Production of microporous biochars by single-step oxidation: effect of activation conditions on CO₂ capture

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Abstract

There is an urgent need to develop materials and processes that reduce the energy penalty associated to the CO₂ capture step. Biochars are appealing adsorbents for post-combustion CO₂ capture applications due to their low cost, stability in moisture conditions and microporous nature. Series of carbon adsorbents were prepared from almond shells and olive stones by single-step activation with air at 400-500 °C, and with lower O₂ concentration in the activating gas, 3-5%, at higher temperatures (500-650 °C). This process entails energy savings compared to conventional activation with carbon dioxide or steam. It has been found that the pore size distribution can be tailored by adequately selecting the activating conditions. Carbons obtained under lower oxygen partial pressures and higher temperatures present narrow microporosity, which is essential for the adsorption of CO₂ at low partial pressures. These appealing low-cost adsorbents have competitive CO₂ working capacities and high CO₂/N₂ equilibrium selectivity in conditions that can be considered representative for post-combustion CO₂ capture, thus showing potential for this application.

Keywords: CO₂ capture, adsorption, biochar, carbon

1. Introduction

In 2010 the United Nations Framework Convention on Climate Change (UNFCCC) Conference Parties (Decision 1/CP.16) approved a non-legally binding commitment to cap global average temperature rises to 2 °C, which is considered consistent with an upper limit of CO₂ equivalent concentration levels in the atmosphere of 450 ppm by 2050. In the least costs scenario, CO₂ Capture and Storage (CCS) will play a vital role in the transition to a low-carbon society [1]. Post-combustion CO₂ capture (PCC), where CO₂ is to be separated from flue gases produced by fuel combustion in the energy sector or industrial processes, is the only option that enables retrofitting of existing facilities, and that can be implemented with a low technological risk in the short term [2-4]. The most likely location for the capture plant is between the flue gas desulfurisation unit and the stack. At this point, flue gases are at near atmospheric pressure and CO₂ represents between 3 and 20% by volume (depending on the fuel used, and if dry or

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wet basis conditions are considered). Amine scrubbing is a mature technology that could be used to separate CO₂ in those conditions. However, it is not implemented so far at utility scale on coal or gas-fired power plants, partly due to its high energy requirements: the most substantial portion of the overall operating cost (above 50%) is the steam consumption of the reboiler, necessary to regenerate the diluted amine solution [5].

Adsorption is a separation technology that presents scope for reducing the energy penalty of the capture step [6-8]. The use of solid adsorbents would avoid the need of heating diluted solvents, and they present higher capacity on a volume basis, which will reduce the size of the necessary equipment. Moreover, they can be regenerated by reducing the overall pressure, without the need of steam. This is of special interest when steam is not available locally, as in the case of cement plants (predicted CO₂ emission by 2020: *ca.*397 million tonnes [9]). Above 461 patents have been published so far dealing on sorbents for CO₂ capture [10]. In 2011, the U.S. Department of Energy co-founded six large projects dealing with PCC sorbent technologies development (21\$ million total investment). Different types of sorbents (hybrid amine sorbents, alumina, carbon materials, MOFs, and sodium carbonate) and processes (thermal swing (TSA), pressure swing (PSA/VSA) or a combination of these) are under evaluation. A 1 MW pilot plant is being designed and constructed to demonstrate solid sorbent-based PCC technology [11].

In general, for gas-phase adsorption applications, the main requirement of the adsorbent is to possess a high micropore volume. Particularly, CO₂ adsorption at subatmospheric pressure is limited to the narrow micropores [12-14]. This is related to the high adsorption potential due to overlapping of the fields from the opposite walls of the pore, arising as a result of dispersion forces [15]. Therefore, an efficient CO₂ adsorbent for post-combustion capture applications, where the partial pressure of CO₂ is low, must present a high volume of narrow micropores (below 1 nm), which is the case of activated carbons and carbon molecular sieves. Other important advantages of carbon materials are their low cost and their high stability in moisture conditions, which make them appealing adsorbents for post-combustion CO₂ capture processes [8, 16-18]. Moreover, these adsorbents can be easily and fully regenerated by simply reducing the pressure of the system (VSA) and/or by increasing slightly the temperature (TSA) [8, 17, 19, 20].

Industrial activated carbons are commonly obtained from naturally occurring carbon precursors like coal, oil, peat, or biomass through a thermal process which is aimed to develop the pore volume of the non-porous precursor [21]. Biomass is a renewable and world-wide

available inexpensive feedstock, and thus an appealing source for the development of post-combustion adsorbents, considering the scale and global character of the problem. Moreover, if any, the carbon footprint of the adsorbent production process is lessened by the CO₂ fixed during the growth of the biomass. Detailed information about carbon production from biomass sources can be found elsewhere [22]. In general, the production of activated carbons from biomass residues is carried out by two main mechanisms, usually referred to as *chemical* and *physical activation*. In brief, the first involves the pyrolysis of the precursor with a chemical activating agent: hydroxides, carbonates, H₃PO₄ or ZnCl₂. Its main drawbacks are the price and the environmental impact of the chemicals, which need to be eliminated after the treatment by thorough washing of the resulting carbon. Physical activation, considered to be more environmentally friendly, is commonly carried out in a two-step process where the carbonaceous raw material is first pyrolysed in inert atmosphere, generally below 800°C, and the resulting char is then partly gasified between 700 and 1000°C with an activating agent that usually consists in steam or carbon dioxide. During physical activation, surface carbon atoms are consumed by the aforementioned oxidising agents (reactions 1-2), leading to the desired texture development.

Oxygen can also be used as an activating agent, with the added advantages of being inexpensive and available everywhere (air). Moreover, due to the exothermic nature of the reaction of oxygen with carbon (reactions 3-4) the activation process presents high energy savings compared to activation with CO₂ or H₂O. However, the exothermic nature of these reactions also makes the activation more difficult to control; this is the main reason of air being less used as an activating agent than CO₂ or H₂O. There are two main ways to control the oxidation rate: lowering the temperature or reducing the oxygen partial pressure [23]. The requirement of a gas mixture with reduced oxygen concentration to carry out the activation opens the way of using residual hot streams, such as flue gas itself, which contains the excess oxygen not consumed by the combustion process.

$$C + \frac{1}{2}O_2 \rightarrow CO \quad \Delta H = -111 \frac{kJ}{mol} \quad (4)$$

Only a few studies dealing with biomass activation using air or oxygen mixtures were found in the literature [23-28]. The activation conditions and feedstock used are summarised in Table 1. In all of them, activation was carried out by the conventional two-step process: first the biomass is pyrolysed in inert atmosphere between 600 and 900 °C, and then the resulting char is oxidised at relatively mild temperatures, between 190 and 600 °C. The activation step is generally accomplished in shorter times than those required for activation with CO₂ or H₂O, which is highly convenient, although reported texture development is moderate. The possibility of carrying out the activation directly, avoiding the carbonisation or pyrolysis step is highly appealing from the energy consumption point of view. However, only one of the works found in the literature explored this option, and it concluded that it was worthy of further study [24]. Single-step activation of biomass with steam [29, 30] or CO₂ [24, 31-33] has shown to produce good quality biomass-based activated carbons, with similar or even better characteristics than those obtained by the more conventional two-step procedure. These favourable results have encouraged the present study, in which biochars are obtained from almond shells and olive stones by direct activation with oxygen mixtures; this implies additional energy savings and shorter reaction times compared to direct activation with CO₂ or H₂O. The environmentally friendly and cheap-to-produce microporous biochars produced by this method present a narrow pore size which makes them appealing adsorbents for post-combustion CO₂ capture applications. Their potential for this particular application is preliminarily evaluated in the present study through the assessment of the equilibrium of adsorption of major flue gas components, CO₂ and N₂, at relevant temperatures (0-100°C) and pressures (0-130 kPa) for the case under study.

Materials and Methods

The biomass feedstocks used in this work are almond shells (A) and olive stones (O) with a particle size between 1 and 3 mm. These materials present low ash content, which is a requirement for adsorbent preparation (see Table 2).

The effect of temperature and oxygen concentration on the oxidation rate of the biomass was first assessed using a thermogravimetric analyser, TGA-DSC1 from Mettler Toledo. Ca. 20 mg of sample was placed in a platinum crucible and heated up to 900°C at a heating rate of 15 °C min⁻¹ under a total flow rate of 10 cm³ min⁻¹ of a gaseous mixture containing 3, 5 or 21% of O₂ (balance N₂).

Isothermal fixed bed experiments were then carried out in batches of *ca.* 3 g of dry biomass using a double jacket quartz reactor in a vertical tubular furnace. The sample was placed at the bottom of the inner tube (I.D.: 2 cm, length: 45 cm) over a porous plate that holds the solid while allowing the exit of tars and gases released during the experiment. Exhaust gases leave the reactor by a gas exit located in the upper part of the outer jacket, while tars remain in the external jacket. The feed gas entered the reactor by the upper part of the inner reactor, thus being heated before contacting the sample. The flow rate and concentration of the feed gas was controlled by means of mass flow controllers from Bronkhorst High Tech. The reactor was initially purged with N₂ for 1 h at room temperature to remove air from the system. At time zero the reactor was introduced into the oven, which was preheated at the desired temperature, and the feed gas was switched to the oxidising mixture (with an oxygen concentration of 3, 5 or 21% (balance N₂) and a total flow rate of 100 cm³ min⁻¹). A thermocouple in contact with the sample allowed monitoring and controlling the temperature during the activation, avoiding thermal runaway. The activation temperatures were selected attending to the oxygen concentration used, based on the information of the non-isothermal tests carried out in the thermogravimetric analyser.

The biochars obtained in the fixed bed reactor were characterised by means of physical adsorption of CO₂ at 0 °C in a volumetric device (samples were evacuated overnight at 100 °C prior to adsorption measurements). The narrow character of the micropores impeded the diffusion of N₂ at -196 °C in most cases. The use of CO₂ as a probe molecule at 0 °C is recommended for the characterisation of the narrow micropores to avoid underestimation of the pore volume by N₂ adsorption at -196 °C [34]. The micropore volume (*W₀*) and the micropore surface area (*S_{DR}*) were determined by the Dubinin-Radushkevich (DR) equation [35] assuming a density of the adsorbed phase of 1.023 cm³g⁻¹, a cross sectional area of 0.187 nm² and an affinity coefficient of 0.36. The average micropore width (*L₀*) was calculated through the Stoeckli-Ballerini equation [36]. The pore size distribution was obtained in the size range of 0.35-1 nm using the Non Local Density Functional Theory (NLDFT) on a slit pore carbon model with graphite like parallel walls, implemented in Quantachrome data analysis software developed by Neimark and Ravikovitch [12].

The CO₂ adsorption performance of the biochars obtained in the fixed bed reactor was assessed at atmospheric pressure and temperatures between 25 and 100 °C in a thermogravimetric analyser TGA92 from Setaram. About 20 mg of sample was dried in 50 cm³ min⁻¹ of Ar flow at 100°C for 1 h, and then allowed to cool down to 25 °C. The amount of CO₂ adsorbed was calculated from the mass gain experienced by the dry sample when it is

exposed to $50 \text{ cm}^3 \text{ min}^{-1}$ of CO_2 flow. Buoyancy effects were corrected. The mass of dry biochar at the end of the heating step (100°C) was taken as the reference mass to avoid underestimation due to Ar adsorption at 25°C . Once CO_2 adsorption equilibrium is attained at 25°C , the furnace temperature is raised at $0.5^\circ\text{C min}^{-1}$ up to 100°C under CO_2 flow to assess the effect of temperature upon the CO_2 adsorption capacity. The biochars were kept at the final temperature of 100°C in CO_2 flow, to assess the adsorption capacity at this temperature and finally regenerated by switching the feed gas to Ar.

Two samples among those that showed most promising for CO_2 capture were selected to assess their potential to carry out CO_2/N_2 separation. With this purpose, the equilibrium of adsorption of pure CO_2 and N_2 was measured between 0 and 120 kPa at 0, 25 and 50°C in a volumetric apparatus TriStar 3000 from Micromeritics.

3. Results and Discussion

3.1. Effect of oxygen concentration: TG-DSC tests

The effect of the oxygen concentration on the mass loss profile of the olive stones is shown in Figure 1a. Three main steps can be differentiated: below 200°C , due to the loss of moisture, between 200 and 400°C , due to the degradation of the biomass structural polymers, and above 400°C , mainly due to the oxidation of the remaining char. Mass loss above 400°C is directly related to the oxygen concentration in the reactive gas: oxidation of the organic matter is nearly completed at 700°C when air is used as the flowing gas, but 27% of the initial mass remains when 3% O_2 is used. No significant differences between the profiles can be appreciated below 400°C . Moreover, up to this temperature, the profiles are also coincident with those obtained in inert atmosphere [37]. Similar findings were found for the almond shells, except for temperatures slightly shifting to lower values (*ca.* 50°C). This implies that the biomass decomposition processes occurring below 400°C are independent of the atmosphere, being driven by temperature (thermal degradation). Two distinct maxima can be differentiated in the DTG curve between 200 and 400°C (Figure 1b): the first is commonly attributed to the decomposition of hemicellulose, and the second to the decomposition of cellulose. Lignin decomposes slowly over a very broad range of temperatures: it starts at a temperature close to that of hemicellulose decomposition and continues up to higher temperatures, making difficult to distinguish its contribution from the other components [38, 39].

Oxidation of biomass in air is globally an exothermic process: the net heat released during heating in air up to 900°C (obtained by integration of the heat flow signal shown in Figure 1c)

is 10.7 and 9.6 MJ per kg of olive stones and almond shells, respectively, which is in good agreement with reported values for the smouldering combustion of different biomasses in air [40]. The DSC signal is endothermic at low temperatures, due to the drying and heating of the biomass, but becomes exothermic above 170 °C (Figure 1c). However, when the partial pressure of oxygen in the reactive gas is reduced, more external energy is required to heat and dry the sample, because gas-phase oxidation reactions of the released volatiles in the vicinity of the sample are less favoured, and the heat released during the subsequent stages is also substantially reduced (see Figure 1c). If necessary, the small energy requirements to carry out the oxidation with low oxygen partial pressures could be satisfied with the combustion of tars and gases produced during the devolatilisation stage.

3.2. Activation in the fixed bed reactor

Series of biochars were prepared from almond shells and olive stones by activation with air at 400 °C and increasing reaction times (series A-21-400-xx and O-21-400-xx, where xx stands for the reaction time in min). To study the effect of temperature, two series were prepared at a higher temperature; this was limited to 450 and 500 °C for almond shells and olive stones, respectively, attending to the profiles obtained in the thermogravimetric analyser (series A-21-450-xx and O-21-500-xx). To evaluate the effect of oxygen concentration, a new set of biochars were prepared from almond shells and olive stones by direct activation with 5% O₂ (balance N₂). The observed oxidation rates in the TG tests carried out at low oxygen partial pressures were significantly lower than those observed in air, which entailed the use of higher temperatures during batch activation: 500 and 650 °C (series A-5-500-xx, A-5-650-xx, O-5-500-xx and O-5-650-xx). A final series of biochars were also obtained from olive stones and almond shells by activation with 3% O₂ at 650 °C (series A-3-650-xx, O-3-650-xx). The experimental conditions evaluated (temperature, oxygen concentration in the activating gas, and reaction time), together with the samples nomenclature are summarised in Tables 3 and 4 for biochars obtained from olive stones and almond shells, respectively.

Figures 2 and 3 show the history of the conversion (X), defined here as weight per cent in dry ash free basis, for the olive stones and almond shells at different oxygen concentrations in the fixed bed reactor. Two stages with markedly different rates can be differentiated: during the first minutes of the experiment (heating up) mass loss occurs very rapidly due to the loss of volatiles (devolatilisation); this is followed by a slower stage, mainly due to oxidation of the remaining solid. As expected, for a given oxygen concentration in the feed gas, increasing the

activation temperature leads to higher conversions. Likewise, at a given temperature, increasing the oxygen concentration leads to higher conversions.

3.2.1. Pore development during activation

Tables 3 and 4 summarise the textural characterisation of the biochars obtained in this study by direct activation with 3, 5 and 21% O₂ of olive stones and almond shells, respectively. Although the term surface area has little significance in the case of narrow micropores and the term pore volume is usually preferred in those cases, the value of the surface area (calculated by the DR method, S_{DR}) has been included in Tables 3 and 4 for comparison purposes with available literature.

3.2.1.1 Activation with air

Micropore volume was progressively developed during the activation of olive stones and almond shells with air at 400 °C (see the increase of W₀ with conversion in Tables 3 and 4).

An increase in activation temperature, for a similar reaction time, led to a significant rise in conversion (lower overall yield). However, no additional gain in texture development was observed. This can be attributed to the fact that the oxidation rate increases to a greater extent with temperature compared to the diffusion rate: the reaction front moves to pores of greater diameter or even to the external surface of the particle, with no significant micropore development.

Carbons with limiting micropore volumes of up to 0.21 cm³ g⁻¹, surface areas of up to 551 m² g⁻¹ and average micropore widths of 0.6-0.7 nm, were obtained in short times (below 55 min) at a relatively low temperature, 400 °C, by direct activation in air.

The microporous volume of sample A-21-400-42 is similar to that obtained by Linares-Solano *et al.* [24] by direct activation of almond shells with air at 400 °C (see Tables 1 and 3-4). However, the carbons presented here were produced in shorter times (42 min vs. 4h) and with higher yield (23 vs. 17 %). Although Linares-Solano *et al.* reported higher texture development by the two-step activation procedure, the latter involved the carbonisation of almond shells at much higher temperature (900 °C). This increases the energy requirements, which become similar to those of activation with CO₂ or H₂O, but with poorer results in terms of texture development.

The micropore volumes of samples O-21-400-55 and A-21-400-42 are slightly above those reported for carbons prepared from nutshell chars by controlled rate activation with air at 306 °C [23] (see Tables 1 and 3-4). The lack of CO₂ adsorption data for the rest of the air-activated-carbons found in the literature (Table 1) prevents direct comparison of the samples.

3.2.1.2. Activation with lower oxygen partial pressures

Activation of olive stones with 5% O₂ at 500 °C led to samples with similar micropore volumes but with higher overall yields than those obtained by activation with air at the same temperature (Table 3). The reduction in the partial pressure of oxygen leads to a reduction in the oxidation rate of the carbon, thus reducing the external carbon burn-off.

The rise in temperature, from 500 to 650 °C, increased the micropore volume and decreased the average micropore width (Table 3). Figure 4 compares the pore size distributions of olive stones activated with 5% O₂ at 500 and 650 °C up to similar conversions (84-85%). The sample obtained at the higher temperature presents greater micropore volume in the narrowest range, between 0.3 and 0.4 nm. Micropore volume in this pore size range is highly desirable for efficient CO₂ adsorption in postcombustion conditions, as will be discussed later.

Similar results were obtained for the almond shells series (Table 4). One-step activation with 5% O₂ at 650 °C achieved micropore volumes of up to 0.22 cm³ g⁻¹ with average micropore widths of 0.5 nm.

These results are comparable to those reported for carbons prepared from nutshell chars by controlled rate activation at 400 °C with an average O₂ concentration of 5% [23] (see Table 1).

The positive results obtained by activation with 5% O₂ at 650 °C encouraged the preparation of two new series of samples by direct activation of olive stones and almond shells at the same temperature but lowering the O₂ concentration in the activating gas to 3%. These conditions led to the sample with the highest micropore volume: O-3-650-110 (0.27 cm³ g⁻¹).

3.2.1.3. Effect of carbonisation

To study the effect of carbonisation, a series of samples were prepared by a two-step procedure: almond shells were first carbonised at 600 °C in N₂ atmosphere (carbon yield: 25%), and the obtained char was then activated at 650 °C with 3% O₂ for 60, 90 and 120 min. These samples were denoted as CA-3-650-xx, where xx stands for the activation time in min. The overall yield (defined as g of final carbon per 100 g of raw biomass) of the two-step procedure for an activation time of 60 min is 21%, which is slightly below that of the direct activation:

22%. The samples obtained by the activation of the carbonised product (CA series) present similar textural features than those obtained by direct activation of the almond shells (see Table 4): limiting micropore volumes of 0.18-0.19 cm³ g⁻¹ and average micropore widths of 0.5 nm. Thus, it was confirmed that direct activation leads to similar results than the carbonisation-activation procedure in terms of textural features but seems more beneficial in terms of time-consuming, cost of N₂, and energy requirements.

3.2.2. CO₂ capture performance of samples prepared in the fixed bed reactor

3.2.2.1. Sample screening: CO₂ capture capacity

The adsorption capacity at 0 °C and 101 kPa is often taken in the literature as an indicative of the potential application of an adsorbent towards CO₂ capture. For instance, high surface area carbon molecular sieves (CMS) have been reported to present CO₂ adsorption capacities as large as 8.6 mmol g⁻¹ at 0 °C and 101 kPa, superior to those of zeolites [41]. However, these conditions are far from being representative of post-combustion capture, where the partial pressure of CO₂ is expected to be below 30 kPa. For instance, the outstanding adsorption capacity of the aforementioned CMS drastically drops to 1.3 mmol g⁻¹ at 10 kPa [41]. The samples developed in the current study present moderate capacities at 0 °C and 101 kPa: up to 3.2 mmol g⁻¹ (see Tables 5 and 6). However, these samples present adsorption capacities up to 1.5 mmol g⁻¹ at 10 kPa, which is above that of the high surface area CMS. This difference is related to the pore size distribution: only the narrower micropores present sufficient potential for adsorbing CO₂ at low pressures. A direct correlation has been reported between the adsorption capacity at 10 kPa and 0 °C and the volume of pores with a diameter smaller or equal to 0.5 nm [13].

Moreover, 0 °C is not a realistic temperature for a real post-combustion capture adsorption process: flue gases exit the wet desulfurisation unit at near 50 °C [42]. Although the adsorption capacity of physical adsorbents decreases with temperature, and thus a low adsorption temperature is desirable, the cost associated to the cooling of the flue gas must be considered. As an example, the most ready-to-use post-combustion capture technology, absorption with amines or ammonia, requires cooling the flue gas between 15 and 40 °C for efficient operation [43]. It is therefore important to assess the CO₂ adsorption performance in a wide temperature range.

Tables 5 and 6 summarise the CO₂ adsorption capacity of the samples at atmospheric pressure and at a temperature of 25 and 100 °C. As expected, as temperature increases the adsorption

capacity of the evaluated samples is reduced. The samples with the highest adsorption capacity in the evaluated temperature range are those activated at 650 °C, and among them, those obtained from almond shells (capacities up to 2.1 mmol g⁻¹ at 25 °C and 0.7 mmol g⁻¹ at 100 °C). This behaviour is related to the high micropore volume of these samples but, above all, to the narrow character of that microporosity, with average pore widths near 0.5 nm for the biochars prepared from almond shells and 0.6 nm for those prepared from olive stones. It has been previously reported that the volume of micropores below 0.6 nm is of maximum importance for the adsorption of CO₂ at 25 °C and atmospheric pressure [14].

As an example, the carbon A-3-650-60 presents similar CO₂ adsorption capacity at 0 °C and 101 kPa than A-21-400-42. However, at higher temperatures (25-100 °C) the CO₂ adsorption capacity is higher for the first sample despite having a lower micropore volume (W_0). This is related to their different pore size distributions: the average micropore width (L_0) of A-21-400-42 is 0.72 nm, while that of A-3-650-60 is only 0.55 nm. The pore size distributions of these two samples, calculated by the NLDFT, are presented in Figure 5. It can be observed that the sample A-3-650-60 has higher micropore volume in the pore size range between 0.35 and 0.52 nm. The combination of reduced oxygen content in the activating atmosphere and higher activation temperature further develop the narrowest pores. These pores present greater adsorption potential thus being more effective for adsorbing CO₂ above 25 °C.

The samples prepared from almond shells by the two-step procedure (series CA-3-650-xx) present similar or slightly lower CO₂ uptakes than those obtained by the single-step procedure (see Table 6). Thus, no advantage over direct activation was observed.

Among the carbons prepared by single-step activation, two were selected for further CO₂ capture studies: A-3-650-83 and O-3-650-110. These cheap-to-produce biochars present moderate CO₂ adsorption capacity at 25 °C and atmospheric pressure, although comparable to that of the commercial activated carbon Norit R2030CO₂ [44] and to that of nitrogen enriched carbons developed from the same precursors by high temperature amination [45, 46]. It should be noted that these latter samples have proven to be very efficient for CO₂/N₂ separation in post-combustion conditions, with superior performance to other materials with higher pore volumes [17, 18].

3.2.2.2. CO₂/N₂ adsorption equilibrium

The adsorption isotherms of pure CO₂ and N₂ on the selected samples at 0, 25 and 50 °C are shown in Figures 6 and 7. Both biochars present significantly higher CO₂ adsorption capacity

than that of N₂ over the entire pressure and temperature range. Note that the shape of the adsorption isotherms of CO₂ and N₂ are markedly different: the first are steeper at low pressures, levelling off as pressure increases, while the second are nearly linearly dependent with pressure in the studied range. This is related to stronger adsorbent-adsorbate interaction forces in the case of the CO₂ molecule, which arise from its stronger quadrupole moment.

The isosteric heat of adsorption of CO₂ and N₂ was estimated from the experimental adsorption data making use of the Clausius-Clapeyron equation:

$$Q_{st} = -R \left[\frac{\partial \ln P}{\partial \left(\frac{1}{T} \right)} \right]_n \quad (5)$$

where Q_{st} is the isosteric heat of adsorption at a selected adsorbed amount n , T is the temperature, P is the pressure of the gas phase and R the universal constant of gases. Plotting $\ln P$ against $\left(\frac{1}{T} \right)$ at constant adsorbed amounts yields a straight line which slope is equal to:

$\left(-\frac{Q_{st}}{R} \right)$. On average, the isosteric heat of adsorption of CO₂ is 31.5 kJ mol⁻¹ for the sample prepared from olive stones and 32.2 kJ mol⁻¹ for the almond shells based sample. For carbon materials (essentially non-polar adsorbents), the isosteric heat of adsorption depends mainly on the pore size distribution: values between 16 and 30 kJ mol⁻¹ have been reported for different types of commercial activated carbons [47, 48]. The relatively high heat of adsorption of the samples under study is attributed to their narrow pore size. Still, this heat of adsorption, which is typical for physisorption processes, is low compared with that of chemisorption. For example, supported amines present heats of adsorption close to 100 kJ mol⁻¹ [49, 50]. The heat of adsorption is a measure of the strength of adsorption: ideally, it should be high enough to have a selective adsorbent but without hindering regeneration. One of the main advantages of porous carbons is that they can be easily regenerated by reducing the pressure of the system in PSA processes, and/or increasing slightly its temperature in TSA processes. The average isosteric heat of adsorption of N₂ is half that of CO₂: 16.7 and 16.5 kJ mol⁻¹ for O-3-650-110 and A-3-650-83, respectively. These values are close to those reported for other adsorbents: 16 kJ mol⁻¹ for BPL activated carbon [48]. The higher isosteric heat of adsorption of CO₂ compared to that of N₂ is related to the stronger adsorption of the CO₂ molecule.

Adsorption models are very useful as they can predict the behaviour of the equilibrium of adsorption in a wide temperature and pressure range (by interpolation or extrapolation of the

data obtained by direct measurement). *Toth* model [51] is commonly used for this purpose due to the simple form of its equation (8) and its correct behaviour at low and high pressures:

$$n = n_m \frac{bP}{(1 + (bP)^t)^{1/t}} \quad (8)$$

Where n represents the amount adsorbed, n_m the saturation capacity, P the pressure of the gas phase, t a parameter that represents the system heterogeneity ($t \leq 1$) and b is the affinity constant which is considered temperature dependent according to Equation 9 [52]:

$$b = b_0 \exp \left[\frac{Q}{RT_0} \left(\frac{T}{T_0} - 1 \right) \right] \quad (9)$$

where b_0 is the affinity at a reference temperature T_0 (taken here as 0°C), Q is a measure of the heat of adsorption, T the evaluated temperature and R the universal constant of gases. The heterogeneity parameter t varies with temperature according to Equation 10 [52]:

$$t = t_0 + \alpha \left(1 - \frac{T}{T_0} \right) \quad (10)$$

The optimal *Toth* parameters, n_m , b_0 , Q , t_0 , and α , presented in Table 7, were obtained by a nonlinear fitting procedure to give the best fit to the experimental data (the total average relative error (ARE [53]) for the three evaluated temperatures was taken as the objective function). As can be seen from Figures 6 and 7, this model describes satisfactorily the equilibrium of adsorption of pure CO₂ and N₂ in the studied range. The parameter Q from *Toth* model is in good agreement with the average isosteric heat of adsorption estimated through the Clausius-Clapeyron equation. The heterogeneity parameter, t , presents a greater deviation from unity in the case of CO₂, indicating a more specific interaction between the carbon surface and the CO₂ molecule than that with N₂. The product $n_m b$ represents the Henry constant in the limit of zero pressure, and it is a measure of the affinity of the adsorbent towards a specific adsorbate at a given temperature at low partial pressures. Note that the value for CO₂ is several orders of magnitude above that of N₂. Comparing the two biochars under study, the almond shells present a greater value of $n_m b$ than the olive stones for CO₂.

A simple criterion for adsorbent selection in PSA processes is the working capacity (difference between the amounts adsorbed at the high pressure adsorption stage and the low pressure evacuation step). This can be preliminarily assessed from the pure component equilibrium adsorption data. As the flue gas is at near atmospheric pressure, a fan will be required to

account for the pressure drop of the PSA unit. A plausible adsorption pressure could be 130 kPa, as this will not increase excessively the operation cost due to compression work [54]. In a PSA process, the adsorbent is regenerated by lowering the pressure of the vessel. As the adsorption step occurs at near atmospheric pressure, subatmospheric pressures are required to recover the adsorbed CO₂. However, the vacuum level during the depressurisation step cannot be excessively low to keep the operation costs as low as possible; 5 kPa seems a reasonable low pressure level according to previous studies [54]. Figure 8 compares the working capacities of the two selected carbons and that of zeolite 13X, for a pressure swing adsorption process operating between an evacuation pressure of 5 kPa and a feed pressure of 130 kPa, at temperatures that could be found in PCC operation (20 and 40 °C), for different CO₂ concentrations in the feed gas. Obviously, as the partial pressure of CO₂ in the feed gas approaches the evacuation pressure, the working capacity tends to zero, and conversely, working capacity increases with the partial pressure of CO₂ in the feed gas. Note that although the absolute adsorption capacity of zeolite 13X is higher than that of the biochars, their working capacities are similar at 20 °C (Figure 8a). At 40 °C (Figure 8b) the order is: zeolite 13X > A-3-650-83 > O-3-650-110. However, heat effects will tend to reduce the working capacity of the adsorbents, and these are expected to be higher for zeolite 13X (due to its higher isosteric heat of adsorption).

The Ideal Adsorption Solution (IAS) theory [55] was used to predict the binary adsorption equilibrium of CO₂ and N₂. MatLab code IAS written by D.D. Do [52] was used to obtain the multi-component CO₂-N₂ prediction using the pure component *Toth* model. Figure 9a compares the binary adsorption isotherms at 25 °C and a total pressure of 130 kPa, calculated by the IAS theory, with the pure component *Toth* model for CO₂ and N₂ for the almond shells based sample. The binary adsorption isotherm of N₂ is well below that of the pure component, while the pure and binary adsorption isotherms of CO₂ are very close. This implies that the presence of N₂ (weak adsorptive) affects little the adsorption capacity of the strong adsorptive, CO₂, while the presence of CO₂ reduces drastically the adsorption of N₂ in a N₂/CO₂ binary mixture. This behaviour is also observed for highly selective adsorbents, such as zeolite 13X, although it is less pronounced for other activated carbons, such as BPL [48].

The equilibrium separation factor for a binary mixture of CO₂ and N₂ is defined by Equation 11 [56], where x refers to the molar fraction in the adsorbed phase and y to the molar fraction in the gas phase. A high separation factor is a key parameter for the screening of adsorbents in a PSA process: the higher the separation factor, the greater product purity is expected [57].

$$S_{CO_2/N_2} = \frac{x_{CO_2}/x_{N_2}}{y_{CO_2}/y_{N_2}}$$

(11)

Figure 9b represents the CO₂/N₂ separation factor for sample A-3-650-83 at a total pressure of 130 kPa between 0 and 50 °C. This decreases with increasing temperature and CO₂ molar fraction in the bulk gas. The equilibrium separation factor of the almond shells sample is very high over the whole studied range, particularly at low CO₂ molar fractions in the gas phase, which is encountered in post-combustion applications. The olive stones char presented a similar behaviour, although the separation factor is below that observed for the almond shells based sample, especially at low CO₂ concentrations in the gas phase (see Figure 10); this is attributed to its wider pore sizes.

According to these results, the biochars presented here show promising features for carbon capture applications in post-combustion conditions.

Conclusions

Biochars have been obtained by activation of almond shells and olive stones with different oxygen concentrations: 3, 5 and 21% (balance N₂) at temperatures between 400 and 650 °C. The use of oxygen as the activating gas entails the use of lower activation temperatures than those required for activation with CO₂ or H₂O. Moreover, single-step activation leads to carbons with similar or even better characteristics than the conventional two-step procedure, which means a new source for energy savings compared to the conventional two-step procedure.

Using low oxygen concentrations (3-5%) and mild temperatures (650 °C), biochars with a relatively high micropore volume in the narrow micropore domain (0.3-0.5 nm) have been obtained. These features are essential for the adsorption of CO₂ at low pressures and above room temperature, which are the characteristic conditions of post-combustion capture. According to a preliminary evaluation based on the equilibrium of adsorption of the major flue gas components, CO₂ and N₂, the obtained biochars exhibit high CO₂/N₂ selectivity in the 0-50 °C temperature range (especially at low CO₂ concentrations in the gas phase) and competitive working capacities for VSA processes, showing potential to be used as CO₂ adsorbents in post-combustion capture processes.

Nomenclature

b Affinity constant of Toth adsorption model

469	b_0	Affinity constant of Toth adsorption model at the reference temperature
470	n	Amount adsorbed ($\text{mol CO}_2 \text{ kg}^{-1}$ adsorbent)
471	n_m	Saturation capacity of Toth adsorption model ($\text{mol CO}_2 \text{ kg}^{-1}$ adsorbent)
472	P	Pressure of the gas phase (kPa)
473	Q	Parameter of Toth model related to the heat of adsorption ($\text{J mol}^{-1} \text{ CO}_2$)
474	Q_{st}	Isosteric heat of adsorption ($\text{J mol}^{-1} \text{ CO}_2$)
475	R	Universal constant of gases ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
476	$S_{\text{CO}_2/\text{N}_2}$	Equilibrium separation factor for CO_2 over N_2
477	t	Heterogeneity parameter of Toth adsorption model
478	t_0	Heterogeneity parameter of Toth adsorption model at the reference temperature
479	T	Temperature (K)
480	T_0	Reference temperature (K)
481	x	Molar fraction in the adsorbed phase
482	y	Molar fraction in the gas phase
483	α	Empirical parameter of Toth adsorption model

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625

626 **Tables and Figures**

627 Table 1. Literature review: activated carbon production by activation with oxygen

Starting material	Nutshell char [23]		Almond shells [24]		Rockrose wood [25]	Eucalyptus sawdust [26]	Almond tree pruning [27]	Olive tree Wood [28]
Carbonisation temperature (°C)	NA	NA	900	None ^a	600	800	600	600
Activation temperature (°C)	306 ^b	400	400	400	600	400	260	400
Activating agent	Air	5.2 ^b % O ₂	Air	Air	Air	Air	Air	Air
Flow rate (cm ³ min ⁻¹)	40	40	90	90	200	NA	167	100
Reaction time (h)	NA	NA	4	4	NA	NA	1	2
S _{BET} (m ² g ⁻¹)	356	645	635	551	370	600	469	481
W ₀ (cm ³ g ⁻¹)	0.18	0.23	0.26	0.19	NA	NA	NA	NA

628 ^aDirect activation (all other samples obtained by a two-step procedure); ^b Average value; NA stands for
629 value not available

630 Table 2. Proximate analysis of biomass feedstocks used in this work

	Proximate analysis (weight %, dry basis)		
	Volatile mater	Ash	Fixed carbon
Olive stones	85.4	0.6	14.0
Almond shells	82.3	1.3	16.4

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633 Table 3. Activation conditions and textural characterisation of samples obtained from olive stones

Sample	% O ₂	Temperature (°C)	Reaction time (min)	Conversion (wt.%, daf)	S _{DR} (m ² g ⁻¹)	W ₀ (cm ³ g ⁻¹)	L ₀ (nm)
O-21-400-30	21	400	30	70.1	400	0.15	0.60
O-21-400-40	21	400	40	76.3	411	0.16	0.61
O-21-400-55	21	400	55	77.8	551	0.21	0.60
O-21-500-24	21	500	24	81.9	538	0.21	0.59
O-21-500-27	21	500	27	82.3	446	0.17	0.58
O-21-500-36	21	500	36	86.5	480	0.18	0.58
O-5-500-45	5	500	45	71.1	466	0.18	0.61
O-5-500-88	5	500	88	76.9	542	0.21	0.62
O-5-500-115	5	500	115	83.9	554	0.21	0.62
O-5-650-40	5	650	40	78.8	528	0.20	0.58
O-5-650-70	5	650	70	80.8	552	0.21	0.57
O-5-650-108	5	650	108	84.9	611	0.23	0.57
O-3-650-83	3	650	83	76.4	562	0.21	0.55
O-3-650-110	3	650	110	83.7	697	0.27	0.57
O-3-650-115	3	650	115	85.9	629	0.24	0.56

634 Table 4. Activation conditions and textural characterisation of samples obtained from almond shells

Sample	%O ₂	Temperature (°C)	Reaction time (min)	Conversion (wt.%, daf)	S _{DR} (m ² g ⁻¹)	W ₀ (cm ³ g ⁻¹)	L ₀ (nm)
A-21-400-28	21	400	28	72.0	329	0.13	0.73
A-21-400-40	21	400	40	76.4	372	0.14	0.68
A-21-400-42	21	400	42	77.3	532	0.20	0.72
A-21-450-26	21	450	26	79.9	388	0.15	0.55
A-21-450-32	21	450	32	85.0	376	0.14	0.52
A-21-450-36	21	450	36	85.4	386	0.14	0.53
A-5-500-73	5	500	73	73.1	340	0.14	0.56
A-5-500-85	5	500	85	77.4	362	0.14	0.64
A-5-500-108	5	500	108	77.7	456	0.17	0.61
A-5-650-38	5	650	38	80.9	485	0.14	0.51
A-5-650-68	5	650	68	83.0	501	0.19	0.50
A-5-650-98	5	650	98	85.8	579	0.22	0.54
A-3-650-60	3	650	60	79.8	466	0.18	0.55
A-3-650-83	3	650	83	80.3	557	0.21	0.49
A-3-650-100	3	650	100	86.4	511	0.20	0.50
CA-3-650-60	3	650	60 ^a	13.7	478	0.18	0.50
CA-3-650-90	3	650	90 ^a	14.9	501	0.19	0.49
CA-3-650-120	3	650	120 ^a	28.1	491	0.19	0.48

^aConversion based on the starting char (dry ash free basis). All the rest are based on the raw biomass (dry ash free basis).

Table 5. CO₂ adsorption capacity of samples obtained from olive stones

Sample	CO ₂ adsorbed (mmol g ⁻¹)			
	0 °C ^a		25 °C ^b	100 °C ^b
	10 kPa	101 kPa	101 kPa	101 kPa
O-21-400-30	0.74	1.95	1.56	0.40
O-21-400-40	0.74	1.99	1.40	0.31
O-21-400-55	0.98	2.77	1.75	0.41
O-21-500-24	1.05	2.66	1.69	0.42
O-21-500-40	0.91	2.22	1.59	0.39
O-21-500-55	0.96	2.38	1.69	0.41
O-5-500-45	0.84	2.2	1.56	0.39
O-5-500-88	0.93	2.64	1.55	0.40
O-5-500-115	0.95	2.68	1.66	0.41
O-5-650-40	1.07	2.28	1.78	0.50
O-5-650-70	1.16	2.74	1.96	0.54
O-5-650-108	1.22	3.12	1.98	0.55
O-3-650-83	1.25	2.85	1.92	0.55
O-3-650-110	1.36	3.10	2.02	0.55
O-3-650-115	1.30	2.84	1.98	0.55

^aVolumetric apparatus; ^bGravimetric

Table 6. CO₂ adsorption capacity of samples obtained from almond shells

Sample	CO ₂ adsorbed (mmol g ⁻¹)			
	0 °C ^a		25 °C ^b	100 °C ^b
	10 kPa	101 kPa	101 kPa	101 kPa
A-21-400-28	0.40	1.43	1.14	0.25
A-21-400-40	0.52	1.64	1.29	0.38
A-21-400-42	0.65	2.37	1.37	0.44
A-21-450-26	0.85	2.03	1.51	0.40
A-21-450-32	0.93	2.06	1.57	0.45
A-21-450-36	0.87	2.01	1.53	0.43
A-5-500-73	0.73	1.69	1.44	0.39
A-5-500-85	0.56	1.71	1.36	0.38
A-5-500-108	0.79	2.36	1.55	0.44
A-5-650-38	0.91	1.93	1.81	0.58
A-5-650-68	1.27	2.76	2.09	0.74
A-5-650-98	1.27	3.20	1.94	0.70
A-3-650-60	1.03	2.41	1.90	0.62
A-3-650-83	1.51	3.11	2.11	0.70
A-3-650-100	1.31	2.84	2.01	0.64
CA-3-650-60	1.22	2.67	1.91	0.62

CA-3-650-60	1.33	2.79	1.97	0.60
CA-3-650-60	1.34	2.81	1.98	0.61

640 ^aVolumetric apparatus; ^bGravimetric

641 Table 7. Optimal parameters for fitting of the temperature dependent Toth equation

	O-3-650-110		A-3-650-83	
	CO ₂	N ₂	CO ₂	N ₂
n_m (mol kg ⁻¹)	7.24	6.19	6.57	4.60
b_0 (kPa ⁻¹)	0.1149	0.0014	0.2893	0.0017
t_0	0.390	0.535	0.354	0.578
Q (kJ mol ⁻¹)	30.70	17.46	32.89	19.02
α	0	0.1131	0	1.927

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Figure 1. Non-isothermal oxidation tests of olive stones carried out in TGA-DSC1 STAR[®] System at a heating rate of 15 °C min⁻¹ under a total flow rate of 10 cm³ min⁻¹ containing 3, 5 and 21% O₂ (balance N₂): (a) TG curve (mass percentage of remaining solid vs. temperature); (b) DTG curve (rate of mass loss vs. temperature); (c) DSC curve (heat flow vs. temperature).

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Figure 2. Conversion history of olive stones in the fixed bed reactor for different oxygen concentrations: (a) 21% O₂; (b) 5% O₂; and (c) 3% O₂ (balance N₂). (Discontinuous lines represent the linear regression of the experimental data).

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Figure 3. Conversion history of almond shells in the fixed bed reactor for different oxygen concentrations: (a) 21% O₂; (b) 5% O₂; and (c) 3% O₂ (balance N₂). (Discontinuous lines represent the linear regression of the experimental data).

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659 (a)

(b)

660 Figure 4. Pore size distribution calculated by the NLDFT-CO₂-carbon model applied to the CO₂ adsorption isotherm
661 at 0 °C of samples O-5-500-115 and O-5-650-108: (a) cumulative pore volume vs. pore width and (b) differential
662 pore volume vs. pore width.

663 (a)

(b)

664 Figure 5. Pore size distribution calculated by the NLDFT-CO₂-carbon model applied to the CO₂ adsorption isotherm
665 at 0 °C of samples A-3-650-60 y A-21-400-42: (a) cumulative pore volume versus pore width and (b) differential
666 pore volume versus pore width.

667 (a)

(b)

668 Figure 6. Adsorption isotherms of CO₂ (a) and N₂ (b) at 0, 25 and 50 °C on sample O-3-650-110 (symbols represent
669 experimental adsorption data and solid lines Toth model fitting).

Figure 7. Adsorption isotherms of CO₂ (a) and N₂ (b) at 0, 25 and 50 °C on sample A-3-650-83 (symbols represent experimental adsorption data and solid lines Toth model fitting).

Figure 8. Comparison of the working capacity of selected samples and zeolite 13X calculated from the pure CO₂ adsorption equilibrium data for an evacuation pressure of 5 kPa and a feed pressure of 130 kPa at: (a) 20 °C and (b) 40 °C. (Adsorption equilibrium data of CO₂ on zeolite13X taken from [58])

Figure 9. (a) Comparison between binary and pure adsorption isotherms at 25 °C on sample A-3-650-83 (solid lines: single component Toth model; dashed lines: binary equilibrium at 130 kPa calculated from the single component Toth model by the IAS theory); (b) Equilibrium separation factor calculated from the binary adsorption equilibrium at a total pressure of 130 kPa between 0 and 50 °C.

Figure 10. (a) Comparison between the CO₂/N₂ separation factor of samples O-3-650-110 and A-3-650-83 at 130 kPa and 25 °C calculated by IAS theory.