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# Thermal Behavior and Kinetics of Raw/Pyrolytic Wood and Coal Blends during Co-combustion Process

Jian DING, Qing-cai LIU, Li-jun JIANG, Guo-qing LIU, Shan REN,
Jian YANG, Lu YAO, Fei MENG
(College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China)

**Abstract**: The thermal properties of raw wood (RW) biomass, corresponding pyrolytic wood (PW) biomass, and their blends with anthracite coal (AC) were evaluated under combustion conditions with a thermogravimetric analysis (TGA) method. The blending ratios of the biomass with AC ranging from 0 to 100 mass% were taken into consideration to investigate the thermal behavior and kinetics of these blends during their co-combustion. For blends with different ratios of the RW to AC and 100% AC (100 AC), two distinct mass loss peaks related to the release or combustion process of the volatiles and the combustion of the char were noted. The addition of a higher ratio of RW or PW into AC can improve the combustion process of the blends. The thermal behavior of the RW/AC or PW/AC blends could not be characterized by a simple linear correlation of their pure material thermal behavior. With the RW/PW addition ratios varying from 25 mass% to 80 mass%, the apparent activation energy of the blends gradually decreased from 48.46 to 34.93 kJ/mol and from 82.74 to 37.81 kJ/mol for the RW/AC and PW/AC blends, respectively, with high correlation coefficient ($R^2$) values ranging from 0.9956 to 0.9984.

**Key words**: thermal property; thermogravimetric analysis; raw wood biomass; pyrolytic wood biomass; apparent activation energy

Biomass is increasingly considered to be a promising feedstock for renewable energy because of the depletion of fossil fuels and the increasing environmental concerns[1]. Biomass has a wide distribution and is a high yield feedstock that accounts for approximately 14% of the world energy supply, especially during the agricultural harvest and forest logging periods[2]. At present, coal is a typical feedstock used for energy production because of its large reserves and high energy density. However, the use of coal has caused concern because of the emission of toxic gases and the fused-ash slagging problem which appears in the bottom of the combustor[3]. Thus, as a promising renewable energy, biomass has attracted more and more attention of researchers and energy institutions. Unfortunately, the use of raw biomass alone will only address some of the problems because it has a high moisture content, is not easy to grind, and has a low density and heating value[4].

The co-combustion of biomass and coal is a promising option to solve the problems mentioned above. In recent years, studies have been reported on issues regarding the co-utilization of biomass and coal[5-7]. However, less attention has been given to the co-combustion behavior comparison regarding the same biomass under different pretreating conditions, especially the pyrolysis process for the biomass, which is necessary to significantly reduce moisture content and enhance energy density value. Therefore, corresponding pyrolytic biomass blends with coal are used to explore the combustion differences between raw wood (RW)-coal and pyrolytic wood (PW)-coal blends.

Thus, in this study, the co-combustion of Chinese anthracite coal, raw wood biomass, and corresponding pyrolytic biomass were carried out in a

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**Biography**: Jian DING, Doctor; **E-mail**: lgq2013@cqu.edu.cn; **Received Date**: September 6, 2015

**Corresponding Author**: Shan REN, Doctor, Lectureship; **E-mail**: shan.ren@cqu.edu.cn

thermogravimetric analyzer. The carbon content of the biomass is lower than that of coal; however, anthracite coal has higher carbon content than any other coals that are available. Blending biomass and coal can relatively enhance the carbon content of the blend, which is closer to that of bituminous or subbituminous coal. There has already been much systematic study on the combustion behavior differences between raw/pyrolytic wood and coal blends. In this study, the co-combustion kinetics of raw/pyrolytic wood and coal blends were investigated under different blending ratios.

## 1 Experimental

### 1.1 Material

Anthracite coal (AC) was provided by a power plant located in Chongqing, China, and the raw wood biomass used was pine powder, which was derived from a wooden furniture factory also located in Chongqing, China. Pyrolytic wood was obtained by the following steps. The raw pine wood was cut into the dimensions of 10 mm×10 mm×40 mm. Then, the wood pieces were pyrolyzed in an inert environment without oxygen at 400 ℃ for 1 h[8]. And nitrogen was used as the carrier gas under a flow rate of 60 mL/min. The raw/pyrolytic wood and coal samples were ground and sieved in order to obtain a particle size of 120 to 150 μm. Five different biomass blending ratios of 0, 25, 50, 80, and 100 mass% were obtained for analysis.

### 1.2 Methods

In this study, a simultaneous thermogravimetric analyzer (STA-449F3, NETZSCH, Germany) was used to examine the combustion characteristics of the samples. For each run, approximately 6 mg of sample and a heating rate of 20 ℃/min were used to avoid heat transfer limitations and minimize the mass transfer effects. After loading the prepared samples into an alumina oxide crucible, a thermocouple was placed close to the sample to monitor the temperature. The sample was then heated from ambient temperature to 900 ℃ under the air flow rate of 60 mL/min to ensure complete contact of the sample and air. To ensure the accuracy and reproducibility of the results, all experiments were carried out in duplicates, at a minimum, to achieve the relative error rate within 5.0%.

Table 1 provides the results of the proximate and ultimate analyses of coal, pyrolytic wood biomass, and raw wood biomass. It shows that the fixed carbon values of the pyrolytic wood material are higher than those of the raw wood material. This implies that the pyrolytic treatment can significantly increase the intensity value of energy density under an inert environment. For a solid fuel, the contents of nitrogen and sulfur are important indexes because they can be transformed into toxic $NO_x$ and $SO_x$ during the combustion process. The contents of nitrogen and sulfur in pyrolytic wood are much lower than those of the raw wood material. However, these values are far below those of coal. Thus, to some extent, the co-combustion of the material blends may achieve considerable environmental benefits.

**Table 1 Proximate and ultimate analysis of anthracite coal and raw/pyrolytic wood biomass** mass%

| Sample | Proximate analysis | | | | Ultimate analysis (ad) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Moisture | Ash | Volatile | Fixed carbon | C | H | O | N | S |
| AC | 5.70 | 12.34 | 12.85 | 69.11 | 78.20 | 4.27 | 15.76 | 1.25 | 0.52 |
| RW | 6.22 | 0.46 | 76.64 | 16.68 | 49.85 | 6.54 | 43.36 | 0.08 | 0.17 |
| PW | 2.25 | 0.81 | 32.45 | 64.49 | 65.04 | 5.31 | 29.57 | 0.03 | 0.05 |

Note: ad means the as determined basis.

### 1.3 Kinetic analysis

In the present work, the kinetically controlled reaction, under the condition of a low heating rate, and the thermogravimetric analysis (TGA) data are used to calculate the kinetic parameters using the Coats-Redfern method, based on the Arrhenius equation. The kinetics of the reaction is given as follows:

$$\mathrm{d}X/\mathrm{d}t = A\exp(-E_a/RT)\cdot f(X) \tag{1}$$

where,

$$X = \frac{(W_0 - W_t)}{(W_0 - W_\infty)} \tag{2}$$

$$f(X) = (1-X)^n \tag{3}$$

$X$ is the conversation rate and can be calculated by Eq. (2)[9-13]; $f(X)$ represents the hypothetical model of the reaction mechanism; $A$ is the pre-exponential or frequency factor; $E_a$ is the apparent activation energy, kJ·mol$^{-1}$; $t$ is the time, min; $R$ is the universal gas constant, 8.314 J·mol$^{-1}$·K$^{-1}$; $T$ is the