Integrating physicochemical information to follow the transformations of biomass upon torrefaction and low-temperature carbonization

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HIGHLIGHTS

- Softwood, hardwood and olive stone heated at 250 and 450 °C were characterized.
- Results from bulk chemical and physical techniques and microscopy were integrated.
- Moderate chemical and structural changes occurred at 250 and drastic ones at 450 °C.
- Differences between hardwood and softwood were subtle, but large for olive stone.
- Greater heterogeneity was observed at torrefaction than at carbonization temperatures.

ARTICLE INFO

ABSTRACT

Morphological and structural changes of different types of biomass after torrefaction and low-temperature carbonization processes have been investigated using a variety of characterization techniques comprising Fourier-Transform infrared spectroscopy (FTIR), gas adsorption at different pressures, thermogravimetry, optical and scanning electron microscopy techniques together with chemical analysis. The biomasses selected included softwood chips (pine), hardwood chips (acacia, eucalyptus, forest residues from eucalyptus) and olive stone. Torrefaction led to the enrichment of carbon and a decrease in reactivity, accompanied by a decrease in the hydrogen- and oxygen-bearing functionalities and a slight increase in aromatization. This was physically reflected in cell-wall shrinkage, resulting in a brittle, well-defined vegetal structure with moderate microporosity, in which slight increase in cell-wall reflectance and significant decrease in fluorescence have been produced. Carbonization at 450 °C in turn led to a further loss of oxygen functionalities and a large increase in aromaticity, reflecting the virtual disappearance of hemicellulose and cellulose. This caused a significant increase in optical reflectance, loss of fluorescence and development of both meso- and microporosity generating an isotropic solid with a disordered structure similar to that of industrial charcoal. The microscopy techniques also showed the heterogeneity of the treated samples in terms of reflectance distribution or fluorescence properties, which cannot be assessed by bulk characterization techniques. They indicated a greater heterogeneity in the sample treated at torrefaction temperatures. The different characterization techniques have revealed minor differences between hardwood and softwood behavior, essentially attributed to resinous impregnations in the latter, whereas greater differences were observed between woods and olive stone due to significant differences in their internal and external structure.

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1. Introduction

Partial substitution of fossil fuels by biomass in industrial processes has become attractive because its utilization could contribute significantly to a reduction in CO_2 from fossil fuels emissions. Nowadays, biomass is considered a neutral C-source because the CO_2 generated by combustion is compensated for by the CO_2 absorbed from the atmosphere during plant growth [1]. Considering biomass as a neutral C-source necessarily requires that forest management is conducted in a sustainable way via a steady and contrasted supply of biomass through energy crops. The partial replacement of fossil fuels by biomass may contribute to protecting the environment in the short-medium term [2]. As regards

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the two major uses of coal (energy generation and metallurgical coke production), biomass is currently used in relatively small-sized boilers for heating purposes but it is gradually being incorporated into large-scale power generation plants in combination with traditional fuels [3]. Charcoal mainly produced in beehive kilns from eucalyptus wood is also used as an energy source and as chemical reducing agent in mini blast-furnaces in Brazil [4–7]. Recently, the use of charcoal in large metallurgical coke-based blast furnaces with pulverized coal injection [8,9], and as an additive in coal blends for metallurgical coke production are also being explored [9–12].

The partial substitution of biomass for coal is not only attractive because of the environmental benefits, but also because some types of biomass, like wood, have low inorganic matter and impurity contents (e.g. sulfur), which are typical contaminants in many processes [13]. However, some features common to raw biomass such as a high moisture, and a high oxygen content, a low heating value and even its fibrous structure, which makes grinding difficult, are often undesirable in industrial processes. These characteristics make it difficult to handle biomass, and increase the energy consumption which is especially disadvantageous when the biomass has to be ground to a pulverized size [14]. Biomass thermal treatment under an inert atmosphere at mild temperature between 200 and 300 °C (torrefaction) and at moderate temperature between 400 and 500 °C (carbonization) improves its characteristics for use as an energy source in different processes [15–18]. Through heating, biomass undergoes chemical, physical and structural transformations whose magnitude depends on the final temperature of the treatment [15,16,19]. The main bulk transformations upon torrefaction are a reduction in hygroscopicity [20–23] and an improvement in grindability [23–26] and energy density [20,27], whereas carbonization leads to greater carbon enrichment, which is preferred for energy purposes [28,29], despite the lower solid yield. Optimum torrefaction conditions have been established for around 30% mass loss, which gave a 20% increase of higher heating value [16].

Among the techniques used for characterization of thermally treated biomass, thermogravimetric analyses have shown little variation in the combustion characteristics of biomass treated at below 300 °C [24,30], and also similar distributions of pore size determined by N_2 adsorption for torrefied and raw biomasses [23]. Structural models based on spectroscopic techniques [23,31] of carbonized biomass suggest a rather aromatic highly conjugated structure with significant amounts of oxygen heteroatoms, which correspond to solids with values of specific surface area of few hundreds depending on the treatment temperature [31]. Both treatment temperature and feedstock have shown to have an impact in the characteristics of the biochars [30,31].

In the present work, the results of chemical, spectroscopic, physical adsorption and microscopic techniques have been integrated to study the transformations occurring in biomasses of different characteristics (softwood and hardwood chips and olive stones) during the thermal treatments of different severity. The main contribution is the combination of results from bulk techniques providing information of the whole sample and quantitative microscopy, able to describe the heterogeneity of the sample.

2. Material and methods

Four types of biomass were selected: softwood chips of *Pinus illiotis* (Pin), hardwood chips of *Acacia mangium* (Aca) and *Eucaliptus saligna* (Euc), the residual biomass from an unselected collection of *Eucaliptus saligna* (Rec), and olive stone from *Olive europaea* (Ols). The wood chips were sieved to 19 mm and the olive stone was maintained at its commercialization size of below 5 mm. Thermal treatments were conducted in a vertical furnace at atmospheric pressure, under a nitrogen flow of 50 mL min^{-1}, at a heating rate of 5 °C min^{-1} up to the target temperature with a holding time of 30 min. Samples were dried at 50 °C before thermal treatment and the amount of sample used in each test was 40 g. Two different target temperatures were selected: 250 °C to generate torrefied biomass and 450 °C to generate charcoal. The suffixes "to" and "ca" identify these samples, respectively.

The samples were subjected to proximate and ultimate analyses as well as tests for total sulfur content and higher heating value (HHV) according to the ISO 17246:2010, ISO 29541:2010, ISO 19579:2006 and ISO 1928:2009 standards, respectively.

The pore surface area of the thermally treated biomasses was determined by gas adsorption isotherms using N_2 at −196 °C and CO_2 at 0 °C as adsorptives with a Micromeritics ASAP 2020 equipment. The samples were outgassed while heated at 5 °C min^{-1} in two steps: (1) up to 90 °C with 1 h holding time; (2) up to 150 °C for the torrefied biomasses and up to 350 °C for the carbonized biomasses, with a holding time of 4 h. The temperatures used for outgassing are well below the temperatures used for the thermal treatment of biomasses and were not expected to modify their porous structure. The Brunauer–Emmett–Teller (BET) theory was applied to the N_2 adsorption data in the interval of relative pressure (P/P_0) 0.05–0.3 to determine the mesopore surface area [32]. CO_2 adsorption isotherms were performed up to a pressure of 0.035 torr to evaluate the micropore surface area. The Dubinin–Radushkevich (D–R) equation [33] was applied to all adsorption data (up to P/P_0 of 0.035), and a value of 0.17 was used for the molecular cross-sectional area.

Fourier-Transform infrared (FTIR) spectra were collected in a Nicolet IR 8700 spectrometer fitted with a mercury-cadmium telluride detector (MCT-A) operating at sub-ambient temperature and a Smart Collector diffuse reflectance (DRIFT) accessory. Spectra were obtained by co-adding 100 scans at a resolution of 4 cm^{-1}. Several FTIR indices derived from the maximum intensity (I) of selected absorption bands were used to assess the changes in the chemical structure of the biomass.

Morphological variations in the biomass upon heating were assessed by using a JEOL JSM 6060 microscope (SEM) and both the physical transformations and morphological changes were determined using a reflected light DMP 4500 optical microscope (OM) equipped with 50× oil immersion objectives. Cell-walls reflectance was measured in the torrefied and carbonized samples following the ISO 7404-5:2009 standard for vitrinite reflectance measurements in coal. Fluorescence spectra of the raw and torrefied biomasses were measured using ultraviolet light excitation and corrected using the spectrum of a quartz-iodine lamp according to the procedure described by Baranger et al. [34]. For each component around 20 spectra were averaged. The parameters used for comparing the different spectra were λ_{max} (wavelength of maximum fluorescence intensity) and the red/green quotient ($Q_{R/G}$ = intensity at 650 nm/intensity at 500 nm).

Combustion at programmed temperature was measured in a TG 7 Perkin–Elmer thermoanalyzer. Approximately 13 mg of sample ground to <212 μm were heated under an air flow of 50 mL min^{-1} from 50 °C to 900 °C at a heating rate of 20 °C min^{-1}. From the first derivative of the weight loss curve (DTG), several combustion parameters were derived: initial burning (Ti), maximum (Tp) and final or burnout (Tf) temperatures, defined as the temperature at which reactivity is 1/5 of the maximum [35], peak temperature, and temperature at which weight loss have ceased, respectively. The maximum reaction rate (ash-free basis) was calculated as $R_{max} = -1/w_0 \, (dw/dt)$, where w_0 is the initial weight of the sample.