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Method for promoting in-situ hydrochar porosity in hydrothermal carbonization of almond shells with air activation

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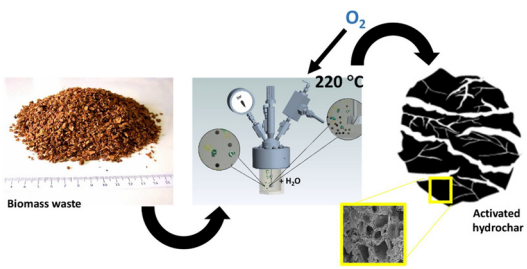
GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a new procedure for *in situ* hydrochar activation during hydrocarbonization of biomass (almond shell) is proposed. This approach suggests the addition of a controlled oxidizing gas stream (i.e. synthetic air) during the process for different periods of time, in order to promote the hydrochar porosity. Characterization of prepared materials revealed a noticeable development of porosity with apparent surfaces areas up to 320 m^2/g. A highlighting variety of functional acid groups especially sensitive to air supply time was confirmed by surface chemistry analysis. Promising preliminary results show the effectiveness of this alternative approach synthesis strategy in converting a low value lignocellulosic biomass into porous materials with potential applications such as adsorption, electrical energy and gas storage or catalysis.

1. Introduction

Last years have witnessed the significant push of hydrothermal carbonization (HTC) as an effective process to produce carbon materials as compared to conventional carbonization of biomass. Apart from being more sustainable and less expensive, it is easier to implement since it require simpler installations and allows the use of high moisture materials [1–3]. Moreover, the carbon capture index is higher when compared with traditional pyrolysis, contributing to the decrease of greenhouse gases emission. While HTC has widely proven to improve the carbon densification and the heating value of biomass, the low porosity development of biomass-derived hydrochars (BDHCs) has delayed the effective and straightforward exploitation of its products for several applications. Therefore, several strategies have been proposed for successful porosity development of BDHCs [4]. The most conventional techniques are post-HTC physical/chemical activations [3,5–12] usually using high temperatures (600–900 °C) under inert conditions or feed of CO_2 [13,14], as well as templating methodologies [2,15]. Using these strategies, BDHCs having up to 3400 m^2/g BET surfaces areas have been reported. Moreover, several studies have been carried out in

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order to find better control over the resulting porosity and surface functionality of the post-activated BDHCs. For instance, Román et al. [16] have recently found that the final yield and type of physical activation can allow a better control over the resulting porosity. Also, Falco et al. [6] have found that the HTC temperature is also an extremely influential parameter affecting the final porosity of BDHCs. Likewise, Jain et al. [3,12] have reported in different studies that pretreatments of biomass with $ZnCl_2$ and H_2O_2 can enhanced significantly the chemical activation of final BDHCs products. In spite of possible drawbacks of post-activation methods, authors agree in the fact that the preparation of highly porous carbon materials from BDHCs products can be very advantageous since they can exhibit special properties in terms of surface functionalities which can make them efficient as a precursor for chemical activation [3,10–12,14,17–19]. However, studies about *in situ* or *one-pot* processes for the BDHCs' production with the aim of tailoring the surface chemistry and or to improve its textural characteristics have been scarcely published. This alternative route could entail several advantages such as savings in energy, preventing or minimizing the generation of chemical wastes or reduce synthesis times in order to produce less expensive carbon materials. Oxidizing gases such as steam, carbon dioxide, air or a mixture of these gases have been widely used as common suitable gasification agents for post-synthesis physical activation of biomass-based charcoal [20–22] and BDHCs [11,13,18,23]. In this work, the injection into the vessel of controlled oxidizing gas streams (i.e. synthetic air) during the HTC process is proposed as an *in situ* BDHCs activation method. As precursor we have used almond shells (AS) that are very abundant wastes in the Southern part of Iberian Peninsula.

2. Materials and methods

2.1. Biomass-based precursor

Almond shell (AS) was used as precursor of BDHCs. The material was supplied by local manufacter (Bioterra Pasat-Profuse, Corte de Peleas, Badajoz, Spain). In successive steps, dry AS were crushed, milled and screen-sieved (1–2 mm). AS were analyzed in terms of their proximate and ultimate analyses (Table 1) following technical specifications reported elsewhere [18]; the lignocellulosic composition of almond shells was determined according to Van Soest method. Also, AS thermogravimetric behavior under both air and nitrogen atmospheres was analyzed with a thermobalance (TA Instruments) using a heating rate of 10 °C min^{-1} and a gas flow of 100 mL min^{-1}, details given elsewhere [23].

2.2. Hydrochar and in situ activated hydrochars production

The production of BDHCs' was done using 100 mL of deionized water and 10 g of AS that was added to a teflon sealed vessel and then inserted into the 0.15 L stainless steel autoclave (Parr), which was then heated in an oven at 220 °C during 20 h. These experimental conditions were selected to obtain a suitable carbon densification with a moderate solid yield (near 65%), as already was demonstrated previously [24]. Maintaining these heating conditions, a controlled synthetic air stream (Linde, HiQ Synthetic Air 5.0 Zero, Purity > 99.9999%) was used as activating agent) was injected inside the vessel at 8 bar through an inlet valve for a precise period of time (between 5 and 30 min). After that, the autoclave was cooled down at room temperature and the BDHCs collected, washed with distilled water and dried in an oven at 110 °C overnight. The BDHCs were denoted as HC-At, where t represents the time of the air stream addition in minutes.

Table 1
Proximate and ultimate analysis of AS raw material.

Proximate analysis (%)				Ultimate analysis (%)				
Fixed Carbon	Moisture	Volatile matter	Ash	C	H	N	S	O[a]
14.2	11.2	73.0	1.6	50.50	6.60	0.20	0.01	42.69

[a] By difference 100-(%C + %H + %N + %S).

2.3. Hydrochar and in situ activated hydrochars characterization

Textural properties of BDHCs were assessed from nitrogen adsorption isotherms at 77 K obtained with an Autosorb-1, Quantachrome. Prior to adsorption analysis, the samples were outgassed at 250 °C for 4 h. The apparent surface area was determined by the BET method (S_{BET}); the total pore volume (V_t) was estimated from the amount of nitrogen adsorbed at the relative pressure of 0.95; the external surface (S_{ext}) was assessed by the α-method [18]; the volume of micropores (V_{mi}) was determined through the Dubinin–Radushkevich equation[25] and the volume of mesopores (V_{me}) was estimated as the difference between V_t and V_{mi}. Surface morphology studies were carried out by scanning electron microscopy with coupled X-Ray Electron dispersion (SEM-EDX, Quanta 3D FEG, FEI). The samples were prepared by depositing about 50 mg of sample on an aluminium stud covered with conductive adhesive carbon tapes, and then coating with Rh-Pd for 1 min to prevent charging during observations. Imaging was done in the high vacuum mode at an accelerating voltage of 30 kV, using secondary electrons under high vacuum conditions. The surface chemistry of hydrochars was studied by FTIR spectroscopy. FTIR spectra were recorded with a PerkinElmer model Paragon 1000 PC spectrophotometer, using the KBr disc method, with a resolution of 4 cm^{-1} and 100 scans.

3. Results and discussion

3.1. Biomass-based precursor analysis

The proximate and ultimate analyses of AS is shown in Table 1. AS display a typical proximate analysis of a lignocellulosic material [18] with high volatile matter content and a fixed carbon content around 15%. Elemental analysis depicted high carbon content and low content in sulphur and nitrogen which could be advantageous regarding the potential subsequent use of the HCs in particular applications such as biofuel [18]. The precursor lignocellulosic analysis gave hemicellulose, cellulose and lignin contents of 25.5, 32.5 and 24.8%, respectively, which is typical for other biomass shells or stones [17,18].

The TG/DTG curves under air and nitrogen atmospheres are displayed in Fig. 1. The thermal degradation in the left up thermogram represents the TG profile in an inert atmosphere (N_2) show at around 160 °C the removal of moisture and the starting of AS devolatilization process for temperatures above 300 °C. It is visible the rapidly decrease of the weigh between 300 and 400 °C followed by slow weigh loss up to 600 °C. According to DTG profile (Fig. 1 left down), the maximum rate of weight loss occurred at around 350 °C. This behavior can be considered a typical pyrolysis curve of lignocellulosic precursors [21]. From the thermogravimetric analysis in air (Fig. 1 right up), three main steps of weight loss can be observed. The first one below 150 °C can be associated with the water evaporation, whereas the second (200–350 °C) and the third (350–600 °C) can be related to the AS combustion process. According to Ghetti et al. [26] the extent of weight loss in these two combustion steps depends on biomass content on hemicellulose and cellulose, and the second combustion step is associated to the lignin content. From 600 °C, the gasification of the entire mass takes place. Similar TG profile have been reported for cherry pits [20]. The DTG profile (Fig. 1 right down) shows clearly the two combustion steps whose height can be directly related to the sample reactivity [26].