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POROUS STRUCTURE AND MORPHOLOGY OF GRANULAR CHARS FROM FLASH AND CONVENTIONAL PYROLYSIS OF GRAPE SEEDS

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Abstract

This work studies the influence of the operating conditions used in the pyrolysis of grape seeds on the morphology and textural properties of the chars resulting. Flash and conventional (<u>283 $\mathrm{Kmin^{-1}}$</u> heating rate) pyrolysis have been used within a wide range of temperature (300-1000 ºC). The effect of a pretreatment for oil extraction has also been studied. The porous structure of the chars was characterized by adsorption of N_2 at 77 K, Ar at 77 K and 87 K, and CO_2 at 273 K and mercury intrusion porosimetry. The morphology was analyzed by scanning electron microscopy. All the materials prepared revealed an essentially microporous structure, with a poor or even negligible contribution of mesopores. Increasing pyrolysis temperature led to higher specific surface areas and lower pore size. The highest specific surface area values occurred within 700-800 ºC, reaching up to 500 m^2g^{-1} with pore sizes in the 0.4-1.1 nm range. No significant morphological changes were observed upon carbonization so that the resulting chars were granular materials of similar size than the starting grape seeds. The hollow core structure of the chars, with most of the material allocated at the periphery of

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the granules can help to overcome the mass transfer limitations of most common (solid or massive) granular activated carbons. The chars showed a good mechanical strength during attrition tests. These chars can be potential candidates for the preparation of granular carbons molecular sieve or activated carbons raw materials.

Keywords: Biomass; Pyrolysis; Microporous carbon; Char; Vitis vinifera.

1. Introduction

Agriculture, forestry and, in generally, biomass residues, are being increasingly considered as alternative resources for energy, chemicals and materials such as activated carbon. These by-products have proved to be promising raw materials for the production of activated carbons because of their availability at a low price [1].

The two main types of conversion processes used to obtain value-added products from biomass are thermochemical and biochemical. Thermochemical conversion of biomass includes gasification, pyrolysis, hydrothermal upgrading and combustion. Pyrolysis provides a solid carbon residue (char) with remarkable differences from starting biomass in composition, porosity, specific surface area, pore structure and physicochemical properties. The textural properties and ash mass fraction of grape seeds provide a useful basis for the preparation of activated carbons by different so-called physical and chemical activation methods, like partial gasification and catalyzed pyrolysis. Chars and activated carbons have been obtained from agricultural and fruit processing residues such as fruit stones, seeds and shells [2 - 4] widely available at low cost. It has been shown that not only the precursor but also the pyrolysis conditions have an important effect on the characteristics of the resulting chars [5, 6], which significantly affect to the quality of the subsequent activated carbons. Thus, starting materials with inadequate ash and/or carbon mass fraction or morphology are not recommended for the preparation of activated carbons. On the other hand operating conditions such as excessive temperature can lead to the collapse of the porous structure by thermal stress [7].

There are a variety of seed-containing fruits that have been considered for the preparation of activated carbons. However, little attention has been paid to grape seeds, even though they represent up to 15 % of the solid residues from the wine industry. Grape seeds are mostly burnt as fuel and in some extent used for cattle feed, despite of the fact that they are the source of oil for human consumption [8, 9], this application being so far minority.

Grape seed is an inexpensive and abundant starting material that has received little attention in spite of the fact that its valorization by pyrolysis can be an interesting source of gas and liquid fuels and carbon materials. The aim and significance of this research is to assess the potential of the carbon materials obtained, stressing the unique morphology of the char and its very narrow micropore size distribution. The granular morphology and this pore size distribution are a much demanded characteristic with the view in applications as activated carbon precursors for molecular sieves with potential use for gas separation [5], CO_2 capture [10] or energy storage [11] since it provides easy handling and low head loss when used in fixed beds.

To achieve a correct and complete characterization of chars and activated carbons with respect to porous structure, N_2 adsorption-desorption at 77K has been widely used for the determination of the main textural parameters such as specific surface area or pore volume by the BET method [12]. However, the low temperature together with the size of N_2 molecule can lead to erroneous determination of the adsorption isotherm in samples with narrow micropores [13]. Ar adsorption at 77 and 87K has been used as an alternative for a better determination of textural properties since the Ar molecule has a higher mobility than N_2 [14]. Still, for samples with narrow microporosity, this characterization is insufficient. For this reason, CO_2 adsorption isotherms at a higher temperature of 273K [15, 16], are used generally as a complement to nitrogen because that higher temperature facilitates the entry of CO_2 into the narrow micropores, even lower than 1nm, allowing a more complete characterization of porosity.

Pore sizes are classified in this study according to the International Union of Pure and Applied Chemistry (IUPAC), that is, micropore (width < 2 nm), mesopore (2 nm < width < 50 nm) and macropore (width > 50 nm). In turn, micropores have been classified in two subgroups, namely ultramicropores (width < 0.7 nm) and supermicropores (0.7 nm < width < 2 nm) [17].

The objective of this work is to study the preparation of granular porous materials from grape seeds by a single pyrolysis step. The influence of seeds pretreatment, pyrolysis temperature and heating rate (flash and conventional pyrolysis) on the porous structure and composition of the chars was evaluated.

2. Materials and methods

The seeds used in this study were collected from grapes of the red variety “Tinta de Toro” harvested for red wine manufacture in Toro (Zamora, Spain). The seeds were separated just after the fermentation of the must (grape juice), and were not treated with any chemical additive. The seeds were washed with distilled water repeatedly until no turbidity was observed, dried at 105 ºC for 1 day and stored at room temperature until use. The sizes of the raw seeds is between 2-3mm.

2.1. Pretreatment

The seeds were separated in two fractions. The first of them was pyrolyzed just after the preparation described above. These seeds were designated as NEX (non-extracted). The other fraction was subjected to n-hexane extraction for 24 h in a Soxhlet apparatus to remove oil [8]. After extraction the seeds were washed with water and dried at 105 ºC for 1 day. These seeds were designated as EX (extracted).

Oil mass fraction of grape seeds depends on grape variety, though the usual range is a mass fraction of 10-16 % of the dry seed [8], though in this instance it is less than 9 %.

2.2. Pyrolysis

Figure 1 shows a schematic diagram of the pyrolysis unit. Pyrolysis was carried out in a vertical quartz tube (68 cm length and 4.8 cm i.d.) placed in a sandwich-type electrical furnace. A 100 mL min^{-1} nitrogen flow (all flows were referred to normal condition) was continuously passed downward. Two K-type thermocouples placed on the furnace wall and at the central part of the reactor (hot zone) were used to control the pyrolysis temperature. A quartz basket with 7-8 g of grape seeds was maintained in the cold zone of the furnace for air removal from where it was displaced to the hot zone by means of a rod. After the heat treatment the basket was cooled in the cold zone and finally the char was recovered and weighted to determine burnoff [18]. The operating variables tested were the heating rate (slow heating (SH): 283 Kmin^{-1} and FH: flash heating) and temperature (300 to 1000 ºC). For the slow-heating samples, the basket was placed in the central part of the reactor, air was purged and then heating of the system was started. For the flash-heating samples, the basket with the grape seeds was kept in the cold zone of the reactor until the central part reached the desired pyrolysis temperature; then the basket was moved into the hot zone and the sample reaches the operating temperature in few seconds after its sudden displacement into the hot zone of the reactor. Flash pyrolysis has been defined as a process characterized by rapid devolatilization in an inert atmosphere, at high heating rate and reaction temperatures between 450 and 1000ºC [19].

Figure 1.

2.3. Samples characterization

Prior to pyrolysis runs, the specimens were characterized by TGA. This technique measures the weight change of a sample with temperature and/or time in a controlled atmosphere, providing characterization of materials that lose o gain weight due to decomposition, oxidation or dehydration. TGA of the seeds was obtained in a Mettler SDTA851^{e} thermobalance in order to learn on the thermal decomposition of this material. A seeds sample weight of about 400 mg was used in TGA runs with a heating rate of 283 Kmin^{-1} under 100mLmin^{-1} N_2 flow. The elemental composition of chars (C, N, H and S) was analyzed by a LECO CHNS-932 apparatus. Specific surface area and pore volume of the chars were measured by adsorption of N_2 at 77 K, Ar at 77 K and 87 K, and CO_2 at 273 K in an automated volumetric gas adsorption Micromeritics Tristar 3020 with a VacPrep 061 degas system. The samples were previously outgassed for 7 h at 150 ºC to an atmospheric pressure. The surface area of the samples was calculated from N_2 isotherms using Brunauer-Emmett-Teller equation (S_{BET}) [12] and the t-method for the micropore volume, whereas Dubinin-Astakhov (DA) model was applied to the CO_2 isotherms to determine the DA surface area (S_{DA}) and micropore volume [20] and the Density Functional Theory (DFT method) was used to calculate the micropore size distribution [21]. A Quantachrome Poremaster 33 mercury porosimeter was used to characterize the meso and macroporous structure of the chars.

The morphology of the grape seeds and the chars was evaluated by Scanning Electron Microscopy (SEM) with a Hitachi S-3000N apparatus. The specimens for SEM observation were metalized with gold to prevent electrical charging during examination using a Sputter Coater SC502. Imaging was done in the high vacuum mode under an accelerating voltage of 20 kV, using secondary electrons. The ash mass fraction of the raw material was determined by calcinations at 800 ºC in a crucible for 2 h.

To obtain samples of the outer layer of chars, the char was subjected to attrition on a sieve (1mm opening) in an Orto Alresa vibrating sifter operating at a frequency of $42 s^{-1}$.

3. Results

Figure 2 shows the TG curve of EX sample at 283 $K min^{-1}$ heating rate until 900 ºC in N_2 atmosphere during 200 min. This curve is representative of all samples showing a greatest weight loss occurs between 300 and 500 ºC. These results indicate that at temperatures below 500 ºC pyrolysis can be considered incomplete. A pyrolysis time of 2 h was considered acceptable for the rest of the study.

Figure 2.

3.1. Influence of pyrolysis variables

Table 1 summarizes the pyrolysis yields (dry oil-free basis). In the 300 to 1000 ºC thermal range, the yield values obtained are from 70 to 30 %. The pyrolysis yield showed as a general trend to decrease when the temperature was increased. Previous studies on biomass pyrolysis show the same trend [22 - 34], showing a high yield of biochar at low pyrolysis temperatures as a results of incomplete pyrolysis [23, 24]. No significant differences were observed between SH and FH samples, although, in general FH provided slightly lower yields. This observation suggests that sudden devolatization gives rise to lower residence time of volatile products within the seeds somewhat diminishing the amount of carbonaceous solid formed upon condensation of pyrolysis products [32, 33].

Table 1.

The elemental composition of the char samples is summarized in Table 2. Consistently with the TG curve (Figure 2) and yield (Table 1), the C percentage of the chars undergoes a significant increase within the 300-500 ºC range up to around 80 % and then a progressively slower thermal decomposition allows approaching to 90 % as a final charring level. Moreover the trend to increase slightly with the pyrolysis temperature is clearly shown even taking into account the results dispersion (around 1-2 %) that is typical of usual heterogeneity of biomass materials. And while carbon percentage increases, hydrogen mass fraction decreased from 6 to less than 1%. Previous studies on pyrolysis of different types of biomass show the same trend in the evolution of C and H relative mass fractions [24 - 28, 35, 36].

The C mass fraction of the EX chars are somewhat higher than those of NEX suggesting that the pyrolysis of the oil fraction generates a carbon residue with lower carbon mass fraction than the oil-free matter of the seeds. No clear influence of the heating rate on the elemental composition of the chars can be concluded in spite of the results in Table 1, where flash pyrolysis (FH) seems to provoke a somewhat more intense thermal decomposition leading to lower yield values. It is important to remark the almost negligible sulphur mass fraction of the starting grape seeds, which even diminishes in the chars. With regard to N mass fraction, a significant reduction is observed upon pyrolysis and the chars show in general percentages lower than 2 %.

The ash mass fraction of the raw material of the NEX and EX seeds are 2 % and 8 % respectively.

Table 2.

3.2. Specific surface area

Figure 3 shows the 77 K N_2 adsorption isotherms of the chars obtained at different temperatures.

Figure 3.

The BET surface areas calculated by N_2 adsorption of the chars are summarized in Table 3. Most temperatures tested show that chars of FH series lead to higher specific surface area than SH series, particularly for the EX series. The highest adsorption values correspond to the chars obtained by flash pyrolysis at an intermediate temperature of 600-700 ºC. Below that temperature a very poorly developed specific surface area can be observed in spite of the fact that devolatilization occurs mostly at lower temperature. The extraction of oil from the grape seeds does not show a clear effect in the development of S_{BET}. The porous structure is dominated by microporosity according to the shape of the isotherms with a sharp increase of N_2 adsorption at low relative pressures followed by a quasi-horizontal branch up to $P/Po \approx 0.95$ (Figure 3).

Table 3.

To complete the characterization of mesoporous range the char samples was also carried out by Ar isotherms at 77 and 87 K. As can be read in Table 3 the results of specific surface area of the isotherms of Ar at 87 K are slightly higher than at 77 K due to the increased mobility of Ar molecules. The low values of specific surface area measured by Ar adsorption reveals the low contribution of mesopores to the surface area and corroborate the results obtained with N_2.

To learn more on the microporous structure of the chars, the CO_2 adsorption isotherms were obtained at 273 K. As an example, Figure 4 shows the CO_2 isotherms of the chars obtained at 800 ºC.

Figure 4.

The Dubinin-Radushkevich and Dubinin-Astakhov equations have been used to describe micropores filling and the energetic heterogeneity of porous solids [37]. But while several studies [38, 39] postulated that the Dubinin-Radushkevich equation applies only to solids with a uniform structure of micropores, others [37, 40 - 43] proposed a modification of this equation when a microporous solid possesses micropores of the same shape but of different sizes. One of them is the well-known Dubinin-Astakhov (DA) equation, which can be applied to the description of the adsorption on structurally heterogeneous solids [20, 44]. In this work the Dubinin-Astakhov method is used because of the heterogeneous structure of the samples and the better regression coefficient obtained in all cases.

The values of surface area obtained from the DA method are summarized in Table 4. These values are significantly higher than those reported in Table 3 from N_2 adsorption, which indicates the existence of a narrow microporosity that become more important as the pyrolysis temperature increases. Temperatures below 500 ºC yielded low values of surface area which is another evidence of the incomplete pyrolysis at those temperatures [23, 24]; understanding this as the incomplete removal of volatile matter from the samples, which affects negatively the development of porosity. The surface area increased with temperature markedly from 400-500 ºC, peaking around 800 ºC for both NEX and EX samples. From 900 ºC the microporous structure seems to collapse during pyrolysis, as evidenced by the dramatic loss of specific surface area. Similarly to the results observed for the BET (N_2) surface area [7, 31, 45]. Flash pyrolysis of the extracted grape seeds yielded the highest values of the CO_2-DA surface area.

Table 4.

3.3. Pore volume

Figure 5 shows the micropore volume (calculated with the t-plot method from N_2 isotherms and with the DA method from CO_2 isotherms) of the chars obtained under different conditions plotted versus pyrolysis temperature. As can be seen no significant development of porosity occurs below 600 ºC. The mesopore volumes were always negligible with adsorbed volumes lower than 0.01 cm^3g^{-1} for all the temperature range.

Figure 5.

The micropore volume from CO_2 isotherms increases with temperature peaking around 800 ºC for both NEX and EX samples. From 900 ºC the microporous structure seems to collapse during pyrolysis, as evidenced by the dramatic loss of porosity [7, 31, 45]. The comparison between N_2 and CO_2 micropore volume indicates that pyrolysis temperatures of 800-900 ºC maximize the contribution of narrow microporosity (microporosity below 1nm width). No significant influence of heating rate and seeds pretreatment was observed in the micropore volume obtained from CO_2 isotherms (Figure 5b).

3.4. Pore size distribution

The pore size distribution (PSD) is a key element in the characterization of porous carbons and a number of methods were developed for the PSD analysis. The density functional theory (DFT) is widely used for the characterization of pore structure of activated carbons and other porous materials [21].

The micropore size distributions calculated from CO_2 isotherms by the DFT method are shown in Figure 6. For simplicity only the range from 600 to 900 ºC of pyrolysis temperature is evaluated since this is the temperature range the relevant porosity development was achieved.

Figure 6.

No significant differences were found in the PSD profiles with heating rate within the NEX or EX series. On the contrary a sharp difference can be seen between the EX and NEX samples in terms of differential pore volume, which is much higher for the EX series. This behavior may indicate that the residue of pyrolyzed oil present in the NEX samples blocks some pores leading to lower development of microporosity in the micropore lower than 1nm. Although Figure 6 shows different PSD profiles depending on the pyrolysis temperature, it can be seen that the micropores show widths falling mainly within the 0.40 to 0.95 nm range for all series. Furthermore these PSD profiles can be considered as bimodal due to the maxima of the adsorbed volume curves observed around 0.55 and 0.9 nm pore width.

Figure 7 shows the mercury intrusion porosimetry characterization of the samples obtained for a pyrolysis temperature of 800 ºC. The plotted data correspond to the volume of intruded mercury in the 0.01 – 2.50 µm pore size range. As can be observed all the samples showed an important contribution of macropores and negligible volume of narrow mesopores. The higher volume was obtained for the samples from flash pyrolysis reaching values above 0.5 cm^3g^{-1} and showing profiles centered around 0.4 µm, while samples obtained by slow heating showed values of adsorbed volume much lower, particularly in the narrow mesopore range, and with a pore diameter centered around 0.2-0.3 µm. The higher porosity of the samples obtained by flash heating can be attributed to sudden release of pyrolysis gases that leads to channeling [46].

Figure 7.

Figure 8 shows the macropore volume determined by mercury porosimetry for the chars prepared by flash pyrolysis at different temperatures. A gradual increase can be observed with pyrolysis temperature peaking around 800 ºC. The porosity is, in general, higher for the chars prepared from extracted seeds.

Figure 8.

3.5. Morphological analysis

The grape seeds were examined by scanning electron microscopy to study their morphology and surface structure. Figure 9 shows the char produced by flash pyrolysis at 800 ºC of extracted seeds. For all the specimens examined the char maintained the granular morphology of the raw seed with no significant changes in size, even upon the most severe pyrolysis conditions, although some of the specimens showed opening of the coat (Figure 9), presumably due to internal overpressure during pyrolysis.

Figure 9.

The outer surface exhibits smooth and homogeneous texture (Figure 10a) resulting from the carbonization of the cuticle tissue of the coat, with no relevant presence of cracks and large macropores, that show that the structure of the outer surface was preserved in the char after pyrolysis [34]. Depending on the applications of the char, the outer layer can be an undesirable resistance for the diffusion of molecules, or can be potentially a barrier for separation. On the contrary, the inner layers exposed by the opening of the outer layers of the coat (Figure 10b) showed a well-developed network of channels and macropores that can provide favorable conditions for diffusion [47].

Figure 10.

The material allocated inside the coat, i.e. albumen and embryo, is mostly removed during pyrolysis due to the high content in volatile components, resulting in a low density or carbon foam-like material, as can be seen in Figure 11a. A closer view of the carbonized coat (Figure 11b) shows that it has an average thickness of around 500 µm, and it is composed of three layers of differentiated structure, all of them with an important presence of channels and macropores. Therefore, the char has a hollow core structure, which together with the macroporous structure can favor the diffusion of molecules in adsorption or catalysis applications [47].

Figure 11.

To study the pore structure of the different layers of the char particles EX800FH sample was subjected to attrition in a vibrating sifter. The samples have a suitable balance between surface area and burn-off, so that the integrity and strength of the particles can be preserved. During the attrition tests three fractions of the powder passing through the sieve openings (<1 mm) were collected at regular intervals of 2 h. The results in Table 5 show a rather homogeneous development of surface area throughout the particle wall. The most noticeable differences can be found for S_{BET}, the outer layers showing significantly lower values of S_{BET}, which suggest the prevailing generation of narrow porosity in the inner layers. In the case of S_{DA} a similar behavior was observed.

It is also remarkable that the char particles have a good resistance to attrition, since only 7.5 % of the initial mass was lost in the first 2 h of the test. This resistance increase in the inner layers. The strength of the particles is of great importance for the sake of handling and performance in potential applications.

Table 5.

4. Conclusions

The influence of operating conditions on the pyrolysis of grape seeds was investigated in order to obtain a granular char with potential application as molecular sieve or precursor of activated carbon. This agricultural by-product appears to be suitable for activated carbons because of their preparation its low sulfur (less than 0.15 %) and ash mass fraction.

The results obtained in this research show that interesting carbonaceous materials can be prepared from grape seeds in a single pyrolysis stage. The resulting chars show a bimodal pore size distribution (micro and macropores). In the optimum conditions, upon oil extraction pre-treatment of seeds followed by flash pyrolysis at 800 ºC, materials with specific surface area around 500 m^2g^{-1}, a micropore volume of 0.2 cm^3g^{-1} and narrow distribution centred within 0.4-0.9 nm. Narrow mesopore volume was negligible and the contribution of macropores was very important (1.1 cm^3g^{-1}). In the case of the chars obtained from grape seeds a hollow core structure is obtained, with most of the adsorbent material allocated at the outer part of the particle thus minimizing the diffusion path. This structure combines the benefits of granular materials with diffusion rates comparable to those of powdered materials.

The pyrolysis process showed a great effect on the final product, and careful selection of carbonization conditions significantly affect to the porous structure of the resulting carbons.

So the results and significance of this research assess the potential of the carbon materials obtained, stressing the unique morphology of the char and its narrow micropore size distribution. It is relevant that the operating conditions that favor the production of the most interesting chars are compatible with the pre-extraction of valuable oil and with the pyrolysis of grape seed to promote gas or liquid products.

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