Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 1 (2009) 1107–1113

Energy Procedia

www.elsevier.com/locate/procedia

GHGT-9

A comparison of two methods for producing CO_2 capture adsorbents

M.G. Plaza, C. Pevida*, B. Arias, J. Fermoso, F. Rubiera, J.J. Pis

Instituto Nacional del Carbón, CSIC. Apartado 73. 33080 Oviedo, Spain

---

Abstract

High capacity CO_2 adsorbents were prepared from a biomass residue, almond shells. Two different methods for producing these adsorbents were compared: activation with carbon dioxide and heat treatment with ammonia gas (amination and ammoxidation). The prepared carbons were physically and chemically characterised. Amination and ammoxidation introduced nitrogen into the carbon structure, up to a 5 wt.%, turning the carbon surface more basic, without the need of carrying out a preoxidation treatment. On the other hand, activation with carbon dioxide led to a significantly higher development of the texture of the samples. The CO_2 adsorption capacity of the adsorbents was meassured in a thermogravimetric analyser. Amination and activation showed to be suitable methods for the production of CO_2 adsorbents. The prepared adsorbents presented a high CO_2 capture capacity, comparable to that of commercial activated carbons, and showed fully reversible adsorption.

Keywords: adsorption; activated carbon; CO_2 capture; surface modification; activation; amination/ammoxidation

---

1. Introduction

Adsorption is a well developed technology used in many industrial applications. However, the application of adsorption in CO_2 capture processes from either pre or post-combustion gas streams, require easily regenerable and durable adsorbents with a high CO_2 adsorption capacity. It has recently been reported that the cost of the capture or separation step in postcombustion CO_2 capture can be reduced by using this technology [1, 2]. Activated carbons present a series of advantages as CO_2 adsorbents: they are inexpensive, insensitive to moisture, present a high CO_2 adsorption capacity at ambient pressure and, moreover, they are easy to regenerate. Furthermore: almost any carbonaceous material can be converted into an activated carbon by a first step of carbonisation followed by a second step of activation. The properties of the final product will depend upon the nature of the starting material, the activating agent, and the conditions of the carbonisation and activation processes. CO_2 is a common activating agent that reacts with carbon at high temperatures releasing gaseous CO. With low CO_2 flow rates and temperatures that

---

* Corresponding author. Tel.: +34-985-119-090; fax: +34-985-297-662.
E-mail address: cpevida@incar.csic.es.

doi:10.1016/j.egypro.2009.01.146

are not excessively high, the consumption of carbon leads to a significant textural development. High flow rates and temperatures cause the external surface of the particle to burn, resulting in a poor porous texture development.

The role of CO_2 as a weak Lewis acid is well established. Consequently it is expected that the introduction of Lewis bases onto the surface of an activated carbon may favour the CO_2 capture performance of these materials. Several works have been published on the incorporation of basic nitrogen functionalities to enhance the adsorption of CO_2 [3-7]. Although the amount of nitrogen in carbon materials is generally low, it can be incorporated into the carbon structure by causing the carbon to react with gaseous ammonia [8-10]. Ammonia reacts with the surface oxides present in the carbon, thereby forming ammonium salts and amine groups that through dehydration and dehydrogenation reactions lead to amides, nitriles, and pyridine- and pyrrol-like functionalities [10, 11]. At high temperatures, ammonia also decomposes forming atomic H and NH and NH_2 free radicals that may gasify the carbon causing HCN, CH_4 and H_2 to be released [12, 13].

The objective of this work was to develop high capacity CO_2 adsorbents from low-cost carbonaceous materials. Two different approaches have been compared: physical activation with CO_2 and heat treatment with ammonia gas.

2. Experimental

Raw almond shells were ground and sieved and a particle size between 1 and 3 mm was selected. Batches of around 15 g of the raw material were then carbonised in a horizontal quartz reactor (i.d. 30 mm) at a 50 cm^3 min^{-1} flow rate of nitrogen, and a heating rate of 15 ºC min^{-1}, up to a maximum temperature of 600 ºC, and held at this temperature for a further 30 min. This stage of the adsorbent preparation process presented an average yield of 24 wt.%.

The resulting char (A) was subjected to different treatments: physical activation with carbon dioxide and treatment with ammonia gas. Both treatments were carried out in batches of around 3 g of char in a quartz microreactor inside a vertical furnace equipped with temperature control. The char was heated in a N_2 flow until the sample reached the treatment temperature, and then, the feed gas was changed to reactive gas.

Activation with CO_2 was conducted at 800 ºC to different degrees of burn-off. Ammonia treatment can be carried out in pure ammonia flow (referred to as amination) or in a mixture of gases containing ammonia and oxygen (ammoxidation) [9]. In this work amination treatment was conducted directly on the chars, without prior oxidation. The char was exposed to a flow rate of 50 cm^3 min^{-1} of ammonia at 800 ºC. For the ammoxidation treatment, the char was brought into contact with a flow rate of 50 cm^3 min^{-1} of a gas mixture consisting of ammonia and air at a ratio of 1:2. The ammoxidation temperature presents a lower upper limit than that of amination due to the high reactivity of carbon towards oxygen. Thus, the ammoxidation temperature was fixed at 300 ºC in order to avoid the combustion of the char. This temperature was selected on the basis of the mass loss profile of the char obtained during heating in air flow in a thermogravimetric analyser. Table 1 summarises the different treatment conditions and the nomenclature used for the resulting samples.

The obtained samples were characterised in terms of texture, chemical composition and surface chemistry. The textural characterisation was carried out by determining the N_2 and CO_2 adsorption isotherms at -196 ºC and 0 ºC, respectively. To compare the relative basicity of the prepared materials, the pH of a suspension containing 0.25 g of sample in 1.5 cm^3 of distilled water was measured once the equilibrium was reached under inert atmosphere. Temperature programmed desorption tests (TPD) were carried out in a thermogravimetric analyser which was coupled to a Fourier Transform Infrared (FTIR) spectrometer via a heated interface to analyse the evolved gases. The CO_2 capture performance of the prepared adsorbents was evaluated by means of a thermobalance Setaram TGA 92, which recorded the mass uptake of the samples when exposed to CO_2.

Table 1 Summary of sample nomenclature and treatment conditions

Sample	Treatment	Temperature (ºC)	Reactive gas	Gas flow rate (cm^3 min^{-1})	Duration of the treatment (h)
A	Carbonisation	600	-	-	-
AA2	Activation	800	CO_2	10	2
AA3	Activation	800	CO_2	10	3
AN2	Amination	800	NH_3	50	2
AN3	Amination	800	NH_3	50	3
ANO	Ammoxidation	300	NH_3/Air	50	2

3. Results and discussion

The chemical analysis of the samples is presented in Table 2. The char shows a low ash and volatile matter content but a high carbon content. It is therefore an adequate precursor for developing carbon adsorbents. The activated and aminated samples present lower volatile matter than the starting char, due to the heat treatment and surface reactions. The hydrogen content also decreases as it is closely related to the volatile matter. On the other hand, the oxygen content increases with activation, probably due to some chemisorption of oxygen during the heterogeneous reaction between the CO_2 and the carbon.

As can be seen from the table, ammonia treatments successfully incorporate nitrogen into the carbon structure. Amination at 800 ºC introduced up to 5 wt.% of nitrogen. This is a significant nitrogen content considering that no preliminary oxidation was carried out and therefore no additional oxygen functionalities –which are thought to control the reaction with ammonia- were incorporated before the treatment with ammonia. Comparison of samples AN2 and AN3 shows that longer treatment times lead to higher nitrogen contents. In contrast the oxygen content decreased after amination, due to the heat treatment and the consumption of oxygen during the reaction with ammonia.

Ammoxidation introduced a similar amount of nitrogen to amination, 4 wt.%. In the case of ammoxidation the reduction in volatile matter content is lower, due to the lower temperature of the treatment. The ammoxidised sample also presents a lower hydrogen content than the starting char. Nevertheless the oxygen content increases, indicating that simultaneous chemisorption of nitrogen and oxygen takes place during the ammoxidation treatment.

Table 2 Chemical analysis of the samples

Sample	pH	Proximate analysis (wt.%, db)		Ultimate analysis (wt.%, daf)			
		VM	Ash	C	H	N	O
A	9.6	13.6	4.7	91.0	2.0	0.4	6.6
AA2	10.4	5.8	5.3	91.1	0.7	0.9	7.3
AA3	11.0	6.0	6.3	90.6	0.6	0.9	7.9
AN2	11.1	3.9	4.7	89.2	0.6	4.5	5.7
AN3	12.0	5.4	6.6	89.9	0.6	5.1	4.4
ANO	10.3	10.4	3.8	87.7	0.5	4.0	7.8

Ammoxidation has been reported to be a more convenient modification technique than amination due to the need for a previous oxidation step in the case of amination. However, in this paper similar nitrogen contents were attained for amination (carried out without any previous oxidation of the carbon) and ammoxidation. Moreover, the nitrogen enriched carbons still contain, in both cases, considerable amounts of oxygen that may add interesting properties to the prepared adsorbent.

The pH values indicate that all the samples have a predominantly basic character. The starting char already presents a basic nature that is reinforced after the different treatments. As expected, amination produced the most basic samples. Ammoxidation, on the other hand, shows a smaller increase in pH, probably due to the different nature of the functionalities introduced into the carbons. Activation also leads to an increase in the basicity of the carbons, which is even greater than that produced by ammoxidation.

To assess the nature of the functionalities formed during the different treatments, temperature programmed desorption (TPD) tests were carried out. Figure 1 summarises the results of the evolved gas analysis by FTIR during the TPD tests of samples A, AA2, AN2 and ANO. The ammoxidised sample is the only one that exhibits evolution of nitrogen species (NH_3 and HCN). This is because amination was carried out at high temperature, and thus nitrogen was incorporated into thermally stable pyridine and pyrrol-type functionalities [3]. ANO presents CO_2 evolution between 150 and 800 ºC and simultaneous evolution of CO, HCN, and NH_3 between 300 and 1000 ºC. The gaseous products evolved at high temperature probably resulted from the decomposition of amides, imides and lactams. The evolution of CO_2 at low temperature (below 320 ºC) can be ascribed to the decomposition of carboxylic acids [14]. AA2 releases CO at high temperature (maximum at 900ºC) indicating the formation of basic pyrone functionalities during the activation process. AN2 also presents the evolution of CO at the same temperature, although in this case the CO may also have resulted from the decarbonylation of lactams formed during amination [9].

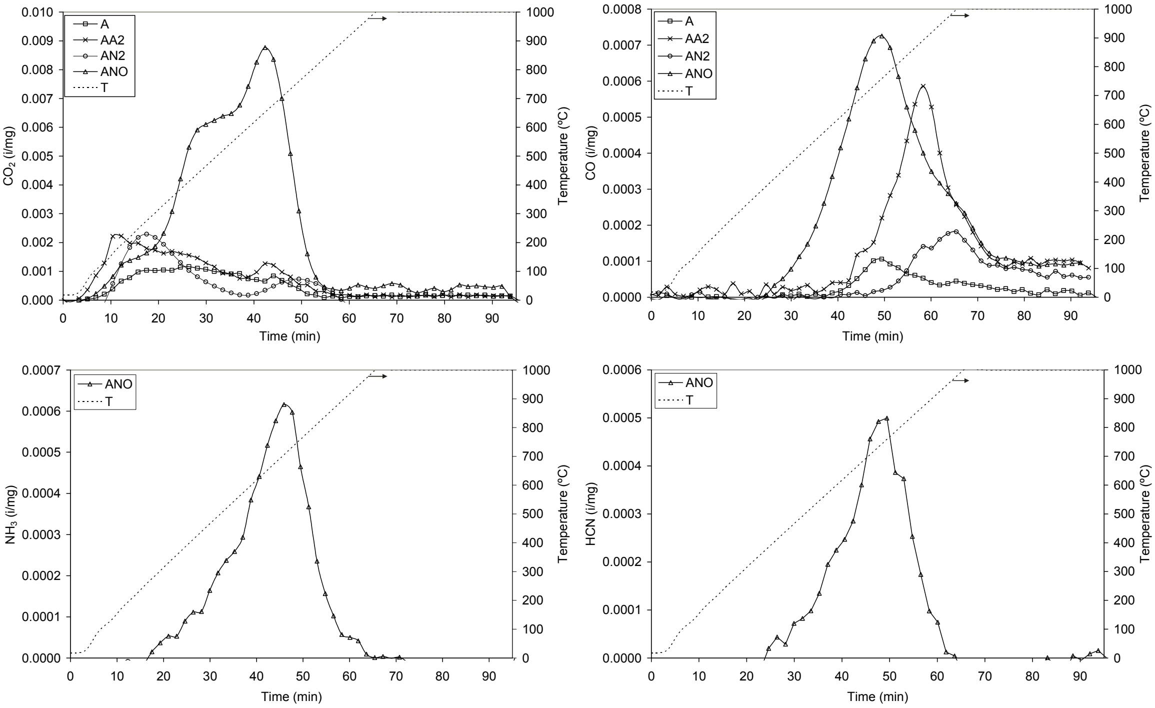

Figure 1. Evolved gas analysis by FTIR during the TPD tests at a heating rate of 15 ºC min^{-1} in 50 cm^3 min^{-1} of Ar flow rate.

Figure 2 shows the N_2 and CO_2 adsorption isotherms at -196 ºC and 0 ºC, respectively, for the prepared almond shell carbons. The char and the ammoxidised sample present negligible textural development. Amination and activation with CO_2 promote the development of porosity in the carbons, mainly in the microporosity domain (type I N_2 adsorption isotherms). The duration of the treatment also influences the textural development: the activated and aminated samples that have experienced longer treatment times, show greater volumes of adsorbed N_2. The curved shape of the CO_2 adsorption isotherms suggests the presence of a narrow microporosity, particularly in the samples with smaller textural development.

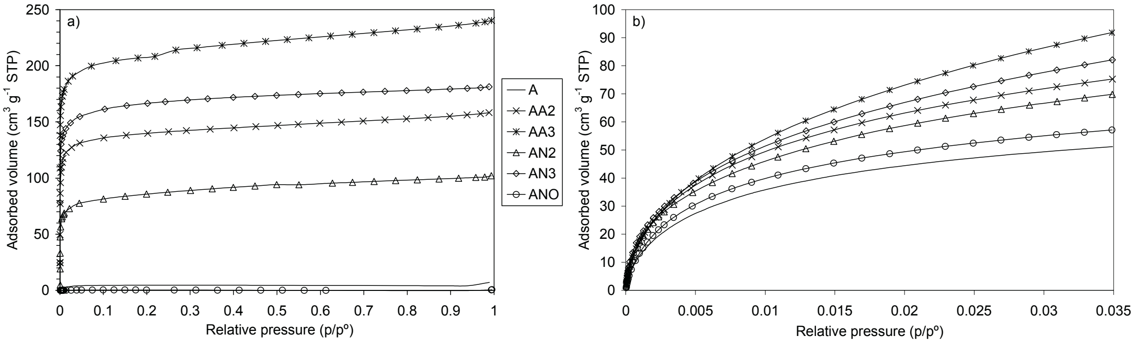

Figure 2. Adsorption isotherms of the samples a) N_2 at -196 ºC, and b) CO_2 at 0 ºC.

The textural parameters calculated from the N_2 and CO_2 adsorption isotherms are summarised in Table 3. It can be observed that activation and amination increase the total pore volume (V_p) and BET apparent surface area (S_{BET}) of the samples, whereas ammoxidation tends to reduce these parameters. In addition, it can be observed that the longer the activation or amination treatment, the greater the increase in V_p and S_{BET}. Maximum values of S_{BET} and V_p were obtained for the sample activated with CO_2 for 3 h (822 $m^2\ g^{-1}$ and 0.371 $cm^3\ g^{-1}$ respectively). CO_2 adsorption isotherms up to atmospheric pressure allow the assessment of narrow microporosity (< 1nm) in the samples. The Dubinin-Radushkevich (DR) equation was applied to determine the volume of narrow micropores (< 0.7 nm) and the micropore surface area (S_{DR}). By using the Stoeckli-Ballerini relation it is possible to evaluate the average narrow micropore width (L_0). It can be seen that the char, A, and the ammoxidised carbon, ANO, exhibit a higher narrow micropore volume (W_0) than total pore volume in nitrogen (V_p). This is due to diffusion restrictions to the adsorption of N_2 at -196 ºC on narrow micropores. Activation, amination and ammoxidation promote the development of the narrow microporosity in the samples. Longer treatments also result in a widening of the microporosity, as can be seen from the shape of the isotherms. Maxima of W_0 and S_{DR} were obtained for the samples activated with CO_2.

Table 3 Helium density and textural parameters calculated from the N_2 and CO_2 adsorption isotherms

Sample	d_{He}	N_2 adsorption at -196 ºC		CO_2 adsorption at 0 ºC		
	($g\ cm^{-3}$)	S_{BET} ($cm^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	W_0 ($cm^3\ g^{-1}$)	S_{DR} ($cm^2\ g^{-1}$)	L_0 (nm)
A	1.60	21	0.011	0.157	411	0.53
AA2	1.93	529	0.245	0.215	562	0.52
AA3	2.00	822	0.371	0.226	593	0.53
AN2	1.93	326	0.157	0.184	481	0.49
AN3	1.98	653	0.280	0.195	510	0.48
ANO	1.60	1	0.001	0.194	508	0.57

Figure 3 summarises the equilibrium CO_2 capture capacities of the samples, measured in a thermogravimetric analyser in a flow of pure CO_2, at two different temperatures: 25 and 100 ºC. The adsorption capacity diminishes with increasing temperature, as might be expected for equilibrium measurements in physisorption processes. The activated and aminated samples present a higher capacity than the starting char, reaching maximum values of up to 9.7 and 3.5 wt.% of adsorbed CO_2 at 25 ºC and 100 ºC, respectively. It is interesting to note that activation and amination lead to similar capacities, even though these samples show substantial differences in their textural properties. The activated samples exhibit a higher narrow micropore volume and therefore they might be expected to present higher CO_2 adsorption capacities. However, aminated samples contain basic nitrogen functionalities that appear to enhance CO_2 adsorption. In contrast, the ammoxidised sample does not show any significant increase in adsorption capacity compared to that of the starting char, despite its high nitrogen content. This is due to the different nature of the nitrogen functionalities introduced by the two ammonia treatments. According to the pH values in Table 2 the fuctionalities introduced seem to be more acidic in the case of the ammoxidised sample. Ammoxidation probably incorporates the nitrogen into amide groups [11], which are considerably more acidic than the pyridinic and pyrrolic nitrogen present in the aminated samples.

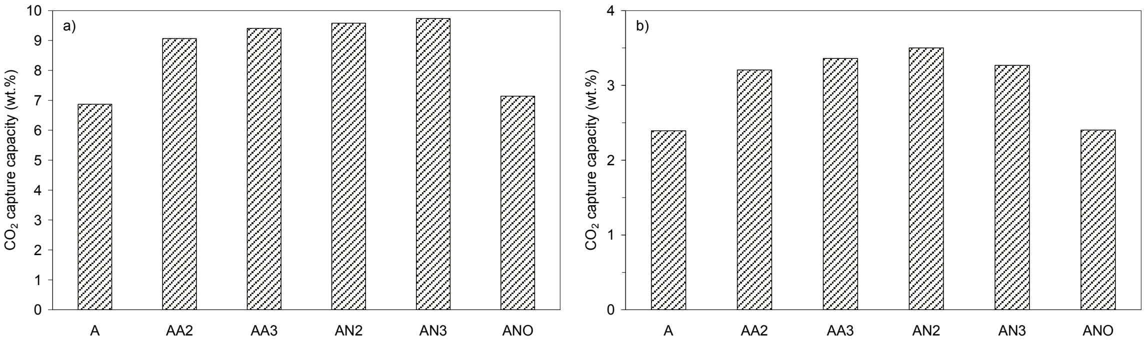

Figure 3. CO_2 capture capacity evaluated in a thermogravimetric analyser in 50 cm^3 min^{-1} of CO_2 flow: a) 25 ºC and b) 100 ºC.

Conclusions

Two methods were considered for the production of CO_2 adsorbents from almond shells: activation with CO_2 and heat treatment with ammonia gas. The prepared adsorbents exhibit significant differences in texture and surface chemistry which influenced their capacity to capture CO_2.

Activation with CO_2 developed microporosity in the samples to a greater extent than amination and ammoxidation, thus enhancing the CO_2 uptake at atmospheric pressure. Ammoxidation introduced 4 wt.% of nitrogen into the carbon matrix. However, the ammoxidised sample did not show a higher CO_2 capture capacity than the starting char. Amination, though, does seem to be a suitable modification technique for obtaining effective CO_2 adsorbents. The aminated samples presented significantly higher capacities than the starting char, and higher in fact than those of the activated samples. Moreover, samples containing up to 4-5 wt.% of nitrogen were produced without the need for carrying out any previous oxidation of the char. This is clearly a significant advantage as it simplifies the production process of the adsorbents.

Acknowledgement

This work was carried out with financial support from the Spanish MEC (Project CTM2005-03075/TECNO). MGP and JF acknowledge the support from the CSIC I3P Program co-financed by the European Social Fund and the PCTI-Asturias, respectively.

References

[1] M. Radosz, X. Hu, K. Krutkramelis, Y. Shen, Flue-Gas Carbon Capture on Carbonaceous Sorbents: Toward a Low-Cost Multifunctional Carbon Filter for "Green" Energy Producers, *Ind. Eng. Chem. Res.* 47 (2008) 3783.

[2] M.T. Ho, G.W. Allinson, D.E. Wiley, Reducing the Cost of CO2 Capture from Flue Gases Using Pressure Swing Adsorption, *Ind. Eng. Chem. Res.* 47 (2008) 4883.

[3] C. Pevida, M.G. Plaza, B. Arias, J. Fermoso, F. Rubiera, J.J. Pis, Surface modification of activated carbons for CO_2 capture, *Appl. Surf. Sci.* 254 (2008) 7165.

[4] M.G. Plaza, C. Pevida, A. Arenillas, F. Rubiera, J.J. Pis, CO2 capture by adsorption with nitrogen enriched carbons, *Fuel* 86 (2007) 2204.

[5] M.G. Plaza, C. Pevida, B. Arias, M.D. Casal, C.F. Martín, J. Fermoso, et al., Different approaches for the development of low-cost CO2 adsorbents, *Journal of Environmental Engineering* In Press (2008).

[6] T.C. Drage, A. Arenillas, K.M. Smith, C. Pevida, S. Piippo, C.E. Snape, Preparation of carbon dioxide adsorbents from the chemical activation of urea-formaldehyde and melamine-formaldehyde resins, *Fuel* 86 (*2007*) 22.

[7] J. Przepiórski, M. Skrodzewicz, A.W. Morawski, High temperature ammonia treatment of activated carbon for enhancement of CO_2 adsorption, *Appl. Surf. Sci.* 225 (2004) 235.

[8] G.M.K. Abotsi, A.W. Scaroni, Reaction of carbons with ammonia: effects on the surface charge and molybdenum adsorption, *Carbon* 28 (1990) 79.

[9] R.J.J. Jansen, H.v. Bekkum, Amination and ammoxidation of activated carbons, *Carbon* 32 (1994) 1507.

[10] B. Stohr, H.P. Boehm, R. Schlogl, Enhancement of the catalytic activity of activated carbons in oxidation reactions by thermal treatment with ammonia or hydrogen cyanide and observation of a superoxide species as a possible intermediate, *Carbon* 29 (1991) 707.

[11] R.J.J. Jansen, H. van Bekkum, XPS of nitrogen-containing functional groups on activated carbon, *Carbon* 33 (1995) 1021.

[12] H.P. Boehm, G. Mair, T. Stoehr, A.R. De Rincon, B. Tereczki, Carbon as a catalyst in oxidation reactions and hydrogen halide elimination reactions, *Fuel* 63 (1984) 1061.

[13] K.B. Bota, G.M.K. Abotsi, Ammonia: a reactive medium for catalysed coal gasification, *Fuel* 73 (1994) 1354.

[14] S. Haydar, C. Moreno-Castilla, M.A. Ferro-García, F. Carrasco-Marín, J. Rivera-Utrilla, A. Perrard, et al., Regularities in the temperature-programmed desorption spectra of CO_2 and CO from activated carbons, *Carbon* 38 (2000) 1297.