



## Investigation on thermal and trace element characteristics during co-combustion biomass with coal gangue



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### HIGHLIGHTS

- The thermochemical behavior of coal gangue and biomass were evaluated.
- The kinetic properties and optimum conditions of their blends were obtained.
- The effects of co-combustion on current combustion application were studied.

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### ABSTRACT

The thermochemical behaviors during co-combustion of coal gangue (CG), soybean stalk (SS), sawdust (SD) and their blends prepared at different ratios have been determined via thermogravimetric analysis. The simulate experiments in a fixed bed reactor were performed to investigate the partition behaviors of trace elements during co-combustion. The combustion profiles of biomass was more complicated than that of coal gangue. Ignition property and thermal reactivity of coal gangue could be enhanced by the addition of biomass. No interactions were observed between coal gangue and biomass during co-combustion. The volatilization ratios of trace elements decrease with the increasing proportions of biomass in the blends during co-combustion. Based on the results of heating value, activation energy, base/acid ratio and gaseous pollutant emissions, the blending ratio of 20–30% biomass content is regarded as optimum composition for blending and could be applied directly at current combustion application with few modifications.

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### 1. Introduction

As the shortage of finite non-regenerated energy (petrochemical resources) and the increasing environmental problems (global warming, surface subsidence, heavy metal pollutions, etc.) during the past decades, the necessity to develop alternative renewable, sustainable and clean energy has become an irresistible trend (Dai et al., 2012; Goldfarb and Liu, 2013; Limayem and Ricke, 2012; Piriou et al., 2013). Biomass as the solar energy in chemical form in plant/animal materials (includes algae, wood, agricultural residues, forestry residues and industrial residues), which is supposed to the best alternative of fossil fuels substitution

(Demirbas, 2005). For the enormous renewable potentially, available abundantly and cost-effective, biomass can be regarded as the main resource for renewable and sustainable energy. Meanwhile, biomass is generally considered as a clean energy for the completely CO<sub>2</sub>-neutral, thereby relieve global warming problems. The underlying hypothesis is that the CO<sub>2</sub> released in the atmosphere during biomass utilization is matched by the amount during photosynthesis (Demirbas, 2005; Gil et al., 2010). Although their potential to substitute for fossil fuels is still uncertainly, biomass is possible to provide a cost-effective and sustainable energy in the future.

Currently, the utilization technologies of biomass materials include both thermochemical (combustion, pyrolysis, liquefaction and gasification) and biochemical (supercritical fluid extraction, anaerobic digestion, enzymatic hydrolysis and esterification) processes (Guo et al., 2012; Kabir and Kumar, 2012; Luo et al., 2014; Piriou et al., 2013). Among these, the direct combustion is account for approximately 97% of the world's bio-energy production

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(Demirbas, 2004). This supply is mainly attributed to the traditional biomass using for heating and cooking in rural areas of developing countries (Demirbas, 2005). However, many studies have been reported that the traditional heating and cooking processes may result in low energy efficiency and high gaseous pollutant emissions during incomplete combustion (Freeman and Cattell, 1990; Mu et al., 2012; Vuthaluru, 2004; Williams et al., 2012). Therefore, the co-combustion of biomass with coal for electricity production has received fairly intensive studies, and suggested that the thermochemical reactivity and combustion properties could be promoted by addition of suitable proportion of biomass (Gil et al., 2010; Goldfarb and Liu, 2013; Haykiri-Acma et al., 2006; Idris et al., 2012; Masnadi et al., 2014; Vamvuka et al., 2003). However, few studies have centered on the co-combustion processes of biomass with high ash content and low heating value fuels (Yadav et al., 2013; Zhou et al., 2014a).

Coal gangue is the industrial residues during coal mining activities (approximately 10–15% of raw coal production), and known as high ash yield, low heating value and low carbon content (Zhou et al., 2014b). With the development of circulating fluidized bed combustion technology, coal gangue could be applied for electricity production by additive suitable percentage of high heating value coal (Pallares and Johnsson, 2006). The high heating value coal could promote the ignition performances and thermal reactivity effectively. Biomass possess higher volatile matter (higher thermochemical reactivity), lower ignition temperature and shorter combustion duration when comparing with fossil fuels (Vassilev et al., 2013, 2014). Biomass may provide a stable flame, and promote the ignition and thermal behaviors effectively when co-firing with coal gangue (Vamvuka et al., 2003; Xu et al., 2014). Meanwhile, the co-combustion of coal gangue with biomass may increase the utilization efficiency of biomass and relieve the rapid consumption of finite fossil fuels and the overload of solid wastes. Although biomass is a potential renewable co-energy source, the thermochemical behaviors are far different from coal gangue (Kirtania and Bhattacharya, 2013). Thus, it is of extremely significance to understand the co-firing behaviors and their influence in combustion efficiency. Meanwhile, the fundamental characteristics of the co-combustion behaviors is of extreme significance for the combustion application. Therefore, it is crucial to carry out a systemic thermochemical analysis of biomass and coal gangue to determine their behaviors in real combustion systems precisely.

Additionally, the atmospheric pollutants ( $\text{NO}_x$ ,  $\text{SO}_x$ , and trace elements) are also of great importance in the utilization approach of biomass (Demirbas, 2005; Williams et al., 2012). The emission amounts and behaviors of pollutants not only influence the removal efficiency of the current atmospheric pollutant control devices, but also relate with the utilization efficiency of biomass. Therefore, the gaseous pollutant emissions and behaviors of these pollutants during co-combustion should be taken into consideration. In this study, the main objectives are to determine (1) the thermochemical characteristics of coal gangue, biomass and their blends via thermogravimetric analysis, (2) the optimum blending ratio and heating rate during co-combustion, (3) the effect of co-combustion on current combustion application.

## 2. Methods

### 2.1. Sampling

In order to represent the chemical characteristics of the Huainan coal gangue, the coal gangue samples (CG) from the floor of No. 7 coal seam of Guqiao Coal Mine, Huainan, China were sampled by cutting channels downwards methods. The agricultural biomass (soybean stalk (SS)) and pine sawdust (SD) were collected from the

farmland and logging camp around the Guqiao Mine, respectively. All the selected samples were kept in the sealed plastic bags immediately to prevent contamination. After taken back to laboratory, both the biomass and coal gangue samples were air dried, crushed and passed through a 200-mesh sieve to homogenize for the subsequent analysis. The proximate and ultimate analyses together with the heating values of the selected samples were determined according to ASTM standards and the results were summarized in Table 1. For the blends samples, biomass was added to coal gangue at weight ratios of 10:90, 20:80, 30:70 and 50:50, respectively. The blends samples, in above proportions, were homogeneously mixed to be representative and precise.

### 2.2. Thermogravimetric analysis

A SDT Q600 thermal analysis system was employed to investigate the thermochemical behaviors of coal gangue, soybean stalk, sawdust and the blends. The precisions of temperature measurement and microbalance sensitivity were  $\pm 0.1^\circ\text{C}$  and  $\pm 0.1\ \mu\text{g}$ , respectively. The heating rate could be ranged from 1 to  $100^\circ\text{C}/\text{min}$ . The analyses were carried out under a  $100\ \text{ml}/\text{min}$  air flow at heating rates ( $H$ ) of 15 and  $60^\circ\text{C}/\text{min}$ , respectively. The combustion temperature was raised from room temperature to  $1000^\circ\text{C}$ . To avoid the mass and heat transfer limitations, approximately 20 mg of the selected samples were applied and dispersed flatly on a crucible. The mass loss (TG) and derivative curves (DTG) representing the function of temperature were recorded under dynamic conditions. Triplicate experiments for each sample were conducted to ensure reproducibility of the results.

### 2.3. Kinetic analysis

The kinetic characteristics (activation energy and pre-exponential factor) on solid reaction could be determined by both differential and integral methods (Bamford and Tipper, 1980). In this study, the integral method was employed to evaluate the kinetic properties of coal gangue and biomass during co-combustion. The fundamental rate equation adopted in all kinetic studied is described as Eq. (1):

$$dx/dt = K(T) \cdot f(x) \quad (1)$$

where  $x$  is the mass conversion ratio during combustion.  $f(x)$  is the hypothetical model, which is decided by the reaction mechanism.  $t$  and  $T$  represent the combustion time (min) and absolute temperature (K), respectively.  $K(T)$  is the reaction rate and could be determined by Arrhenius equation as Eq. (2):

$$K(T) = A \cdot \exp(-E/RT) \quad (2)$$

where  $A$ ,  $E$ , and  $R$  are the pre-exponential factor ( $\text{min}^{-1}$ ), activation energy (kJ/mol), and the universal gas constant ( $8.314\ \text{J}/(\text{K mol})$ ), respectively. Once the combustion is applied using a non-isothermal thermogravimetric analysis, the heating rate ( $H$ ,  $\text{k}/\text{min}$ ) is constant and could be described by the following relationship as Eq. (3):

$$H = dT/dt = (dx/dt) \cdot (dT/dx) \quad (3)$$

Substitution of Eq. (3) in Eq. (1) and arrangements into Eq. (4):

$$dx/f(x) = (A/H) \cdot \exp(-E/RT) \cdot dT \quad (4)$$

Integrating both sides of Eq. (4) gives Eq. (5):

$$g(x) = \int_0^x dx/f(x) = (A/H) \int_{T_0}^T \exp(-E/RT) dT \quad (5)$$

$g(x)$  is the integral conversion function. Since  $E/RT \gg 1$ , the right side of Eq. (5) could be substituted into Eq. (6):

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