EFFECT OF PYROLYSIS TEMPERATURE ON THE TEXTURAL PROPERTIES AND THE ACTIVATION MECHANISM OF PORK BONE DERIVED HYDROXYAPATITE

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***Abstract*— Calcium hydroxyapatite was produced from pork bones through a three step procedure including pre-pyrolysis, chemical impregnation with K_2CO_3 and pyrolysis. The effect of pyrolysis temperature on the porosity development of the material was investigated. The specific surface area (SSA) decreases as charring temperature increases. It is observed that the chemical treatment with K_2CO_3 is inefficient at mild pyrolysis conditions, in the 550-700ºC range. On the contrary, micropore, mesopore and macropore formation is enhanced by chemical activation with K_2CO_3 at about 800ºC. The reactions involved during the chemical activation step were analysed by mass spectrometry. It was concluded that treatment with K_2CO_3 favours the release of water and CO. this phenomenon was related to SSA and pore volume development. On the contrary, activation at 900 ºC caused a remarkable reduction in SSA, especially for K_2CO_3 treated samples, due to excessive ongoing of the above reactions as deduced from the pyrolysis gases.**

***Keywords*— Hydroxyapatite; Bone char; Chemical activation; Physicochemical characterization; TG-MS.**

I. INTRODUCTION

Owing to its desirable structural stability, ionic substitution ability and acid–base properties, the use of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) (HAp) has recently increased. HAp is a versatile material and recently it has been successfully used for the adsorption of organic pollutants (Ciobanu *et al*., 2014) and metals (Kim and Lee, 2014; Sicupira *et al.*, 2014) from liquid effluents, as a support in photocatalytic systems (Chun *et al.*, 2014) and also in electrochemical (Goodman *et al.*, 2013) and biomedical applications (Sobczak-kupiec *et al.*, 2013).

Many methods of synthesizing HAp have been reported, such as solid-state reaction, sol–gel, wet synthesis and hydrothermal methods (Guo *et al*., 2013; Salviulo *et al.*, 2011). However, the procedures employed were relatively complicated and it has been proven difficult to obtain controlled morphology with these methods. Hard tissues in animals represent an abundant source of natural HAp (Larsen *et al*., 1993; Singh, 2012). If adequate methods are developed, the use of waste animal bones is a promising alternative choice for the production of HAp-based porous materials.

Pyrolysis constitutes one of the most reliable treatment methods for the animal bones left over. The solid fraction obtained (char) contains about 70–76 wt% calcium hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, 9–11 wt% carbon and 7–9 wt% $CaCO_3$. The apatite crystals in bones can act as natural template for the formation of abundant pores. Furthermore, this process could be economically feasible as well as environmentally friendly.

Difficulties have been reported in the production of materials based on natural HAp with large specific surface area (SSA). Doostmohammadi *et al*. (2012) reported a surface area value of 2.2 m^2/g, obtained by the charring of bovine bones in air atmosphere at 700 ºC. Hassan *et al.* (2008) achieved an area of 72 m^2/g from the pyrolysis of camel bones in inert atmosphere at 800ºC. Murillo *et al*. (2011) reported some of the largest BET values, of about 127 m^2/g, through the pyrolysis of chicken bones in nitrogen atmosphere at 800 ºC.

Chemical activation represents an alternative for improving the textural and surface properties of bone char. It requires lower temperature and results in higher yield than physical activation only (Lillo-Ródenas *et al.*, 2003; Phan *et al*., 2006). In a previous work our research group (Iriarte-Velasco *et al.*, 2015a; 2015b) concluded that the chemical activation with K_2CO_3 significantly enhances the textural properties of bone char. However, there are still important gaps in the fundamentals of the process, regarding the optimization of preparation conditions and the reaction mechanisms that take place. The activation temperature is one of the most important factors. Sobzak *et al.* (2009) investigated the textural properties of pig bone calcined in air atmosphere. Calcinations in the 650 – 900 ºC range caused variations in S_{BET} values in the 44 – 3 m^2/g range.

In this study a porous material, mainly composed of natural HAp, has been produced by using pork bones as raw material. To the best of the authors' knowledge, there is no study in the literature regarding the effect of the pyrolysis temperature on the production of natural HAp through the activation of pork bones with K_2CO_3. The specific objectives of the present work can be described as follows: i) investigate the effect of pyrolysis temperature on porosity development within the bone char; ii) identify the reactions that occur during the chemical activation process; and iii) determine how such reactions contribute to the evolution of porosity and specific surface area.

II. METHODS

A. Preparation of bone char

Pork chop bones were pre-pyrolysed at 450 ºC to remove meat and fat. Pre-pyrolysed bones were then contacted with a solution containing 0.05M K_2CO_3 at an

impregnation ratio (r) of 1 mmol $K_2CO_3/g_{precursor}$. This impregnation ratio was selected because it results in an adequate pore development (Iriarte-Velasco *et al.*, 2015a) and implies environmentally and economically sustainable conditions. Finally, impregnated samples were pyrolysed in nitrogen atmosphere at different temperatures (550, 700, 800 and 900 ºC). More details about the preparation procedure are given elsewhere (Iriarte-Velasco *et al.*, 2014). Thermal treatment conditions (precharring and pyrolysis) were as follows: heating rate of 10 ºC/min until the predetermined temperature was reached, which was held constant for 1 hour, nitrogen flow of 120 mL/min, corresponding to 8 minutes of residence time in furnace. The obtained bone char was left to cold down in nitrogen atmosphere. A part of the precursor material (precharred bone) was pyrolysed without–chemical treatment (BCO). K_2CO_3-treated samples were coded as BCK.

B. Characterization of bone char

A porosimeter (ASAP 2010, Micromeritics) was used to determine the textural properties, by means of nitrogen adsorption/desorption at 77 K. BET surface area, and pore area and volume were determined. Micropore surface and volume were measured from density functional theory (DFT), while values in the mesopore and macropore ranges were measured based on the Barrett, Joyner & Halenda method (BJH).

In order to investigate the reactions occurring during the activation process, thermogravimetric analysis (TG) coupled to mass spectrometry (MS) was conducted. TG analyses were performed with a Setsys Evolution (Setaram) thermal analyser. About 70 mg of impregnated samples were put into the alumina crucible and heated under helium atmosphere from room temperature up to 1000 ºC, using a heating rate of 10 ºC/min. The thermal analyser exhaust gases were analysed on-line by mass spectrometry (MKS, Cirrus 3000). The following compounds were collected continuously: H_2 (m/z=2), CH_4 (m/z=15), H_2O (m/z=18), CO (m/z=28) and HCN (m/z=27).

III. RESULTS AND DISCUSSION

A. Specific surface area and volume

Figure 1 shows the nitrogen adsorption desorption curves. All isotherms exhibited the presence of a hysteresis loop, which is a characteristic feature of the Type IV isotherm. The downward displacement of the curve with the increased calcinations temperature was indicative of the collapse of porous structure. For chemically activated samples, this effect was intensified at the highest temperatures investigated.

Figure 2 shows the total specific surface area (SSA) and pore volume (V_p) of biochars. Figure 3 exhibits the fractional surface areas. Complementary textural data are presented in Table 1. The following regions have been considered, based on the location of valleys in the pore size distribution (not shown): micropores, SSA_I (D_p<1.7 nm); small mesopores, SSA_{II} (1.7<D_p<5.0 nm)

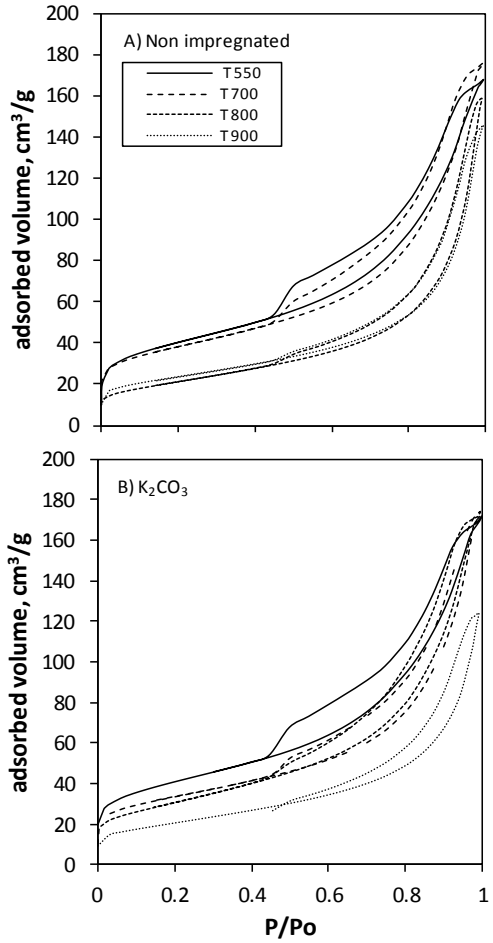

Figure 1. Nitrogen adsorption-desorption isotherms.

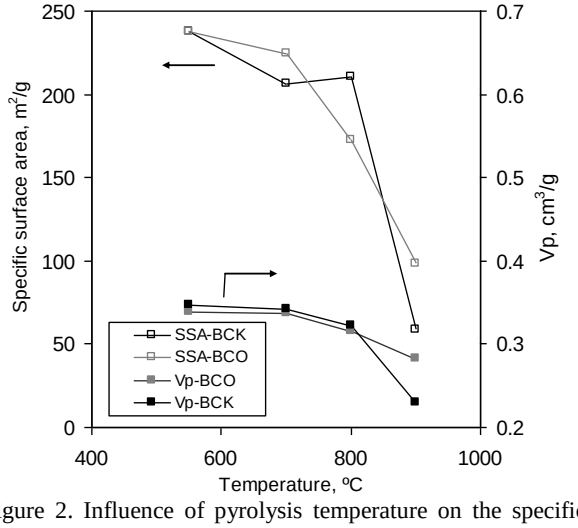

Figure 2. Influence of pyrolysis temperature on the specific surface area (SSA) and pore volume (V_p) of K_2CO_3 treated (BCK) and non-treated (BCO) bone char.

and the sum of large mesopores and macropores SSA_{III} (D_p>5.0 nm).

The maximum SSA (237 m^2/g) was obtained for non-treated sample pyrolysed at mild temperature, 550ºC. At that temperature, there are no significant differences between treated and non-treated (BCO) samples. A significant variation in SSA is observed as temperature varies. For BCO, specific surface area continu-

Table 1. Textural properties of the prepared biochars. T, ºC; S_{BET}, m^2/g; dp, Å; V, cm^3/g.

	T	S_{BET}	dp	V_I	V_{II}	V_{III}
BCO	550	142	70	0.021	0.07	0.19
	700	134	80	0.021	0.05	0.21
	800	76	107	0.017	0.03	0.22
	900	83	102	0.003	0.03	0.20
BCK	550	145	74	0.022	0.07	0.20
	700	117	89	0.017	0.04	0.23
	800	115	109	0.023	0.05	0.20
	900	75	125	n/d	0.01	0.17

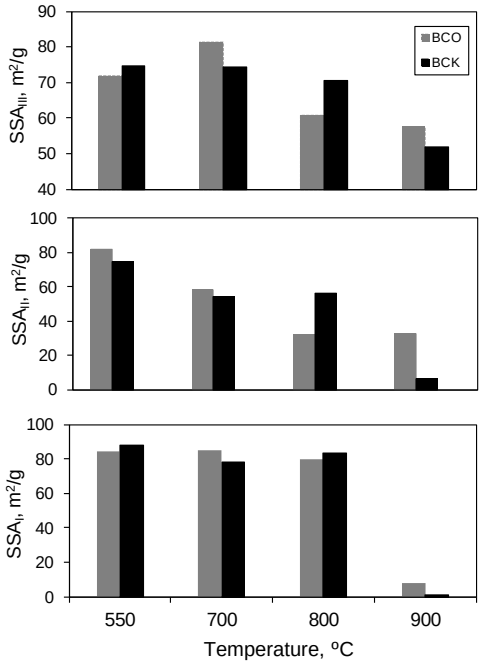

Figure 3. Influence of pyrolysis temperature on the fractional surface area of non-treated (BCO) and K2CO3 (BCK) treated bone char. r=1 mmol/g.

ously decreases with charring temperature within all the temperature range investigated (550 to 900 ºC). The decrease is more pronounced at high temperatures.

Several authors (Deydier *et al*., 2005) have also reported a dramatic decrease in surface area of calcined meat and bone meal, from 18 to 2 m^2/g, as temperature was increased from 550 to 900ºC. On the contrary, Ayllon *et al*. (2006) reported a dissimilar behaviour. According to their data, the specific surface area of meat and bone meal char had a local maximum at 450 ºC, and it dropped off at about 500 ºC. From 600 to 900 ºC, the SSA increased again, up to a maximum value of 37.7 m^2/g at 900ºC. The discrepancy in the influence of temperature could be due to either differences in source material or in the experimental set-up.

For K_2CO_3-treated sample, as activation temperature increases (in the 500-800 ºC range), the SSA of the final product is reduced, though the decrease is less pronounced, as compared to BCO. This behaviour is mainly attributed to a better preservation of the meso and macro range structure, as shown in Figure 3. In this way, at 800 ºC, the sample treated with K_2CO_3 shows larger surface area. As compared to BCO, the mesopore and macropore surface area of BCK were 78% (57 vs 32 m^2/g) and 15% (70 vs 61 m^2/g) larger, respectively. This suggests that the activation with K_2CO_3 requires temperatures of about 800 ºC to effectively enhance the textural properties of biochar. If the activation temperature is further raised to 900 ºC, total SSA and V_p are drastically reduced from 210 to 59 m^2/g and from 0.272 to 0.179 cm^3/g, respectively. This is likely due to pore widening processes which cause an almost complete suppression of surface area at dp<5 nm (Figure 3) whereas macropores still remain.

B. Thermogravimetric analysis

The results of the thermogravimetric (TG) and differential TG (dTG) analysis of non-treated and K_2CO_3-impregnated samples are shown in Figure 4. In the dTG curves one main peak (with its maximum near 470 ºC) and other small peaks (at around 100, 225, 800 and 900 ºC) are detected. The inorganic component of bone is primarily hydrated calcium phosphate, hydroxyapatite (HAp). At about 450 ºC, HAp begins to dehydroxylate to form oxyhydroxyapatite, or $Ca_{10}(PO_4)_6(OH)_{(2-2x)}O_x$, where x = vacancy.

This decomposition process is gradual and takes place over a range of temperature (Tanaka *et al*., 1997). The intense mass loss from around 275 °C to 600 °C is attributed to that process. Furthermore, the decomposition of collagen has also been associated to this mass loss (Etok *et al*., 2007). Figure 4 reveals that mass loss within this range is significantly intensified by K_2CO_3 treatment.

At above 600 ºC a broad step of continuous mass loss exists related to the thermal decomposition of inorganic constituents of bone. This peak is centred at about 800 ºC for non-treated bone char (mass loss of 3.5 %), whereas it is displaced to a higher temperature of about 900 ºC (mass loss of 5.6 %) for chemically treated sample. The activation of samples (both impregnated and non-impregnated) was performed within this range and despite the relatively low mass loss observed at high temperatures for both non-treated and K_2CO_3 treated sample, the textural properties were significantly altered. The decrease in surface area at pyrolysis temperatures above 600 ºC could be explained by an increase of HAp crystallite size (Guo *et al*., 2013). At high temperatures, changes in the crystalline structure have been reported, even with minimum loss of components. Dimovic *et al*. (2009) prepared a biochar using bovine bones. They reported a decrease of SSA, from 71 to 2 m^2/g, when increasing temperature in the 600 - 1000 ºC range. The–weight loss was low, about 3 %, which is very similar to the present work.

C. TG-MS analyses

In order to better understand the activation mechanism the following species were monitored in pyrolysis gases: H_2O, H_2, CO, CH_4 and HCN. The results are shown in Figure 5. Chemical treatment increases dramatically the release of H_2O and CO whereas that of H_2, CH_4 and HCN is diminished. The main release of water starts at

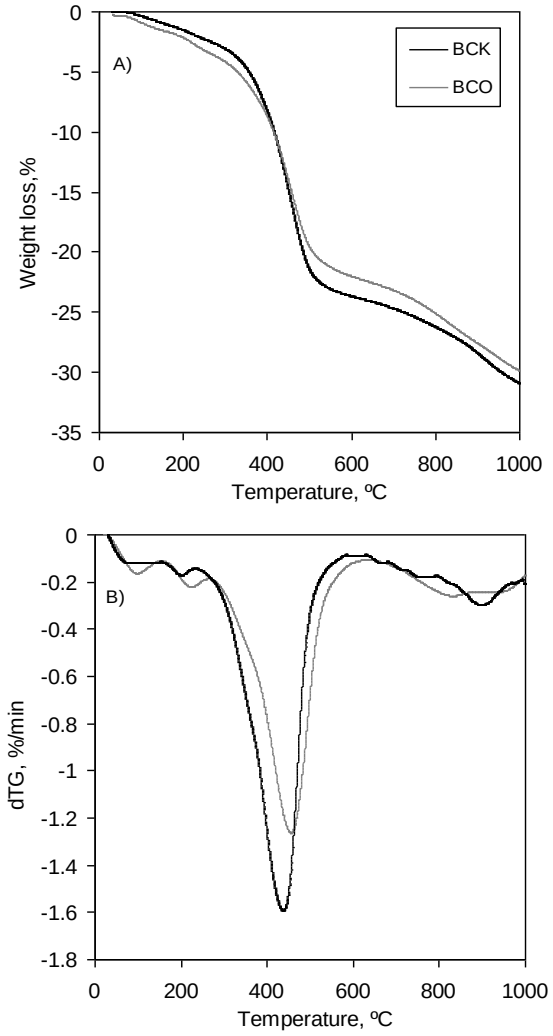

Figure 4. Thermogravimetric analysis of non-impregnated and chemically impregnated samples of bone char. A) TG curves; B) dTG curves.

about 400 ºC, and could be partially ascribed to the decomposition of the surface P-OH groups of HAp by dehydration (Eq. 1), which takes place in the 400-700 ºC range (Tanaka *et al*., 1997). The OH^- species provided by K_2CO_3 (Iriarte-Velasco *et al*., 2014) could also react according to following mechanism:

$$2P-OH \leftrightarrow P-O-P+H_2O \quad . \qquad (1)$$

The release of water observed below 200 ºC is associated to desorption of adsorbed water. The fact that the peak for the K_2CO_3 impregnated samples was lower could be related to the aforementioned dehydration capability of K_2CO_3 during the impregnation step.

Regarding the release of CO, McKee (1983) and Lillo-Ródenas *et al*. (2004) studied the gasification of graphite by alkali metal and found that K_2CO_3 was reduced in inert atmosphere by carbon as follows:

$$K_2CO_3 + 2C \rightarrow 2K + 3CO \, . \qquad (2)$$

Another source of CO is the RWGS reaction (Eq. 3). This reaction has been reported during the pyrolysis of carbonaceous precursors, and would take place mainly at temperatures higher than 700 ºC (Chen and Lin, 2013; Iriarte-Velasco *et al.*, 2014; Prabowo *et al*., 2014).

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad (3)$$

As shown in Figure 5, the release of CO during the activation of non-impregnated sample occurs in two stages, in the 400-600 ºC and 700-1000 ºC ranges. For the chemically treated sample it takes place much more intensely and only at the lowest temperature range. The occurrence of the RWGS reaction requires the presence of both CO_2 and H_2. Nevertheless, CO_2 was not detected in pyrolysis gases. It is hypothesized, that the rapid transformation of CO_2 into CO, according to the RWGS reaction, would cause both the absence of CO_2 and the drop-off in H_2 release at around 700 ºC (Figure 5). This hypothesis is also supported by the role of K as promoter of the RWGS reaction (Jacobs and Davis, 2010).

The release of CO_2 is well documented. Both the $CaCO_3$ constituent of bone char and the incorporated K_2CO_3 can undergo thermal decomposition (Eqs. 4-5) in the 600- 1000 ºC range (Lehman *et al*., 1998; Wang and Thomson, 1995).

$$CaCO_3 \leftrightarrow CaO + CO_2 \qquad (4)$$

$$K_2CO_3 \leftrightarrow K_2O + CO_2 \qquad (5)$$

The increased release of H_2O and CO suggests that K_2CO_3 can act through different mechanism; i) as dehydration agent; or ii) being reduced by carbon and releasing CO and thereby increasing the specific surface area and specific pore volume. Both processes involve gasification reactions and thus, are expected to have an impact on the textural properties of the prepared material. Also, when activation temperature reaches the boiling point of potassium 800 °C, it can diffuse into the precursor structure, causing the deformation of pore structure. These phenomena could be involved in porosity development. However, they could also cause the collapse of pores and a drastic reduction in SSA, as observed for the K_2CO_3 treated sample activated at 900 ºC (Figure 2), likely by excessive ongoing of such reactions.

CH_4 and HCN could be formed following a reaction pathway similar to that described by Robau-Sánchez *et al*. (2005):

$$6OH^- + 5.5C + N_2 \leftrightarrow 2CN^- + 2CO_3^{-2} + 1.5CH_4 \qquad (6)$$

The above mechanism implies the reaction of structural carbon and nitrogen with a source of OH^- ions. Figure 5D,E reveal the evolution of CH_4 and HCN which exhibit a well defined peak at temperatures between 400 and 600 ºC, with its maximum at around 500 ºC. The shape of the curves suggests a main common source, reaction Eq. (6). The observed tail in the CH_4 release curves could be ascribed to additional mechanisms of CH_4 formation, such as the methanation of CO and CO_2 (Iriarte-Velasco *et al.*, 2014).

The release of water observed belowThe reduced release of these compounds during the charring of K_2CO_3 treated samples could be attributed to the preferential oxidation of carbon by the activating agent through Eq. (2). In this way, the consumption of much

part of the carbon content in bone char would limit the

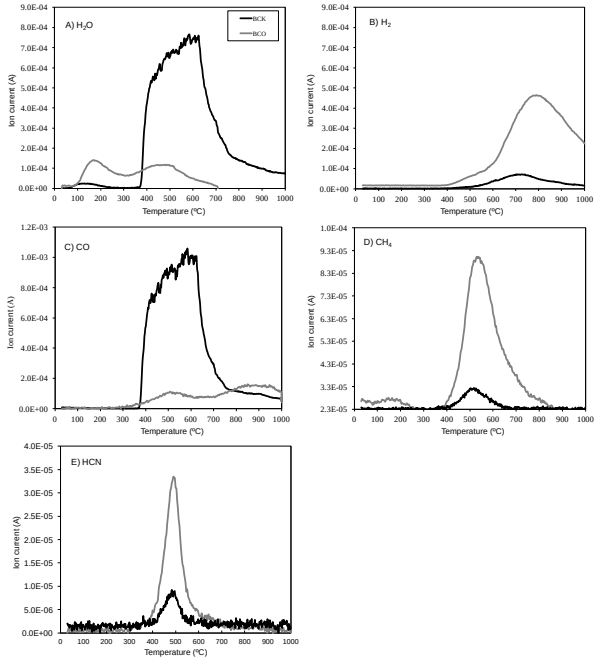

Figure 5. Temperature dependence of pyrolysis products for K_2CO_3 impregnated and non-impregnated bone char.

occurrence of Eq. (2) and therefore would explain the limited release of cyanide and CH_4 as observed for the sample impregnated with K_2CO_3.

III. CONCLUSIONS

The results presented demonstrate that chemical treatment with K_2CO_3 enhances pore development more than physical activation when pyrolysis is carried out at 800 ºC, mainly in the mesopore and macropore range. At lower temperatures, in the 550-700 ºC range, the chemical treatment was inefficient. At higher temperatures, of about 900 ºC, the shrinkage in the bone char structure was more pronounced resulting in a drastic reduction in surface area and-pore volume.

The investigation of pyrolysis gases by TG-MS reveals an increased release of H_2O and CO during the charring of K_2CO_3-treated bone char. The release of H_2O is related to the decomposition of HAp structure. The release of CO is partly attributed to the enhanced gasification of carbon in bone char through its reaction with K_2CO_3. The obtained results encourage further investigation into the application of TG-MS as a technique to control the textural properties of biochars produced by the pyrolysis of waste material.

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