Different approaches for the development of low-cost CO$_2$ adsorbents
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Abstract

Different carbon materials were tested as precursors for the production of CO$_2$ adsorbents. The chemical modification of the surface of the prepared adsorbents was studied by means of three different approaches: impregnation with amines, electrophilic aromatic substitution and heat treatment in the presence of ammonia. The samples were chemically characterized and the porous texture was evaluated from the N$_2$ adsorption isotherms at -196 °C. The CO$_2$ adsorption capacities of the adsorbents at 25 and 100 °C were evaluated in a thermogravimetric analyzer. In general, the incorporation of basic nitrogen functionalities enhanced the CO$_2$ capture capacities of the modified carbons but this increase depended on the textural properties of the support and the surface
modification methodology. CO₂ adsorption capacities of up to 111 mg CO₂/ g at room temperature were attained. All the tested samples were completely regenerated when subjected to heat treatment at 100 ºC under inert atmosphere.

CE Database subject headings: Carbon dioxide capture; Adsorption; Waste management; Surface chemistry-modification

INTRODUCTION

The increasing demand for energy is causing a rise in the emissions of greenhouse gases (GHGs) and growing environmental concern over global warming and climate change. CO₂ is by far the most important GHG. As a result of anthropogenic CO₂ emissions, atmospheric concentrations have risen by 35 % from the pre-industrial level of 280 ppm to 387 ppm in 2008, primarily as a consequence of the use of fossil fuel. Because of the risk and cost of using non-fossil alternatives such as nuclear, biomass, solar energy, etc., at their current stage of development, these energy sources would be unable to satisfy the need for energy that at present is supplied by fossil fuels. Hydrogen could be used as a substitute for fossil fuel but currently around 96 % of the hydrogen produced commercially originates from fossil fuels. No significant change to the production of hydrogen from renewable power sources is likely to take place in the near term. In this scenario, CO₂ capture and storage (CCS) technologies are crucial to achieving a significant reduction in atmospheric CO₂ concentrations. According to the IPCC Special Report on CO₂ Capture and Storage, CCS will contribute to 15-55 % of the cumulative mitigation effort worldwide until 2100 (IPCC 2005). CO₂ emissions in power generation can be reduced by three different routes that are at different stages of development: post-combustion, pre-combustion and oxy-fuel combustion. Among the technologies considered for post and pre-combustion capture, absorption, adsorption, membrane separation and cryogenic distillation are the most promising (IPCC 2005).
Amine scrubbing is currently the preferred technology due to its higher state of development. The main drawback of absorption is the energy penalty due to the high regeneration costs. Adsorption, on the other hand, entails lower energy requirements and is commercially used in many industrial applications. The development of a new generation of adsorbents that adsorb CO$_2$ efficiently, will undoubtedly enhance the competitiveness of adsorptive separation for CO$_2$ capture in flue gas applications (IPCC 2005). Low-cost adsorbents are desirable, particularly in post-combustion capture where CO$_2$ in the flue gas is in low concentration, and the gas stream once free of CO$_2$ has no further commercial or industrial use. Two techniques with great potential for CO$_2$ adsorption at large scale are pressure/vacuum swing adsorption (PSA/VSA) and temperature swing adsorption (TSA). In both cases, the adsorption rates depend on temperature, partial pressures of CO$_2$, the CO$_2$-adsorbent interaction, the pore size and the surface area of the adsorbent (Ruthven et al. 1994; Yang 1997). Thus, efficient CO$_2$ adsorbents need to have a high capacity and selectivity for CO$_2$, great diffusivity, fast rates of adsorption, and high regenerability. Zeolites have shown promising results for separating CO$_2$ from gas mixtures and could potentially be used in PSA processes (Díaz et al. 2008; Majchrzak-Kuçeba et al. 2005; Siriwardane et al. 2005). However, the presence of water inhibits the CO$_2$ adsorption capacity of zeolites. On the other hand, activated carbons do not require any moisture removal and usually present a lower heat of adsorption that results in lower energy requirements for regeneration (Yang 1997). Due to these advantages, activated carbons would appear, a priori, to be suitable adsorbents for CO$_2$ removal; (http://www.norit-ac.com/; Maroto-Valer et al. 2005; Sircar et al. 1996; Siriwardane et al. 2001). Moreover, enhancement of CO$_2$ adsorption has been achieved on modified activated carbons with increased basicity (Przepiorski et al. 2004).
This work focuses on the development of CO$_2$ adsorbents from different low-cost carbon precursors with different textural properties. Various methodologies were employed to modify the surface chemistry of the prepared adsorbents and so increase their affinity towards CO$_2$.

**EXPERIMENTAL**

**Adsorbent preparation**

Three different starting materials were used to develop CO$_2$ adsorbents: biomass residues (AOS), sewage sludge (L), and pet coke (PC). These precursors were subjected to carbonization under inert atmosphere and ulterior activation with CO$_2$. The main objective of the carbonization-activation steps is to develop porosity in the carbon precursors. For the carbonization step about 20 g of sample was placed in a quartz reactor (i.d. 30 mm) and heat-treated in a horizontal tube furnace under an inert atmosphere of nitrogen (100 cm$^3$ min$^{-1}$ flow rate) at temperatures between 850 and 900 °C. After carbonization, the resultant chars were subjected to physical activation with CO$_2$ at a selected temperature ($T_{act}$) for a time defined by the burn-off degree (b.o %) to be achieved. The activation temperature for each char was selected by obtaining the CO$_2$ reactivity profiles of the chars in a thermogravimetric analyzer. Activation was conducted in batches of 5-9 g that were placed in a quartz reactor and heat-treated in a vertical tube furnace at temperatures between 900 and 1000 °C up to different degrees of burn-off. The activated samples were denoted as Precursor-AT$_{act}$(b.o. %), so that, for example, PC-A1000(20 %) stands for the pet coke treated at 1000 °C in CO$_2$, with 20% degree of burn-off.

**Surface chemistry-modification**

The CO$_2$ adsorption capacity can be increased if a high textural development is combined with an adequate surface chemistry that enhances the affinity of the adsorbent.
towards CO₂. Commercial amine scrubbing applied to the separation of CO₂ is based on
the reaction of an acid gas, CO₂, with basic amines (i.e., monoethanolamine-based
solvents commercialized by Fluor Daniel Inc., ABB Lummus Crest Inc., Dow Chemical
Co., etc.). The aim of this work was to attach amino-type functionalities to the surface
of the carbons to promote their CO₂ adsorption capacity. For this purpose, three
different approaches were studied: wet impregnation with amines, functionalization
with amino groups by electrophilic aromatic substitution (EAS) and heat treatment in
the presence of ammonia gas and/or mixtures of ammonia-oxygen.

Amine impregnation was accomplished using a wet impregnation method adapted from
Xu et al. (Xu et al. 2003). The experimental procedure followed in this work has been
described elsewhere (Plaza et al. 2007).

Functionalization by EAS was conducted by a method adapted from Yantasee et al.
(Yantasee et al. 2004). The first step involved aromatic nitration of the carbonaceous
support: a mixture of concentrated sulphuric and nitric acids was prepared by carefully
adding 30 cm³ of sulphuric acid (96 %) to 30 cm³ of nitric acid (65 %). Then, 5 g of the
selected carbon support was added to the acid mixture and stirred at a temperature of
50 ºC overnight. The mixture was filtered, washed with distilled water and then air dried
at 60 ºC. The second step consisted in reducing the attached nitro groups to amine
functionalities using sodium hydrosulphite (Na₂S₂O₄) as reducing agent in a basic
media. Thus, 3 g of nitrated sample was added to a mixture of 50 cm³ of distilled water
and 20 cm³ of ammonia solution (25 %) and allowed to stir for 10 min. Then, 12 g of
Na₂S₂O₄ was added to the mixture which was left to stir overnight at room temperature.
The resulting product was filtered and washed. In order to eliminate a possible excess of
sodium hydrosulphite in the filtrate, the carbon was allowed to stir in 100 cm³ of
distilled water at 50 ºC for 1 h, and then it was filtered and washed again. This process
was repeated three times in order to purify the product. Finally, the carbon was air dried at 60 °C.

Heat treatment with ammonia gas (amination) and ammonia-oxygen mixtures (ammonoxidation), was carried out in a vertical tube furnace at 400 °C. Around 3 g of dried carbon was placed in a quartz reactor and held under N₂ flow. Once the sample had reached the desired temperature, the flow was changed from N₂ to NH₃, or to 8% NH₃ in air, and held for 2 h. Then the sample was removed from the furnace and cooled to 100 °C. Finally, the flow was changed back to N₂ until room temperature was reached.

**Characterization of the samples**

Ultimate analysis was carried out in order to determine the chemical composition of the carbons. Helium density was measured in an Accupyc 1330 at 35 °C. Textural characterization of the samples was carried out by physical adsorption of N₂ at -196 °C in a Micromeritics Tristar 3000. The samples were outgassed at 100 °C under vacuum for 24 h prior to density and adsorption measurements. The apparent surface areas \( (S_{BET}) \) were calculated from the physical adsorption of N₂, and the total pore volumes \( (V_p) \) were evaluated using Gurvitsch’s rule \( (p/p^0 = 0.99) \) (Gurvitsch 1915). According to the IUPAC classification the mesopore volume \( (V_{meso}) \) comprises pores between 2 and 50 nm. The mesopore volume was calculated by applying the DFT method to the N₂ isotherms, assuming slit shaped pores and low-regularization (Olivier 1998; Seaton et al. 1989). Micropore volumes \( (W_0) \) were calculated by the Dubinin-Radushkevich (DR) method from the N₂ adsorption isotherms (assuming an affinity coefficient of 0.34) (Dubinin 1966). The average pore width \( (D) \) was estimated assuming slit shaped pores by means of the expression \( 2V_p/S_{BET} \). The acid/basic character of the samples was
estimated by means of the Point of Zero Charge (pH_{PZC}) using a mass titration method adapted from Noh et al. (Noh et al. 1989).

The modified samples were subjected to temperature programmed desorption (TPD) tests using a Setaram TGA 92 thermogravimetric analyzer (TG) coupled to a Nicolet Nexus Fourier Transform Infrared (FTIR) spectrometer through a heated interface. This set-up allowed the analysis of the gases evolved during the TPD tests. In each experiment 20 mg of sample was heated at 15 °C min\(^{-1}\) up to 1000 °C under an Argon flow rate of 50 cm\(^3\) min\(^{-1}\). The final temperature was maintained for 30 min.

**CO\(_2\) adsorption capacity**

The CO\(_2\) capture capacity of the samples at atmospheric pressure was evaluated in the thermogravimetric analyzer. CO\(_2\) uptakes were determined from the mass evolution profiles when the samples were exposed to 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 and then allowed to cool to 25 °C. Afterwards, Ar was changed to 50 cm\(^3\) min\(^{-1}\) of CO\(_2\) and the temperature was held at 25 °C for 1 h to assess the CO\(_2\) capture capacity at this temperature. Next, the temperature was increased at a heating rate of 0.5 °C min\(^{-1}\) to 100 °C, and the mass change was recorded to evaluate the influence of temperature on the CO\(_2\) capture capacity of the adsorbents. The samples were then kept at 100 °C for 1 h to assess the CO\(_2\) capture capacity at this temperature, and finally the flow was switched to Ar in order to regenerate the sample.

**RESULTS AND DISCUSSION**

**Chemical analysis**

Table 1 shows the proximate and ultimate analyses of the carbon precursors used in this work, i.e. pet coke (PC), sewage sludge (L), and air-oxidized olive stones (AOS). These carbon precursors present significant differences in their chemical compositions. L has
the highest volatile matter and ash contents. A high volatile matter content will reduce the solid yield in the carbonization step and a relatively low carbon content will also limit the extent of activation. L is a residue with significant disposal problems so that its conversion to a precursor of CO₂ adsorbents should be regarded as a promising alternative to disposal. On the other hand, PC and AOS exhibit high carbon contents and low levels of ash and volatiles, and are thus potentially better precursors for developing high porous carbons than L.

**Textural characterization**

Figure 1 shows the N₂ adsorption isotherms at -196 °C for the initial chars and for the chars activated with CO₂. From these isotherms the extent of microporosity (pore diameter < 2 nm) and mesoporosity (2nm < pore diameter < 50 nm) development in the samples can be assessed. Physical activation of the chars produced carbons with a wide range of textural development: non porous carbons (PC), mesoporous carbons with some microporosity (L) and microporous carbons with some mesoporosity (AOS). The activated olive stone chars show the highest textural development, their microporosity increasing with the degree of burn-off, as can be observed from the N₂ adsorbed volumes at relative pressures of less than 0.1. Pet coke chars activated with CO₂ present little textural development. A more aggressive activation method, such as chemical activation with KOH, would be required to develop porosity in this carbon (Wu et al. 2005). Thus, pet coke was discarded in this work as a carbon precursor for the production of CO₂ adsorbents. The textural parameters calculated from the N₂ adsorption isotherms at -196 °C are summarized in Table 2. Helium densities of around 2 g cm⁻³ were obtained for the majority of the activated samples, with the exception of the samples obtained from sewage sludge that present helium densities of 2.6 g cm⁻³ due to the large ash content of the L char (72 wt. %). Significant apparent BET surface
areas, greater than 1000 m$^2$ g$^{-1}$, were calculated for the olive stone activated chars, taking into account that commercial activated carbon grades have surface areas between 500 and 1500 m$^2$ g$^{-1}$ (http://www.norit-ac.com/). In contrast, sewage sludge activated chars present discrete values of apparent surface area, up to 140 m$^2$ g$^{-1}$, due to the intrinsic limitations of these materials.

Mesoporosity develops to some extent in most of the samples, but more so in the sewage sludge activated carbons. Physical activation with CO$_2$ generates mainly microporosity in the activated olive stones. Surface modification reduces the pore volumes in the treated samples. EAS acts preferentially over mesoporosity, resulting in a 32% reduction in mesopore volume with respect to the parent char, while the micropore volumes appear to be more influenced by amination and ammoxidation. In addition, heat treatment with ammonia of the AOS char reduces the apparent BET surface areas to 764 m$^2$ g$^{-1}$. The average pore sizes of the samples (D) obtained from L and PC fall within the range of mesoporosity, while the olive stone carbons present average pore sizes within the microporosity range (pores < 2nm).

**Surface modification**

In the light of the results of previous studies on wet impregnation with amines of activated alumina (Plaza et al. 2008) and commercial activated carbons (Plaza et al. 2007), linear polyethylenimine (PEI) with an average molecular weight of 423 g mol$^{-1}$ was the amine chosen for this work. L-A850(40%) and AOS-A900(45%) were the samples selected for amine impregnation. L-A850(40%) presents a wide pore size (average pore width of 2.4 nm) suitable for impregnation. It has previously been reported that mesoporous molecular sieves with 2.75 nm pore diameter size had a synergetic effect on the adsorption of CO$_2$ by PEI (Xu et al. 2002). AOS-A900(45%) was selected due to its high pore volume (0.612 cm$^3$ g$^{-1}$). The amount of PEI used for
impregnation was 10 % mass/mass with respect to the support for L-A850(40%), and 5 % for AOS-A900(45%). The prepared samples are referred to as L-A850(40%)-PEI and AOS-A900(45%)-PEI.

In this work the main objective of the surface modification was to enhance the capacity of the adsorbents for capturing CO₂ by complementing a good textural development with suitable surface chemistry and thereby increasing the affinity of the adsorbent towards CO₂. Thus, the char resulting from the carbonization of the air-oxidized olive stones was selected for functionalization by EAS and also for heat treatment with ammonia gas (amination and ammoxidation at 400 °C), due to its high textural development. The modified olive stone chars are denoted as AOS-NH₂, AOS-N400 and AOS-NO400, respectively.

Table 3 shows the results of the chemical characterization of the air-oxidized olive stones prepared by the three different surface modification methodologies. The nitrogen contents of the modified samples increase with respect to the parent materials, particularly for the activated sample impregnated with PEI.

The acid/basic character of the samples, determined by the pH_{PZC}, points to an increase in the basicity of the activated olive stone char impregnated with PEI, with respect to the parent sample, which already presents a considerable basic character (pH_{PZC} = 10.7). Given the relatively high oxygen content of the char, its basicity may come from the presence of basic oxygen groups. Acidic oxygen groups, such as carboxyls, lactones and phenols are thermally labile and thus eliminated during the carbonization step; only carbonyls resist this heat treatment. The thermal decomposition of these groups leads to the formation of active sites capable of fixing oxygen, upon re-exposure to air, in the form of ether groups that combined with the thermally stable carbonyls form pyrone type structures (Papirer et al. 1987).
Functionalization by EAS decreased the basicity with respect to the starting char. The sample with the lowest pH_{PZC} is AOS-NH₂. Given its high oxygen content, this could be due to the incorporation of acidic oxygen surface groups during the nitration step, which is carried out in a strong oxidizing solution of concentrated nitric and sulphuric acids.

The ammonia-treated samples, AOS-N400 and AOS-NO400, present a slight decrease in their basic character compared to that of the starting char. The reduction in basicity of the aminated and ammoxidized samples may be due to the reduction in oxygen content with respect to the starting char, assuming that this oxygen content was present in the form of basic oxygen surface groups.

In order to obtain more information about the surface chemistry of the samples, TPD tests on the modified olive stone carbons were carried out, and the evolved gases were analysed in a FTIR spectrometer. The main gas species to evolve from the samples during heating under inert atmosphere were NH₃, H₂O, CO₂ and CO. CO₂ and CO come from the decomposition of oxygenated surface groups commonly present in activated carbons, whereas NH₃ must derive from the decomposition of the nitrogen surface functionalities introduced into the samples during the different treatments. The evolution of NH₃ during the TPD tests is presented in Figure 2. In the AOS-NH₂ sample NH₃ evolves at the lowest temperature (200 °C) while in the aminated (AOS-N400) and ammoxidized (AOS-NO400) samples NH₃ evolves at around 700 °C. In the sample impregnated with PEI, AOS-A900(45%-PEI), NH₃ evolves in an intermediate temperature range (ca. 400 °C), corresponding to the decomposition temperature of PEI (Plaza et al. 2008). This indicates that the original polymer is unaltered when it is immobilized on the carbon surface.

The differences observed in the ammonia profiles of the olive stone modified chars suggest that different nitrogen functionalities are introduced into the samples, depending
on the method employed for the surface modification. Nitrogen is incorporated into more labile amino-type functionalities by electrophilic aromatic substitution, while amination and ammoxidation incorporate thermally more stable nitrogen (amides, imides, etc.) (Jansen et al. 1994). On the other hand, impregnation with PEI introduced amine functionalities which are stable in an intermediate temperature range.

**CO₂ adsorption capacity**

Table 4 summarizes the CO₂ capture capacities at atmospheric pressure evaluated in the thermogravimetric analyzer at 25 and 100 ºC. The CO₂ uptakes are expressed in terms of mass of CO₂ / mass of dry adsorbent. For all the tested samples, except for L-A850(40%)-PEI, the highest CO₂ capture capacities are attained at room temperature. In fact, it is characteristic of common adsorption processes that capacity decreases with increasing adsorption temperature. Olive stone based adsorbents display the greatest CO₂ uptakes at 25 ºC, attaining a maximum of 111 mg of CO₂ per gram of adsorbent in the case of AOS-A900(45%). The high capacity of these materials is due to their large micropore volume, which is responsible for CO₂ adsorption at room temperature. The activated sewage sludge, on the other hand, presents reduced CO₂ capacities, due to its low micropore volume. Maximum CO₂ uptake by the sewage sludge carbons is achieved for sample L-A850(40%)-PEI at 100 ºC -25 mg CO₂ per gram of adsorbent-. The same tendency of increasing CO₂ uptake with temperature, has also been observed for liquid PEI (Plaza 2007). This suggests that the PEI impregnated onto the carbon support is controlling the CO₂ capture behavior of this sample and that the polymer has been only slightly modified by the support, as was observed in the NH₃ profile during the TPD tests. In a equilibrium-controlled process, a decrease in CO₂ uptake with temperature should have occurred due to the exothermic character of the PEI-CO₂ reaction (Satyapal et al. 2001). The increase in CO₂ uptake with temperature observed

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO₂ Uptake at 25 ºC (mg CO₂/g adsorbent)</th>
<th>CO₂ Uptake at 100 ºC (mg CO₂/g adsorbent)</th>
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<td>AOS-A900(45%)</td>
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</tr>
<tr>
<td>L-A850(40%)-PEI</td>
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</tr>
</tbody>
</table>

Table 4: CO₂ capture capacities at atmospheric pressure evaluated in the thermogravimetric analyzer at 25 and 100 ºC.
for PEI and L-A850(40%)-PEI is attributed to a diffusion-controlled process. In other words the rate of sorption is governed by the diffusion of CO2 through the polymer film, a phenomenon which is favored at higher temperatures.

The temperature programmed adsorption profiles of sample L-A850(40%)-PEI and the parent sample L-A850(40%) are presented in Figure 3. The rate of CO2 adsorption at 25 ºC is slower for the sample impregnated with PEI. However, minor differences in CO2 uptakes of both samples are observed at 25 ºC. As the temperature rises, the behaviour of the two samples diverges: while in the case of the parent activated sewage sludge CO2 uptake gradually decreases with temperature, for the sample impregnated with PEI it increases. This shows that the mechanism of CO2 capture is different for each sample: on the activated carbon, L-A850(40%), physical CO2 adsorption takes place, while for the PEI impregnated carbon, chemical interactions between CO2 and the immobilized PEI seem to occur, these interactions being more noticeable at higher temperatures. This behavior has been observed in other mesoporous adsorbents impregnated with PEI, such as activated alumina (Plaza et al. 2008), MCM41 (Xu et al. 2002), and fly-ash derived carbons (Arenillas et al. 2005). Xu et al. (Xu et al. 2002) concluded that CO2 adsorption at room temperature on MCM-41 impregnated with PEI is a diffusion-controlled process. This may explain the slower rates of CO2 adsorption at 25 ºC observed for L-A850(40%)-PEI.

Air-oxidized olive stone chars were subjected to different treatments: physical activation with CO2 and surface modification by impregnation, electrophilic aromatic substitution and heat treatment with ammonia gas. The parent sample (AOS char) shows a significant uptake of CO2, reaching 91 and 34 mg CO2 per gram of adsorbent at 25 and 100 ºC, respectively (cf. Table 4). These values match those obtained with commercial activated carbons (Heuchel et al. 1999; Siriwardane et al. 2001; van der
Vaart et al. 2000). Physical activation with CO₂ enhances the capture capacity of the olive stone chars at room temperature. This is most probably due to the substantial textural development caused by the activation and, more specifically, to the generation of microporosity. Previous studies have confirmed that the adsorption of CO₂ at atmospheric pressure is restricted to narrow microporosity (< 1 nm) (Martin-Martinez et al. 1995).

The sample modified by electrophilic aromatic substitution (AOS-NH₂), increases the CO₂ uptake with respect to the AOS char at 25°C, although its capacity decreases at 100 °C. A similar behavior was observed for the aminated and ammoxidized samples. On the other hand, impregnation of the activated olive stone char with PEI, AOS-A900(45%)-PEI, reduces the uptake of CO₂ at both 25 °C and 100 °C with respect to the activated olive stone char, probably due to partial blockage of the micropore volume by the PEI polymer. Moreover, this sample follows the general trend of decreasing CO₂ capacity with increasing sorption temperature, as might be expected for an equilibrium controlled process. The difference observed in the behavior of the impregnated AOS and L may be attributed to the different pore size distributions of both supports. While L-A850(40%) presents an average pore size of 2.4 nm, capable of effectively hold the amine polymer for enhanced CO₂ capture purposes, AOS-A900(45%) presents an average pore size of only 0.8 nm. Impregnation with amines does not seem to be an adequate technique for modifying microporous materials.

In summary, the surface modification of the olive stone char has different effects on capture capacity depending on the method used. In order to examine in greater depth the influence of the nitrogen functionalities on the CO₂ uptake, capacities were normalized by the micropore volumes (W₀) assessed from the N₂ adsorption isotherms at -196 °C (see Table 4). The samples heat-treated with ammonia at 400 °C, i.e. AOS-N400 and
AOS-NO400, display the greatest CO\textsubscript{2} uptakes / W\textsubscript{0} at 25 °C, followed by AOS-NH\textsubscript{2}. This indicates that surface chemistry may contribute to the enhancement of CO\textsubscript{2} uptake at 25 °C, this effect being even more pronounced in the case of the aminated and ammoxidized samples. At 100 °C the effect of the introduced functionalities is not as noticeable.

It seems therefore that for the olive stone samples CO\textsubscript{2} uptake is controlled by the physical adsorption of CO\textsubscript{2}. The introduction of nitrogen functionalities, particularly through amination, increases the affinity of the adsorbent towards CO\textsubscript{2} and thus compensates for the loss in microporosity in the modified samples with respect to the parent char. In the case of impregnation with PEI, blockage of the porous system may account for the substantial decrease in CO\textsubscript{2} uptake.

It is clear that modification of the surface chemistry influenced the performance of the modified samples to capture CO\textsubscript{2}. However, different effects were observed depending on the support employed: whereas modified olive stones increased CO\textsubscript{2} uptake at 25 °C with respect to the parent chars, the impregnated sewage sludge enhanced the CO\textsubscript{2} capture capacity at 100 °C.

In addition, all the samples studied rapidly regenerated at 100 °C when the flow was switched from CO\textsubscript{2} to Ar, as illustrated in Figure 3 for the sewage sludge samples.

**CONCLUSIONS**

Activated carbons prepared from different carbon precursors have been tested as CO\textsubscript{2} adsorbents. Physical activation was found to increase the capacity of the carbons to capture CO\textsubscript{2} at room temperature due to enhanced textural development. Surface modification of the carbons was carried out in order to improve the affinity of the adsorbents towards CO\textsubscript{2}. At higher temperatures the CO\textsubscript{2} capture capacity of a mesoporous carbon may be enhanced by impregnation with PEI. In the case of the
impregnated sewage sludge, CO$_2$ uptake at 100 °C was eight times higher than that of the parent activated sewage sludge. On the other hand, the CO$_2$ capacity of the adsorbents at room temperature appears to be enhanced by electrophilic aromatic substitution, amination and ammoxidation. Of the surface modification methodologies employed, the functionalities introduced by amination appear to have the greatest influence on the capture capacity of the adsorbents. However, the main drawback of this procedure is the loss of microporosity due to the heat-treatment with ammonia.

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<th>Sample</th>
<th>Proximate Analysis (wt.%, dry basis)</th>
<th>Ultimate Analysis (wt.%, dry basis)</th>
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<tbody>
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<td></td>
<td>VM</td>
<td>FC</td>
</tr>
<tr>
<td>PC</td>
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<tr>
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<td>AOS</td>
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VM: volatile matter; FC: fixed carbon; * calculated by difference
Table 2. Textural parameters and helium density of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>d$_{He}$ (g cm$^{-3}$)</th>
<th>S$_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>V$_p$ (cm$^3$ g$^{-1}$)</th>
<th>V$_{meso}$ (cm$^3$ g$^{-1}$)</th>
<th>V$_{meso}$/V$_p$</th>
<th>W$_0$ (cm$^3$ g$^{-1}$)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC char</td>
<td>1.79</td>
<td>0</td>
<td>0.001</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PC-A1000(20%)</td>
<td>1.97</td>
<td>11</td>
<td>0.038</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.9</td>
</tr>
<tr>
<td>PC-A1000(40%)</td>
<td>2.01</td>
<td>9</td>
<td>0.030</td>
<td>0.012</td>
<td>0.40</td>
<td>0.005</td>
<td>6.7</td>
</tr>
<tr>
<td>L char</td>
<td>2.49</td>
<td>91</td>
<td>0.098</td>
<td>0.024</td>
<td>0.24</td>
<td>-</td>
<td>2.2</td>
</tr>
<tr>
<td>L-A850(20%)</td>
<td>2.49</td>
<td>127</td>
<td>0.147</td>
<td>0.045</td>
<td>0.31</td>
<td>-</td>
<td>2.3</td>
</tr>
<tr>
<td>L-A850(40%)</td>
<td>2.59</td>
<td>137</td>
<td>0.167</td>
<td>0.065</td>
<td>0.39</td>
<td>-</td>
<td>2.4</td>
</tr>
<tr>
<td>AOS char</td>
<td>2.01</td>
<td>859</td>
<td>0.420</td>
<td>0.050</td>
<td>0.12</td>
<td>0.329</td>
<td>1.0</td>
</tr>
<tr>
<td>AOS-NH$_2$</td>
<td>1.79</td>
<td>853</td>
<td>0.395</td>
<td>0.034</td>
<td>0.09</td>
<td>0.321</td>
<td>0.9</td>
</tr>
<tr>
<td>AOS-N400</td>
<td>2.02</td>
<td>788</td>
<td>0.369</td>
<td>0.046</td>
<td>0.12</td>
<td>0.305</td>
<td>0.9</td>
</tr>
<tr>
<td>AOS-NO400</td>
<td>2.00</td>
<td>764</td>
<td>0.348</td>
<td>0.043</td>
<td>0.12</td>
<td>0.295</td>
<td>0.9</td>
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<tr>
<td>AOS-A900(20%)</td>
<td>2.11</td>
<td>1089</td>
<td>0.549</td>
<td>0.060</td>
<td>0.11</td>
<td>0.412</td>
<td>0.7</td>
</tr>
<tr>
<td>AOS-A900(45%)</td>
<td>2.14</td>
<td>1179</td>
<td>0.612</td>
<td>0.094</td>
<td>0.15</td>
<td>0.431</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Table 3. Chemical characterization of the modified olive stone samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ultimate analysis (wt.%, dry basis)</th>
<th>pH_{PZC}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>AOS-A900(45%)</td>
<td>89.2</td>
<td>0.0</td>
</tr>
<tr>
<td>AOS-A900(45%)-PEI</td>
<td>88.9</td>
<td>0.9</td>
</tr>
<tr>
<td>AOS char</td>
<td>89.2</td>
<td>0.3</td>
</tr>
<tr>
<td>AOS-NH₂</td>
<td>85.4</td>
<td>0.5</td>
</tr>
<tr>
<td>AOS-N400</td>
<td>88.6</td>
<td>0.4</td>
</tr>
<tr>
<td>AOS-NO400</td>
<td>90.3</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* calculated by difference
Table 4. CO₂ capture capacity of the samples at atmospheric pressure

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO₂ capture capacity (mg CO₂ g⁻¹ of adsorbent)</th>
<th>CO₂ capture capacity /W₀ (mg CO₂ cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T = 25°C</td>
<td>T =100 ºC</td>
</tr>
<tr>
<td>L-A850(40%)</td>
<td>14</td>
<td>5</td>
</tr>
<tr>
<td>L-A850(40%)-PEI</td>
<td>14</td>
<td>25</td>
</tr>
<tr>
<td>AOS char</td>
<td>91</td>
<td>34</td>
</tr>
<tr>
<td>AOS-NH₂</td>
<td>99</td>
<td>27</td>
</tr>
<tr>
<td>AOS-N400</td>
<td>98</td>
<td>31</td>
</tr>
<tr>
<td>AOS-NO400</td>
<td>93</td>
<td>31</td>
</tr>
<tr>
<td>AOS-A900(20%)</td>
<td>103</td>
<td>31</td>
</tr>
<tr>
<td>AOS-A900(45%)</td>
<td>111</td>
<td>30</td>
</tr>
<tr>
<td>AOS-A900(45%)-PEI</td>
<td>87</td>
<td>23</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1. $N_2$ adsorption isotherms at -196 °C of the initial and activated chars.

Figure 2. NH$_3$ evolution during the TPD tests of the modified AOS carbons.

Figure 3. Temperature resolved CO$_2$ adsorption tests for the sewage sludge activated char and the corresponding sample impregnated with PEI.
**Fig. 2.** NH$_3$ evolution during the TPD tests of the modified AOS carbons

**Fig. 3.** Temperature resolved CO$_2$ adsorption tests for the sewage sludge activated char and the corresponding sample impregnated with PEI