product purity and recovery. Integrating the two-stage VPSA process produced a CO_2 purity of 95.01%, CO_2 recovery of 90.04%, CO_2 productivity of 0.1165 g CO_2 /g ads.h, and total energy consumption of 993 kJ/kgCO_2.

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