Evaluation of a novel multibed heat-integrated vacuum and temperature swing adsorption post-combustion CO₂ capture process

M.G. Plaza^{*} and F. Rubiera

Instituto Nacional del Carbón, INCAR-CSIC, C/Francisco Pintado Fe 26, 33011 Oviedo, Spain

^{*}Corresponding author: m.g.plaza@incar.csic.es

Abstract

A novel multibed heat-integrated vacuum and temperature swing adsorption process has been designed to capture 85% of the CO₂ emitted by an advanced supercritical coal fired power plant of 820 MW_e taken as reference, and to produce a concentrated product with 95% of CO₂ using a microporous carbon obtained from olive stones. The overall performance of the post-combustion CO₂ capture process has been evaluated from the results of the dynamic simulation of the process at cyclic steady state, using a detailed non-isothermal non-equilibrium dynamic fixed-bed adsorption model that takes into consideration competitive adsorption between the main flue gas components: N₂, CO₂ and H₂O. The proposed process operates between 30 °C and 1.05 bar and 80 °C and 0.05 bar. The specific heat duty of the process, 2.41 MJ_{th} kg⁻¹ CO₂, which is lower than the benchmark amine absorption technology, can be satisfied using waste heat. On the other hand, its electricity consumption, 1.15 MJ_e kg⁻¹ CO₂, is higher. Increasing the pressure of the production step reduces significantly the energy demand of the process, but also its capture rate. Substantial improvements in performance can be expected from adsorbent development. Adsorption is an environmentally benign technology with great potential to mitigate CO₂ emissions from industrial processes with unused waste heat sources.

Keywords: CO₂ capture, adsorption, simulation, post-combustion

1. Introduction

The Beyond 2 °C Scenario (B2DS) of the International Energy Agency (IEA) is in line with the midpoint of the ambition range of the Paris Agreement, *i.e.*, limiting future temperature increase to 1.75 °C by 2100. According to the B2DS, over 11 Gt of CO₂ will need to be captured and stored by 2060 [1]. However, current annual capacity is only around 35 Mt. CO₂ capture and storage still needs to be deployed globally and urgently to achieve climate targets.

Coal continues to provide 40% of the electricity production, with over 2000 GW_e of installed capacity and 1000 GW_e under planning stage. It is unlikely that these facilities will close in a time frame consistent with climate goals, so the retrofitting of such units with post-combustion CO₂ capture technologies is the IEA's recommended approach in a cost-effective energy scenario [2]. Only two post-combustion capture units have been installed so far in coal fired power plants at commercial scale: the first entered in operation in 2014 at Boundary Dam Power Station, in Canada [3], and the last (and largest), at Petra Nova plant, in Texas, US, by the end of 2016 [4]. Both facilities make use of amine absorption technology. Despite the technology development carried over the last decades, amine scrubbing still presents a series of drawbacks such as toxic emissions, corrosion problems and energy intensity, not to forget issues related to solvent production, such as a high carbon footprint [5].

Adsorption-based separation processes have lower environmental impact as they do not present toxic emissions, and sustainable adsorbents can be developed from biomass feedstocks. These processes do not present corrosion problems, and they do have potential to reduce the energy penalty of the CO₂ capture step, being an appealing alternative to the benchmark post-combustion CO₂ capture technology. In fact, there is a high patent activity related to adsorption-based CO₂ capture processes with large companies involved, that demonstrates the economic interest of the practice [6].

One of the distinguishing characteristics of adsorption-based separation processes is that they present great design flexibility. Several post-combustion CO₂ capture processes have been proposed up to date that differ in the adsorbent used (supported amines, supported potassium carbonates, zeolites, carbons, alumina, etc.), the method of regeneration (temperature, pressure, concentration driven or a mixture of them), and the gas-solid contact type (fixed, moving, fluidized or rotary adsorbers). Table 1 provides an overview of those that have reached demonstration stage at pilot scale in coal fired power plants. Most of them [10-15] are under active development either to reduce their energy requirements and/or to improve their removal efficiency and CO₂ purity. In general, fixed-bed adsorbers are used in pressure driven processes, whereas circulating solids are preferred for temperature driven processes due to the associated thermal inertia. Comparison between the different processes is not straightforward, as they present different levels of complexity, different removal rates and CO₂ purities, different sources of energy (low-temperature heat, high-temperature heat, electricity), and also due to the lack of sufficient data to make a fair comparison. However, all the processes shown in Table 1 have something in common: they have demonstrated the feasibility to capture the CO₂ emitted by a real coal-fired power plant using adsorption technology.

Table 1. Demonstration of post-combustion CO₂ capture adsorption processes at pilot scale in coal fired power plants

Type of process	Type of adsorber	Flue gas flow rate	Flue gas pretreatment	Adsorbent	Adsorption conditions	Regeneration conditions	CO ₂ capture rate (%)	CO ₂ purity (%)	Energy consumption	Reference
Dual stage: I. PTSA II. PSA	Fixed-bed I: 4 beds II: 4 beds	1000 Nm ³ h ⁻¹	dehydration (2-bed PSA alumina unit)	Ca-X zeolite	≈ 1 bar	0.05-0.15 bar 50-100 °C	90	99	2.02 MJ _e kg ⁻¹ CO ₂ + unused waste heat	[7]
VPSA	Fixed-bed (3 beds)	46 Nm ³ h ⁻¹	dehydration (alumina unit)	Zeolite 5A (282 kg)	1.2 bar 20 °C	0.05 bar	79	85	2.37 MJ _e kg ⁻¹ CO ₂ ^a	[8]
Dual stage VPSA	Fixed-bed (I: 3 beds) (II: 2 beds)	35 Nm ³ h ⁻¹	dehydration (2-bed TSA alumina unit)	I: zeolite 13X APG (261 kg) II: activated carbon beads (68 kg)	I: 1.17 bar II: 1.22-1.26 bar	I: 0.07-0.08 bar II: 0.2 bar	90.2	95.6	2.44 MJ _e kg ⁻¹ CO ₂ ^a + waste heat for alumina regeneration	[9]
DR-VPSA	Fixed-bed (4 beds divided into 2 sections)	100 Nm ³ h ⁻¹	cooling; compression; dust, SO _x , and NO _x removal; drying (glycerol)	Two types of activated carbons: AC1 & AC2 (270 kg + 270 kg)	1.6 bar 18 °C	0.05-0.1 bar	44.6	87.5	3.52 MJ _e kg ⁻¹ CO ₂ ^a	[10]
TSA (KIERDRY)	Riser	35,000 Nm ³ h ⁻¹	compression; desulfurization; humidity control	K ₂ CO ₃ based sorbents	70-80 °C	140-200 °C	>80	>95	4-5 MJ _{th} kg ⁻¹ CO ₂	[11]
TSA (ADAorb TM)	3 staged fluidized bed in bubbling regime	0.38 kg/s	desulfurization; compression; cooling	amine-based ion-exchange polymers (BN)	40 °C	120 °C	90	89.4	4.75 MJ _{th} kg ⁻¹ CO ₂ ^b	[12]
TCSA (ACS)	Moving bed	120 m ³ h ⁻¹	cooling (DCC)	carbon beads	50-60 °C	120 °C	67	93		[13]
CSA	Simulated moving bed (10 beds)	0.63 kg/s	heating with boiler feed water	alkalized alumina	1 bar ≈130-140°C	≈130-140°C				[14]
TCVSA (VeloxoTherm TM)	Rotary adsorber		cooling (DCC)	Structured carbon adsorbents	40 °C	100 °C 0.9 bar		90		[15]

^a VPSA blower & vacuum pumps considered only; ^b Regeneration energy only. PTSA: pressure and temperature swing adsorption; PSA: pressure swing adsorption; VPSA: vacuum pressure swing adsorption; DR: dual reflux; TSA: temperature swing adsorption; TCSA: temperature and concentration swing adsorption; CSA: concentration swing adsorption; TCVSA: temperature, concentration and vacuum swing adsorption; DCC: direct contact cooler.

In this work a novel multibed heat-integrated vacuum and temperature swing adsorption (VTSA) process that makes use of a sustainable microporous carbon adsorbent, has been designed to capture at least 85% of the CO₂ emitted by a coal-fired power plant taken as reference and to deliver a product with 95% CO₂ (dry basis) or greater. The reference power plant, used for comparison purposes, is that previously used within the HiPerCap project (EU funded; FP7-ENERGY-608555) to compare different post-combustion technologies: an advanced supercritical coal-fired power plant of 820 MW_e (gross) [16]. The use of a common reference case and set of assumptions facilitates the comparison of radically different competing technologies on a fair basis.

In an adiabatic VSA process the productivity is reduced due to the inherent exothermic nature of adsorption; *i.e.*, the adsorbent is heated during adsorption and cooled during regeneration, reducing its working capacity. In the here proposed VTSA process, the adsorbent is regenerated by countercurrent evacuation combined with mild indirect heating. The heating pursues to enhance the regeneration of the adsorbent, reducing the level of vacuum required to meet the recovery target, and thus reducing the electricity consumption of the process [7]. The use of indirect heat transfer in tube bundle adsorbers [17] allows reducing the cycle time compared to direct heat transfer, thus increasing productivity, and saving thermal energy within the process [18] through heat recovery, *i.e.*, the enthalpy stored in one adsorber can be used to heat another adsorber in a different step of the cycle, making use of a thermal fluid that circulates between the vessels [19].

The overall performance of the proposed VTSA post-combustion CO₂ capture process has been evaluated through process simulation. This is a powerful tool that can be used to assess preliminarily the feasibility of a specific technology for a determined application with a low investment cost. The dynamic model of the adsorption process used to run the simulation takes into consideration competitive adsorption between main flue gas components, *i.e.*, N₂,

CO₂ and H₂O. Competitive adsorption should be considered in the design of adsorption based separation processes, although it is generally neglected due to the added complexity of the model. In the case of post-combustion CO₂ capture, the flue gas is saturated with H₂O; in these conditions, the equilibrium adsorption capacity of H₂O is generally large, and the influence of H₂O should either be considered in the design of the adsorption process or the flue gas should be dried prior to enter the capture unit. When hydrophilic adsorbents are used, the second approach is generally followed, as shown in Table 1; otherwise large amounts of water would be strongly adsorbed making regeneration uneconomic. The use of hydrophobic carbons with relatively low adsorption capacity and affinity towards H₂O pretends to avoid the dehumidification of flue gas and its associated costs. The feasibility of this approach has been demonstrated at real coal-fired power plants, where the carbon-based adsorption unit is placed directly after a direct contact cooler [13], withstanding even high sulfur levels [15].

2. Materials and methods

2.1. Adsorbent

The adsorbent used to run the process simulations in the present study is a microporous carbon obtained by direct oxidation of an abundant residue from the food industry: olive stones [20]. This adsorbent presents the characteristic moderate adsorption capacity towards CO₂ of carbon adsorbents [21], but also relatively low adsorption capacity and affinity towards H₂O [22] that makes it an interesting candidate for adsorption-based post-combustion CO₂ capture processes [23].

2.2. Description of the evaluated VTSA post-combustion capture process

The VTSA post-combustion CO₂ capture process proposed and evaluated in the present work consists in a multibed heat-integrated process, which simplified flowsheet is presented in Figure 1.

Figure 1. Simplified flowsheet of the VTSA post-combustion CO₂ capture process.

As shown in Figure 1, the desulfurized flue gas from the reference power plant, G1, is slightly pressurized to overcome the pressure drop of the capture unit using a blower (FGB). Then, the flue gas is cooled down to *circa* 30 °C using a cooler (FGC), which in practice will most likely be a direct contact cooler. Due to the temperature drop, part of the H₂O fed with G1 condenses (C-1). Flue gas cooling has shown to reduce the overall energy consumption of adsorption-based post-combustion capture processes, due to the increase achieved in the working capacity of the adsorbent [18].

Up to this point the flowsheet of the VTSA process is similar to that of the benchmark absorption process. However, absorption is a steady state process where the flue gas is continuously fed to the absorber column and the liquid solvent circulates between the absorber and the stripper columns. On the other hand, in the VTSA process, the solid remains stationary and the flue gas, which is also continuously fed to the capture unit, is fed alternatively to adsorber A1 or A2 through an automated valve system. Therefore the design and layout of post-combustion CO₂ capture processes by absorption and fixed-bed cyclic adsorption differ substantially.

The adsorbers considered in the present work are vertical tube bundle adsorbers, where the adsorbent is packed inside the tubes and a thermal fluid circulates outside the tubes and parallel to them. Thin tubes (with an internal diameter of 3 cm) are considered to avoid thermal gradients in the radial direction of the tubes and to achieve fast temperature swings. The height of the tubes was set to 0.7 m to limit the overall pressure drop and to reduce cycle time according to previous TSA design experience [18]. The operating temperature range of the VTSA process (30-80 °C) entails using water as the heat transfer fluid, which presents the advantages of a large heat capacity, availability, lack of toxicity and low cost.

During the *feed step*, the cooled flue gas (G1-2) is fed to one of the adsorbers, which is either being pressurized or in adsorption mode. During adsorption, a waste stream of decarbonized gas (W) is produced. A buffer tank (WBT) provides a continuous flow rate of waste gas to the stack of the power plant.

In order to operate in a continuous basis, the adsorbent needs to be cyclically regenerated. This is accomplished during the *regeneration or production step*, by closing the waste outlet and recovering the concentrated CO₂ product from the feed end by means of evacuation coupled with indirect heating. A vacuum pump or product blower (PB1) delivers a concentrated CO₂ product at 1.1 bar (P-2). To save thermal energy within the process, the enthalpy of P-2 is used to preheat the adsorbers' heating water (AHW-3) in a cross heat exchanger, labelled as HX in Figure 1. The outlet product, P-3, is further cooled to near 30 °C using cooler PC1, which knocks out the condensate C-2. The resulting product, P-4, is fed to a buffer tank (PBT) that provides a continuous flow rate of product (P-5), which is compressed by blower PB2 and cooled by cooler PC3, to deliver the final product at 2 bar and near 30 °C. These conditions mimic those of the product of the absorption process taken as reference, to facilitate the comparison of the performance of both technologies. A buffer tank, CBT, collects

all the knocked out condensates and provides a continuous flow rate of condensate (C) out of the process.

The minimum pressure achieved during the regeneration step was set to 0.05 bar in order to achieve sufficient recovery, according to the results from a parametric study carried out by running a batch of simulations of VTSA processes up to cyclic steady state (CSS). This is a common vacuum level in adsorption-based post-combustion CO₂ capture processes, as shown in Table 1. The inlet temperature of the adsorbers' heating water, 80 °C, opens up the prospect to use low-temperature waste heat as the heating source. This is a significant advantage over the benchmark technology, which uses condensing steam above 120 °C to regenerate the amine solvent; such steam needs to be extracted from the power cycle or produced in an independent boiler unit.

By the end of the regeneration step the adsorbent is hot; this is progressively cooled during the feed step using the adsorbers' cooling water (ACW-1) that is fed to the shell of the adsorber at the same temperature as the flue gas and cocurrently to it. The enthalpy of the cooling water that exits the adsorber at the beginning of the feed step, ACW-2, is used to preheat the parallel adsorber prior to the production step.

In order to recover CO₂ with high purity, an intermediate *rinse (R) step* is carried out between the adsorption and the regeneration steps. During this step, a fraction of the product, R-1, is used to sweep the N₂ present in the gas phase by the end of the adsorption step. At the same time, the adsorbent is indirectly preheated using the enthalpy of ACW-2 to save thermal energy within the process. To avoid condensation of H₂O in the bed, which is initially cold from the adsorption step, R-1 is extracted after knocking out the product condensate C-2. Prior to enter the adsorber, the rinse stream is heated by a heater (RH) up to the temperature of ACW-2. The temperature rise experienced by the adsorbent during the rinse step reduces the rinse flow rate requirements, as the equilibrium adsorption capacity of CO₂ decreases with

increasing temperature for a given partial pressure of CO₂. The effluent produced during the rinse step, R-3, is recirculated in order to meet the imposed recovery target. A buffer tank (RBT) is used to provide a continuous flow rate of R-3, which is mixed with the cooled flue gas (G1-2) to make up the adsorbers feed.

The adsorbers' cooling and heating water (ACW and AHW, respectively) circulates in two separate closed loops by means of centrifugal pumps (ACWP and AHWP, respectively). ACW is cooled using external cooling water from the cooling towers of the reference power plant in a separate cooler (ACWC) prior to enter the adsorber. A storage tank provided with a heating system (AHWT&H) is used to store AHW when this is not circulating, and to adjust its temperature prior to be fed to the adsorber, using a source of waste heat.

The cycle schedule of the proposed VTSA process is shown in Figure 2. Each adsorber goes through the following steps in series: pressurization with feed, adsorption, rinse, and production, completing a full cycle in 240 s. With this schedule, an even number of adsorbers (at least 2) are required to treat the flue gas from the power plant in a continuous basis.

FEED: PRESSURIZATION & ADSORPTION		RINSE	PRODUCTION
RINSE	PRODUCTION	FEED: PRESSURIZATION & ADSORPTION	

Figure 2. Cycle schedule of the proposed VTSA process.

2.3. Evaluation of the performance of the VTSA post-combustion capture process

The performance of the post-combustion CO₂ capture process has been evaluated from the dynamic simulation of the VTSA process, which was carried out until the CSS was achieved. At CSS the concentration and temperature profiles along the bed at a given cycle time becomes the same at each subsequent cycle.

The VTSA model used in the present work is based on a detailed one dimension non-isothermal non-equilibrium dynamic fixed-bed adsorption model that has been previously validated with experimental results obtained in a laboratory scale fixed-bed vacuum pressure

and temperature swing adsorption (VPTSA) unit. These included: (i) dynamic breakthrough experiments with N_2/CO_2 mixtures with varying composition at different temperatures [21]; (ii) dynamic breakthrough experiments with synthetic flue gas mixtures containing N_2 , CO_2 and H_2O with varying relative humidity at different temperatures that departed from a fully regenerated adsorbent and from an adsorbent initially saturated with H_2O [22]; and (iii) VTSA cycles with synthetic flue gas mixtures containing N_2 , CO_2 and H_2O [23]. This model takes into consideration competitive adsorption between N_2 , CO_2 and H_2O making use of the Ideal Adsorption Solution (IAS) theory [24]. The competitive adsorption between the main flue gas species, *i.e.*, CO_2 , N_2 and H_2O , is generally neglected in simulation studies due to the added complexity to the model. However, even a carbon adsorbent can adsorb a significant amount of H_2O at equilibrium with a gas phase with high relative humidity, and this has an adverse impact in the adsorption capacity towards CO_2 [22]. Therefore, it is mandatory to consider competitive adsorption in the cyclic adsorption model used to design adsorption-based post-combustion CO_2 capture processes [23].

To reduce the computational effort of the dynamic simulations only CO_2 , N_2 and H_2O were considered in the gas phase. The simulations were run with the actual composition of CO_2 and H_2O of the desulfurized flue gas of the reference power plant and the amount of N_2 was calculated by difference. This is a good approximation, as O_2 and N_2 have shown to behave similarly in likewise adsorbents [25], and trace components are not expected to be a problem for carbon adsorbents [26].

Simulations were carried out for a single tube to reduce the simulation time: it is assumed that every tube in the bundle behaves equally. The VTSA model includes a single-phase jacket heat exchanger that embraces the tube packed with the adsorbent. The material and energy balances that constitute the model account for three different phases: the solid adsorbent, the gas phase, and the heat transfer fluid. The following assumptions were made: the energy

balance of the wall of the tubes can be neglected; the adsorber vessels are thermally insulated from ambient air; gas flow within the packed tubes can be described as axially dispersed plug flow; the pressure of the gas phase inside the packed tubes can be calculated locally as a function of the gas velocity using the Ergun equation; radial dispersion within the tubes is negligible; and the solid linear driving force approximation is valid.

VTSA process simulations were carried out using Aspen Adsorption V8.0. The spatial derivatives were approximated using the upwind differentiating scheme (USD1) with 100 nodes along the adsorber axis. Average values of the molecular diffusivities and the heat capacities were considered for each step. The overall heat transfer coefficient between the gas phase and the liquid water used as heat transfer fluid was assumed constant.

The main design parameters used to run the simulations are summarized in Table 2 with specific reference to their source. These have been either taken from previous studies to facilitate technology comparison or specifically selected in this work according to simulation results.

Table 2. Design parameters used to simulate the VTSA post-combustion CO₂ capture processes

Parameter	VTSA	Units
Length of the tubes packed with the adsorbent	0.7 ^a	m
Diameter of the tubes packed with the adsorbent	0.03 ^a	m
Wall width between the adsorbent and the heat transfer fluid	1 ^a	mm
Overall heat transfer coefficient	2000 ^a	W m ⁻¹ K ⁻¹
Molar flow rate of the desulfurized flue gas from the reference power plant (G1)	27217 ^b	mol s ⁻¹
Conditions of the desulfurized flue gas from the reference power plant (G1)	Pressure	1.05 ^b bar
	Temperature	47 ^b °C
	Composition	
	CO ₂	13.60 ^b % mol
	H ₂ O	10.16 ^b % mol
	N ₂	76.24 ^c % mol
Temperature of the cooled flue gas (G1-2)	30.78 ^d	°C
Pressure of the decarbonized flue gas vented to the stack (W)	1.05 ^b	bar
Inlet temperature of the adsorbers' cooling water (ACW-1)	30.78 ^d	°C
Inlet temperature of the adsorbers' heating water (AHW-1)	80 ^d	°C
Flow rate of the adsorbers' cooling water (ACW)	27337 ^d	kg s ⁻¹
Average flow rate of the adsorbers' heating water (AHW)	22781 ^d	kg s ⁻¹
Total duration of the feed (pressurization & adsorption steps)	120 ^d	s
Duration of the rinse step	20 ^d	s
Duration of the production step	100 ^d	s
Superficial velocity of the feed gas at the adsorber inlet	0.26 ^d	m s ⁻¹
Superficial velocity of the rinse gas at the adsorber inlet	0.24 ^d	m s ⁻¹
Linear valve coefficient used to simulate the evacuation step	0.07 ^d	mol s ⁻¹ bar ⁻¹
Pressure of the stream P-1	0.05 ^d	bar
Pressure of the stream P-2	1.1 ^d	bar
Temperature of the stream P-4	30.78 ^d	°C
Pressure of the CO ₂ product delivered by the capture unit (P)	2 ^b	bar
Temperature of the CO ₂ product delivered by the capture unit (P)	30.78 ^b	°C

^a [18]; ^b [16]; ^c calculated by difference; ^d values used in this work according to utilities'

specifications and simulation results

The results from the dynamic simulations of the VTSA process at CSS were used to upscale the process to treat the full molar flow rate of the flue gas from the reference power plant. The

performance of the post-combustion CO₂ capture process is assessed in terms of the CO₂ purity of the product (in dry basis), the CO₂ capture rate, the productivity of the VTSA process, and the energy consumption of the overall process.

The product purity, the capture rate and the productivity are defined by Equations 1, 2, and 3, respectively.

$$CO_2 \text{ purity of the product (\% mol, db)} = \frac{F_{CO_2,P}}{F_{CO_2,P} + F_{N_2,P}} \times 100 \quad (1)$$

$$\text{Capture rate (\%)} = \frac{F_{CO_2,P}}{F_{CO_2,G1}} \times 100 \quad (2)$$

$$\text{Productivity} \left(\frac{\text{kg } CO_2}{\text{kg of adsorbent} \times h} \right) = \frac{\dot{m}_{CO_2,P}}{M_A} \quad (3)$$

where $F_{CO_2,P}$ represents the molar flow rate of CO₂ in the final product that leaves the capture unit, $F_{N_2,P}$ represents the molar flow rate of N₂ in the final product that leaves the capture unit, $F_{CO_2,G1}$ represents the molar flow rate of CO₂ that enters the capture unit with the flue gas, $\dot{m}_{CO_2,P}$ represents the mass flow rate of CO₂ in the final product that leave the capture unit expressed in kg h⁻¹, and M_A represents the total mass of adsorbent expressed in kg.

The energy requirements were calculated for the full scale capture process using Aspen Plus software. The total heat duty of the process was calculated from the sum of the heat duty of the adsorbers' heating water heater (AHWT&H) and the rinse heater (RH). The total cooling duty of the process was calculated from the sum of the cooling duties of the flue gas cooler (FGC) and the product coolers (PC1 and PC2). The electricity requirements were calculated from the sum of the consumption of the flue gas blower (FGB), the product blowers (PB1 and PB2), and the centrifugal pumps required to circulate the adsorbers' cooling and heating water (ACWP and SHWP, respectively), using the specifications shown in Table 3. In order to facilitate comparison with other post-combustion processes, the specific energy demand was calculated as the energy demand per kg of CO₂ captured.

Table 3. Specifications of the auxiliary equipment

Equipment	Parameter	value	Units
Blowers	Isentropic efficiency	75 ^a	%
	Driver efficiency	95 ^a	%
Centrifugal pumps	Hydraulic efficiency	80 ^a	%
	Driver efficiency	95 ^a	%
	Pressure change	0.4 ^b	bar
Coolers, heaters and cross heat exchanger	Pressure drop (gas)	2 ^a	%
Power plant's cooling water	inlet temperature	20.78 ^a	°C
	outlet temperature	30.53 ^a	°C
Coolers/condensers and cross heat exchanger	Minimum temperature approach	10 ^b	°C

^a[16]; ^b[18]

However, the comparison between different post-combustion technologies is not so straightforward. Specific terms, like the *Specific Energy Penalty of Avoided CO₂* (SEPAC), which is defined by Equation 4 [16], have been defined to enable fair comparisons. SEPAC measures the reduction in the net power output of the reference power plant due to capture, normalized by the amount of CO₂ avoided.

$$SEPAC = \frac{NEO_{ref} - NEO}{\phi_{CO_2,ref} - \phi_{CO_2}} \quad (4)$$

where *NEO* is the net electric output of the power plant in MW_e, ϕ_{CO_2} is the emitted flow of CO₂ in kg s⁻¹, and *ref* states for the reference power plant without capture.

The calculation of SEPAC requires the determination of the net electric output of the capture plant integrated with the reference power plant, which is out of the scope of the present work. However, the value of SEPAC for the VTSA process was estimated assuming that the heat duty of the VTSA process can be entirely satisfied using waste heat (with no added penalty for the power plant efficiency).

3. Results and discussion

3.1. Results from the simulation of the VTSA process at CSS

Figure 3 represents the history of pressure, temperature, and relative humidity of the gas phase inside a packed tube at three different heights: at the feed entrance (FE), at the waste gas outlet (WO) and at an intermediate position (IP) during a full VTSA cycle once CSS has been achieved.

Figure 3. History of pressure (a), temperature (b), and relative humidity (c) of the gas phase at CSS during a full VTSA cycle. FE: feed entrance; IP: intermediate position; WO: waste gas outlet.

As can be seen from Figure 3a, the pressure increases linearly at the beginning of the feed step because the gas outlet of the adsorber is kept closed until the adsorption pressure is reached. The pressure remains approximately constant at near 1.05 bar during the adsorption and rinse steps, until the beginning of the production step, when it drops down to 0.3 bar very rapidly and then more slowly towards 0.05 bar.

Figure 3b shows that the temperature inside the adsorber decreases from 80 °C to near 32 °C during the first 30 s of the cycle and remains approximately constant during the rest of the feed step mainly due to the indirect cooling carried out by the adsorber's cooling water. Then, during the rinse step, the temperature raises up to approximately 53 °C due to the direct and indirect heating, but also to the exothermic adsorption of CO₂. Subsequently, at the beginning

of the production step, the temperature increases up to 80 °C due to the external heating carried out by the adsorbers' heating water.

As can be seen from Figure 3c, the maximum relative humidity is reached at the feed entrance by the end of the feed step; at this cycle time, the relative humidity of the gas phase in the rest of the bed is negligible because nearly all the H₂O is adsorbed at the bed entrance, as it will be discussed later. The figure shows a sharp drop of the relative humidity at the beginning of the rinse and regeneration steps that is due to the temperature rise. It is important to bear in mind that during the whole VTSA cycle only the bed entrance is exposed to a noticeable humidity.

Figure 4 represents the profiles for the amount of N₂, CO₂, and H₂O adsorbed at CSS of the VTSA process by the end of the feed, rinse and production steps, which correspond to cycle times of 120 s, 140 s, and 240 s, respectively.

Figure 4. Profiles for the amount adsorbed of N₂ (a), CO₂ (b), and H₂O (c) at CSS by the end of the feed, rinse and production steps, which correspond to cycle times of 120 s, 140 s, and 240 s, respectively.

Figure 4a shows that the amount of N₂ adsorbed is maximum by the end of the feed step at the bed outlet, decreases drastically during the rinse step, and is negligible by the end of the production step. Comparing Figure 4a and Figure 4b is clear that the amount of CO₂ adsorbed is significantly greater than that of N₂ during the full cycle.

Figure 4b shows a moderate CO_2 loading by the end of the feed step, which was expected for the adsorbent evaluated [21]. The amount of CO_2 adsorbed becomes maximum by the end of the rinse step at the bed entrance, which is the product end during the subsequent production step. Note that the adsorbent is not fully regenerated by the end of the production step, as expected for this type of processes. Reducing further the residual loading of CO_2 would require the use of higher vacuum and/or temperature.

From Figure 4c it can be seen that the loading of H_2O is significant only at the feed entrance during the feed and rinse steps, *i.e.*, most of the water adsorbed during the adsorption and rinse steps is desorbed during the regeneration step, resulting in a rather small H_2O hold-up during the VTSA process. This is relevant, as hydrophilic adsorbents would not be regenerated in the relatively mild conditions evaluated here. It is also important to notice that the maximum H_2O loading achieved during the VTSA cycle is significantly lower than the equilibrium capacity of the carbon at high relative humidity [22].

Figure 5 represents the profiles for the molar fraction of N_2 , CO_2 and H_2O in the gas phase at CSS for the VTSA process by the end of the feed, rinse and production steps, which correspond to cycle times of 120 s, 140 s, and 240 s, respectively.

Figure 5. Profiles of the molar fraction of N_2 (a), CO_2 (b), and H_2O (c) in the gas phase at CSS by the end of the feed, rinse and production steps, which correspond to cycle times of 120 s, 140 s, and 240 s, respectively.

As can be seen from Figure 5a the molar fraction of N_2 in the gas phase is maximum by the end of the feed step; the gas composition at the bed entrance during this step is close to the flue gas composition. However, by the end of the rinse step the vast majority of N_2 has been swept out from the bed, and only the gas phase at the bed outlet remains rich in N_2 . Figure 5a also shows that the molar fraction of N_2 in the gas phase at the bed inlet increases by the end of the production step. This can solely be attributed to the desorption of N_2 during the production step. However, due to the low absolute pressure at this stage of the cycle (near 0.05 bar), the actual amount of N_2 in the gas phase is very low.

The molar fraction of CO_2 in the gas phase, shown in Figure 5b, is minimum by the end of the feed step and maximum by the end of the rinse step. Although CO_2 is the most abundant component in the gas phase by the end of the production step, the amount of CO_2 remaining in the gas phase is low.

Figure 5c shows that the gas phase is essentially free of H_2O during the full VTSA cycle: only the bed entrance presents noticeable H_2O content in the gas phase, *i.e.*, all the H_2O fed is adsorbed, as shown in Figure 4c.

3.2. Assessment of the overall performance of the VTSA post-combustion CO_2 capture process

The process performance parameters of the VTSA post-combustion CO_2 capture process are summarized in Table 4. Two additional post-combustion CO_2 capture processes have also been included in the table for comparison purposes: an advanced absorption case taken as the reference case within HiPerCap project (CESAR1) [16] and a fixed-bed TSA process [18], that have been developed for the same reference power plant using a common set of assumptions.

Table 4. Performance of different post-combustion CO₂ capture technologies evaluated using a common basis.

Parameter	VTSA ^a	TSA ^b	CESAR 1 ^c	Units
Purity of the CO ₂ product (dry basis)	95.0	95.6	≥95	% vol.
CO ₂ capture rate	85.3	85.4	90	%
Specific heating duty	2.41	3.59	3.02	MJ _{th} kg ⁻¹ CO ₂
Specific cooling duty ^d	3.00	3.36	3.37	MJ _{th} kg ⁻¹ CO ₂
Specific electricity consumption ^d	1.15	0.13	0.09	MJ _e kg ⁻¹ CO ₂
SEPAC ^d	1.15		0.78	MJ _e kg ⁻¹ CO ₂
Productivity	0.32	0.40	-	kg _{CO2} kg _{adsorbent} ⁻¹ h ⁻¹

^aThis work; ^b[18]; ^c[16]; ^dexcluding CO₂ product compression above 2 bar

As can be seen from Table 4, the VTSA process fulfils the established targets for the CO₂ capture rate and the CO₂ product purity: it captures 85% of the CO₂ emitted by the reference power plant with a final product purity of 95% CO₂ (dry basis).

The specific heat duty of the VTSA process is lower compared to the benchmark absorption technology and the TSA process mainly due to the milder thermal swing considered in the present work (30-80 °C vs. 30-120 °C and 30-130 °C, respectively). Moreover: due to the lower operating temperature of the VTSA process, its specific heat duty might be satisfied using low grade heat from unused waste heat sources within the power plant. This is an important advantage against the benchmark technology, which makes use of steam extracted from the power cycle to regenerate the solvent, thus reducing the gross electrical output of the power plant.

It is also interesting to highlight that the specific cooling duty of the VTSA process is lower than that of the benchmark absorption technology. This is of high relevance, as cooling water availability is one of the major constraints to the retrofit of thermal power plants with CO₂

capture units using amine absorption technology. However, it must be born in mind that the cooling requirements of the power plant (without capture) and those of the capture plant are not necessarily additive. For example, the integration of the reference power plant with the reference absorption case leads to an increase in the overall cooling duty of only 19% (excluding the compression of the product above 2 bar), which is significantly lower than that expected for an additive behavior: 63% [16]. Nevertheless, the integration of the reference power plant with the VTSA capture plant is out of the scope of the present work.

The specific electricity consumption of the VTSA process is the highest of the three processes included in Table 4, due to the added mechanical work required to compress the CO₂ product from subatmospheric pressures. The main electricity consumer of the VTSA process is the blower PB1, which increases the pressure of the product at the adsorber outlet from 0.05 bar up to 1.1 bar, consuming 90% of the electricity requirements of the VTSA process. Part of the heat generated during this mechanical compression is used to preheat the adsorbers' heating water in the cross heat exchanger. This entails saving 0.95 MJ_{th} kg⁻¹ CO₂, which represents 39% of the total heat duty of the VTSA process. The specific electricity consumption of the VTSA process is lower than that reported for other pressure driven adsorption processes demonstrated at coal fired power plants (see Table 1).

As can be seen from Table 4, the *SEPAC* of the VTSA process is higher than that of the reference absorption case. However, it must be born in mind that the latter makes use of an advanced solvent with reduced energy consumption: the typical regeneration duty of a conventional absorption process making use of 30% MEA is around 4 MJ_{th} kg⁻¹ CO₂ [27]. The development of advanced adsorbents with greater working capacities would lead to a lower *SEPAC*.

Table 4 shows that the productivity of the evaluated process is somewhat lower than that of the TSA process. Note that the TSA process makes use of carbon monoliths, which entailed

using higher feed flow rates [18]. However, the productivity of the VTSA process is high compared to other post-combustion CO₂ capture processes by VTSA reported in the literature and evaluated with dry synthetic flue gas mixtures [28-30] mainly due to the shorter cycle time used in the present work. Higher productivities could be achieved using adsorbents with higher CO₂ working capacities. This might be the case of Mg-MOF-74 [31], although the later would require a dehumidification stage prior to the capture unit [32].

Table 5 summarizes the main inputs and outputs of the VTSA capture plant, which is delimited by a dashed line in Figure 1. The global mass balance closes within -0.19%. The external cooling water requirements of the capture plant (ECWRCP) have been calculated from the cooling duties of FGC, PC1, PC2 and ACWC, following the specifications of Table 2.

Table 5. Summary of the main inputs/outputs of the VTSA capture unit.

Parameter	value	Units
Mass flow rate of CO ₂ captured	138.9	kg s ⁻¹
Mass flow rate of inlet flue gas (G1)	794.0	kg s ⁻¹
Mass flow rate of decarbonized gas delivered to stack (W)	601.6	kg s ⁻¹
Mass flow rate of product (P)	144.9	kg s ⁻¹
Mass flow rate of condensate (C)	49.0	kg s ⁻¹
Total mass of adsorbent	1539	t
External cooling water requirements of the capture plant (ECWRCP)	10228	kg s ⁻¹
Electrical requirements of the capture plant (ERCP)	159	MW _e
Heating duty of the capture plant (HDCP)	334	MW _{th}

Effect of production pressure

As discussed above, the major electricity consumer of the previously evaluated VTSA process is the blower PB1, which compresses the product from 0.05 bar to 1.1 bar. To evaluate the effect of the production pressure on the overall performance of the post-combustion CO₂ capture

process, two additional simulations were carried out changing solely the pressure of the production step. The results are summarized in Figure 6.

Figure 6. Effect of production pressure over the main process performance parameters: CO₂ capture rate, CO₂ purity, specific heating duty of the capture plant (SHDCP), and specific electricity requirements of the capture plant (SERCP).

As expected, as the pressure of the production step increases, the CO₂ capture rate decreases because the adsorbent is less thoroughly regenerated; *i.e.*, the residual loading of CO₂ increases. On the other hand, the CO₂ purity of the product increases slightly with the production pressure, from 95.0% to 96.7%.

The electricity requirements of the capture plant decrease by 55 % as the production pressure increases from 0.05 bar to 0.2 bar. The reduction in the specific electricity requirements of the capture plant is somewhat lower, 33%, because these are referred to the amount of CO₂ captured. On the other hand, the heating duty of the capture plant increases by 13 %, and the specific heating duty by 68%, because the temperature of the compressed product (P-2) decreases, and thus, the amount of heat that can be recovered in the cross heat exchanger.

The *SEPA*C decreases from $1.15 \text{ MJ}_e \text{ kg}^{-1} \text{ CO}_2$ to $0.77 \text{ MJ}_e \text{ kg}^{-1} \text{ CO}_2$ when the production pressure increases from 0.05 bar to 0.2 bar, becoming lower than that of the reference absorption case. However, in view of the need for rapid and significant emission cuts, and the likeliness that we need to go towards Negative Emission Technologies in the future [33], reducing the capture rate to 60% to save energy, is probably not the most interesting pathway. Instead, identifying industrial processes with an abundance of low-temperature waste heat (e.g. some metallurgical industries) should be the path to pursue.

Conclusions

A novel multibed heat-integrated vacuum and temperature swing adsorption process has been designed to capture at least 85% of the CO_2 emitted by an 820 MW_e (gross) advanced supercritical coal-fired power plant with a purity equal or greater than 95% (dry basis). The overall performance of the post-combustion CO_2 capture process has been evaluated from the results of the dynamic simulation of the adsorption process at cyclic steady state. The specific heat duty of the process, $2.41 \text{ MJ}_{th} \text{ kg}^{-1} \text{ CO}_2$, is lower than that of the benchmark technology. Moreover, due its low operating temperature range, $30\text{--}80^\circ\text{C}$, its heat demand can be satisfied using low-grade heat. However, the specific electricity consumption of the process, $1.15 \text{ MJ}_e \text{ kg}^{-1} \text{ CO}_2$, is higher than that of the benchmark technology, mainly due to the use of vacuum to regenerate the adsorbent. Increasing the absolute pressure of the production step reduces significantly the electricity requirements of the adsorption process, but also its capture rate. The specific energy penalty of avoided CO_2 , which provides a fair comparison between different post-combustion technologies, becomes competitive with an advanced solvent technology taken as reference for an absolute production pressure of 0.2 bar. However, a capture rate of near 60% does not seem sufficient to achieve climate goals. The adsorbent considered in the present work is a biomass-based carbon adsorbent; significant

performance improvements can be expected through the development of advanced adsorbents with higher working capacities.

Nomenclature

A	adsorber
ACS	advanced carbon sorbent technology
ACW	adsorbers' cooling water
ACWC	adsorbers' cooling water cooler
ACWP	adsorbers' cooling water pump
AHW	adsorbers' heating water
AHWP	adsorbers' heating water pump
AHWT&H	adsorbers' heating water tank and heating system
B2DS	beyond 2 °C Scenario of the International Energy Agency
C	condensate
CBT	condensate buffer tank
CSA	concentration swing adsorption
CSS	cyclic steady state
db	dry basis
DCC	direct contact cooler
DR-VPsA	dual reflux vacuum pressure swing adsorption
ECWRCP	external cooling water requirements of the capture plant (kg/s)
ERCP	electricity requirements of the capture plant (MW _e)

FE	feed entrance
FGB	flue gas blower
FGC	flue gas cooler
F_i	molar flow rate of species i (mol s^{-1})
G1	desulfurized flue gas from the reference power plant
G1-2	cooled flue gas
HDCP	heating duty of the capture plant (MW_{th})
HX	cross heat exchanger
IEA	International Energy Agency
IP	intermediate position
M_A	total mass of adsorbent of the capture unit (kg)
$\dot{m}_i$	mass flow rate of species i (kg h^{-1})
NEO	net electric output (MW_e)
P	CO_2 product delivered by the capture unit at 2 bar and near 30 °C
PB	product blower
PBT	product buffer tank
PC	product cooler
P-i	intermediate product streams
PSA	pressure swing adsorption
PTSA	pressure and temperature swing adsorption
R	rinse

RBT	rinse buffer tank
ref	reference power plant without capture
RH	rinse heater
SEPAC	specific energy penalty of avoided CO ₂ (MJ _e kg ⁻¹ CO ₂)
SHDCP	specific heat duty of the capture plant (MJ _{th} kg ⁻¹ CO ₂)
SERCP	specific electricity requirements of the capture plant (MJ _e kg ⁻¹ CO ₂)
TCVSA	temperature, concentration and vacuum swing adsorption
TSA	temperature swing adsorption
VPSA	vacuum pressure swing adsorption
VPTSA	vacuum pressure and temperature swing adsorption
VSA	vacuum swing adsorption
VTSA	vacuum and temperature swing adsorption
W	waste gas (decarbonized flue gas vented to the stack)
WO	waste gas outlet
WBT	waste buffer tank
ϕ_{CO_2}	emitted flow of CO ₂ (kg s ⁻¹)

Acknowledgements

M.G.P. acknowledges the Spanish Government for a Ramon y Cajal contract (RyC-2015-17516).

References

- [1] IEA. Energy Technology Perspectives 2017. Catalysing Energy Technology Transformations. International Energy Agency, 2017.

- [2] IEA. 20 years of carbon capture and storage. Accelerating future deployment. Paris, France. International Energy Agency, 2016.
- [3] K. Stéphenne, Start-up of world's first commercial post-combustion coal fired CCS project: contribution of Shell Cansolv to SaskPower Boundary Dam ICCS project. *Energy Procedia*, **63** (2014), pp.6106-6110.
- [4] D. Greason. Petra Nova carbon capture. The future of Carbon Capture, Utilization, and Storage (CCUS): status, issues, needs. Washington, US, 2017.
- [5] P. Luis, Use of monoethanolamine (MEA) for CO₂ capture in a global scenario: Consequences and alternatives. *Desalination*, **380** (2016), pp.93-99.
- [6] J. Luis Míguez, J. Porteiro, R. Pérez-Orozco, D. Patiño, S. Rodríguez, Evolution of CO₂ capture technology between 2007 and 2017 through the study of patent activity. *Appl Energy*, **211** (2018), pp.1282-1296.
- [7] M. Ishibashi, H. Ota, N. Akutsu, S. Umeda, M. Tajika, J. Izumi, A. Yasutake, T. Kabata, Y. Kageyama, Technology for removing carbon dioxide from power plant flue gas by the physical adsorption method. *Energ Convers Manage*, **37** (1996), pp.929-933.
- [8] Z. Liu, L. Wang, X. Kong, P. Li, J. Yu, A.E. Rodrigues, Onsite CO₂ capture from flue gas by an adsorption process in a coal-fired power plant. *Ind Eng Chem Res*, **51** (2012), pp.7355-7363.
- [9] L. Wang, Y. Yang, W. Shen, X. Kong, P. Li, J. Yu, A.E. Rodrigues, CO₂ capture from flue gas in an existing coal-fired power plant by two successive pilot-scale VPSA units. *Ind Eng Chem Res*, **52** (2013), pp.7947-7955.

- [10] D. Wawrzyńczak, I. Majchrzak-Kucęba, K. Srokosz, M. Kozak, W. Nowak, J. Zdeb, W. Smółka, A. Zajchowski, The pilot dual-reflux vacuum pressure swing adsorption unit for CO₂ capture from flue gas. *Sep Purif Technol*, **209** (2019), pp.560-570.
- [11] K. Kim, K.S. Kim, S. Yang, J.B. Lee, T.H. Eom, Y.H. We, C.K. Ryu, Performance improvement of a 10 MW_e dry CO₂ capture pilot plant by analyses of sorbents. *Journal of Energy and Power Sources*, **4** (2017), pp.1-8.
- [12] S. Sjostrom, J. Denney, C. Senior, W. Morris. Evaluation of solid sorbents as a retrofit technology for CO₂ capture. Final technical report DOE Award DE-FE004343, 2015.
- [13] SRI. Pilot-scale evaluation of an advanced carbon sorbent-based process for post-combustion carbon capture. 2016 NETL Project Review Meeting 2016.
- [14] J. Elliott, F. Yi. Sorbent based post-combustion CO₂ slipstream testing. 2017 NETL CO₂ Capture technology project review meeting. Pittsburgh, US, 2017.
- [15] D. Greeson. NRG CO2NCEPT - Confirmation of the novel cost-effective emerging post-combustion technology. DE-FE0026581 Final technical report, 2016.
- [16] H.M. Kvamsdal, G. Haugen, J. Brown, P. Wolbers, R.J. Drew, P. Khakharia, M. Nienoord, P.L. Fosbøl, Reference Case and Test Case for Benchmarking of HiPerCap Technologies. *Energy Procedia*, **114** (2017), pp.2642-2657.
- [17] G.S. Duarte, B. Schürer, C. Voss, D. Bathen, Modeling and simulation of a tube bundle adsorber for the capture of CO₂ from flue gases. *Chemie Ingenieur Technik*, **88** (2016), pp.336-345.

- [18] M.G. Plaza, F. Rubiera, C. Pevida, Evaluating the feasibility of a TSA process based on steam stripping in combination with structured carbon adsorbents to capture CO₂ from a coal power plant. *Energy & Fuels*, **31** (2017), pp.9760-9775.
- [19] L. Joss, M. Gazzani, M. Mazzotti, Rational design of temperature swing adsorption cycles for post-combustion CO₂ capture. *Chem Eng Sci*, **158** (2017), pp.381-394.
- [20] M.G. Plaza, A.S. González, J.J. Pis, F. Rubiera, C. Pevida, Production of microporous biochars by single-step oxidation: Effect of activation conditions on CO₂ capture. *Appl Energy*, **114** (2014), pp.551-562.
- [21] M.G. Plaza, I. Durán, N. Querejeta, F. Rubiera, C. Pevida, Experimental and simulation study of adsorption in postcombustion conditions using a microporous biochar. 1. CO₂ and N₂ adsorption. *Ind Eng Chem Res*, **55** (2016), pp.3097-3112.
- [22] M.G. Plaza, I. Durán, N. Querejeta, F. Rubiera, C. Pevida, Experimental and simulation study of adsorption in postcombustion conditions using a microporous biochar 2. H₂O, CO₂, and N₂ adsorption. *Ind Eng Chem Res*, **55** (2016), pp.6854-6865.
- [23] M.G. Plaza, I. Durán, F. Rubiera, C. Pevida, Adsorption-based Process Modelling for Post-combustion CO₂ Capture. *Energy Procedia*, **114** (2017), pp.2353-2361.
- [24] A.L. Myers, J.M. Prausnitz, Thermodynamics of mixed-gas adsorption. *AIChE J*, **11** (1965), pp.121-127.
- [25] M.G. Plaza, A.S. González, C. Pevida, F. Rubiera, Influence of water vapor on CO₂ adsorption using a biomass-based carbon. *Ind Eng Chem Res*, **53** (2014), pp.15488-15499.

- [26] S. Sjostrom, H. Krutka, Evaluation of solid sorbents as a retrofit technology for CO₂ capture. *Fuel*, **89** (2010), pp.1298-1306.
- [27] K. Li, W. Leigh, P. Feron, H. Yu, M. Tade, Systematic study of aqueous monoethanolamine (MEA)-based CO₂ capture process: Techno-economic assessment of the MEA process and its improvements. *Appl Energy*, **165** (2016), pp.648-659.
- [28] M.G. Plaza, S. García, F. Rubiera, J.J. Pis, C. Pevida, Post-combustion CO₂ capture with a commercial activated carbon: Comparison of different regeneration strategies. *Chem Eng J*, **163** (2010), pp.41-47.
- [29] L. Wang, Z. Liu, P. Li, J. Yu, A.E. Rodrigues, Experimental and modeling investigation on post-combustion carbon dioxide capture using zeolite 13X-APG by hybrid VTSA process. *Chem Eng J*, **197** (2012), pp.151-161.
- [30] M.G. Plaza, A.S. González, C. Pevida, F. Rubiera, Green coffee based CO₂ adsorbent with high performance in postcombustion conditions. *Fuel*, **140** (2015), pp.633-648.
- [31] N.A.A. Qasem, R. Ben-Mansour, Energy and productivity efficient vacuum pressure swing adsorption process to separate CO₂ from CO₂/N₂ mixture using Mg-MOF-74: A CFD simulation. *Appl Energy*, **209** (2018), pp.190-202.
- [32] N.A.A. Qasem, R. Ben-Mansour, Adsorption breakthrough and cycling stability of carbon dioxide separation from CO₂/N₂/H₂O mixture under ambient conditions using 13X and Mg-MOF-74. *Appl Energy*, **230** (2018), pp.1093-1107.
- [33] IPCC. Global warming of 1.5 °C: an IPCC Special Report on the impacts of global warming of 1.5 °C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat

of climate change, sustainable development, and efforts to eradicate poverty. IPCC Special Reports, Intergovernmental Panel on Climate Change (IPCC), 2018.

Accepted for publication in Applied Energy