Fuel 180 (2016) 256–262

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Influence of minerals on the thermal processing of bamboo with a suite of carbonaceous materials

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HIGHLIGHTS

- Biomass was co-processed with carbonaceous materials with different mineral content.
- Synergy between biomass and different carbonaceous materials was evident.
- Minerals (Na, K and Ca) showed catalytic effect on co-pyrolysis and co-combustion.

ARTICLE INFO

Article history:
Received 8 February 2016
Received in revised form 31 March 2016
Accepted 1 April 2016

Keywords:
Biomass
Carbonaceous material
Thermal processing
Kinetic study
Synergy

ABSTRACT

This study focuses on the impacts of minerals naturally existed in different carbonaceous materials on the thermal processing of their blends with bamboo. Combustion characteristics, such as ignition temperature, peak temperature and burnout temperature, were studied using Thermogravimetric Analysis (TGA) to understand how thermal processing was affected by blending with different types of carbonaceous materials. Kinetic parameters, i.e., activation energy and pre-exponential factors, were determined for both combustion and pyrolysis processes. Synergy was observed in the co-pyrolysis of bamboo and carbonaceous materials. The blending of bamboo was found to have positive influence on ignition and burnout performance of all blends. It was showed that when graphite, activated carbon and coal were blended with bamboo by 50:50 wt%, ignition temperature of the blends dropped by 466, 90 and 142 °C, respectively and burnout temperature dropped by 82, 39 and 37 °C respectively. It was found that K and Na in biomass and Ca in coal acted as catalysts and enhanced the overall co-combustion process and resulted in significant synergistic effect.

1. Introduction

Co-processing of biomass with coal is a promising approach to reduce the use of fossil fuels [1] as well as to address environmental pollution problems [2] due to its carbon-neutral nature.

Although coal is derived from biomass, the thermal properties of coal and biomass are very different. It is therefore necessary to understand thermal behavior of biomass if it is to be co-processed with coal in large scale. In the past few decades, kinetics of co-combustion and co-pyrolysis of coal and biomass has drawn significant attention worldwide. Much work has been carried out to investigate the influence of operating conditions [3], coal rank [4,5] and types of biomass on the combustion [6] and pyrolysis [5] of coal and biomass blends. It was found that activation energy for biomass to decompose decreased with the increase in the percentage of torrefied biomass [7], and synergistic effects, the enhanced interactions between coal and biomass, existed during the co-pyrolysis of coal and biomass [8,9] which resulted in changes in the yield of volatiles and the value of activation energy [10].

Work was also conducted to determine kinetic parameters of thermal processing of biomass [10–13]. Minerals in ash were found to have catalytic effects on the co-processing of coal and biomass [14]. However, to date, very little work has been carried out to understand how minerals naturally existed in coal and biomass contribute to the synergistic effect and affect the thermal co-processing of coal with biomass. Since co-firing has become a general practice in western countries, the understanding of such is of great importance in the selection of biomass to be co-fired with coal to achieve a desired combustion performance in utility boilers.

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http://dx.doi.org/10.1016/j.fuel.2016.04.001
0016-2361/

In this study, to understand the role of minerals naturally existed in bamboo in the co-processing of bamboo with a suite of carbonaceous materials, one coal and two different carbonaceous materials, i.e., activated carbon and graphite, were blended with bamboo and tested. Characteristics of pyrolysis and combustion of bamboo blended with these carbonaceous materials were investigated in detail using Thermogravimetric Analysis (TGA). Kinetic studies on combustion and pyrolysis were also carried out to find out how thermal processing was influenced by minerals and the blending of biomass with different carbonaceous materials.

2. Experimental

2.1. Sample preparation

The biomass sample used in this study was bamboo (BB, acquired from Huzhou, Zhejiang Province), a type of biomass widely available in China, especially in south China. The other materials used were Mengxi coal (MC), a coal mined from the western part of China's Inner Mongolia, activated carbon (AcC) and graphite powder (GR, analytical grade), both purchased from Sinopharm Chemical Reagent Co., Ltd. These three carbonaceous materials are of significantly different mineral compositions as well as mineral content.

All the samples were prepared following British Standard for sample preparation [15]. Approximately 1.0 kg of each sample (except graphite) was grinded into a size range of −106 μm for future use. Bamboo was blended with Mengxi coal, activated carbon and graphite at three different mass ratios, i.e., 10, 30, 50 wt %. Ash samples of bamboo, Mengxi coal, activated carbon and graphite were also prepared based on British Standard [16].

2.2. Proximate analysis and ultimate analysis

Proximate analysis was carried out using a TGA (NETZSCH STA 339 F3) following the procedures adopted elsewhere [17]. Ultimate analysis was carried out using a PE 2400 Series II CHNS/O elemental analyzer (Perkin Elmer). About 2–3 mg of fine powder of a sample was used for each test and was manually grinded further prior to testing to eliminate the influence of size on diffusion during testing. Carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) content of samples were determined directly, while oxygen (O) content was calculated by difference.

2.3. Characterization of ash samples

Morphology of ash sample was observed using a scanning electron microscope (SEM, Zeiss Sigma VP, Germany). Elemental composition of ash sample was characterized using an energy dispersive X-ray spectroscopy (EDS, Oxford X-act, UK) attached to the SEM.

Phase composition of ash samples was measured using a powder X-ray diffraction (XRD, Bruker D8 advanced A25). The Coupled Two Theta/Theta was selected as the scanning type with Two Theta range from 10° to 100° at a 0.01° step in a 0.1 s interval.

2.4. Pyrolysis and combustion experiments

Pyrolysis and combustion tests were carried out using the TGA. About 5–10 mg of a sample was used for each test and was manually grinded further prior to testing to eliminate the influence of size on diffusion during thermal processing. During pyrolysis test, the sample was heated in nitrogen atmosphere from ambient temperature to 110 °C and was kept isothermal at the temperature for 20 min to ensure a complete removal of moisture. The sample was then further heated to 800 °C at three different heating rates, i.e., 5, 20 and 50 °C/min. In combustion test, the sample was heated from ambient temperature to 900 °C at a heating rate of 20 °C/min in air with a flow rate of 20 ml/min.

2.5. Kinetic study

Kinetic study of pyrolysis and combustion processes was carried out based on the Arrhenius equation. Activation energy and pre-exponential factor were calculated using TGA data collected from previous study, the method of which is detailed elsewhere [12].

3. Results and discussion

Results of proximate and ultimate analyses are listed in Table 1. It is clear that graphite had the highest carbon content of 96.1 wt%, followed by activated carbon, Mengxi coal and bamboo, which were of a carbon content of 91.4, 76.8 and 49.9 wt%, respectively. Carbonaceous materials, i.e., Mengxi coal, activated carbon and graphite, are of significantly different ash content.

3.1. Characteristics of pyrolysis of blends

Fig. 1 shows the thermogravimetric (TG) and differential thermogravimetric (DTG) profiles of the pyrolysis of Mengxi coal, bamboo and Mengxi coal/bamboo blends at a heating rate of 5 °C/min. Theoretical TG and DTG curves were calculated using the TG and DTG data of parent coal and biomass based on the assumption that additive property applies.

From Fig. 1, it is clear that the devolatilization of bamboo started at around 180 °C while for Mengxi coal, it took place at a much higher temperature (300 °C). The rapid mass change of bamboo, as shown in Fig. 1, was due to the decomposition of cellulose and hemicellulose. The decomposition of these two components overlapped as hemicellulose started to decompose mainly at a temperature range of 250–370 °C whilst cellulose decomposes at a temperature range of 300–400 °C [18]. When the temperature was over 400 °C, the mass change was less significant as the degradation of lignin in biomass was slow and occurred in a broad temperature range of 250–550 °C [13].

As shown in Fig. 1, theoretical TG and DTG curves fitted reasonably well with the experimental data, which suggests that no significant synergy existed between Mengxi coal and bamboo during devolatilization.

Table 1
Proximate and ultimate analyses of raw materials.

Properties	Bamboo	Mengxi coal	Activated carbon	Graphite
Moisture content (wt%)	3.7	5.9	6.0	0.3
Proximate analysis (wt%)[a]				
Volatile	76.8	35.0	14.6	2.8
Fixed carbon	16.5	52.1	80.8	95.8
Ash	6.6	13.0	4.6	1.4
Ultimate analysis (wt%)[a,b]				
C	49.9	76.8	91.4	96.1
H	6.5	4.8	1.6	0.1
O[c]	37.0	15.8	3.7	3.0
N	6.0	1.6	0.2	0.1
S	0.6	2.2	3.1	0.7

[a] Dry basis.
[b] Ash free basis.
[c] By difference.