Carbon foam prepared by pyrolysis of olive stones under steam

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Abstract

The experimental conditions for the pyrolysis of olive stones to produce a swelling of the particle and eventually the formation of carbon foam are described and discussed. The greatest expansion of the material occurred when 200–300 g of precursor, in the presence of steam at a pressure of 1 MPa, is introduced into a 1000 ml stainless steel reactor placed inside a sand-bath furnace previously heated to 500 °C. In a few minutes the pyrolysis begins and this exothermic process leads to a more rapid pyrolysis. A relationship between heating rate and degree of foaming for the resulting char is observed. The carbon foam obtained exhibits a low density, 0.2–0.3 g/cm³, due to the presence of meso and macropores, mainly those of size larger than 1 μm. A mechanism is suggested to explain the formation of the foam as a combination of a softening of the precursor and a fragmentation of the biopolymers to produce a “melt”. A fast increase in temperature reduces the viscosity of the “melt” and facilitates the fragmentation to volatiles, responsible for the swelling of the particles and the formation of the foam.

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1. Introduction

Biomass pyrolysis is a thermal process usually employed in the preparation of fuels, chemicals and charcoal. It also constitutes the first step in the preparation of thermally (or physically) activated carbon. Briefly, the precursor, with an approximate composition of 50 wt% C, 6 wt% H and 44 wt% O, decomposes upon increasing temperature, releasing H₂O, CO₂, CO and a great variety of hydrogen and carbon rich compounds, so that the remaining solid is enriched in aromatic carbon while adopting a structure typical of non-graphitizable carbons [1]. The char yield of the process is near 25 wt%, although this value depends on the selected operation conditions. In general, low heating rates and high pressure facilitate secondary reactions and the conversion to char, while fast pyrolysis using high inert gas flow increases the amount of organic volatiles.

Studies on pyrolysis of cellulosic and lignocellulosic materials indicate that the largest transformations take place in the 200–400 °C temperature range, these being accompanied by a fast evolution of gases and an enhancement of the solid's temperature. As the particles of precursor shrink it is assumed that the decomposition products of the constituting polymers (mainly cellulose, hemicellulose and lignin) react to form a series of linked chemical bonds and the solid, which becomes richer in carbon, progressively gets rigid. The evolved gases leave the solid through the channels present in the structure of the vegetal, thus enabling the shrinkage of particles and the maintenance of the precursor appearance [2]. Consequently, the formation of carbon foam by pyrolysis of these precursors is not common and it has not been previously reported.

Since the first development of carbon foam from thermosetting organic polymers, advances in finding new precursors and the preparation of carbon foam from coal [3], mesophase pitch [4,5], polyimide [6], etc., have been described. The use of lignocellulosic precursors, due to its low cost, can constitute an interesting alternative.

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Although there are no publications related to the preparation of carbon foam from cellulosic and lignocellulosic materials, some authors [7] have reported that during the flash pyrolysis of almond shells pretreated at 300 °C, a dilatation of 20% occurred instead of the expected shrinkage. In a similar way, the expansion of the particles after the flash pyrolysis of milled cedar sawdust has been described [8].

This work analyses the pyrolysis conditions required for the expansion of a granular lignocellulosic material such as olive stones, in order to obtain carbon foam. The process involves the transformation of the precursor grains into a block of continuous material in which the grain boundaries cannot be distinguished.

2. Experimental

2.1. Thermal treatment

The precursor, olive stones, ground to a uniform particle size (3.5 mm), is loaded in a glass tube (65 mm internal diameter) which is introduced into a 1000 ml stainless steel reactor placed inside a sand-bath furnace previously heated to 500 °C. A thermocouple inserted in the centre of the bed of the precursor registers the solid temperature during pyrolysis, and another thermocouple placed near the outlet of the reactor (5 cm below) detects the temperature of the gases evolved during pyrolysis. The system can operate at pressures as high as 1.5 MPa, and controlled depressurisation is possible. The heat transfer to the reactor is carried out using a fluidised sand bed furnace which is previously heated to 500 °C. A scheme of the system was already published [9].

Table 1 presents the conditions selected for pyrolysis. As an example, experiment 1 has been carried out as follows: the glass tube charged with 200 g of the precursor is introduced at room temperature into the reactor which already contains 25 ml of water. Next, the reactor is filled with nitrogen at 1 MPa and introduced in the sand-bath furnace

where it is externally heated. Pressure is kept constant inside the reactor during the experiment, as the gas outlet has a pressure control valve. When the temperature of the solid reaches 500 °C, the furnace is removed and the reactor is depressurised.

In the majority of the experiments (see column 2 in Table 1), 25 ml of water were incorporated into the reactor, around the glass tube, in order to generate a steam-rich atmosphere before the beginning of the pyrolysis. In experiments 10 and 11 sodium chloride was dissolved in the 25 ml of water. In addition to the environment in which the reaction takes place (experiments 1–5), other conditions such as pressure (experiments 1, 6, 7) or the amount of precursor (experiments 1, 8, 9) have been modified. In the experiments 12 and 13 the furnace has also been heated to 500 °C but the pyrolysis was interrupted at 150 °C and 220 °C, respectively.

2.2. Dimension change and porosity

The thermal treatment introduces visible changes in the product obtained, either because the precursor grains swell, or because the grains aggregate to form foam. In the majority of the experiments the final block of material is constituted by areas with the aspect of foam and other more external areas which are granular, both types of area being easy to separate. The degree of foaming is defined as the weight percentage of the char obtained as foam (Table 1).

The bulk density of the foam has been determined by weighting a block of known dimensions. The volume of large meso and macropores has been quantified by mercury porosimetry (Carlo Erba 200), and the surface and cavities produced during pyrolysis have been examined by SEM (Jeol JSM-840). For the chars obtained mainly in granular form (5, 6, 7 and 11), the average particle diameter has been determined using a photographic system, and counting and sizing a representative amount of particles. The bulk density of granular chars has also been determined

Table 1
Pyrolysis conditions

Experiment	Initial atmosphere	Amount of precursor (g)	Pressure (MPa)	Temperature (°C)	Degree of foaming (%)
1	N ₂ + H ₂ O	200	1.0	500	73
2	CO ₂ + H ₂ O	200	1.0	500	80
3	Air + H ₂ O	200	1.0	500	69
4	O ₂ + H ₂ O	200	1.0	500	27
5	N ₂	200	1.0	500	0
6	N ₂ + H ₂ O	200	0.1	500	0
7	N ₂ + H ₂ O	200	0.5	500	5
8	N ₂ + H ₂ O	50	1.0	500	59
9	N ₂ + H ₂ O	300	1.0	500	82
10	N ₂ + NaCl(aq) ^a	200	1.0	500	84
11	N ₂ + NaCl(aq) ^b	200	1.0	500	0
12	N ₂ + H ₂ O	200	1.0	150	32
13	N ₂ + H ₂ O	200	1.0	220	47

^a NaCl aqueous solution, 5 wt%.

^b NaCl aqueous solution, 20 wt%.

by weighting a calibrated volume filled with the char (method ASTM D 2854-89).

2.3. Structure and chemical nature

The chemical nature and composition of the chars 1 and 5 have been determined by the following techniques: elemental analysis (Carlo Erba CHNSO EA1108), FTIR spectroscopy (Matson Infinity Gold spectrometer) and XPS, model VG-Microtech Multilab 3000. As the chars at 500 °C are semi-carbonized, the results obtained are rather erratic. In order to obtain representative values a large amount of the char has been milled to a particle size below 100 µm and the analyses have been carried out using four different portions of the sample and the results averaged.

3. Results and discussion

3.1. Experimental conditions that lead to the formation of carbon foam

Fig. 1 plots the variation of the temperature for both the furnace, solid and gas outlet during the pyrolysis for experiments 1 and 5 of Table 1. The initial temperature of the furnace, 500 °C, slightly decreases when it gets in contact with the reactor, which is originally at room temperature. Since the reactor mass is rather large in respect to that of precursor, the temperature profile of the furnace for all experiments is very similar.

In experiment 5, the profile shows that the solid's temperature increases faster as from 10 min, with a pseudo-step at around 150–200 °C and reaching 23 °C/min for the temperature range 200–400 °C. Gas temperature also increases as from 10 min, but the profile shows a maximum at around 200 °C. The most intense transformations of the precursor seem to end at about 400 °C, when the solid's temperature increases more slowly and the gas temperature remains constant.

Experiment 1 uses the same conditions as 5, but with the addition of 25 ml of water to the reactor. This seems to affect the solid temperature profile in two ways: (a) the pseudo-step (change in heating rate) at 150 °C, is shorter in experiment 1; and (b) the heating rate in the temperature range 200–400 °C is 45 °C/min for the experiment 1, almost double than for experiment 5. The gas temperature profile in both experiments is similar, the only difference being the small maximum found at 5 min from the start of experiment 1, due to the boiling of the water.

The char yield after experiment 5 was 35 wt%, slightly higher than 33 wt% from experiment 1. Nevertheless, the more marked differences are in the physical shape of the product. Whereas all the char of experiment 5 is in granular shape, 27 wt% of solid 1 is granular and the rest, 73 wt%, constitutes a whole block. The granular part of the sample is located near the internal lateral walls of the glass tube inside the reactor, whereas the block occupies the centre and bottom of the tube. When the block is fractured, no interparticulate spaces are observed and the porous structure seems to be completely different to the cellular structure of the precursor.

Fig. 2 includes the temperature profiles of experiments 1R and 5R, carried out in a similar way as experiments 1 and 5, but without precursor. The similarity between the two later profiles, in agreement with the small differences in thermal conductivity for nitrogen and steam [10], indicates that the heat transfer rate from the furnace to the precursor is the same in experiments 1 and 5. Therefore, the observed differences in the solid's temperature profiles plotted in Fig. 1 are due to differences in the heat generated during pyrolysis.

The shape of the temperature profiles for the solid in most experiments is similar to that described in Fig. 1 for solids 1 and 5. However, some samples exhibit a different profile, as shown in Fig. 2 for experiments 4, 8 and 11. For instance, the high concentration (20 wt%) of NaCl in experiment 11 enhances the boiling temperature of the

Fig. 1. Evolution of sand-bath furnace temperature, solid temperature and gas outlet temperature during pyrolysis.

Fig. 2. Influence of pyrolysis conditions on the temperature profiles for the solids.

solution but also the heat demand to carry out the phase change. As a result, the temperature remains almost constant for some minutes and the heating rate for the solid in the 200–400 °C range is lower than for experiment 10, for which the NaCl concentration is 5 wt%. In experiment 4, oxygen stabilises intermediate products of pyrolysis, which require extra heat for their decomposition. Finally, the profile of experiment 8 is intermediate of the profiles of experiments 1 (Fig. 1) and 1R as the method to measure temperature is very sensitive to the amount of precursor introduced, which was smaller in run 8. The shape of this curve constitutes a proof of the difficulties in measuring experimentally the real temperature of the solid. Therefore, all the profiles shown in Figs. 1 and 2 must be considered as an approximation to the real temperature of the solid.

Fig. 3 presents the degree of foaming as a function of the heating rate of the solid deduced from the linear portion of the temperature profile in the temperature range 200–400 °C. The relation found indicates that a minimum heating rate of 30 °C/min is necessary to initiate the formation of the foam, which is extensive for heating rates higher than 50 °C/min. Thus, during experiment 10, similar to experiment 1 but incorporating 5 g NaCl to the 25 ml of water, a heating rate of 74 °C/min is reached after the initial 10 min (Fig. 2), with an 84 wt% of foam being formed.

When the heating rate is below 30 °C/min the chars are essentially granular, although the particle size is larger than that obtained in a conventional pyrolysis. Thus, the average particle diameter of the precursor, 3.5 mm, is reduced to 2.6 mm in a traditional pyrolysis at 500 °C, whereas for the chars obtained in experiments 5, 6, 7 and 11, a larger particle size is obtained, 3.0, 2.8, 3.2, and 2.8 nm, respectively. Therefore, it can be concluded that the swelling of the particle is an intermediate step for the formation of the foam.

The values for the degree of foaming in Table 1 indicate that, with the experimental system used here, the formation of the carbon foam during pyrolysis is favoured when

steam is generated in the presence of inert gas (experiments 1–5), under a pressure of 1.0 MPa (experiments 1, 6, 7), and filling with the precursor at least 2/3 of the reactor's volume (experiments 1, 8, 9). Besides, if the boiling point of water is increased by the addition of NaCl (experiments 1, 10, 11), the degree of foaming increases, but it is inhibited if the concentration of salt in the solution is high. Finally, it must be pointed out that the expansion occurs from the beginning of pyrolysis (experiments 1, 12, 13).

No relation between the char yield and the degree of foaming has been found. Just to comment that the char yield of experiment 5 was 35 wt%, while in the rest of the experiments, where steam was generated before pyrolysis, the char yield is 32–33 wt%. This indicates that steam facilitates the extraction of volatiles, possibly the more soluble ones [11], due to the increase in the extraction strength of water at 1 MPa and temperatures above 200 °C and also to the increase in the flow of gas at the outlet of the reactor produced by the addition of 25 ml of water. In any case, the char yield obtained with this faster pyrolysis is lower than that obtained at the same temperature using a controlled heating rate of 1 °C/min at 1.0 MPa, 41–42 wt% [12], and similar to that obtained in a conventional ambient pressure pyrolysis at 500 °C (31 wt%).

3.2. Density and appearance

The char obtained in experiment 1 was constituted by 73 wt% foam and 27 wt% granular char and Fig. 4 shows the SEM images of foam (a–c) or granular (d) sections. A transversal cut of the foam block (a) shows that a continuous mass with a different appearance to the precursor is forming, where no grain boundaries can be detected. A higher magnification image (b) shows the existence of voids/pores with size in the range of several tens of microns and even up to 100 µm. Observing the surface with more detail (c), a smooth texture is visible, in contrast to that of a char prepared in a conventional pyrolysis, which is rough and reflects the cellular structure of the precursor [13,14]. A group of fissures and blisters can be observed in the surface of the granular fraction (d), the aspect of which suggests that they have been generated by the release of gases throughout a liquid of high viscosity. In the same way, a labyrinth of holes has formed in the fractured grain, some of them exhibiting an unusual large size. The images of the rest of the chars are similar to those of Fig. 4, taking into account that the lower the degree of foaming the lower is the size of the voids.

The bulk density of the fraction of carbon obtained as foam ranges from 0.32 to 0.22 g/cm³, values that can be considered low since there is not any free space between the particles, whereas the bulk density for the granules is higher (0.48–0.31 g/cm³). In both cases, a linear decrease of bulk density with the degree of foaming is observed, the decrease being more pronounced for the granular fraction. This means that increasing degree of foaming leads to

Fig. 3. Relation between degree of foaming and heating rate of the solid.

Fig. 4. SEM images of a section of char 1 in foam shape (a–c) and in granular

a logical lower amount of char in granular form, the granules being more swollen and, consequently, more porous.

The micropore volume of these chars, estimated from the adsorption isotherms of N_2 at 77 K and CO_2 at 273 K, is rather low, approximately $0.02 \text{ cm}^3/\text{g}$. Consequently, the low density of the carbon foam may be caused by the presence of macro and mesopores, which have been evaluated by mercury porosimetry; this technique yields curves for cumulative pore volume (see Fig. 5) in the size range $15 \mu\text{m}$ to 7 nm (pressure range, $0.1\text{--}20 \text{ MPa}$). Since the foams have voids larger than $15 \mu\text{m}$ (and even up to $100 \mu\text{m}$, see Fig. 4) the pore volume in the $100\text{--}15 \mu\text{m}$ has also been determined; for this measurement the picnometer containing the sample was filled with mercury under vacuum and the drop in the calibrated capillary was measured when the picnometer is exposed to atmospheric pressure. This value has been added to those obtained in the porosimetry curves, to build up Fig. 5.

In general terms, the pore volume for carbon foams is much higher than for the granular char 5, exceeding in some cases the value of $4 \text{ cm}^3/\text{g}$; most (60–80%) of the pore volume corresponds to macropores with a size larger than $1 \mu\text{m}$, visible under an optical microscope. The comparison of the curves 1–4 shows the evolution of porosity along foaming. Thus, the transition from low to medium degree of foaming (curves 4 and 3) produces a preferential development of the pores in a size range of $30\text{--}300 \text{ nm}$, whereas for the largest foaming (curves 1 and 2), the differences are

Fig. 5. Volume distribution of meso and macropores (mercury porosimetry) for several carbon foams and granular chars.

observed in the larger pore size, indicating that pores of increasing size are produced during the expansion. This effect is more noticeable when comparing the curves for foams 8, 1 and 9 (degree of foaming of 59%, 73% and 82%, respectively), where the formation of pores smaller than $10 \mu\text{m}$ is followed by formation of pores of larger dimensions.

3.3. An interpretation of the foam formation

The above results indicate that the pyrolysis of a large amount of precursor at high pressure and in the presence of steam occurs fast and leads to the formation of a carbon foam.

Olive stones have three major constituents: the natural polymers lignin (39%), hemicellulose (25%) and cellulose (36%). Its structure can be referred as a composite where the cellulosic fibres are held together in a lignin and hemicellulose matrix. In order to expand the precursor, the experimental conditions must facilitate: (i) the softening of the matrix, especially the lignin, as it is the main responsible for the mechanical resistance of the precursor, (ii) depolymerization of some components into an intermediate product which can be considered a “melt” of high viscosity, and (iii) foaming by the volatile matter evolved from the melt before polymerization into a solid occurs.

Previous work [15] reported that the lignin softens in the presence of steam even at 90 °C without a significant decomposition and this fact is used in the manufacture of shaped furniture. Consequently, the precursor particles may be soft when pyrolysis begins, thus allowing for the expansion of the precursor as from the first stages of pyrolysis, as it could be observed in experiments 12 and 13 (where pyrolysis was interrupted at 150 and 220 °C, respectively).

On the other hand, if part of the precursor is to be transformed into intermediate “melt” and then into volatiles one has to admit that fragmentation of biopolymers is taking place in addition to dehydration. It is well known that if the heating rate experimented by the solid is high, as in the so-called fast pyrolysis, the depolymerization/fragmentation reactions compete with dehydration reactions, which are almost exclusive during conventional pyrolysis [16–20]. The studies carried out with cellulose indicate that fast pyrolysis produces depolymerization to give the monomer levoglucosan, oligomers and other volatile compounds. It is probable that at high pressure the volatiles remain in the particle as a liquid, which boils or decomposes to gases when the temperature is increased. This will cause a local pressure increase within the particle, allowing first for its expansion and then for the formation of the foam.

Although the pyrolysis carried out in this work cannot be considered fast pyrolysis, the heating rate for the solid is high and the results of Fig. 3 seem to indicate that the larger the heating rate the larger is the transformation from granular to foam. According to Mok and Antal [21], the char produced in the transformation of the products of the depolymerization of cellulose is soft and fluffy, as suggested by Fig. 4c. However, the char from the dehydration has a strong structural integrity and retain the precursor shape, as it is usually observed in the char obtained in a conventional pyrolysis of the same precursor.

The experiment 1 of Fig. 1 can be interpreted according to the model of biomass decomposition [20]: the heat supplied to the reactor is first employed to evaporate the 25 ml

of water, increasing its partial pressure and, since it retards dehydration, it softens the precursor’s matrix. When the precursor reaches a temperature around 150 °C there is a pseudo-step that can be interpreted as a scission of the biopolymers of the precursor (endothermic process) to produce the high viscosity “melt” which undergoes dehydration, an exothermic process. This exothermic process leads to a faster pyrolysis and facilitates further fragmentations to produce monomers and/or dimers [16]. These volatiles initially remain as liquid because of the pressure inside the reactor, but boiling or decomposition take place when the temperatures increases, thus producing the expansion of the particles. Such expansion is large enough to put into contact neighbouring particles and, if the local temperature is high enough, as in the centre of the reactor, the viscosity of the “melt” will facilitate their coalescence (see Fig. 4c).

The behaviour described above is different from the one found in a conventional pyrolysis because in the latter the dehydration reactions predominate, thus favouring the formation of stable cross-linked bonds. The gases (mainly H₂O, CO₂ and CO) are released to the exterior of the particle through the transport channel of the vegetal material and the particle does not swell but it shrinks.

To analyse if the degree of expansion is related to the composition of the chars obtained at 500 °C, Table 2 collects the data corresponding to char 5 (0% foaming) and char 1 (73% foaming).

XPS and elemental analysis results indicate that the foam contains lower oxygen content than the same product in granular shape, the differences being more marked in char 5. In a similar fashion the FTIR spectra of char 1 (granular) and char 5 exhibit a slight enhancement in the signal at 1100–1300 cm^{−1}, indicative of the C–O bond. Therefore, it is possible to assume that the “melt” have lower viscosity when the oxygen content is low, thus facilitating the formation of the foam. For the same reason, one can expect a trend relating the formation of the foam to the aromaticity of the chars. However, there is no agreement between the results obtained with the different techniques. Thus, the results from elemental analysis and FTIR spectra seem to indicate that the aromaticity is higher in the foam than in the granular fraction, although the aromaticity quantified by the relative intensity of the band C_{1s} at 284 eV does not follow the same order. Therefore, some additional experiments are needed to clarify the chemical changes that lead to the formation of a foam.

Table 2
Oxygen content and aromaticity of some chars

Char	FTIR	XPS		Elemental analysis	
	C–H _{arom} (%)	Oxygen (wt%)	C _{1s} 284 eV (%)	H/C (at%)	O (wt%)
1 foam	62	13	82	44	13
1 granular	45	15	87	48	14
5	30	17	83	52	16

431 **4. Conclusions**

432 The formation of carbon foam along the pyrolysis of
 433 olive stones is facilitated when a reactor containing 200–
 434 300 g of precursor under 1 MPa of inert gas and steam is
 435 introduced into a furnace heated at 500 °C. Although the
 436 heat transfer from the furnace to the precursor is fast,
 437 the exothermicity of the own pyrolysis makes the solid
 438 heating occur at a higher rate, a minimum of 30 °C/min
 439 heating rate being needed to initiate the foam formation,
 440 and of 50 °C/min for this to occur extensively.

441 As the micropore volume of the foam is negligible, its
 442 low density (0.2–0.3 g/cm³) is due to the presence of meso-
 443 pores and macropores, 60–80% of the pore volume corre-
 444 sponding to pores with a size superior to 1 µm. In general,
 445 a parallelism between degree of foaming and the produc-
 446 tion of pores of increasing size is observed.

447 A mechanism is suggested to explain the formation of
 448 the foam as a combination of a softening of the precursor
 449 and a fragmentation of the biopolymers to produce an
 450 intermediate that can be considered as a “melt”. A fast
 451 increase in temperature reduces the viscosity of the “melt”
 452 and facilitates further fragmentation to volatiles, the
 453 expansion of which swells the particles to produce the
 454 foam.

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