Evaluation of ammonia modified and conventionally activated biomass based carbons as CO₂ adsorbents in postcombustion conditions

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Abstract

Low cost carbons obtained from biomass residues, olive stones and almond shells, were evaluated as CO₂ adsorbents in postcombustion conditions (low CO₂ partial pressure). These carbons were prepared from biomass chars by means of two different methods: physical activation with CO₂ and amination. All the prepared carbons present a high CO₂ adsorption capacity at 303 K, although carbons developed from almond shells show a superior CO₂/N₂ selectivity (lower N₂ adsorption) than those obtained from olive stones. In general, activated samples present faster adsorption kinetics due to the presence of transport pores, although they have lower densities. On the other hand, aminated samples have narrower porosities but higher volumetric capacities. Among the samples studied, aminated almond shells were selected as the most promising adsorbent, due to their high CO₂ adsorption capacity and selectivity and their good adsorption kinetics. To assess the performance of these samples in cyclic adsorption/desorption processes, basic two-step cycle configurations were evaluated by the following regeneration strategies: temperature swing adsorption (TSA), vacuum swing adsorption (VSA) and a combination of both (VTSA). Aminated almond shells showed no sign of deactivation after 13 h of continuous TSA cycling between 303 and 373 K, nor during VSA or VTSA cycling.

Keywords: CO₂ capture; postcombustion; adsorption; biomass; VTSA

1. Introduction

An extensive application of Carbon Capture and Storage (CCS) will be required to mitigate climate change in the short to medium term, until an alternative energy scenario emerges. CCS is an active field of research, since it is a well established technology with a wide variety of industrial

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applications, one of whose objectives is to reduce the cost of the capture process. Adsorption is one of the available technologies with the potential to achieve cost reductions [1-3]. Within the field of CO₂ capture by means of adsorption, research has been focused on maximising the efficiency of the process and minimising the associated costs. Two main adsorption technologies are viewed as feasible in the case of CO₂ post-combustion: Temperature Swing Adsorption (TSA) and Pressure Swing Adsorption (PSA). In TSA, the adsorbent is regenerated by increasing the temperature of the bed. This may be accomplished by harnessing the low heat steam from the power plant in indirect heating exchangers [4], or by passing an electric current through the solid (Joule effect), a method commonly referred to as Electrical Swing Adsorption (ESA) [5, 6]. Due to the high flowrate and low pressure of the flue gases, it would be uneconomical to compress them for a conventional PSA process. The PSA processes proposed for application in post-combustion would operate between a pressure close to atmospheric during the adsorption stage and a reduced pressure during adsorbent regeneration [1, 7-13]. Because a vacuum is used in these processes, they are commonly referred to as Vacuum Swing Adsorption (VSA).

Many adsorbents have been proposed for CO₂ adsorption including zeolites, activated carbons, silicas, hydrotalcites, metal oxides, MOFs, etc. [14-16]. Activated carbons and zeolites have been widely studied due to their competitive CO₂ adsorption capacities (at relatively low temperatures), high CO₂/N₂ selectivity, and excellent regenerability [16]. Carbon adsorbents have the added advantages of easier regeneration, superior cyclic stability in actual flue gas (saturated with moisture and with typical flue gases contaminants, such as NO_x and SO₂ [3]), and an appealing low cost [2, 6, 17]. Moreover, the surface chemistry of an activated carbon can be easily modified to further enhance CO₂ adsorption. CO₂ is known to react with primary and secondary amines to form carbamates [18, 19]. The specific nature of this reaction is the core of CO₂ capture by chemical absorption with aqueous amine solutions. To overcome the problems related to this technology (mainly its high energy requirements and corrosion problems) while keeping its high selectivity, hybrid sorbents have been prepared by impregnation of solid supports with amines [20-25]. Although impregnation with amines can be an effective modifying technique for a mesoporous support [20, 25], they tend to block the entrance to the micropores of activated carbons, partially cancelling the positive effect of their favourable surface chemistry [24]. Other drawbacks of amines are: high volatility, tendency to degrade in the presence of oxygen, leaching and deactivation in the presence of sulphur components in the flue gas. Alternatively, the adsorption of acidic CO₂ may be enhanced by the presence of other basic nitrogen functionalities

on the carbon surface: CO₂ is a weak Lewis acid (electron-acceptor) that can interact with electron-donors, such as nitrogen surface groups. Apart from impregnation, nitrogen-rich carbons can be obtained by the pyrolysis of N-containing polymers [26-28], by chemical reaction [29, 30] or by heat treatment with ammonia gas in the presence or absence of oxygen (respectively referred to as ammoxidation and amination) [31-36]. Among these, amination at high temperature has shown to be an efficient technique for modifying the surface of carbons: it introduces highly stable nitrogen heteroatoms into the carbon matrix leading to basic carbons with increased delocalised electrons, and at the same time develops the narrow microporosity of the carbons, enhancing CO₂ adsorption [32-35]. Additionally, this technique can be easily implemented on an industrial scale and can make use of low-cost feedstock [33, 34].

In previous studies, our group dealt with the development of low cost CO₂ adsorbents from biomass residues: olive stones and almond shells [33, 34]. Both of these are relatively abundant agricultural by-products, and have proven to be a good feedstock for activated carbon production in the past [37-40]. The previous studies dealt with the preparation and characterisation of carbons and provided a preliminary assessment of their CO₂ capture capacity by means of gravimetric experiments. In the present paper, selected materials have been tested in a purpose-built fixed-bed adsorption unit for separating CO₂ from CO₂/N₂ binary mixtures, which are more representative of postcombustion conditions.

2. Experimental

The carbons evaluated in the present paper were obtained from olive stones and almond shells. The raw biomass was ground and sieved to a particle size between 1 and 3 mm and then carbonised in a N₂ flow at 873 K. The carbonised olive stones and almond shells will be denoted by the letters O and A, respectively. Two different samples were prepared from each carbonised product. The first series of samples were obtained by conventional physical activation with 10 cm³ min⁻¹ of CO₂ up to a 40 % of burn off (activation was carried out at 1073 and 973 K for O and A, respectively), giving rise to samples OA and AA. The second series of samples were obtained by treating the char with ammonia at 1073 K for 2 h, and will be referred to here as ON and AN. A more detailed description of the amination process can be found elsewhere [32-34].

Pure N₂ and CO₂ equilibrium adsorption isotherms were obtained in a volumetric TriStar 3000 apparatus from Micromeritics. Prior to the adsorption measurements the samples were vacuum degassed overnight at 373 K.

Fixed bed adsorption experiments were carried out in a purpose built adsorption unit described in detail elsewhere [41]. The adsorber consists of a stainless steel reactor 9 mm in diameter and 203 mm in height (maximum solids height 157 mm) equipped with temperature and pressure control. The composition of the outlet gas stream was measured by a dual channel micro-gas chromatograph (micro-GC), CP 4900 from Varian, fitted with a thermal conductive detector (TCD) using He as carrier gas. The TCD response was calibrated using standard mixtures of CO₂ and N₂ of known compositions.

CO₂ breakthrough curves of the studied samples were obtained at 303 K and 130 kPa, using a feed flowrate of 34 cm³ min⁻¹ (standard conditions, 273 K and 100 kPa) with 17 % (vol) of CO₂ in N₂. The adsorber was initially fed in at the desired N₂ flowrate, CO₂ having been added to the nitrogen flow at time zero. The adsorbent was regenerated by heating the bed up to 373 K for 1 h in 10 cm³ min⁻¹ of N₂ flow. CO₂ breakthrough capacities were calculated by applying a mass balance to the adsorber and subtracting the gas present in the void fraction.

Finally, cyclic adsorption-desorption experiments were performed on the sample with very promising results being obtained during the binary breakthrough tests. The cycle time was fixed to simulate an operation with two columns of equal length for the adsorption and desorption steps. The time was set according to the information obtained in the breakthrough tests. Three different cycle configurations were evaluated by modifying the regeneration conditions but keeping the other parameters constant: cycle time (18 min), feed flowrate (34 cm³ min⁻¹), feed composition (17% of CO₂ in N₂), and adsorption operating conditions (303 K and 130 kPa). In the first configuration, the solid was regenerated by externally heating the solids up to 373 K in a small flowrate of nitrogen (2.6 cm³ min⁻¹), as in a basic TSA operation. The second regeneration strategy involved evacuating the bed down to a final pressure of 5 Pa at a constant temperature of 303 K, as in a basic VSA cycle. Finally, the third type of regeneration evaluated involved simultaneously evacuating the bed down to 5 Pa and mildly heating it up to 323 K.

3. Results and discussion

3.1. Adsorption equilibrium of pure CO₂ and N₂

Determining the adsorption equilibrium of each component is essential in the design of an adsorption process. The CO₂ and N₂ adsorption isotherms of samples O, OA, ON, A, AA and AN at 303 K are presented in Figure 1. All the carbons present a higher CO₂ adsorption capacity than N₂ over the whole pressure range. In general, the N₂ isotherms exhibit an almost rectilinear shape (Henry-type), characteristic of weak adsorbate-adsorbent interaction forces, whereas the CO₂ adsorption isotherms can be classified as Type I, i.e., they are representative of stronger adsorbate-adsorbent interactions. This difference can be attributed to the larger electric quadrupole moment of the CO₂ molecule (about three times that of the N₂ molecule [42]), due to the strong dipole moment of carbonyl bonds. The activated samples present higher CO₂ adsorption capacities than the aminated samples at pressures above 30 kPa, due to the contribution of a wider microporosity (which is absent in the aminated samples; see references [33, 34] for further details). However, it must be borne in mind that these pressures are above the partial pressure of CO₂ in typical flue gases. It is also important to note from Figure 1b that the samples obtained from the olive stone char, OA and ON, present a higher N₂ adsorption capacity than those obtained from the almond shell char, AA and AN, not forgetting that minimum N₂ adsorption is desirable in order to maximise the purity of the CO₂ product.

If the adsorption of N₂ and CO₂ were independent, as suggested by some authors [43], the adsorption capacity of a binary mixture would be that of the pure components. In this case, the CO₂/N₂ equilibrium selectivity (defined as the ratio of the molar fractions in the adsorbed phase to those of the gas phase at equilibrium) for an equimolar gas mixture of CO₂ and N₂ would be given by the ratio of the amount of pure CO₂ adsorbed over that of N₂ adsorbed at a given pressure. This “ideal” CO₂/N₂ equilibrium selectivity decrease with increasing pressure (see Figure 2). As expected, the carbons obtained from almond shells present a higher CO₂ selectivity than those obtained from the olive stones over the whole pressure range. It should also be noted that the aminated samples exhibit higher selectivities at low pressures than the corresponding activated samples. This is very important for their application to postcombustion capture, in which CO₂ is present at low partial pressures. This higher selectivity could be attributed to the presence of the nitrogen heteroatoms on the carbon matrix (N content *ca.* 4 wt%), which contribute to increase the system of delocalised π electrons of the carbon, combined with a narrower porosity.

Sips model (Equation 1) reproduces the experimental CO₂ adsorption isotherms fairly well. This model, which is frequently used for modelling purposes in gas separation processes, is as follows:

$$q = q_m \frac{(bP)^{1/n}}{1 + (bP)^{1/n}} \quad (1)$$

where q represents the adsorbed concentration, q_m represents the maximum adsorbed concentration, b is the affinity parameter, P is the pressure, and n is a parameter that characterises the heterogeneity of the system. Parameters b and n can be considered temperature dependant as shown in Equations 2 and 3 [44]:

$$b = b_0 \exp \left[\frac{Q}{RT_0} \left(\frac{T_0}{T} - 1 \right) \right] \quad (2)$$

$$\frac{1}{n} = \frac{1}{n_0} + \alpha \left(1 - \frac{T_0}{T} \right) \quad (3)$$

where T_0 is the reference temperature, b_0 and n_0 are the affinity and heterogeneity parameters at the reference temperature, α is a constant, and Q is a measure of the heat of adsorption. These parameters were estimated from a non-linear least squares fit of the experimental adsorption isotherms of CO₂ at 273 K and 303 K to Equations 1-3, using 273 K as the reference temperature. The resulting parameters are presented in Table 1. The goodness of the fit can be observed in Figure 3, where the dots represent the experimental adsorption isotherms of CO₂ at 273 and 303 K, and the solid lines represent the optimised Sips model. Although Q is only a rough estimation of the heat of adsorption since only two adsorption temperatures were used, the heat of adsorption thus estimated lies between 20 and 30 kJ mol⁻¹ in all cases, which are typical values for physisorption processes.

Although the adsorption of N₂ at 303 K is almost linear, Henry's law fails to describe accurately the experimental data. However, N₂ adsorption at 303 K can be satisfactorily fitted to the Sips model. To overcome the absence of a limiting adsorption capacity with increasing pressure, the value of q_m for N₂ was set to be that of CO₂ (the molar volumes of N₂ and CO₂ are similar). The optimal b and n parameters for N₂ adsorption were obtained by a non-linear least squares fit of the adsorption data at 303 K. The goodness of the fit can be appreciated in Figure 4, where the dots

represent the experimental adsorption data at 303 K, and the solid lines represent the optimised Sips model.

The Sips model for multicomponent adsorption can be written as:

$$q_i = q_m b_i P_i \frac{\sum (b_k P_k)^{1/n}}{1 + \sum (b_k P_k)^{1/n}} \quad (4)$$

where P_i represents the partial pressure of component i in the mixture. The thermodynamic consistency of equation 4 implies that parameter n should be equal for all the components in the mixture. However the fit with equal n failed to reproduce the experimental adsorption of N_2 and CO_2 . As an approximation, n was taken as the mean value of the optimal values of n for CO_2 and N_2 adsorption at 303 K. According to this model, the selectivity (ratio of the adsorbed concentrations divided by that of the partial pressures in the gas phase) is equal to the ratio of the affinity parameters. For illustrative purposes the ratio of the CO_2 and the N_2 affinity parameters at 303 K have been included in Table 1. It should be noted that the chars present the highest CO_2 selectivity, followed by sample AN. The trends discussed above persist: almond shells are more selective than olive stone carbons, and aminated samples are more selective towards CO_2 than activated samples.

3.2. Breakthrough experiments with CO_2/N_2 binary mixtures

The term breakthrough curve refers to the response of a bed (initially free of adsorbate) to a step change in the adsorbate concentration at the bed inlet. In an ideal plug flow system with negligible axial dispersion and very fast heat and mass transfer processes, the outlet concentration response would replicate the input discontinuity with a time delay that corresponds to the bed hold-up. However, in a real system the breakthrough front will be generally more spread, so that measurement of time delay will provide information about equilibrium and dispersion of response information about adsorption kinetics. In general, the overall rate of adsorption is controlled by mass (or heat) transfer resistances rather than by intrinsic adsorption kinetics [45, 46].

Table 2 summarises the characteristics of the adsorbent bed. The bed density was calculated from the mass of dry adsorbent loaded into the column and the volume of the resulting bed. It should be noted that aminated samples present a significantly higher bed density than the activated samples, which is a very important point from a practical point of view, as this would reduce the

volume of the adsorbers required in the final application. Furthermore, the total void space of the aminated bed is smaller, which means that less feed gas will remain behind in the voids of the saturated bed at the end of the adsorption step (the purity of the product will therefore be greater in the subsequent regeneration step, and rinse requirements will be reduced).

Figures 5 and 6 show the CO₂ breakthrough curves of the studied carbons at 130 kPa and 303 K for a feed consisting in 34 cm³ min⁻¹ (STP) of a binary mixture of 17 % CO₂ in N₂. The evolution with time of the effluent CO₂ molar fraction ($y_{CO_2, effluent}$) is presented. At the beginning of the experiment all the incoming CO₂ is adsorbed, and only N₂ exits the bed, ($y_{CO_2, effluent} = 0$). After several minutes, the mass transfer zone reaches the bed outlet and CO₂ is detected in the effluent stream ($y_{CO_2, effluent} > 0$). After sufficient time, the bed becomes saturated (attains equilibrium) and the effluent concentration meets that of the feed ($y_{CO_2, effluent} = 0.17$).

Figure 5 represents ten consecutive CO₂ breakthrough curves for the olive stone carbons. All the curves overlap, indicating a very good repeatability of the experimental results and completely reversible adsorption, while the adsorbent shows no decay in capacity after 10 consecutive adsorption-desorption cycles. The olive stone char (O) presents the broadest breakthrough curve (Figure 5a), whereas the activated sample (OA) shows the steepest curve (Figure 5b). This seems to indicate that intraparticle diffusion is the mass transfer rate limiting mechanism. The char presents only incipient microporosity [33], and consequently high resistance to CO₂ diffusion in the narrow pores. In contrast, the activated sample (OA), exhibits wider pores that were formed during the activation process so that intraparticle mass transfer resistance is substantially reduced. The aminated sample (ON) displays an intermediate behaviour; it still shows greater resistance to mass transfer (broader curve) than sample OA due to the narrower character of its porosity [33]. High mass transfer resistances are undesirable, as it signifies a greater length of unusable bed (LUB) [45, 47].

Figure 6 represents the CO₂ breakthrough experiments corresponding to the almond shell carbons. Again a good reproducibility of results is observed for several consecutive runs, testifying to the good cyclability of these materials. The curve corresponding to the almond shell char (A) presents the same broad character that was previously observed for the olive stone char, due to the absence of transport pores. However, in this case, both the aminated (AN) and activated almond (AA) carbons show a desirable abrupt profile, which is a sign of reduced mass transfer resistances.

The CO₂ breakthrough capacities are below the corresponding values for pure CO₂ adsorption at the same partial pressure, implying that N₂ is partly co-adsorbed with CO₂, which reduces the pore volume available for CO₂ adsorption. Experimentally obtained CO₂ adsorption capacities from a binary mixture of 17 % CO₂ in N₂ lie in between the adsorption capacities predicted for pure CO₂ adsorption and for binary CO₂/N₂ adsorption by the multicomponent Sips model (see Table 3). The underestimation of CO₂ adsorption capacity by the multicomponent Sips model can be attributed to lateral interactions between the adsorbed molecules (which are greater in the case of CO₂) resulting in a reduction of the amount of N₂ coadsorbed.

AN shows the highest CO₂ adsorption capacity of the studied carbons: 0.82 mol kg⁻¹, which is even greater than that of the reference commercial carbon evaluated under the same operating conditions (0.77 mol kg⁻¹ [41]). Sample AA also presents a high CO₂ adsorption capacity, 0.80 mol kg⁻¹. However, if the density of the bed is also taken into account, sample AN has a CO₂ volumetric capacity of 327 mol m⁻³, which is significantly greater than that of AA (227 mol m⁻³). This is an important point, as it may help to decrease the volume of the adsorbers required for the final application. For this reason, sample AN was selected for trying out shorter adsorption-desorption cycles, that are more representative of real operation conditions.

3.3. Cyclic adsorption experiments with CO₂/N₂ binary mixtures

Table 4 summarises the operation conditions of the cyclic adsorption experiments performed on sample AN. The cycle time was set to 18 min in all cases and was equally divided into two steps: adsorption (I) and desorption (II). Only the conditions during the regeneration step differ between the three different cycles evaluated: TSA, VSA and VTSA.

The TSA cycles were carried out for almost 13 uninterrupted hours (41 consecutive cycles) without any sign of adsorbent deactivation. Figure 7 represents the evolution of pressure, temperature and effluent CO₂ molar fraction during cycles 10, 20 and 40; the experimental data of the different cycles overlap perfectly, demonstrating the reproducibility of the results and the good cyclability of AN. At the beginning of the adsorption step the feed meets a hot bed (373 K), which is externally cooled to 303 K during the adsorption step. As the bed temperature falls, its adsorption capacity increases, and the effluent become more deeply decarbonised (the purity of the N₂ varies during the adsorption step, with an average value of 95 %). Near the end of the adsorption step

the CO₂ concentration in the effluent rises slightly, indicating that CO₂ is about to break through the adsorber. At this point (9 min), the desorption step starts. The feed is then switched to a small purge of N₂ (2.6 cm³ min⁻¹, STP) and the adsorbent rapidly heats up to 373 K. The concentration of CO₂ at the bed outlet then experiences a rapid increase, reaching a maximum (ca. 78 % CO₂ in less than 3 min). Although CO₂ continues to desorb thereafter, the CO₂ concentration at the bed outlet starts to tail, the regeneration step concluding after 9 min (45 % CO₂).

Extending the desorption time would increase the recovery of CO₂ and adsorbent's working capacity, but only at the expense of the purity of the CO₂. In the conditions evaluated, the working capacity of AN was reduced to 0.46 mol kg⁻¹. Although this cycle was not optimised (using the simple configuration outlined above), the CO₂ was successfully concentrated from 17 to 59 % (vol) resulting in an average CO₂ recovery of 68 %. There are several ways in which the purity of the product could be further increased to meet storage specifications. A rinse step could be added with part of the CO₂ enriched stream. This rinse would displace the N₂ present in the bed voids and the adsorbed phase would be enriched in CO₂ due to the increase in CO₂ partial pressure. This would increase the purity of the CO₂ during the next regeneration step. The use of a diluting gas could be completely eliminated if electrical or indirect heating were used. It should also be borne in mind that, even for an optimised cycle, it is likely that two stages would be necessary to meet storage specifications [10, 11]. The operation of the second unit would be greatly facilitated due to the increase in CO₂ partial pressure, and the volume of the installations would also be smaller due to the reduction in feed flowrate already attained. The productivity of the cycle, defined as the amount of CO₂ produced per kg of adsorbent and cycle time, for the simple TSA cycle presented here was around 1.5 mol kg⁻¹ h⁻¹. These results are clearly much better than those obtained using a reference commercial carbon with a similar cycle configuration [41].

Figure 8 presents the VSA cycle carried out at 303 K. During the adsorption step, the bed is first pressurised together with the feed up to 130 kPa. Once adsorption pressure is attained, a decarbonised effluent with an average purity of 98 % starts to exit the bed. Although no signs of breakthrough are observed in the composition of the effluent, a small increase in temperature can be observed by the end of the adsorption step, indicating that the thermal wave accompanying CO₂ adsorption has reached the thermocouple placed near the bed outlet, and that the bed is being almost fully used. During the regeneration step the bed is evacuated down to 5 Pa. Due to the initial cold state of the bed, the working capacity (0.59 mol kg⁻¹) and the extent of effluent

decarbonisation are greater than in the evaluated TSA cycle. Cycle productivity and carbon recovery can be estimated by assuming that all the CO₂ adsorbed during step I is desorbed during step II (there is no hold up). The overlapping experimental data in Figure 8 confirm that the cyclic steady state has been reached. The productivity of the evaluated VSA cycle is 2.0 mol kg⁻¹ h⁻¹ with a CO₂ recovery of 90 %. The performance of AN gave better results than those obtained with the reference commercial activated carbon [41]. The level of vacuum, which will have a profound effect on the operating cost of the final process [8], will be optimised in future studies.

Figure 9 represents the VTSA cycle, in which a combination of mild heat and a vacuum was used to regenerate the adsorbent. No signs of deactivation were observed for 12 consecutive cycles. The vacuum level during the regeneration step was kept at 5 Pa, so that this cycle could be compared with the previously evaluated VSA cycle. The only difference between both cycles is that the bed is heated up to 323 K during the regeneration step and cooled to 303 K during the pressurization step. By the end of the adsorption step, a small increase in the temperature can again be observed, indicating that the bed is being almost fully used. Due to the mild heating of the adsorbent up to 323 K, the adsorbent is regenerated a little more compared to VSA, and as a consequence the working capacity is increased from 0.59 to 0.64 mol kg⁻¹. The decarbonised effluent presents an average purity of 99 %, which is the highest obtained for the three evaluated cycles. Furthermore, this VTSA cycle also shows the highest productivity (2.1 mol kg⁻¹ h⁻¹) and CO₂ recovery (97 %).

In order to choose the most suitable regeneration strategy a detailed cost study of optimised cycles would be necessary, but this is beyond the scope of the present work. However, it has been demonstrated that sample AN is a promising adsorbent for CO₂ capture, as it leads to better results than those obtained with a reference carbon under similar cycle configurations. It has also been shown that sample AN responds very well both under temperature and vacuum swing cycling conditions, with no signs of deactivation.

Conclusions

A series of carbons obtained from biomass residues (olive stones and almonds shells) by physical activation and amination have been tested as potential adsorbents for postcombustion capture conditions (low CO₂ partial pressure).

Pure CO₂ and N₂ adsorption isotherms were obtained at 303 K. Although activated samples present a higher textural development, their CO₂ adsorption capacity only surpasses that of the aminated samples above 30 kPa, which is above the typical partial pressure of CO₂ in flue gases. Moreover the aminated samples show a higher selectivity at low partial pressures, due to their narrower porosity and their favourable surface chemistry. It was also found that the carbons obtained from olive stones present a higher N₂ adsorption, and as a consequence a lower CO₂ selectivity than those obtained from almond shells.

Binary breakthrough curves achieved at 303 K and 130 kPa using a binary mixture of 17 % CO₂ in N₂ demonstrated that the prepared carbons can successfully separate CO₂/N₂ mixtures. Although the biomass chars are highly selective towards CO₂, their adsorption dynamics are too slow for practical applications. Activated samples exhibit fast adsorption kinetics due to the presence of transport pores, although the high porosity of the activated samples also leads to low bed densities and thus low volumetric capacities. In contrast, aminated samples have higher bed densities, leading to higher volumetric capacities, but narrower pores that might impede diffusion through the pore network. Sample AN, obtained by amination of almond shell char, showed not only the highest CO₂ capacity on a volumetric basis (near 330 mol CO₂ m⁻³ adsorber), but also fast adsorption dynamics, and can thus be considered the most promising candidate for carrying out CO₂ capture in postcombustion applications.

The performance of sample AN was further evaluated in simple adsorption/desorption cycles, under different regeneration conditions: temperature, vacuum, and a combination of both (TSA, VSA and VTSA). AN showed no signs of deactivation after 13 h of continuous TSA cycling between 303 and 373 K (over 40 cycles). Using this basic TSA cycle CO₂ was concentrated by a factor of 3.5. AN also demonstrated excellent cyclability under vacuum regeneration, leading to productivities of up to 2.1 mol kg⁻¹ h⁻¹ and CO₂ recoveries of up to 97 %. Although these are only basic cycles that still need to be optimised, the results are promising as they surpass those obtained with a reference commercial activated carbon.

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Tables

Table 1. Optimal Sips model parameters for CO₂ and N₂ adsorption on carbons O, OA, ON, A, AA, and AN

	CO ₂ adsorption at 273 and 303 K					N ₂ adsorption at 303 K		Selectivity
	q _m (mol kg ⁻¹)	b _{273K} (kPa ⁻¹)	n _{273K} (-)	Q (kJ/mol)	α (-)	b _{303K} (kPa ⁻¹)	n _{303K} (-)	
O	3.16	0.02680	1.34	23	0.21	0.00045	1.09	22
OA	9.66	0.00649	1.54	25	0.59	0.00063	1.12	3
ON	5.29	0.01183	1.56	21	0.27	0.00116	1.06	4
A	3.10	0.03045	1.34	29	0.00	0.00048	1.07	18
AA	13.74	0.00199	1.77	22	0.31	0.000152	1.14	5
AN	7.10	0.00803	1.72	26	0.20	0.000322	1.10	8

Table 2. Physical properties of the samples studied and fixed bed characteristics

	O	OA	ON	A	AA	AN
N content (wt%, dry ash free basis)	0.3	0.6	3.6	0.4	0.9	4.5
BET Surface Area (m ² g ⁻¹)	-	909	390	-	831	588
Helium density (kg m ⁻³)	1649	2052	1920	1598	1982	1902
Apparent density (kg m ⁻³)	820	670	880	710	480	760
Mass of adsorbent (g)	3.94	2.98	3.97	3.33	2.68	3.48
Bed density (kg m ⁻³)	442	330	463	379	284	399
Bed void fraction	0.46	0.51	0.47	0.47	0.41	0.48
Total void fraction	0.73	0.84	0.76	0.76	0.86	0.79

Table 3. Comparison between the experimental CO₂ breakthrough capacities (mol kg⁻¹) and the Sips model predictions (303 K and 130 kPa, 17 % CO₂ in N₂)

	O	OA	ON	A	AA	AN
CO ₂ breakthrough capacity	0.60	0.77	0.76	0.51	0.80	0.82
Pure CO ₂ adsorption Sips model	0.75	1.01	0.96	0.70	1.11	1.08
Binary CO ₂ /N ₂ adsorption Sips model	0.64	0.62	0.58	0.58	0.58	0.65

Table 4. Operation conditions for the adsorption/desorption cycles carried out with carbon AN

Cycle type	t _c (min)	y _{CO₂}	Q _i (cm ³ min ⁻¹)	T _i (K)	P _i (kPa)	Q _{ii} (cm ³ min ⁻¹)	T _{ii} (K)	P _{ii} (kPa)	CO ₂ recovery (%)	Productivity (mol kg ⁻¹ h ⁻¹)
TSA	18	0.17	34	303	130	2.6	373	120	68	1.5
VSA	18	0.17	34	303	130	0	303	0.005	90	2.0
VTSA	18	0.17	34	303	130	0	323	0.005	97	2.1

Figures

Figure 1. Equilibrium adsorption isotherms of CO₂ (a) and N₂ (b) at 303 K over carbons O, OA, ON, A, AA, and AN.

Figure 2. CO₂/N₂ equilibrium selectivity calculated as the ratio between the amount of pure CO₂ adsorbed at equilibrium and that of N₂ at a given pressure.

Figure 3. Sips fitting to the CO₂ adsorption isotherms of carbons O, OA, ON, A, AN and AO at 273 and 303 K (dots represent the experimental data and solid lines represent the model's prediction).

Figure 4. Sips fitting to the N₂ adsorption isotherms of carbons O, OA, ON, A, AN and AO at 303 K (dots represent the experimental data and solid lines represent the model's prediction).

Figure 5. CO₂ breakthrough curves (evolution of the CO₂ molar fraction at the bed outlet) at 303 K and 130 kPa (feed: 34 cm³ min⁻¹ (STP), 17% CO₂ in N₂) over the olive stones carbons: a) O, b) OA, and c) ON.

Figure 6. CO₂ breakthrough curves (evolution of the CO₂ molar fraction at the bed outlet) at 303 K and 130 kPa (feed: 34 cm³ min⁻¹ (STP), 17% CO₂ in N₂) over the almond shell carbons: a) A, b) AA, and c) AN.

Figure 7. TSA cycles for sample AN: evolution of temperature, pressure and CO₂ molar fraction at the bed outlet during cycles 10, 20 and 40.

Figure 8. VSA cycles for sample AN: evolution of pressure, temperature and CO₂ molar fraction at the bed outlet during cycles 7 and 9.

Figure 9. VTSA cycles for sample AN: evolution of pressure, temperature and CO₂ molar fraction at the bed outlet during cycles 9 and 11.