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Influence of temperature and particle size on structural characteristics of chars from Beechwood pyrolysis

Jie Yu^{a,b}, Lushi Sun^{a,b}, César Berrueto^{b,1}, Beatriz Fidalgo^{b,2}, Nigel Paterson^b, Marcos Millan^{b,*}

^a State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

^b Department of Chemical Engineering, Imperial College, London SW7 2AZ, UK

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ABSTRACT

This work investigates the effect of temperature and particle size on the product yields and structure of chars obtained from the pyrolysis of Beechwood Chips (BWC), a lignocellulosic biomass. BWC of three different size fractions (0.21–0.50 mm, 0.85–1.70 mm and 2.06–3.15 mm) were pyrolyzed at atmospheric pressure and temperatures ranging from 300 to 900 °C in a fixed bed reactor. Tar and gas yields increased with increasing temperature, while char yield decreased, particularly between 300 and 450 °C. The effect of particle size was mostly observed at temperatures lower than 400 °C as a larger char yield for larger particles due to intraparticle reactions. At higher temperatures the larger surface area in the char fixed bed favoured reactions increasing char and gas yields from the smaller particles. Pyrolysis chars were characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Raman spectroscopy. Loss in oxygenated functional groups and aliphatic side chains with increasing temperature was revealed, along with an increase in the concentration of large aromatic systems, leading to a more ordered char structure but no significant graphitization. The changes in char nature at high temperature led to a loss in their combustion reactivity. Raman spectra indicated that the temperature needed to completely decompose the cellulose structure increased with biomass particle size and the enhanced intraparticle reactions in pyrolysis of large particles was likely to give rise to amorphous carbon structures with small fused ring systems.

1. Introduction

Biomass as a renewable fuel resource for energy production is likely to play a major role to replace fossil fuels, help meet the increasing energy demand and reduce CO₂ emissions. Pyrolysis is not only the first set of reactions undergone by biomass in combustion and gasification [1,2], but it can also be an effective process to produce a solid fuel without the large amount of oxygen and moisture present in the biomass, which reduce its heating value and represent a drawback to its use.

Therefore, the study of pyrolysis is of great importance, not only because it affects the yields of the pyrolysis products, but also the char reactivity in subsequent processes [3–7]. Among the various uses of chars from biomass pyrolysis a route, to a char that can be used as a substitute to pulverized coal in steel making in electric arc furnaces has recently been reported [8]. The suitability of biomass-derived char for electric arc furnace applications depends on its structure, heating value and reactivity, which are all affected by the pyrolysis process.

The influence of biomass pyrolysis operating conditions on the developing char structure caused by the release of volatiles from the biomass matrix has been the subject of several studies [3,4,6,7]. Generally, smaller particle size and higher heating rate leads to less char yields. Temperature has a great effect on char yields and properties [5]. The structural properties of a char are determined by the parent biomass and pyrolysis operating variables, such as heating rate, peak temperature, residence time and particle size, and the type of pyrolyser, as there can be significant differences between chars from fixed beds, fluidized beds and entrained flow reactors [9,10]. These variables affect char reactivity due to their effect on elemental composition, functional groups, surface area, carbon microstructure, and agglomeration of inorganic matter, which plays a catalytic role in gasification and combustion.

Biomass grinding into the small particle sizes required for many applications is energy intensive. Therefore, selecting an appropriate biomass particle size has an impact on process economics. Understanding the effect of pyrolysis temperature and particle size on

* Corresponding author.

E-mail address: marcos.millan@imperial.ac.uk (M. Millan).

¹ Current address: Catalonia Institute for Energy Research, IREC, C/Marcel·lí Domingo, 2, 43007 Tarragona, Spain.

² Current address: Bioenergy and Resource Management Centre, Cranfield University, Cranfield MK43 0AL, UK.

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the structure of chars is useful to select and optimize pyrolysis conditions to produce high quality chars for different processes, including their use in electric arc furnaces. Hence, the present work investigates the combined effect of temperature and particle size on the product yields and char structure from BWC pyrolysis. A novel adaptation of a Gray King (GK) apparatus has been used to produce chars. This configuration enables an assessment of the extent of reactions of the evolving volatiles both intraparticle (before volatiles are released from a particle) and interparticle (where volatiles generated in one particle react over other particles in the bed). Structural characteristics of raw biomass and the biomass chars are studied by a range of advanced analytical methods to investigate changes in char structure with conditions of formation. FTIR, XRD and Raman spectroscopy provide an insight into char structures [7,11–18], and the influence of char structural changes on combustion reactivity has been investigated by thermogravimetric analysis.

2. Experimental section

2.1. Sample preparation

A sample of BWC was ground by a biomass shredder and sieved to three different particle size fractions: 0.21–0.50 mm, 0.85–1.70 mm and 2.06–3.15 mm. Before each experiment, the samples were placed in a vacuum oven, dried overnight at 35 °C and then stored in a desiccator cabinet until used. Elemental analysis of the samples was carried out using a Vario EL-2 elemental analyzer. Proximate analysis (TGA2000, Las Navas) was conducted to determine moisture, volatile matter, fixed carbon, and ash contents. Approximately 3–4 mg of sample was heated to 50 °C and held at that temperature for 10 min under N₂ atmosphere (40 mL min⁻¹). Afterwards, temperature was increased in two steps: (i) to 110 °C at 10 °C min⁻¹ and held for 30 min in order to record moisture; (ii) to 900 °C at 10 °C min⁻¹ and held for 30 min to measure volatile matter contents. Temperature was then decreased to 800 °C at 10 °C min⁻¹ and held for 10 min under the same flowrate of N₂. Next, the sweep gas was switched to air (40 mL min⁻¹) and held for 40 min in order to register fixed carbon and ash contents. The detailed analysis of the BWC sample is shown in Table 1.

2.2. Pyrolysis set-up and procedure

A laboratory scale quartz reactor (length: 300 mm, inner diameter: 20 mm) was set up in a fixed bed configuration for this study according to the layout shown in Fig. 1. This reactor was adapted from the standard Gray-King assay test [19]. For each run, 2–3 g of BWC was placed in a wire mesh cage inside the quartz tube reactor at room temperature and heated, by means of a furnace, to the pyrolysis peak temperature, at a heating rate of about 50 °C min⁻¹. Several

temperatures in the range 300 and 900 °C were evaluated. Once the peak temperature was achieved, it was kept constant for 15 min before the quartz reactor was removed from the furnace and allowed to cool. Two thermocouples were used to monitor temperature at the front and rear of the biomass bed. A flow rate of 1.2 L min⁻¹ of helium was used to sweep the volatile products out of the reactor and into the tar trap. The tar trap was composed of a glass U-tube immersed in a liquid nitrogen bath, which condensed most of the tar. An external cotton-filled filter was placed downstream from the tar trap to remove any residual tar mist. The tar collected in the cold trap system was formed over a temperature range from the onset of volatile release up to the peak temperature. The primary char in the cage and tar in the U-tube and tar trap system filter were the main recovered products at the end of each pyrolysis run. Only traces of tar and secondary char were observed in the reactor outlet tube section. The solid residues were collected and weighed to calculate the char yield as a percentage of the initial biomass weight. Tar yield was calculated from the difference in weight between the tar trap system and reactor before and after each run and reported as a percentage of the initial biomass weight. Gas yield was calculated by difference.

2.3. Characterization of chars and tars

XRD spectra of the char samples were obtained using a PANalytical B.V. X'Pert Pro multipurpose X-ray diffractometer (40 mA, 40 kV, Cu KR). Samples were scanned in a step-scan mode with a step size of 0.01° over an angular 2θ range of 10–90°. The apparent microcrystallite diameters (La) were calculated using Warren's formula [20]:

$$La = \frac{1.84\lambda}{B \cos(\theta)}$$

where λ is the X-ray wavelength, θ is the Bragg angle and B is the breadth at half-maximum intensity in radians.

The main organic functional groups in the char particles were analyzed using an FTIR spectrometer (Bruker, VERTEX 70, Germany). The samples were first powdered in an agate mortar and then mixed with KBr to prepare transparent wafers. The mixture of char and KBr powder was dried overnight in an oven at 105 °C. FTIR spectra were obtained with 4 cm⁻¹ resolution and 32 scans between 4000 and 400 cm⁻¹.

Raman measurements were conducted with a Confocal Raman Microspectroscope (Type: Renishaw RM-1000), using an Ar+ laser beam at 514.4 nm, with spectral resolution 1 cm⁻¹ and laser power of less than 0.4 mW (at the samples) was used as an excitation source. Raman spectra were measured in the range of 800–1800 cm⁻¹.

A PerkinElmer Thermogravimetric Analyser (TGA) Pyris 1 was used to determine combustion reactivity of biomass chars. Approximately 2–3 mg of solid sample were heated from 50 to 400 °C at a heating rate of 50 °C min⁻¹ in an inert N₂ atmosphere (40 mL min⁻¹). Next, the sweep gas was switched to air (40 mL min⁻¹) for the combustion reaction and temperature was increased at a rate of 15 °C min⁻¹–900 °C and held for 5 min. Half-life temperature (T_{50%}) and maximum reactivity temperature (T_{Rmax}) were determined from the TGA data as char reactivity indices. T_{50%} is defined as the temperature at which 50% of the combustible material has reacted. The T_{Rmax} is the temperature at which the weight loss rate presents its maximum. Shifts of these values towards higher temperatures indicate lower sample reactivity.

Molecular size distributions of the tars were compared by size exclusion chromatography (SEC) analysis carried out using a 300 mm long, 7.5 mm i.d., polystyrene/polydivinylbenzene-packed, Mixed-D column (Polymer Laboratories, U.K.). The chromatograph was operated at 80 °C and 1-methyl-2-pyrrolidinone (NMP) as the mobile phase with a flow rate of 0.5 mL min⁻¹. Signal detection was carried out using a Knauer diode array Smartline 2600 detector, with UV absorbance at 300 nm.

Table 1
Proximate and ultimate analysis of the BWC sample (%).

Sample	Beechwood
Proximate analysis ^a (%)	
Moisture	11.6
Ash	0.5
Volatile Matter	75.0
Fixed Carbon	12.9
Ultimate analysis ^b (%)	
Carbon	45.5
Oxygen (by difference)	48.1
Hydrogen	6.1
Nitrogen	0.08
Sulphur	0.21

^a As used basis.

^b Dry ash-free basis.

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