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Investigating co-firing characteristics of coal and masson pine

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ABSTRACT

Co-firing characteristics of masson pine and coal was determined using thermogravimetric analysis at different heat rates in an air atmosphere. The kinetic parameters were calculated using Kissinger-Akahira-Sunose and Coats-Redfern method. Pollutant emission and ash characteristics were also investigated. Results showed that all samples had two separated combustion zones during co-firing process except for coal, corresponding to volatile and char combustion. CO_2 had the highest releases and SO_2 had the lowest release. The chemical compositions and thermodynamic properties of blend ash were similar with coal ash. The optimum blend ratio was 20% masson pine and 80% coal because it had the similar kinetic parameters and ash characteristics with coal. Furthermore, it also had a lower pollutant emission. The results from this research will be helpful to develop masson pine as fuel products in China.

1. Introduction

Bio-fuels have gotten more and more concerns due to fossil fuel crisis and environment pollution in the past few years [1,2]. The data from the Energy Technology Perspective (ETP) shows that bio-fuel demand will reach 32×10^{18} J by 2050 around the world [3]. At the same time, European also expects that biomass energy will replace 20% of gross energy consumption by 2020 [4]. However, the utilization of bio-energy in various regions is still very limited. In industrialized countries, the contribution of biomass to energy consumption is only 4%. In developing countries, around 22% of energy originated from biomass, but the majority of them are non-commercially traditional applications [5]. According to data from the Chinese energy development report in 2003, the electricity production is main rely on the coal combustion in power station. The environmental impacts of coal combustion have led to more and more researches on alternative and renewable fuels. Forestry and agricultural residues is about 0.9 billion tones every year in China [6]. Masson pine is one of the four types of fast-growing forestry plants and has been widely cultivated in China. Now it has been used to produce wood products, such as furniture, wood based-panel, paper, etc. These processes have produced abundant wastes of masson pine, having great potential as bio-energy resources of the future.

Coal utilization is main through combustion in energy power station to electricity generation due to its characteristics of higher heat value (HHV) and large-scale reserves [7,8]. It occupied 62% of energy consumption of China in 2016. Currently, the using of biomass as fuel is main rely on (1) carbonization of biomass to charcoal; (2) gasification of biomass to gaseous products; (3) liquefaction of biomass to liquid products; (4) co-firing with coal; (5) direct combustion for electricity generation [9,10]. It is well known that there are still some disadvantages in gasification, liquefaction and direct combustion. For example, the higher H/C and O/C of biomass materials affect the properties of gasification and liquefaction products. The lower HHV decreases the efficient of combustion in direct combustion [11,12]. However, combustion is the mostly direct and simple way to utilize coal and biomass, especially in some rural areas now [13].

Co-firing of biomass with coal has proved to be an effective utilization option for reducing greenhouse gas emissions. Many researchers have investigated the co-firing of biomass and coal. Seongyool et al. investigated the effects of biomass blending with two types of pulverized coal under air and oxy-fuel conditions. They found that the ignition temperature was governed by the fuel composition. However, the burnout temperature depended on the oxidant ingredients rather than on the fuel components [14]. Gil et al. investigated the thermal characteristics of coal, pine sawdust and their blends. They found that volatiles were released and

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burned at 200–360 °C for pine sawdust. Its char combustion occurred at 360–490 °C. In contrast, coal was characterized by only one combustion stage at 315–615 °C [15]. Wang et al. found that HCl, SO_2, CO_2 and NO_X emissions were closely related to the volatile combustion and char reacting stages during co-firing of coal/wheat straw. The emission of SO_2, and NO_X had two characteristic peaks. The first peak occurred around 320 °C for all blends. However, the second peak shifted towards higher temperatures as the coal content was increased in the blends. The CO_2 emission was mainly produced in the char combustion stage and purely increased with the carbon content in the blends [16]. Luan et al. investigated composition and sintering characteristics of ashes from co-firing of coal and biomass. Sintering temperature decreased with increase in the mass ratio of biomass to coal with a non-linear relationship [17].

It is well known that the physical structure and chemical composition will influence the combustion process of fuels. Despite these previous researches were very helpful in understanding co-firing of biomass/coal, masson pine is a type of different forestry resources. To the best of our knowledge, there is a lack of sufficient information concerning co-firing of masson pine and coal. In this research, the co-firing characteristics of masson pine and coal was therefore determined using thermogravimetric analysis (TGA) at a heat rate of 10 °C/min, 20 °C/min, 30 °C/min and 40 °C/min in an air conditions. The kinetic parameters including activation energy, pre-exponential factor and degree of fitting were calculated using Kissinger-Akahira-Sunose (KAS) and Coats-Redfern (CR) method. The pollutant emission, such as carbon dioxide (CO_2), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2), and ash characteristics were also investigated. The results from this research will be helpful to develop masson pine as fuel products in China.

2. Materials and methods

2.1. Materials

Masson pine *(Pinus massoniana Lamb.)*, aging with 20 years, was taken from Anhui province, China. The initial moisture content was about 9.5%. Coal was taken from Hebei province, China. They were broken down and screened to get 250–425 μm particles using a Wiley Mill. Masson pine was uniformly mixed with coal with different blend ratios (10% masson pine/90% coal, 20% masson pine/80% coal, 30% masson pine/70% coal and 40% masson pine/60% coal). The materials were dried at temperature105 °C until the mass stabilized.

2.2. Determination of co-firing of masson pine/coal

Combustion characteristics were determined in terms of global mass loss though TA Instrument, TGA Q 500 thermogravimetic analyzer (TA Instrument, USA). Samples were evenly and loosely distributed in an open pan with an initial weight of about 5–8 mg. Temperature variation was controlled from room temperature (30 ± 5 °C) to 800 °C with 10 °C/min, 20 °C/min, 30 °C/min and 40 °C/min of heating rates under 60 ml/min of air flows. Weight loss of the samples was continuously recorded during the process. Three replicates of each TGA experiment were performed.

2.3. Combustion kinetics parameter

The fundamental rate equation used in all kinetics studies is generally described as:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

Where, k is the rate constant and f(α) is the reaction model, a function depending on the actual reaction mechanism. Eq. (1) expresses the rate of conversion, dα/dt at a constant temperature as a function of the reactant conversion loss and rate constant. In this study, the conversion rate α is defined as:

$$\alpha = \frac{(w0 - wt)}{(w0 - wf)} \tag{2}$$

Where, w_t, w_0 and w_f are time t, initial and final weight of the sample, respectively. The rate constant k is generally given by the Arrhenius equation:

$$k = A\exp\left(\frac{-Ea}{RT}\right) \tag{3}$$

Where, Ea is the apparent activation energy (kJ/mol), R is the gas constant (8.314 J/K mol), A is the pre-exponential factor (min^{-1}), T is the absolute temperature (K). The combination of Eqs. (1) and (3) gives the following relationship:

(1) Kissinger-Akahira-Sunose (KAS) method

The KAS method is based on Eq. (4), used as a non-isothermal model because it can obtain accurate activation energy [18,19].

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{A \cdot E_a}{R \cdot g(\alpha)}\right) - \frac{E_a}{R \cdot T} \tag{4}$$

Where, g(α) is the integral reaction model and is constant at a given value of conversion: $g(\alpha) = n^{-1}\cdot(-1+(1-\alpha)^{-n})$ for reaction-order models, and the frequency factor was calculated considering n = 1. β is the heating rate. The plot is $\ln(\beta/T^2)$ versus 1/T and α is from 0.2 to 0.8, where the slope is equal to $(-E_a/R)$ and the frequency factor was calculated considering n = 1 [4].

(2) Coats-Redfern (CR) method

Coats-Redfern method [20] is based on Eq. (5), used as a isothermal model.

$$\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right) = \ln\left[\frac{A \cdot R}{\beta \cdot E_a}\left(1 - \frac{2 \cdot R \cdot T}{E_a}\right)\right] - \frac{E_a}{R \cdot T} (\text{for } n = 1) \tag{5}$$

In the plot of $\ln(-\ln(1-\alpha)/T^2)$ versus $1/T^2$ (for n = 1) the slope gives $-E_a/R$, and the intercept is $\ln[A \cdot R/\beta \cdot E_a(1-2RT/E_a)]$. But, by assuming $2RT \ll E_a$, then the intercept can be arrange as $\ln(A \cdot R/\beta \cdot E_a)$, where A can be calculated [21,22].

2.4. Determination of pollutant emission

Pollutants from combustion process were observed in terms of global mass loss though thermogravimetry (TA Instrument, USA) coupled with Fourier transform infrared spectrometer (Bruker IFS 66/S, Bruker Optics, Billerrica, MA). A helium sweep gas flow of 500 Nml/min was used to bring the evolved combustion gases from the TGA directly to the gas cell which was heated to 150 °C. The system collected FTIR spectra every 30s and the sample temperature and mass were logged every 3s. The sample pan was placed close to the end of the furnace, where a steeply decreasing temperature profile existed. This, combined with the high gas flow, minimized the residence time of the evolved gases in the hot zone. In the experiment, 20 mg samples were heated from 50 °C to 1000 °C at heating rate 20 °C/min under air conditions. A minimum of two samples