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Effect of temperature and pressure on characteristics and reactivity of biomass-derived chars

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HIGHLIGHTS

- The effect of pressure on chars produced at low pyrolysis temperatures was studied.
- Special attention was devoted to the oxidation reactivity of the produced chars.
- Pyrolysis conditions and secondary char formation affected char porosity/reactivity.
- Secondary char formation becomes more important with pyrolysis temperature/pressure.
- The temperature interval 350–450 °C may be key in the tar repolymerization process.

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ABSTRACT

This study evaluates the influence of pyrolysis temperature (350–450 °C) and pressure (0.1–2.0 MPa) on product yields and char properties. Spruce chars were produced under slow pyrolysis conditions in a fixed bed reactor. Special attention was devoted to the study of the oxidation reactivity of the produced chars, and its relationship with the evaluated char properties. The obtained results showed that the effect of the pyrolysis condition on char production and in particular on the mechanism of secondary char formation strongly influenced the char reactivity. Additionally it has been observed that the interval of temperature between 350 and 450 °C may be key in the mechanism of tar repolymerization. The information provided in this study is of great interest for the determination of optimal operation conditions and the design of new gasification concepts or the development of bioenergy carriers via pyrolysis technologies.

1. Introduction

Biomass is considered a renewable energy source with high potential to contribute to the growing needs for sustained energy supply, offering advantages such as (Brewer and Brown, 2012; EREC, 2010): (i) it is a widespread resource, (ii) reduces greenhouse emissions, (iii) brings about an increment in rural incomes and restoration of degraded lands, and (iv) represents an economical option versus oil and coal. However, the production of bioenergy on a large-scale still faces some barriers. These drawbacks are related to the geographical dispersion of biomass resources and to its moderate energy density, high oxygen content, hydrophilic properties and water content (van der Stelt et al., 2011), resulting in high transportation costs and technical difficulties for the biomass conversion processes to operate optimally. A possible approach to reduce the impact of these factors is to apply a thermal pretreatment to biomass (torrefaction/pyrolysis) in order to produce a carbonaceous solid product, commonly referred to as torrified biomass or char. This product presents higher energy density than biomass and very low moisture and hydrophilicity, and can be transported and stored more efficiently to be used in different energy applications (e.g. gasification). Although nowadays combustion is the dominant process, gasification is more efficient for power production and expands the versatility of biomass through the production of syngas for the synthesis of second generation biofuels (SNG, FT liquids, methanol, dimethylether, etc.) (Asadullah et al., 2003). According to these assumptions, within the next years the development of bioenergy carriers and the implementation of large-scale biomass technologies are expected.

Mild pyrolysis is one of the thermal pretreatments that are commonly applied in order to improve biomass properties as solid fuel. During pyrolysis, biomass is subjected to temperatures above 300 °C (typically in the range from 300 to 650 °C), in absence of oxidizing agent. The yields and properties of the different pyrolysis products strongly depend on the operating conditions and reactor

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configuration (Berrueco et al., 2014a; Cetin et al., 2004; Cordella et al., 2013; Kandiyoti et al., 2006; Manyà, 2012; Neves et al., 2011).

In order to optimize char production it is necessary to carefully select the conditions to be used in the pyrolysis process. The biomass pyrolysis step should ideally aim to give high yield of char with high reactivity. However, the process conditions needed for increasing char yield tend to decrease its reactivity. In order to obtain high char yields, tar release must be minimized, and this is achieved through promoting repolymerization reactions. However, repolymerization reactions produce stable and non-porous char deposits, which present poor gasification properties (Kandiyoti et al., 2006; Berrueco et al., 2014a). The main operating parameters governing the characteristics of the chars (as well as the other pyrolysis products) for a given type of biomass are temperature, heating rate, particle size, pressure, reaction time and the configuration of sample and reactor (Antal and Grønli, 2003; Berrueco et al., 2014a; Cetin et al., 2004; Cordella et al., 2013; Kandiyoti et al., 2006; Manyà, 2012; Neves et al., 2011). The pyrolysis problem at hand (i.e. enhancement of char formation during the pyrolysis process) may best be studied in a fixed bed reactor. This reactor configuration enables the operation at conditions that would tend to maximize the char yield, i.e. high pressures, relatively low heating rates and varying bed depths, which can be used to maximize the interaction between the evolving tars and the solids.

In this study the influence of pyrolysis temperature (350–450 °C) and pressure (0.1–2.0 MPa) on the product yields and char properties was evaluated. Spruce wood pyrolysis was investigated under slow heating rate (10 °C min^{-1}) in a fixed bed reactor. Special attention was paid to the chemical and physical characterization of the chars and the relation between composition and structure of the chars and their oxidation reactivity. The data provided will be of relevance for future pyrolysis studies and the design of new gasification concepts to enable a clean conversion of solid fuels into high-quality products.

2. Methods

2.1. Biomass preparation and characterization

Wood spruce sieved to a particle size range of 250–500 μm was used as biomass sample. The proximate and ultimate analyses of the samples were carried out using a LECO Thermogravimetric analyzer (TGA 701) and a LECO TruSpec CHN-S-O analyzer, respectively. The proximate analysis was conducted following the standard method ASTM D7582 for moisture, volatile matter and fixed carbon determination. The lower heating value was determined in an isoperibolic LECO Automatic calorimetric bomb (AC 600), according to the ASTM D5865-07 standard test method. Halogens (HCl, HF, HBr) and phosphorous (H_3PO_4) were recovered by washing the calorimetric bomb with Milli-Q water and quantified by ionic chromatography (DIONEX ACS 1100) according to the EN-15408:2011 standard method. The results of the biomass analyses appear gathered in Table 1. These data will be useful to assess the variations between the raw and pyrolyzed feedstock.

2.2. Setup and procedure for pyrolysis experiments

Pyrolysis experiments were performed in a laboratory-scale fixed bed reactor (PID Eng & Tech, Spain) made of stainless steel (305 mm in length and 13 mm i.d.). Temperature was measured by a thermocouple placed inside the biomass bed. The reactor was settled in a hot box and externally heated by a radiant furnace. The gas flowed downstream across the reactor and, after leaving the reaction zone, went through a cold trap and a coalescing filter, to retain condensable liquids. The cold trap, packed with stainless steel mesh, was cooled with a mixture of ice and water. Finally, the pyrolytic gas was collected in a Tedlar gas-sampling bag to be analyzed after the experiment. The gas composition and flow rate were measured by means of an online micro GC (Agilent 490) and a Bronkhorst High-Tech flowmeter, respectively.

2.2.1. Experimental procedure

The biomass samples weighting approximately 1.5 g were held on a porous plate placed inside the reactor. Prior to the beginning of the experiment, nitrogen (Praxair, Inc.) was forced through the reactor at atmospheric pressure during a period of 30 min to remove any presence of oxygen and guarantee a non-oxidative environment.

After the purging period, the nitrogen flow was set at 50 NmL min^{-1} (experiment flow conditions), and the system was pressurized to the desired value. When the target pressure was reached, the reactor was heated at 10 °C min^{-1} and the final temperature was held for 15 min. The gas collection bag was then detached from the system and the gas composition was analyzed in the micro GC. The reactor was cooled down under pressure, the nitrogen flow stopped and the solid and liquid products recovered and weighted. Specifically, tar was recovered by washing the reactor, downstream pipes and the cold trap with acetone. The solvent was then removed by purging with N_2 at room temperature until the tar was totally dry.

2.3. Gas and char analyses

An online micro GC (Agilent 490) was used to quantify the composition of the gas collected in the gas-sampling bag during the experiments. The chromatograph configuration includes three different channels that analyze the permanent gases (H_2, O_2, N_2, CO, CO_2 and CH_4) and hydrocarbons up to C_5. Further details can be found elsewhere (Berrueco et al., 2014b).

The proximate and ultimate analyses of the recovered chars were carried out following the same procedure cited above for the biomass sample characterization.

The char morphology was studied using a scanning electron microscope SEM (JEOL JSM 6400). Samples were mounted on a cylindrical aluminium stub (10 mm o.d., 10 mm high) glued to a carbon tab and then gold-coated under vacuum for 3 min with a Sputter Coater (Emitech K575X).

The pore structure and total surface area of each char sample were determined through CO_2 adsorption at 0 °C using a Quantachrome Autosorb-iQ-C sorption analyzer. All char samples were degassed in vacuum (10^{-5} Torr) at 300 °C during at least 3 h prior to analysis. Surface areas and pore size distributions of the chars were calculated using the Dubinin–Radushkevich (DR) equation.

2.4. Reactivity analysis

Char samples were analyzed to establish their reactivity at low temperatures in an O_2–N_2 atmosphere. Oxidation reactivity analyses were conducted in a Mettler Toledo TGA/DSC 1 microbalance equipped with a 34-positions sample robot. The produced biomass chars were ground and sieved to a particle size of 100–106 μm. The samples (about 1.5 mg) were evenly distributed in the crucibles (Al_2O_3 crucibles, 70 μl) as a very thin layer. During the analyses the chars were heated under nitrogen atmosphere at a constant heating rate of 20 °C min^{-1} up to the analysis temperature, followed by a 5 min period for temperature stabilization. After this period the atmosphere was switched to an O_2 (5 vol.%)–N_2 mixture and the analyses were performed under isothermal conditions at 320, 350 and 450 °C. All the analyses were carried out at