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Development of low-cost biomass-based adsorbents for postcombustion CO_2 capture

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ABSTRACT

In this work a series of carbon adsorbents were prepared from a low-cost biomass residue, olive stones. Two different approaches were studied: activation with CO_2 and heat treatment with gaseous ammonia. The results showed that both methods are suitable for the production of adsorbents with a high CO_2 adsorption capacity, and their potential application in VSA or TSA systems for postcombustion CO_2 capture. It was found that the presence of nitrogen functionalities enhances CO_2 adsorption capacity, especially at low partial pressures.

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1. Introduction

Currently the energy system is mostly based on fossil fuels combustion; coal being the dominant fuel, power generation is responsible for about 1/3 of all anthropogenic CO_2 emissions. Moreover, related emissions are increasing rapidly due to the current growth in global energy demand. At the same time, there is an urgent need to stabilise the concentration of CO_2 in the atmosphere before permanent and severe damage to the climate system is done [1]. Although important measures are being taken, such as increasing the share of renewables, or improving the efficiency of energy conversion processes, it is widely accepted that Carbon Dioxide Capture and Storage, commonly referred as CCS, will be necessary if the demand for energy is to be satisfied, without contributing to global warming in the forthcoming years, while alternatives to fossil fuels are developed.

The capture or separation step is the main contributor to the overall cost of CCS [2]. At present, the preferred technology to carry out the separation of CO_2 in postcombustion applications is amine scrubbing. However, this technology presents a series of drawbacks, such as the high energy requirement for the regeneration of the solvent. Other technologies in a lesser stage of development that seek to reduce the cost associated to the capture step, include adsorption with activated carbons or zeolites. Recently it was reported that the cost associated to CO_2 capture can be reduced below the amine base case by using the technology of adsorption [3,4].

Activated carbons present a series of advantages as CO_2 adsorbents: a high adsorption capacity at ambient pressures, ease of regeneration, low-cost, and insensitiveness to moisture. These materials can be obtained from almost any carbonaceous product by carbonisation followed by an activation step. The adsorption capacity of an activated carbon is mainly governed by its texture, but it is also strongly influenced by the surface chemistry. The presence of nitrogen functionalities in the carbon surface have been reported to be effective in the adsorption of acid gases, such as H_2S and SO_2 [5,6]. Attention has also been given to the introduction of nitrogen functionalities into the carbon in order to enhance CO_2 adsorption capacity [7–13]. Among other possibilities, nitrogen can be introduced into the carbon matrix by reaction with gaseous ammonia at high temperatures [14–20].

In this study two different approaches for developing efficient carbon dioxide adsorbents were compared: activation with carbon dioxide, and heat treatment with gaseous ammonia, which will be referred to from now on as amination. The main objective of amination is the introduction of basic nitrogen functionalities to enhance CO_2 adsorption.

2. Experimental

A biomass by-product from the Spanish food industry, olive stones (OS), was selected as starting material for the preparation of the activated carbons. The olive stones were ground and sieved, and a particle size between 1 and 3 mm was selected. First, carbonisation was carried out at 600 °C under an inert atmosphere of N_2. An average char yield of 24% was obtained. The resulting char was denoted as GKOS.

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A first series of samples were prepared by activation of the char with 10 $cm^3\ min^{-1}$ of carbon dioxide at different burn-off degrees (20%, 40% and 50%). The temperature of activation was set at 800 °C, based on previous tests in a thermogravimetric analyser. The activated samples were referred to as GKOSAX, where *A* represents activation, and *X* the degree of the burn-off.

A second series of samples were obtained by heat treating the char with 50 $cm^3\ min^{-1}$ of ammonia gas at four different temperatures: 400, 600, 800 and 900 °C. The soaking time was 2 h in all cases. These samples were denoted as GKOSNY, where N stands for NH_3, and *Y* represents the temperature of the treatment.

Chemical characterisation of the samples involved the determination of the proximate and ultimate analyses, and the estimation of the point of zero charge (pH_{PZC}) by a mass titration method adapted from Noh and Schwarz [21].

All the samples were characterised by physical adsorption of N_2 and CO_2 at −196 °C and 0 °C, respectively, in a volumetric apparatus (Micromeritics Tristar 3000). Prior to the adsorption measurements, the samples were outgassed overnight at 100 °C under vacuum. The use of both adsorbates provides complementary information about the porous texture of the samples: the adsorption of CO_2 at 0 °C and up to 1 bar is restricted to pores narrower than 1 nm, whereas N_2 adsorption at −196 °C covers wider pore sizes but presents diffusion limitations in the narrowest pores. The apparent surface area of the samples was evaluated from the N_2 adsorption isotherms by applying the BET equation in the linear form proposed by Parra et al. [22]. The mesopore volume (V_{meso}) was assessed from the N_2 adsorption isotherm by the Density Functional Theory (DFT), assuming slit shape pores geometry and non regularisation [23]. The narrow micropore volume (W_0) (pore width below 0.7 nm) was estimated from the CO_2 adsorption isotherms at 0 °C by the Dubinin–Radushkevich method [24].

The CO_2 capture capacity of the adsorbents was evaluated in a Setaram TGA 92 thermogravimetric analyser. CO_2 uptakes were determined from the mass evolution profiles when the samples were exposed to a gas flow containing CO_2. Prior to the adsorption measurements, the samples were dried at 100 °C in 50 $cm^3\ min^{-1}$ of Ar for 1 h.

3. Results and discussion

As can be seen from the chemical analyses presented in Table 1, the raw biomass shows high volatile matter and low ash and sulphur contents. After carbonisation, the char exhibits a carbon content above 90% and a low ash content, being a suitable precursor for activated carbon production. The oxygen content is substantially reduced during the carbonisation step, as it is associated to the volatile matter of the biomass. However, the char still shows a noticeable oxygen content that may play an important role not only in adsorption processes but also in surface reactions with ammonia.

The point of zero charge experiences an increase after carbonisation, mainly as a consequence of the loss of surface functionalities. The char has a pH_{PZC} of 8.7, which indicates the dominant basic character of its surface. This basicity may result from basic surface oxides formed after carbonisation [25], or from non-heteroatomic Lewis base sites, that are characterised by regions of π electron density on the carbon basal planes [26].

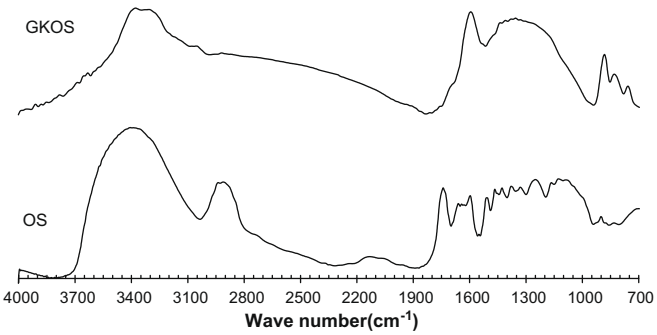


Fig. 1. DRIFT spectra of the starting olive stones (OS) and the carbonised product (GKOS).

Fig. 1 shows the DRIFT spectra of the raw olive stones, OS, and of the carbonised product, GKOS. In the spectrum of the raw biomass, it can be observed the presence of IR bands associated to aliphatic carbon (near 2900 cm^{-1}), phenolic groups (3000–3600 and 1000–1200 cm^{-1}) and also a band at 1740 cm^{-1} compatible with the presence of carboxyl or lactone groups [27,28]. The bands at 2900 and 1740 cm^{-1} have disappeared completely as a consequence of the carbonisation treatment, indicating an increase in the aromaticity of the carbon and the loss of labile carboxylic acids. The spectrum of the char also shows an intensification of the band at 1600 cm^{-1} that can be associated to quinone groups [27,28]. This band, together with the overlapping bands between 1000 and 1500 cm^{-1} have also been attributed to carboxyl-carbonate structures [29,30]. The presence of these basic oxides helps to explain the basicity of the char and its relatively high oxygen content.

3.1. Activation

3.1.1. Characterisation of the activated samples

Activation with carbon dioxide is an oxidative treatment that eliminates C atoms from the char by means of a heterogeneous reaction that releases gaseous CO. During the gasification reaction, some oxygen may be chemisorbed on the carbon surface, forming C(O) surface complexes [31]. To study the type of oxygen functionalities present in the samples, temperature programmed desorption tests (TPD) were carried out in a thermogravimetric analyser coupled to an Omnistar™ mass spectrometer. It is well known that upon heating in an inert atmosphere, the oxygen surface complexes of carbonaceous materials decompose, releasing CO_2 and CO [32]. CO_2 results from the decomposition of carboxyls, lactones and anhydrides, while CO comes from anhydrides, phenols, carbonyls, quinones and pyrones [20,32,33].

Fig. 2 shows the profiles of evolved CO_2 and CO for samples GKOS and GKOSA50, in the course of heating at 15 °C min^{-1} in 50 $cm^3\ min^{-1}$ of Ar. The char presents two maxima in the CO_2 profile: at around 350 and 700 °C. Low temperature CO_2 is commonly attributed to the decomposition of carboxyls, while higher temperature CO_2 is associated to the decomposition of lactones or

Table 1
Chemical analyses of the raw biomass (OS) and the resulting char (GKOS).

Sample	pH_{PZC}	Proximate analysis (%, db)			Ultimate analysis (%, daf)				
		VM	Ash	FC*	C	H	N	S	O
OS	6.2	85.4	0.8	13.8	51.6	6.0	0.2	0.5	41.7
GKOS	8.7	9.8	1.6	88.6	93.0	2.2	0.3	0.0	4.5

VM: volatile matter; FC: fixed carbon.
* Calculated by difference; db: dry basis; daf: dry ash free basis.

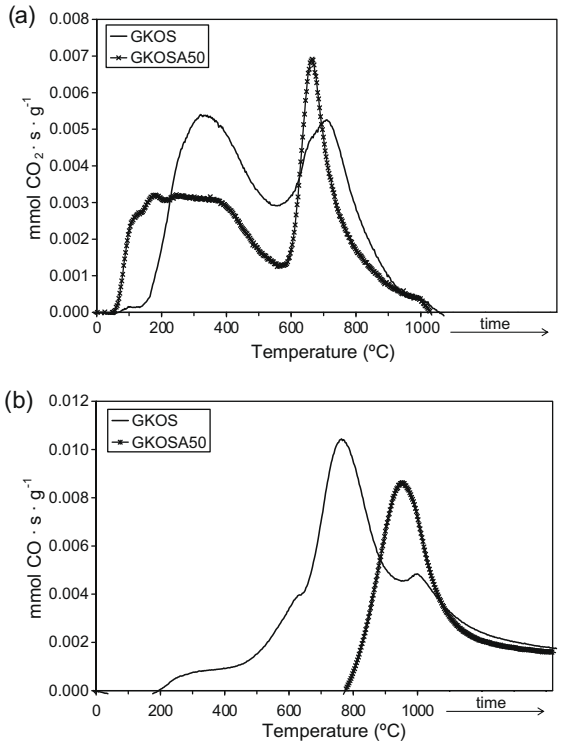


Fig. 2. (a) CO_2 and (b) CO evolution profiles during temperature programmed desorption tests in 50 cm^3 min^{-1} of Ar (heating rate 15 °C min^{-1} up to 1000 °C).

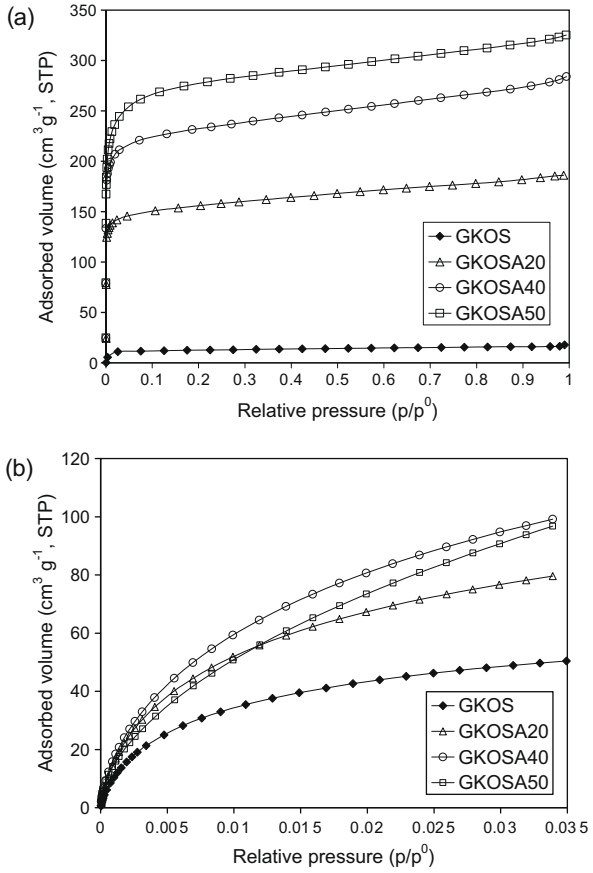


Fig. 3. Adsorption isotherms of activated olive stones: (a) N_2 at −196 °C and (b) CO_2 at 0 °C.

anhydrides [27]. However, as previously discussed, the DRIFT spectrum of GKOS does not show any characteristic band at 1750 cm^{-1}, typical of those species. The presence of carboxyl-carbonates was also reported [29,30]. These groups could release CO_2 upon heating, which would explain the CO_2 emissions from GKOS. GKOSA50 presents similar CO_2 evolution regions to GKOS, but it also shows CO_2 contributions at lower temperatures. This low temperature CO_2 may result from the decomposition of labile carboxyls formed by oxygen chemisorption after the activation process [34]. Similarly to GKOS, the narrow peak at 670 °C cannot come from the decomposition of anhydrides, as there is no simultaneous evolution of CO. However, the largest change in oxygen functionalities after activation can be observed from the CO profile. The CO profile of GKOS presents a maximum at 770 °C, which can be attributed to the decomposition of phenols, there being a shoulder at 630 °C which may be related to quinones [35], in good agreement with the DRIFT spectrum. On the other hand, GKOSA50 shows a single peak centred at 950 °C that matches a smaller shoulder in the CO profile of GKOS. This high temperature CO has been attributed to pyrone groups [35].

As can be seen in Table 2, activated samples have higher values of pH_{PZC} than the corresponding char. This increase in surface basicity may partly be a consequence of the extended heat treatment at a temperature higher than that of the carbonisation step. However, it may also be due to the formation of basic pyrone-type functionalities during the activation process [36]. The presence of these basic oxygen functionalities can have an enhancing effect on the adsorption of acidic CO_2, as has been demonstrated for SO_2 [36,37].

The N_2 adsorption isotherms of the activated olive stones are shown in Fig. 3a. All the activated samples presented type I nitrogen adsorption isotherms, characteristic of microporous materials. From the amount of adsorbed nitrogen it can be seen that activation with carbon dioxide substantially develops the texture of the starting char. The textural parameters calculated from the N_2 adsorption isotherms of the activated samples are summarised in Table 2. It can be seen that the char presents higher narrow micropore volume (W_0) than total pore volume in nitrogen (V_p). This is due to diffusion restrictions on the adsorption of N_2 at −196 °C on narrow micropores [38]. As activation proceeds, the microporosity widens, allowing the N_2 to enter the pores as reflected by the increase in V_p. Activation with CO_2 leads to the continuous development of the char porous structure resulting in BET appar-

Table 2
Point of zero charge and textural characterisation of the activated samples.

Sample	pH_{PZC}	N_2 adsorption at −196 °C			CO_2 adsorption at 0 °C
		S_{BET} (m^2 g^{-1})	V_p[a] (cm^3 g^{-1})	V_{meso}[b] (cm^3 g^{-1})	W_0 (cm^3 g^{-1})
GKOS	8.7	43	0.026	–	0.173
GKOSA20	9.8	613	0.288	0.046	0.294
GKOSA40	9.5	909	0.437	0.073	0.296
GKOSA50	9.6	1079	0.502	0.066	0.246

[a] Total pore volume estimated by the amount of adsorbed nitrogen (as liquid) at p/p^0 = 0.99.
[b] Volume of mesopores (2 < pore width < 50 nm) obtained from the DFT method.

ent surface areas of up to 1079 $m^2 g^{-1}$ and total pore volumes of up to 0.5 $cm^3 g^{-1}$. The predominantly microporous character of the samples is reflected by the small contribution of the mesopore volume to the total pore volume, even for high degrees of burn-off.

Fig. 3b shows the CO_2 adsorption isotherms of the activated olive stones. It can be observed that the shape of the isotherms tends to be more rectilinear as the burn-off increases. This is due to the gradual widening of the micropores with activation. For low burn-off degrees, the formation of narrow microporosity prevails (see the increase in W_0 in Table 2). However, as the activation process proceeds, the narrow micropores widen, resulting in wider microporosity (pore widths below 2 nm) and mesoporosity (pore widths between 2 and 50 nm). Thus, from the point of view of sample texture, activation results in the continuous increase of V_p with burn-off degree, while W_0 goes through a maximum for GKOSA40, decreasing at higher burn-off degrees.

3.1.2. CO_2 capture tests of the activated samples

Table 3 summarises the CO_2 capture capacities of the activated samples at 25 °C and 100 °C, obtained in 50 $cm^3 min^{-1}$ of CO_2. The CO_2 uptakes are expressed in terms of mass of CO_2 per mass of dry adsorbent. As might be expected for a physisorption process, the adsorption capacity of the carbons decreases with increasing adsorption temperature. All the activated samples present higher CO_2 capture capacities than that of the initial char at both temperatures, due to the substantial textural development during activation. Moreover, at 25 °C, CO_2 capture capacity reaches values of up to 10.7 wt.%, which is greater than that of commercial activated carbons tested under the same experimental conditions [7]. Even at 100 °C, the samples still present significant capacities of up to 3.2 wt.%. This is a very interesting advantage, as the cooling of flue gas that is required prior to the adsorption unit can be reduced if the capture step can be carried out at higher temperatures. The possibility of using lower adsorption temperatures would increase the working capacity of the adsorbents making it possible to reduce the size of the adsorption equipment. However cooling costs would then increase. Therefore, these parameters would need to be balanced in order to optimise the cost of the capture step.

Production yields of the olive stone activated carbons exceed in all cases 12%, which is above the yield of commercial wood-based carbons [39]. However, an increase in the burn-off degree would be justified, economically speaking, if a significant increase in the working capacity of the adsorbent was attained. Thus, in the case of olive stones, increasing the burn-off above 40% could not be justified by an increase in CO_2 adsorption capacity.

Table 3
Product yield of the activated samples and CO_2 capture capacity at 25 and 100 °C in pure CO_2 (50 $cm^3 min^{-1}$).

Sample	Product yield (%)	CO_2 capture capacity (wt.%)	
		25 °C	100 °C
GKOS	24	5.8	1.5
GKOSA20	19	8.9	2.9
GKOSA40	15	10.5	3.2
GKOSA50	12	10.7	3.2

3.2. Amination

3.2.1. Characterisation of the aminated samples

Table 4 summarises the chemical and textural characterisation results of the aminated samples. Amination significantly increases the amount of nitrogen incorporated into the carbon matrix. This nitrogen fixation comes from the reaction of ammonia with carbon surface oxides to form ammonium salts and amine groups that, upon dehydration and dehydrogenation produce amides, nitriles and pyridine or pyrrole-like functionalities [16,40]. The nitrogen content obtained is relatively high, considering that the chars were not subjected to oxidation prior to the ammonia treatment, as is customary in the literature [19]. Nitrogen fixation seems to be favoured at high temperatures, as the maximum nitrogen content was obtained for the sample aminated at 800 °C. The pH_{PZC} of the samples also increases after amination, parallel to the incorporation of nitrogen, reflecting the basic nature of the functionalities formed. Previous studies carried out by our group have shown that the type of nitrogen functionality incorporated may vary with the temperature of ammonia treatment: in the case of the samples obtained above 600 °C, nitrogen is incorporated onto the layer system of the carbon as thermally stable pyrrol and pyridinic-type functionalities, while in the case of the samples obtained at lower temperatures, nitrogen might be forming amide-like functionalities [7].

Fig. 4a shows the N_2 adsorption isotherms of the aminated olive stones. It can be seen from the isotherms that amination has caused the porous structure of the char to develop by partial gasification. Ammonia is known to decompose at high temperatures producing atomic H and NH_2 and NH radicals that react with the carbon releasing gaseous H_2, CH_4, HCN and $(CN)_2$ [14,18]. The gasification becomes more important as the temperature increases, producing a continuous increase in the BET surface area and in the total pore volume. From the CO_2 isotherms in Fig. 4b, it can be seen that the formation of new microporosity is important at 800 °C. Below this temperature, the CO_2 isotherms of the initial char and the aminated samples at 400 and 600 °C are almost coincident. By comparing the narrow micropore volume (W_0), obtained from the CO_2 adsorption isotherms, with the total pore volume (V_p), obtained from the N_2 adsorption isotherms, presented in Table 4, it can be observed that the total pore volume is smaller in all the samples. As it has been previously discussed, this is due to diffusion limitations impeding the entry of the N_2 molecule at −196 °C into the narrow micropores. Thus, the new microporosity formed by gasification with ammonia is of very narrow size.

The total production yields of the aminated samples are presented in Table 5 (*g* of adsorbent per 100 g of raw biomass). Only the samples aminated at high temperatures present lower yields than the char, due to the contribution of gasification. Even so, the yields are still above those of the activated samples (cf. Table 3).

Table 4
Chemical and textural characterisation of the aminated samples.

Sample	N (%, db)	pH_{PZC}	N_2 adsorption at −196 °C		CO_2 adsorption at 0 °C
			S_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)	W_0 ($cm^3 g^{-1}$)
GKOSN400	0.88	8.9	152	0.065	0.183
GKOSN600	2.58	9.2	232	0.100	0.174
GKOSN800	3.64	11.3	390	0.164	0.200
GKOSN900	3.06	10.9	442	0.189	0.209

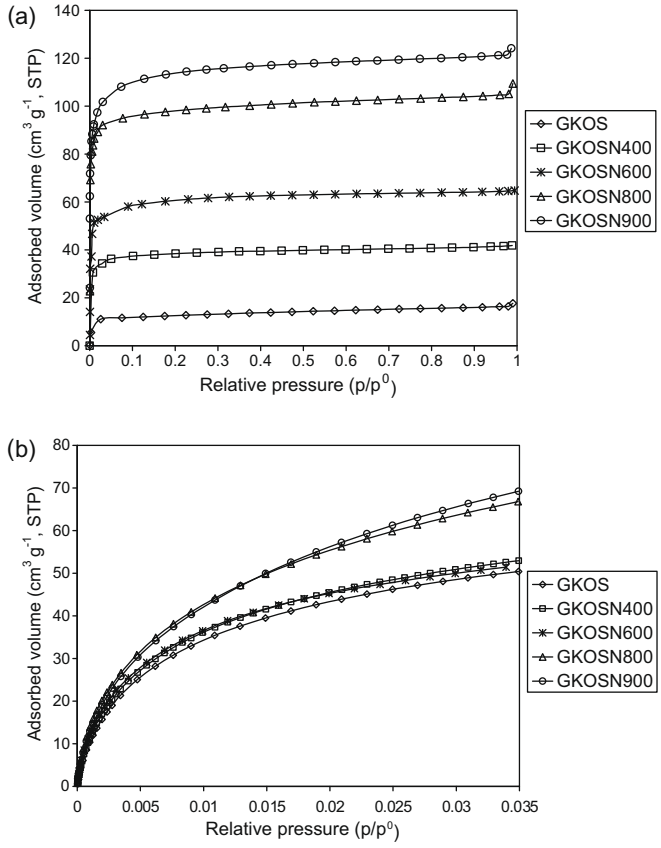


Fig. 4. Adsorption isotherms of aminated olive stones: (a) N_2 at −196 °C and (b) CO_2 at 0 °C.

Table 5
Product yield of the aminated samples and CO_2 capture capacity at 25 and 100 °C in pure CO_2 (50 cm^3 min^{-1}).

Sample	Product yield (%)	CO_2 capture capacity (wt.%)	
		25 °C	100 °C
GKOS	24	5.8	1.5
GKOSN400	24	6.8	1.9
GKOSN600	23	7.1	2.1
GKOSN800	22	8.6	2.6
GKOSN900	19	7.3	2.5

3.2.2. CO_2 capture tests of the aminated samples

Table 5 summarises the CO_2 capture capacity of the aminated samples in 50 cm^3 min^{-1} of CO_2 flow at 25 and 100 °C. Again, a decrease in adsorption capacity with increasing temperature can be observed. The maximum capacities were obtained at both temperatures for the sample aminated at 800 °C. This sample is also the one with the highest nitrogen content, which is thought to be the main cause of its high CO_2 uptake. Moreover, the adsorption capacity of GKOSN800 is very similar to that of the sample activated to 20% burn-off, GKOSA20, although the latter experienced significantly higher textural development as a result of which higher CO_2 adsorption capacities might have been expected. Thus, the introduction of nitrogen functionalities seems to be playing an important role in CO_2 adsorption.

Adsorption is favoured at low temperature and high adsorbate partial pressures. Hence, the working capacity of the adsorbents in a real postcombustion application, where CO_2 is diluted in a flue gas containing mainly nitrogen, will be lower than that achieved in pure CO_2. In order to study the behaviour of the adsorbents in more realistic postcombustion conditions, adsorption tests in a gas mixture containing 15% CO_2 and 85% N_2 at 40 °C and 1 bar were carried out in a thermobalance for selected samples. This temperature was chosen as being feasible if the capture unit is to be placed after the desulphuration step in the power plant.

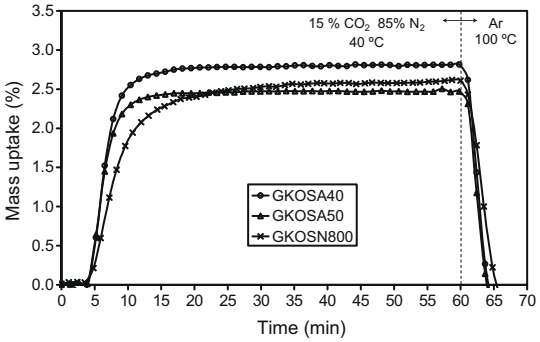


Fig. 5. CO_2 capture tests in a gas mixture containing 15% CO_2 and 85% N_2.

Samples were completely regenerated by changing the feed gas to Ar and increasing the temperature to 100 °C. The corresponding mass profiles are presented in Fig. 5. In these conditions, the capture capacity of the adsorbents is reduced to below 3 wt.%. However, it is important to note that the sequence of increasing CO_2 capture capacity has been altered. In pure CO_2 the adsorption capacity of the samples followed the order: GKOSA50 ≈ GKOSA40 > GKOSN800 while for a CO_2 concentration of 15% the relative order was: GKOSA40 > GKOSN800 > GKOSA50. This would seem to indicate that the effect of the surface area of the carbon becomes less important as the partial pressure of CO_2 decreases. On the other hand, other factors, such as the presence of nitrogen functionalities or a narrower pore size distribution, seem to play a more important role. GKOSA40 presents a lower total pore volume and surface area than GKOSA50, but narrower pore sizes that appear to be more efficient for adsorbing CO_2.

4. Conclusions

Basic activated carbons with a CO_2 capture capacity of up to 10.7 wt.% at 25 °C and up to 3.2 wt.% at 100 °C in pure CO_2 were produced from olive stones, a low-cost biomass by-product, by means of activation with carbon dioxide. These capacities exceed those of commercial activated carbons. The basic surface oxides formed during the carbonisation and activation processes may have a beneficial effect on the adsorption of CO_2. The pore size distribution has been shown to play an important role in CO_2 adsorption, especially at low partial pressures.

Heat treatment with gaseous ammonia is proposed as an alternative pathway to produce efficient CO_2 adsorbents. Nitrogen was successfully incorporated into the carbon structure without the need for a previous oxidation step, and it has been demonstrated to have an enhancing effect on CO_2 adsorption. The effect of the temperature of the treatment was also studied. 800 °C was found to be the optimum temperature, as CO_2 adsorption capacity and nitrogen incorporation reach the maximum values. CO_2 capture capacities of up to 8.6 wt.% at 25 °C and 2.6 wt.% at 100 °C in pure CO_2 were obtained for the aminated samples. These values are similar to, or even substantially greater at temperatures above ambient, than those of commercial activated carbons. Amination has other advantages over activation including shorter soaking times and higher production yields per gram of initial biomass. What is more, adsorption tests in a gas mixture containing 15% of CO_2 revealed that the effect of surface nitrogen is more noticeable at lower partial pressures of CO_2.

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