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Textural and fuel characteristics of the chars produced by the pyrolysis of waste wood, and the properties of activated carbons prepared from them

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ABSTRACT

Chars were obtained by the pyrolysis of waste wood samples of different origin – silver fir (*Abies alba*), holm oak (*Quercus ilex*), stone pine (*Pinus pinea*) and Pyrenean oak (*Quercus pyrenaica*) – at 600 °C in a pilot scale installation. The thermo-chemical characteristics of the resulting materials were fully investigated using a combination of standard techniques. The char yield ranged from 23 wt% to 29 wt%, depending on the precursor wood. The recovery of C achieved was 42–51 wt%, increasing with the hemicellulose content of the wood. In addition, the chars had low volatile matter (8–12 wt%) and ash (2.0–8.5 wt%) contents. The higher heating values of the chars were relatively high (31–35 MJ kg^{-1}) and comparable to that of a semi-anthracite (silver fir and stone pine chars) or medium-volatile bituminous coal (holm and Pyrenean oak chars). Their combustion intervals, and ignition, volatilization and burnout temperatures, were similar to those of commercial coals. The chars had a microporous structure (pore size < 2 nm) with BET surface areas in the range 314–405 $m^2 g^{-1}$. Their treatment by CO_2 at 800 °C resulted in activated carbons with pore sizes below 0.89 nm and BET surface areas of 543–815 $m^2 g^{-1}$.

1. Introduction

World demand for energy in 2050 will be double that of 2000 – a demand that cannot be met by nuclear and fossil fuels combined [1]. Dwindling fossil fuel reserves and the lack of will to use nuclear energy in many countries means that other sources of energy must be found. These energy sources should also be CO_2-neutral [2]. As part of the drive to find and use new energy resources, the EU has set a 2020 goal for substituting 10% of traditional fuels by biofuels [3]. The production of char from biomass has generated much interest in this respect since these fuels sequester carbon [4].

The so-called "second generation" technologies for the production of fuels allow the use of a wide range of non-food cellulosic biomass feedstocks. These include silvo-agricultural wastes, e.g., forest waste (current production of which is about 3 billion tonnes per year [5]), straw, bagasse, corn stover, sawmill residues, and paper manures, as well as purpose-grown energy crops [6,7]. Cellulosic biomass normally consists of cellulose, hemicellulose and lignin in the proportions 35–50%, 15–25% and 15–30% respectively [6]. Biomass can be thermochemically transformed via direct combustion [8,9], gasification, co-gasification with coal [10] or pyrolysis [11]. The latter is an attractive way of producing biofuels in the form of bio-oil, biochar and biogas [12], and is very efficient compared to the other methods. In pyrolysis, the biomass is heated in the absence of oxygen, decomposing it into a solid residue (char), vapour/aerosol, and gas. While the vapour/aerosol can be quickly condensed to bio-oil, and the uncondensed gases can be used to make electricity via the turning of gas turbines, the char is generally defined as a by-product [13]. However, while it typically only makes up about 15 wt% of the final products, it accounts for some 25% of the energy of the biomass feedstock [14]; it might therefore have potential as a fuel if burned under optimum combustion conditions.

The quality of pyrolytically produced char as a fuel depends on the original plant species, the dimensions of the pieces of waste material pyrolyzed, the type of pyrolytic kiln used, and the type of pyrolysis undertaken [15]. It can be burned alone or in combination with other fuels [16], but in recent years it has also been assessed as a carbon sequestration agent [16–18], a soil amendment agent [19], in the production of activated carbon (via heating in a reactive atmosphere containing water vapour, air or CO_2, or via chemical activation with $ZnCl_2$, KOH and H_3PO_4) [20,21], as a component of functional textiles (e.g., in nano-carbon-laced fabrics), and in shielding against electromagnetic radiation [22]. Biochars may also have applications in animal feeds. In vivo studies have

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shown that the pores of certain biochars can retain mycotoxins, aflatoxin B1, zearalenon, vomitoxin and *E. coli*. The incorporation of 1–5% biochar in feedstuffs can provide important health benefits to young animals [23,24].

Many of the reports published on chars derived from the pyrolysis of biomass have focused on different energy recovery processes (combustion, gasification, co-gasification), and on the sequestration of CO_2 and its applications in agriculture as a soil corrector. Few have examined the textural characteristics of these chars or compared those obtained from different types of waste wood (WW).

In the present work, four types of char were prepared from different types of WW in a pilot pyrolysis plant. The aims of this study were to examine their textural properties (relating the results obtained to the initial characteristics of the WW), to determine the fuel properties of the chars, and to compare the textural properties of the activated carbons made from them.

2. Experimental

2.1. Waste wood

The WWs used in this work came from forestry cleaning and conservation work in the Catalonian Pyrenees, and consisted of silver fir (*Abies alba*), holm oak (*Quercus ilex*), stone pine (*Pinus pinea*) and Pyrenean oak (*Quercus pyrenaica*). Approximately 500 kg of each WW were crushed, producing chips of dimensions $250 \times 100 \times 50$ mm.

2.2. Thermo-chemical properties of the initial wood samples

Proximate and ultimate analyses of the WWs were performed following standards ISO562 and ISO1171 respectively. A CHNS 923 Elemental Analyser (Leco, Germany) operated at a combustion temperature of 1100–1200 °C was used for elemental analysis on a dry basis (d.b.). Total carbon, nitrogen, sulphur and hydrogen contents were determined in accordance with standard ASTMA D-5773. The oxygen content was determined using a VTF-900 apparatus (Leco, Germany).

The lignin and cellulose contents were determined by the TAPPI T22 method [25] and the Kushner procedure [26] respectively. The higher heating value (HHV) of the WWs was evaluated using a C4000 (Ikaweeme, India) automatic bomb calorimeter.

2.3. Pyrolysis

The chars were prepared by the pyrolysis of the WW samples in a Grauthermic-CSIC technology pilot plant [27] with several fixed bed reactors in parallel and a system for energetically revalorizing the pyrolysis gases produced. This fixed bed reactor consisted of six vertical, tubular, stainless steel reactors (length 1510 mm, wall thickness 6 mm, external diameter 154 mm). Pyrolysis was performed in the normal atmosphere inside the reactors, without the addition of nitrogen. Each reactor had a capacity of 12 kg and was fed through a PN-16 3-type valve. Batches of WW (72 kg) were heated (via propane gas combustion) over a reactor residence time of 4 h at 600 °C ± 10 °C. Previous studies [28,29] have shown this temperature to return the best results in terms of non-condensed gas [≈100 $Nm^3\ h^{-1}$ at 400 °C compared to ≈150 $Nm^3\ h^{-1}$ at 600 °C)] and electricity production [≈434 kW h t^{-1} at 400 °C compared to ≈563 kW h t^{-1} at 600 °C]).

The pyrolysis gas flowed out by natural convection and was cooled in two successive condensers (water- and cryogenically-cooled respectively) to recover the bio-oil. The condensers were composed of a number of stainless steel tubes, the upper and lower part of each being equipped with a small chamber for the expansion of gases and bio-oil collection. The gas temperature at the entrance of the first condenser was near 250 °C, and about 100 °C at the exit. The gas reached the second condenser at 45 °C. Gas condensation is enhanced by a cryogenic cooling system to guarantee a gas temperature below 5 °C in the second condenser. The condensed oils (bio-oils) were collected in a deposit equipped with a level-maintaining valve and a pump.

The non-condensed gases were filtered and led to a Totem® (Total Energy Module) turbine for the production of electricity. After completing the pyrolytic process, the reactors were cooled for 4 h, opened, and the char removed by aspiration. To avoid the oxidation of the char in the air, the samples were immediately stored in vacuo in polyethylene bags.

The composition and yield (by weight) of the bio-oil and char fractions were determined; the difference between the sum of these weights and that of the WW corresponds to the weight of the non-condensed gas. Each result presented in this paper is the mean value of the data obtained in at least two experiments.

Representative samples of the different chars were milled in a Pulverisette 6 ball mill (Fristsch, Germany) in an N_2 atmosphere to a particle size of < 40 μm. The milled samples were stored in vacuo in polyethylene bags until use.

2.4. Thermochemical properties of the chars

The chars were subjected to proximate and elemental analysis and the determination of their HHVs, as described for the initial wood samples (see Section 2.1).

The inorganic impurities in the chars were analyzed using an AA-630 atomic absorption/emission spectrometer (Shimadzu, Japan), employing a deuterium lamp for background correction. Zn, Fe, Mn, Al, Ca, Mg and Si concentrations were estimated by atomic absorption; K and Na were evaluated by atomic emission.

2.5. Structural and textural properties

X-ray diffraction analysis was undertaken using a D8 Discover diffractometer (Kα Cu radiation, 30 mA, 40 kV) (Bruker, Germany) over the 2θ angular range of 10–100°. The different mineralogical phases were identified using the Match Phase Identification programme (Powder Diffraction software v. 1.11d) (Crystal Impact GbR, Germany).

The porosity characteristics of the chars and activated carbons were examined by N_2 adsorption at 77 K using a Coulter SA1100 automatic adsorption analyser (Beckman Coulter, USA). The porous features were evaluated by analysis of the corresponding isotherms using the Brunauer–Emmet–Teller (BET) equation, Dubinin's theory, the comparison plot, and the DFT method [30]. The total surface area was estimated from the average values obtained using the Dubinin–Radushkevich theory, comparison plot and DFT methods.

The chars were morphologically characterized by scanning electron microscopy (SEM) using JSM 6500 F field emission microscope (Jeol, Japan). Powdered samples were embedded in a polymer resin and coated in graphite for all observations.

2.6. Activation of the chars

Representative samples of the chars were placed in a quartz reactor, containing a porous plate, under N_2 (100 ml min^{-1}). Activation was performed under a CO_2 atmosphere (74 ml min^{-1}) at 800 °C in a electric oven (Carbolite, Germany) for 6.5 h.

The reactivity (R, % h^{-1}), was determined from equation (1):

$$R = \left(\frac{m_i - m_a}{m_i}\right)\frac{1}{t_a}100 \quad (1)$$