



Evolved gas analysis and slow pyrolysis mechanism of bamboo by thermogravimetric analysis, Fourier transform infrared spectroscopy and gas chromatography-mass spectrometry



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ABSTRACT

Slow pyrolysis of bamboo is an important conversion pathway to produce biofuels and chemicals such as biomass-derived fertilizer precursor (biochar). In this study, evolved gas analysis during pyrolysis of bamboo was conducted by a combination of TG, FTIR and GC-MS to establish a detailed pyrolysis mechanism of bamboo biomass. The main decomposition temperature zones were 300–400 °C and it reached the maximum mass loss intensity at 350 °C based on DTG curves. The main functional groups escaped from biomass during pyrolysis were –OH, –CH₂, –CH₃, C=O, C–O, and –COOH. The main compounds during pyrolysis of bamboo were acetic acid and 2-propenoic acid, ethenyl ester at 300 °C, 2-oxo-propanoic acid and 1-hydroxy-2-propanone at 350 °C and acetic acid and acetic acid ethenyl ester at 400 °C. Evolved gas analysis indicated that components in bamboo occurred in different temperatures and pyrolysis mechanisms and resulted in distinguishing pyrolysis product emission characteristics.

1. Introduction

Bamboo is an important biomass resource, which is widely in the area of Asian and has the advantages of fast growth and low ash content (Posom and Sirisomboon, 2017). It is an important source of bioenergy, which can be transformed into liquid biofuels, biochemicals and biomaterials by many process pathways including pyrolysis (Jiang et al., 2012), hydrothermal liquefaction (Chang et al., 2016), gasification/Fischer-Tropsch synthesis (Buragohain et al., 2010) and hydrolysis/fermentation (Yuan and Wen, 2017). Pyrolysis is an important option because of mild operation temperature and polygeneration of many products (biochar, bio-oil and biogas) (Yang et al., 2016), especially high-value bamboo-derived biochar. However, biomass has different contents of cellulose, hemicellulose and lignin, which have different pyrolysis characteristics and pyrolysis pathways/mechanisms (Cao et al., 2014). For examples, these biomass components have different pyrolysis temperature zones such as 315–400 °C for cellulose, 220–315 °C for hemicellulose and 160–900 °C for lignin (Yang et al., 2007). To discriminate the pyrolysis mechanisms, many analysis methods have been developed including thermogravimetric analysis (TG) (Hu et al., 2016), Fourier transform infrared spectroscopy (FTIR) (Posom et al., 2017), gas chromatography-mass spectrometry (GC-MS)

(Dong et al., 2015) and their hyphenated utilization (Chen et al., 2015a,b; Jiang et al., 2012).

Pyrolysis characteristics and kinetics for bamboo pyrolysis can be inferred by thermogravimetric analysis. The main pyrolysis temperature ranges are between 300 and 500 °C, which are indicated by many thermogravimetric curves. Pyrolysis profiles of bamboo biomass can be divided into three reactions (hemicellulose, cellulose and lignin) corresponding to the activation energy of 175.6, 199.7 and 158.4 kJ/mol (Chen et al., 2017). Thermogravimetric analysis also indicates that fungal pretreatment greatly enhances the thermal degradation of bamboo and decreases the negative effect of extractives on pyrolysis (Yu et al., 2015). Microwave heating reduces the decomposition activation energy during moso bamboo pyrolysis and a kinetic compensation effect has also been indicated (Dong and Xiong, 2014). Microwave hydrothermal pretreatment can also removes more acetyl groups in hemicellulose compared to conventional hydrothermal pretreatment, which is suitable for upgrading the pyrolysis oil quality (Dai et al., 2017).

Except pyrolysis characteristics from TG, FTIR can also be used to evaluate pyrolysis characteristics. TG-FTIR analysis of moso bamboo shows that the main pyrolysis products include absorbed water, methane gas, carbon dioxide, acids and aldehydes, ammonia gas, etc

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(Jiang et al., 2012). The FTIR absorption of the volatiles of lignin pyrolysis is lower than those from hemicellulose, cellulose, holocellulose and bamboo indicating lower gas yield and higher residual yield of lignin pyrolysis (Cao et al., 2014). It also indicates that the main oxygen-containing functional groups in biochar gradually decrease, while the degree of aromatization increases at a higher pyrolysis temperature (Chen et al., 2016). The main chemical structure of lignin can also be evaluated and the typical lignin patterns is –OH, –CH, C=O and C–H and the main differences in fingerprint region are due to the different proportion of guaiacyl unit, syringyl unit and *p*-hydroxyphenyl unit in lignin (Chen et al., 2015b).

Comparing with macroscopic analysis of TG and FTIR, GC–MS can give detailed compound distribution based on evolved gas analysis during bamboo pyrolysis processes. The main chemical components of the bamboo bio-oil analyzed by GC–MS are grouped into seven classes: acids, ketones and aldehydes, furans, phenols, guaiacols, syringols and sugars (Cheng et al., 2015). Acetic acid and phenolic compounds are the main organic components in bio-oil of moso bamboo pyrolysis (Chen et al., 2014). Results from Py-GCMS indicate that aromatic compounds are the major volatiles of lignin pyrolysis (Cao et al., 2014).

Based on all of these research results from TG, FTIR and GC–MS, some bamboo pyrolysis mechanisms have been established (Cao et al., 2014; Chen et al., 2015a,b; Oyedun et al., 2013). For example, many pyrolysis kinetic models have been established such as distributed activation energy model, detailed lumped kinetic model, chemical percolation devolatilization model and kinetic monte carlo model (Wang et al., 2017). However, the pyrolysis mechanisms of bamboo are still not clear, shortage of key information and need detailed researches and illustration. In this study, pyrolysis of bamboo was conducted by a combination method of thermogravimetry, Fourier transform infrared spectrometer and gas chromatography-mass spectrometry (TG-IR-GCMS) to reveal the emission characteristics of evolved gas. The pyrolysis mechanisms were established at gradually increased pyrolysis temperatures. It will provide basic information for bamboo biofuel application and process optimization of large-scale bamboo-based pyrolysis plants.

2. Materials and methods

2.1. Materials

As one of important biomass sources, bamboo has the advantage of fast growth and low ash content with high value-add by-products such as bamboo shoots during their growth. Bamboo specie (*Phyllostachys pubescens*) was used in this research, which was collected from Xianning of Hubei Province, P.R. China. Bamboo stems were cut into short pieces with sticks scissions and then dried in 24 h to keep a constant weight. Then dried sample was ground by a micro plant grinder and the powder of sample was sieved by a sifter of 40 meshes (0.38–0.25 mm).

The proximate analysis, ultimate analysis and chemical composition of samples were shown in Table 1. The heating value of sample was tested by a bomb calorimeter (PARR1281, USA). Elemental analysis (Elementar Vario EL, Germany) of sample was conducted to measure the content of C, H, N, S, and O in the samples. The main components of sample are cellulose, hemicellulose and lignin with little extractive and ash. Their content was measured by the two-step acid hydrolysis method, which can refer to NREL technical report for detailed operation and description (Sluiter et al., 2012).

2.2. Pyrolysis experiments and evolved gas analysis

Evolved gas analysis means measurement of the gases evolved from a sample being heated by a thermal analyzer (Zeng et al., 2015) and these gases can be released from reactions such as evaporation, boiling, separation, or from the combustion/pyrolysis of a material. It is often conducted based on hyphenated techniques, which couple two or more

Table 1

Proximate analysis, ultimate analysis and chemical composition of bamboo.

Items	Content	Measure standards
Water (%)	10.41	GB/T 212-2001
Ash (%)	2.10	GB/T 212-2001
Volatile (%)	73.05	GB/T 212-2001
Fixed carbon (%)	14.44	GB/T 212-2001
C (%)	45.06	GB/T 476-2001
H (%)	4.58	GB/T 476-2001
O (%)	37.53	GB/T 476-2001
N (%)	0.28	GB/T 476-2001
S (%)	0.04	GB/T 214-1996
Heat value (MJ/kg)	17.57	/
Cellulose (% _d)	45.13	NREL
Hemicellulose (% _d)	25.66	NREL
Lignin (% _d)	22.49	NREL
Extractive (% _d)	4.97	NREL

instruments to greatly increase the power of analyses and save precious time by acquiring more information from a single run. In this study, pyrolysis experiments were conducted by a hyphenated equipment of TG, FTIR, and GCMS to reveal the emission characteristics of evolved gas at 300 °C, 350 °C and 400 °C, which included gaseous bio-oil and non-condensable gas during biomass pyrolysis. Thermogravimetric experiments (TGA 8000, PerKinElmer, USA) were conducted at inert (N₂) environment with the heating rates of 10, 15 and 20 °C/min. For each experiment, about 10 mg dried biomass sample was used and placed in the sample cell. The pyrolysis temperatures were ranged from room temperature to 600 °C and the TG-DTG curves were both recorded at these temperature zones. The evolved gas during thermal mass loss process was analyzed by online FTIR and GC–MS. The temperature of transmission line (TL9000, PerKinElmer, USA) between TGA and FTIR/GC–MS was maintained at 280 °C to avoid the condensation of evolved volatile.

The evolved gas was analyzed online by Fourier transform infrared spectroscopy (Frontier FT-IR, PerKinElmer, USA), which was conducted at the range of 4000–400 cm⁻¹ with the interval of 1 cm⁻¹. Pure nitrogen was used as the carrier gas and held at a flow rate of 30 mL/min. The FTIR absorption was recorded in the whole experiment process and finally 3D FTIR absorption spectrums were established against pyrolysis temperature and wave number. Some special compound absorption peaks such H₂O, CH₄, CO₂, CO and compounds including C=O bond were also extracted from the 3D FTIR spectrums to illustrate their variation during the whole pyrolysis process.

For online GC–MS analysis of evolved gas (Clarus SQ8, PerKinElmer, USA), an Elite-5MS chromatographic column (30 m length and 0.25 mm i.d.) was used and column flow rate (He) was 1 mL/min. Inlet temperature, quadrupole and detector temperature were 280 °C, 230 °C and 150 °C respectively. The oven temperature increased from 50 °C to 300 °C with the heating rate of 10 °C/min. Another five minutes was maintained before and after the programed temperature process. The mass spectrometer scan range was from 40 to 500 mass units, and derived compounds were identified using the mass spectral library (NIST 08).

3. Results and discussion

3.1. TG characteristics and pyrolysis peak simulation

Thermogravimetric analysis can evaluate thermal decomposition characteristics of biomass samples at different pyrolysis temperatures, which give mass loss curves and its mass loss rate curves (i.e. TG and DTG curves) with increased operation temperatures. TG and DTG curves of bamboo pyrolysis were shown in Fig. 1, which were overlapping curves because biomass samples had complex composition including cellulose, hemicellulose and lignin. The main pyrolysis

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