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Thermal behavior and the evolution of char structure during co-pyrolysis of platanus wood blends with different rank coals from northern China

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HIGHLIGHTS

- Synergistic effects were observed during co-pyrolysis of platanus wood and coal.
- Non-additivity performance on activation energy values of the blends was found.
- The evolution of char structure was studied applying Raman spectroscopy.
- The platanus wood blending ratio significantly affected co-pyrolysis char structure evolution.

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ABSTRACT

Co-thermochemical conversion of biomass and coal has been extensively investigated as an effective means to reduce the emission of greenhouse gas. Successful evaluation on the thermal behavior and product characteristics of the co-pyrolysis process is of crucial importance for predicting performance and improving efficiency of this technology. In this study, thermal behavior of platanus wood, two different rank coals (Pingzhuang lignite and Shenmu bituminous) and their blends during pyrolysis were studied via thermogravimetric analyzer. Raman spectroscopy technique was further employed to study the evolution of char structure. Thermogravimetric experiments indicated that the pyrolysis characteristics of their blends cannot be accurately forecasted based on individual component and blending ratio. The non-additive behavior of thermogravimetric curves of the blends suggested the existence of synergistic effects, which can promote the volatiles yields during the co-pyrolysis process. The most obvious synergistic effects were observed when the coal blending ratios were 30% for Pingzhuang lignite and 50% for Shenmu bituminous, respectively. In addition, iso-conversional method was used to solve activation energy. Non-additivity performance in the mean activation energy values of the blends was observed. The Raman results revealed that as the platanus wood blending ratio increased the Raman peak intensities of the char samples from pyrolysis of the blends also increased, which was probably attributed to the competition of oxygen-containing groups increment and disproportional impact of alkali and alkaline-earth metal species. The intensity ratios of some major Raman bands can provide useful information on char structure evolution. The generation of smaller aromatic rings structures (3–5 fused rings) was favored in these char samples with the higher platanus wood blending ratio.

1. Introduction

Biomass has been attracting great attention nowadays as a renewable and clean energy source with CO_2-neutral property, which also supplies approximately 14% of global energy [1,2]. At present, thermochemical conversion is one of the most promising means for utilizing energy stored in biomass efficiently due to its superior adaptability of feedstock and variety of products [3]. However, the seasonal supply nature, wide distribution and heterogeneity of biomass make it difficult to steadily and continuously produce electricity in biomass based power plants, which remarkably limits its widespread applications. Co-thermochemical conversion of biomass and coal can solve these problems and utilize coal in a cleaner method [4,5]. As the fundamental and initial step of co-gasification and co-combustion, co-pyrolysis has significant effects on the performance of the further process. Furthermore, co-pyrolysis can also be considered as a single co-thermochemical conversion process to produce a variety of fuels and chemicals [4,6]. Therefore, it is meaningful to

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Nomenclature

A	pre-exponential factor (s^{-1})
A_G/A_{all}	band area ratio between G band and all the 10 Raman bands (–)
$A_{(VR+VL+GR)}/A_D$	band area ratio of the sum of V_R, V_L and G_R bands to D band (–)
D_i	devolatilization index (mg min^{-1} °C^{-3})
E	activation energy (kJ mol^{-1})
E_m	mean activation energy (kJ mol^{-1})
$f(\alpha)$	reaction mechanism function (–)
m_0	initial weight of sample (mg)
m_t	instantaneous weight of sample (mg)
m_∞	final weight of sample (mg)
R	universal gas constant (J mol^{-1} K^{-1})
R_d	instantaneous weight loss rate (mg min^{-1})
R_{max}	maximum weight loss rate (mg min^{-1})
t	time (s)
T	temperature (K)
T_{in}	initial devolatilization temperature (°C)
T_{max}	temperature of maximum weight loss rate (°C)
$\Delta T_{1/2}$	temperature interval when R_d equals to half of R_{max} (°C)
$W_{Experimental}$	experimental weight loss value (–)
$W_{Calculated}$	calculated weight loss value (–)
ΔW	deviation of experimental and calculated weight loss value (–)
α	conversion fraction of sample (–)
β	heating rate constant (°C min^{-1})

Abbreviations

PW	platanus wood
PZ	Pingzhuang lignite
SM	Shenmu bituminous
TGA	thermogravimetric analyzer
DTG	derivative thermogravimetric
EDS	energy dispersive spectrometry
KAS	Kissinger–Akahira–Sunose
RMS	root mean square
AAEM	alkali and alkaline-earth metal

conduct the research on the characteristics of biomass and coal in their co-pyrolysis process so as to design and operate co-thermochemical utilization system.

As a precondition for product yield management and performance improvement, thermal behavior is regarded as a key characteristic for co-pyrolysis process. Several studies have been focused on the thermal behavior and kinetic analysis of a variety of coals blended with different biomasses, such as sawdust [7], cypress wood chips [8], and pine chips [9] from forestry residues, cherry pit [10], hazelnut shell [11], sugar beet pulp [12], straw [13], corn and sugarcane [14] from agricultural residues. However, due to the great varieties and heterogeneity of biomass, different conclusions on the thermal behavior were obtained by different researchers. Several researchers reported that the volatiles yields exceeded the expected values calculated from individual samples based on additive behavior during co-pyrolysis, which can be named as synergistic effects [13–17]. Nevertheless, some researchers were against the presence of synergistic effects during co-pyrolysis [8,18]. To summarize, it seems that there is no general regulations that can be used to predict thermal behavior of biomass and coal in their co-pyrolysis process. Furthermore, as far as we know, no investigation has been reported about thermal behavior in pyrolysis process for coal blended with platanus wood (PW), an abundant urban landscaping woody biomass with remarkable heat value in China. The PW is from *Platanus acerifolia* which is extensively applied in the city landscaping, known as the king of roadside trees in the world. These trees are planted in a lot of Chinese cities due to its great trunks, strong resistance to contamination and good environmental adaptability [19]. Because of the rapid growth rate, they are periodically pruned every year, and a large number of waste PW is produced in the pruning process. To investigate co-pyrolysis of PW and coal blends as a worthy method for producing secondhand energy, there is still an unsatisfied demand to study thermal behavior and kinetics of their blends during pyrolysis process.

To improve the efficiency of co-pyrolysis, many works have been also devoted to the evolution of gaseous and liquid products attributed to their wide applications in industry, but there are only a few researches concerning the characteristics of co-pyrolysis chars. Some investigators found that the physical characteristics of the char samples, such as pore size and specific surface area, were improved by adding biomass during pyrolysis process resulting in the conversion promotion of the char [20]. Furthermore, study on the evolution of carbon structure, an important factor influencing product distributions and reactivity of the char in further gasification or combustion process, is rarely conducted. Compared to the char from pyrolysis of individual biomass or coal, the structure evolution of the char samples from pyrolysis of the blends is more sophisticated because the influence of volatiles–char interactions [21]. Besides, the reaction of char conversion is normally the rate-limiting procedure for integrated co-gasification or co-combustion process [21,22]. Therefore, obtaining a clear understanding of carbon structure evolution for co-pyrolysis chars is indispensable for promoting the co-thermochemical conversion process efficiency.

In the present work, co-pyrolysis characteristics of PW blends with two different rank coals have been investigated to obtain an overall knowledge about the co-thermochemical conversion process. The thermal behavior and kinetic analysis of PW, two different rank coals and their blends were evaluated using a thermogravimetric analyzer. The efforts were also devoted to investigate if there existed synergistic effects between PW and coal during co-pyrolysis process. The kinetics parameters were computed by the Kissinger–Akahira–Sunose (KAS) method. The effects of PW on char structure evolution and elementary composition were investigated by Raman spectroscopy and energy dispersive spectrometry analyses, respectively. The aim of this study is to gather data and obtain knowledge, which can be useful in modeling, designing, and running of co-thermochemical utilization technology for the blends of biomass and coal.

2. Materials and methods

2.1. Samples

The PW was obtained from the street of Xi'an, Shaanxi Province, China. Two different rank coals were selected for this study including Pingzhuang lignite (PZ) and Shenmu bituminous (SM). Both the two types of coals are typical in northern China. The samples were first broken, then sieved to fine particles of less than 74 μm. The tested blends were prepared with three different PW/coal blending ratios including 70:30, 50:50 and 30:70, and the uniformity of the blends was ensured by subsequent rolling at a constant speed of 300 rpm for more than 12 h. The proximate, ultimate and chemical ingredients analysis results of the raw samples are presented in Table 1. Identification of the major structure of PW, i.e. holocellulose (the sum of the cellulose and hemicellulose), and lignin