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Research article

Effect of pyrolysis temperature on char structure and chemical speciation of alkali and alkaline earth metallic species in biochar

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ABSTRACT

To investigate the effect of pyrolysis temperature on char structure and chemical speciation of alkali and alkaline earth metallic (AAEM) species in biochar, experiments were carried out in an entrained flow reactor with nitrogen to reduce volatile–char interactions. Pyrolysis was conducted at temperatures ranging from 500 °C to 900 °C. Raman, Fourier transform infrared and X-ray photoelectron spectroscopies were used to identify the char structure and functional groups. The assessment of the chemical speciation of AAEM species in the biochar was carried out by chemical fractionation analysis and inductively coupled plasma mass spectrometry. Pyrolysis between 500 and 900 °C results in ring condensation, which produces large aromatic ring systems containing six or more fused benzene rings. In addition, C–O and C–C linkages form through thermal polycondensation and cyclization to produce stable aromatic rings, which shows C═C stretching bands in the FTIR. Conjugated aromatic carbonyl/carboxyl C═O groups disappear at temperatures higher than 700 °C, and the relative concentration of carbonyl oxygen from quinines increases gradually with increasing temperature. More than 50% of K and Na in the sawdust and chars prepared at 500–900 °C exists as ions, while most of the Ca (65%) and Mg (60%) are bound in organic compounds. The release of K and Na occurs mainly in the form of inorganic salts and hydrated ions, while volatilization is the main release mechanism for Ca and Mg in the organic compounds.

1. Introduction

The structure of char and chemical speciation of alkali and alkaline earth metallic (AAEM) species (e.g., K, Na, Mg and Ca) in the char are important because they influence char reactivity in biomass thermochemical conversion processes [1–4]. Numerous techniques can be applied to study changes in the structural features of biochar. However, there are limitations with all the techniques currently available, and none can explain the transitions of biochar adequately. For example, Raman spectroscopy has been used extensively to characterize the structural features of biochar by correlating the Raman bands to structural parameters [3,5]. However, it is ineffective for analyzing specific functional group changes. While Fourier transform infrared spectroscopy (FTIR) has been used to examine cross-linking in organic compounds and various bonds in O-containing functional groups present in chars [6,7], it is of limited use for less-polar aromatic structures and sp^3–sp^3 or sp^3–sp^2 cross-linked structures. X-ray photoelectron spectroscopy (XPS) has been useful for characterization of biochars [8], but it is mainly valid for surface analysis.

Volatilization of AAEM species during the pyrolysis of biomass is strongly dependent on the temperature [9–12]. Most recent research has focused on the absolute quantity of volatized AAEM species during pyrolysis. AAEM species are present as various chemical compounds in biomass, including as different salts, minerals and organic compounds. The chemical speciation of AAEM species is known to influence the rate of devolatilization of lignocellulose during pyrolysis and can modify the distribution of syngas, tar and char through catalytic activity [11,13]. However, there are few reports on the effect of the pyrolysis temperature on the chemical speciation of AAEM species in biochar. Sequential extraction by chemical fractionation analysis (CFA) could be useful for studying solid-phase speciation of trace metals in biochars [14].

Li et al. [15–17] found that the char structure and volatilization of AAEM species were strongly influenced by volatile–char interactions during pyrolysis in a fluidized-bed/fixed-bed quartz reactor. In the present study, to study the effect of pyrolysis temperature alone, an entrained flow reactor with nitrogen was used to decrease the concentration of biomass volatiles in the reactor to less than 5% and eliminate the influence of the volatile–char interactions. Using this reactor, the effects of pyrolysis temperature on the char structure and volatilization of AAEM species were investigated. Raman, FTIR and XPS spectroscopic techniques were used to identify the functional groups and structural features of the biochar.

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Table 1
Proximate and ultimate analyses of sawdust.

Proximate analysis				Ultimate analysis				
M_{ad} (wt.%)	A_{ad} (wt.%)	V_{ad} (wt.%)	FC_{ad} (wt.%)	C_{ad} (wt.%)	H_{ad} (wt.%)	$O_{ad.(diff.)}$ (wt.%)	N_{ad} (wt.%)	$S_{t,ad}$ (wt.%)
9.49	0.96	77.13	12.42	38.34	6.17	44.58	0.37	0.09

Note: diff. = by difference, ad = air dried basis.

2. Experimental

2.1. Samples

Manchurian walnut, which is abundant in Northeast China, was used in the experiments. The proximate and ultimate analyses data for the Manchurian walnut sawdust are listed in Table 1. After drying the sawdust at 105 °C overnight, it was crushed further and sieved to a particle size of 0.15–0.25 mm. A schematic diagram of the entrained flow reactor is shown in Fig. 1. The diameter of the reactor was 100 mm and the length of the reaction zone was 1510 mm. The reactor is described in detail in an earlier study [18]. The pyrolysis temperatures were 500 °C, 600 °C, 700 °C, 800 °C and 900 °C. Nitrogen gas at room temperature and different flow rates (8.00 L/min, 7.18 L/min, 6.33 L/min, 5.70 L/min and 5.28 L/min) was used to maintain a residence time of 4.2 s at the different pyrolysis temperatures. After the reactor temperature reached the target temperature and stabilized, biomass particles were fed into the reactor at a rate of 1.0 g/min. The biomass particles were introduced through a water-cooled probe to avoid the release of volatiles before the particles reached the target temperature zone.

2.2. Analysis of the char structure

2.2.1. Raman analysis

Raman spectra were recorded using an inVia confocal micro Raman spectrometer (Renishaw, New Mills, UK) equipped with a charge-coupled device 1040 × 256 camera. The camera was used to focus the excitation laser beam on the sample and to collect the Raman signal in the back-scattered configuration. The structural features of the char were characterized using an excitation laser at 633 nm. The char sample was mixed and ground with spectroscopic grade potassium bromide (KBr) to reduce thermal emission. Spectra were recorded in the range of 800–1800 cm^{-1}.

2.2.2. FTIR analysis

The functional groups were analyzed using a Nicolet 5700 FTIR (Thermo Fisher Scientific, Waltham, MA). The samples and KBr were dried at 105 °C in an oven for 12 h and then mixed together in a 1:120 ratio. The mixture was ground to a fine powder (ø < 2 μm) under an infrared lamp. KBr pellets were formed (10 Mpa, 1 min) and analyzed in the FTIR. All the spectra were obtained at a resolution of 4 cm^{-1} in the range from 400 to 4000 cm^{-1}. Thirty-two scans were collected for each spectrum. The spectra were corrected for H_2O and CO_2 and ambient air. Before analysis of each sample, the spectrum of the background was measured to reduce interference.

2.2.3. XPS analysis

XPS analysis of pyrolysis char was performed using a K-Alpha spectrometer (Thermo Fisher Scientific) equipped with monochromatic Al Kα X-rays at 1486.6 eV. To exclude effects on the binding energies because of the changing of the sample during XPS, the data were corrected by a linear shift with the maximum peak of the C1s binding energy of the adventitious carbon corresponding to 284.6 eV.

2.3. CFA of AAEM species

Assessment of the chemical speciation of AAEM species in the sawdust and chars was carried out by CFA [14,19,20]. Samples were dried at 105 °C overnight. Each sample was extracted successively with deionized water (H_2O), 1.0 mol/L ammonium acetate (NH_4Ac) and 1.0 mol/L hydrochloric acid (HCl). In the first extraction, water-soluble compounds, such as K and Na salts, dissolved. Ion exchangeable elements

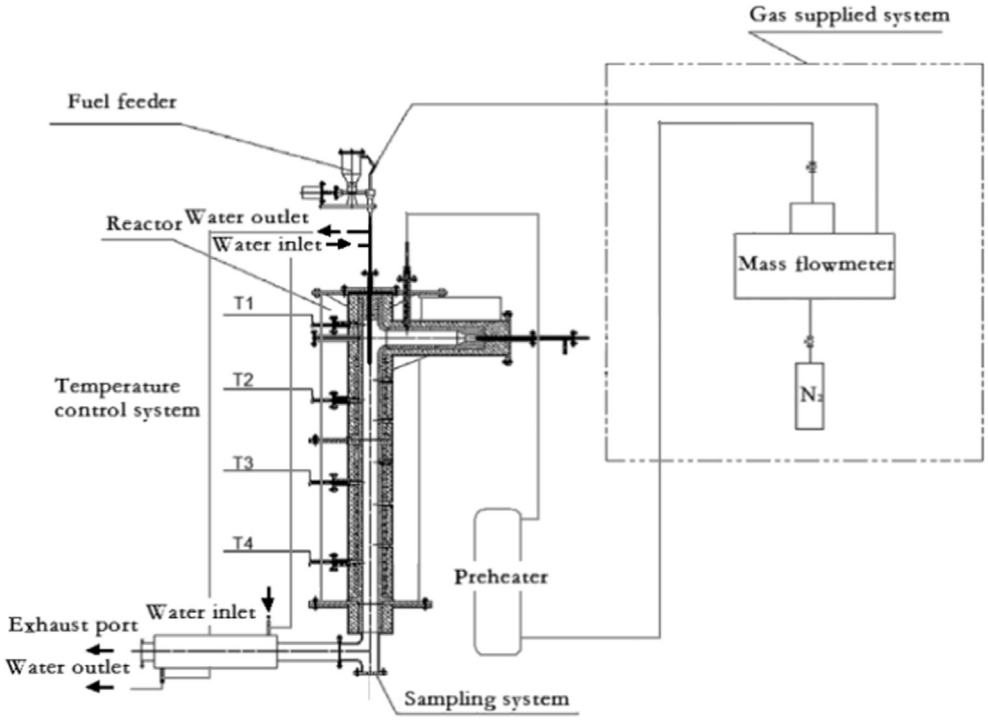

Fig. 1. Schematic diagram of the entrained flow reactor.

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