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Thermal behavior and kinetic analysis of co-combustion of waste biomass/low rank coal blends

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ABSTRACT

The thermal decomposition behavior of Shenhua bituminous coal (SB), Rice husk (RH), Pine sawdust (PS) and their blend during combustion were investigated by using the thermal analysis method. The apparent kinetic parameters of combustion process were estimated by fitting the experimental data to the double parallel reactions *n*th order rate model. The results showed that the combustion characteristics of the two kinds of biomass residues with low degree of order are higher than that of bituminous coal. For blend of bituminous coal with biomass residues, the ignition performance could be improved by increasing content of biomass residues, but the comprehensive combustion characteristics first decreases and then increases, with its lowest value occurring at addition content of 60%. Meanwhile, through comparison between theoretically calculated and experimentally measured data, it is concluded that there's a synergistic effect during combustion process of biomass and coal blend. Through kinetic analysis, it is found that the combustion processes of coal, biomass and their blends could be well represented by the double parallel reactions *n*th order rate model, and for the two stages in combustion, with an increase of biomass content both activation energies first decrease and then increase. Both stage activation energies of the RH blend have lowest value when RH ratio of 60% (first stage 140.2 kJ/mol, second stage 136.9 kJ/mol), but for the SP blend the first stage lowest activation energies was PS ratio of 20% with a value of 143.1 kJ/mol and the second stage's was a PS ratio 40% with a value of 143.9 kJ/mol.

1. Introduction

With industrialization process of China, consumption of fossil fuels continuously increases. Statistics in 2014 depicted that, China consumed 1962.4 million tons of oil equivalent to coal, 4035.4 million barrels of petroleum, and 185.5 billion cubic meters of natural gas, which systematically accounted for 50.6%, 12.4%, 5.4% for total world consumption, respectively [1]. The burning fossil produces enormous amounts, of CO_2, NO_x and SO_2. Beginning in 2010, China surpassed the US to become the world's biggest CO_2 emitters, accounting for almost one-third of the total emissions in 2013 [2]. Therefore, China has become a focus of global effects to reduce of CO_2 emissions amidst increasing international pressure [3]. Meanwhile, China is a big agricultural country with abundant biomass resources and annual yields of forestry and agricultural residues reaches 1.6 billion tons. If only half of them could be used as fuel, they are equal to 0.4 billion tons of standard coal [4–6]. Biomass stores solar energy in chemical energy form and it is renewable with abundant resource, low pollutant emission as well as carbon neutrality. However, biomass resource has its own disadvantages, such as large difficulty to collection, low density of energy, large investment and low utilization efficiency, so biomass resource is not efficiently utilized in China and much of them is processed by open burning which not only wastes resource but also causes environmental problems [7–9]. If biomass resource could be efficiently utilized, it would have great meaning for sustainable development of economy and society. Many investigations have been made for comprehensive utilization of biomass resource such as combustion, pyrolysis and gasification [10–13], and among them co-combustion with coal is one of the promising alternatives for the utilization of biomass fuels [14–17].

Main constituents and structure of biomass are different from coal. From proximate analysis, compared with coal, water and volatile contents in biomass are higher and solid carbon content

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is lower. From elemental analysis, compared with coal, oxygen content in biomass is much higher which makes calorific value of coal is higher than that of biomass [16]. From the viewpoint of substance comprises, coal is formed by metamorphic process of ancient plant under high temperature, high pressure, and oxygen deficient condition, and its maceral ingredient contains liptinite, vitrinite, and inertinite [18]. However, the main constituents of biomass are cellulose, hemicelluloses and lignin [19]. Considering molecule structure, coal is composed by aromatic series, aliphatic series and arcus adiposus, and for coal with different metamorphic degree, basic structure unit as well as condensation degree are also different [20]. But for biomass, the main constituents are glucose, polysaccharide, amino acid, protein, as well as much alkane, arene, aldehydes, ketone, organic acid and alcohol compound [21]. Due to different structure and constituents for coal and biomass, there are large differences between combustion process of them. It was concluded by Liu et al. [14,22–23] that there are two significant peaks in weight loss curve of biomass during combustion process, while for coal there is only one peak. Ignition and burn out temperatures of biomass are lower than that of coal, and the maximum combustion rate as well as mean combustion rate of biomass are higher. Differences between structure and combustion characteristics might lead to synergistic effect in co-combustion process. According to results on the combustion behavior of corncob, bituminous coal and hard wood by Liu et al. [14], it was found that addition of biomass could improve combustion characteristics of bituminous coal and there's mutual promotion effect in combustion process. However, from results of Zhou et al. [24,25], in co-combustion process of coal and biomass, no significant mutual promotion effect was found. It could be concluded from these literatures that in combustion process the influence of biomass on coal is not fully clear yet, and further study is needed.

Thermogravimetric analyzer, mass spectrometry analyses, fluidized bed reactor, tube reactor are frequently used techniques for investigation of combustion of biomass and coal [26–29]. Thermogravimetric analyzer and mass spectrometry analyses were used by Zhang et al. [26] to research co-combustion characteristics and pollutant emission feature of tobacco stem and high sulfur bituminous coal. Combustion behavior of biomass was researched by Yang et al. [27] through fluidized bed reactor, and influences of primary air flow, secondary air flow, feeding rates and bed temperature on combustion efficiency were analyzed. Gungor [28] investigated the effect of the biomass share on CO, NO_x and SO_2 emissions when co-firing coal and biomass in CFBs by using a developed model. Cofiring characteristics of torrefied biomass and coal were studied through drop tube reactor by Ndibe et al. [29], and the forming characteristics of SO_2 and NO_x during combustion process were also investigated. Among the above methods, thermogravimetric technique is widely applied due to its simplicity to get large amounts of data. Through thermogravimetric analysis, combustion characteristic values, such as ignition temperature, burn out temperature, reaction peak temperature, maximum combustion rate, mean combustion rate and burning time, could be obtained. Also, according to weight loss curves under different temperatures, combustion kinetic parameters such as activation energy, pre-exponential factor, reaction order as well as mechanism function, could be ascertained. Combustion mechanism of biomass and coal could be investigated in depth through kinetics analysis, and also combustion rate as well as reaction process could be predicted. These data are of significant importance for understanding the co-combustion mechanism of biomass and coal, which is beneficial for improving combustion efficiency as well as designing and operating of combustion furnace. Many investigations have been done on co-combustion of biomass and coal, and the vast majority of them can be classified as either 'model-free' or 'model-fitting'. In the conventional approach for estimating kinetic parameters (activation energy, pre-exponential factor and reaction order) from conversion curve via model-fitting analysis, it is usually assumed a certain reaction order, and then the differential or integral form of the rate equation is applied until a straight line plot can be obtained by linear regression. Coats and Redfern [30], Freeman and Carroll [31], and Duvvuri et al. [32] methods are often used for these kinds of study. But it is recognized that these methods suffer from two main drawbacks, especially when only a single heating rate is applied. Different values of the kinetic parameters can be obtained to describe the same reaction curve, which leads to an uncertainty in terms of interpretation of the results. On the other hand, it generally tends to yield one set of kinetic parameters for the whole range of conversion, but does not take into account the complexity of mechanisms during combustion of materials [33]. With the increase of calculating capability of computers, a more complicated but more accurate method involving non-linear least squares optimization of multiple heating rates has been increasingly considered [23,34,35].

In the present study, Shenhua bituminous coal (SB), Rice husk (RH), Pine sawdust (PS) have been analyzed by proximate analysis, ultimate analysis, X-ray diffraction analysis, FTIR analysis and scanning electron microscopy techniques to obtain the similarities and differences between coal and biomass. In addition, the combustion characteristics of biomass and their blends with different weight ratio of the biomass/coal have been investigated by thermogravimetric analysis (TGA). Ignition temperature, burnout temperature, reaction peak temperature, ignition index and comprehensive combustion index of different samples were obtained. Moreover, the double parallel reactions *n*th order rate model was also established and used to evaluate the kinetic parameters for combustion curves of different samples. The resultant data may be used to enhance the understanding of the combustion of biomass/coal and also provide a basis for further applying biomass on blast furnace or power station with high efficiency.

2. Material and methods

2.1. Material preparation and analysis

Rice husk (RH) and Pine sawdust (PS) are the sustainable agricultural and forestry remnants which are very abundant in China. On the other hand, Shenhua bituminous coal (SB) which is a typical low quality coal with low calorific value and high ash content is generally used in blast furnace injection in the Huabei region of China. Therefore, the two biomass materials and coal material were adopted and studied in this work. Prior to experiments, the coal and biomass materials were firstly dried at room temperature, and then ground to <2 mm and held in a drying oven at 378 K for 12 h. Dry samples were further ground by a shredder and sieved by vibrating screens. Afterward, the particle sizes of samples were selected to that lower than 0.074 mm by using standard test sieve for experiments.

The proximate, ultimate and calorific analysis were performed. The proximate analysis was performed in accordance with the standard procedures of Chinese standard GB/T 212-2001. The elemental analysis was carried out using an elemental analyzer. The weight percent of carbon, hydrogen, nitrogen and sulfur in samples can be detected simultaneously, and the weight percent of oxygen was determined by difference. The higher heating values (HHVs) of the samples were measured by means of a bomb calorimeter. The characteristics of samples are listed in Table 1. The ash of the raw materials was prepared by air oxidation at 1088 K in a muffle furnace according to the Chinese standard (GB/T 212-2008). The ash chemical composition was determined by XRF-18000 produced