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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 (283 K min^{-1} heating rate) pyrolysis have been used within a wide range of temperature (300–1000 °C). 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 °C, reaching up to 500 m^2 g^{-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 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.

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

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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 77 K 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 87 K 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 273 K [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 1 nm, 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 °C for 1 day and stored at room temperature until use. The sizes of the raw seeds are between 2 and 3 mm.

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 °C 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*

Fig. 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 K min^{-1} and FH: flash

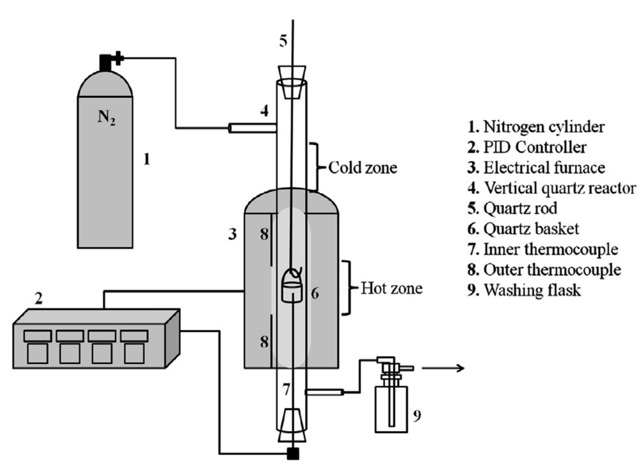

Fig. 1 – Schematic diagram of pyrolysis system.