Combustion Characteristics of Biomass and Bituminous Coal Co-firing in Non-isothermal and Isothermal Conditions

Meijing Chen, a Baojun Yi, a,b,* Zhigang Li, a and Qiaxia Yuan a,b

A thermogravimetric method was used to study the combustion of bituminous coal (BC), diverse biomass (wood chips: WC, chaff: CH), and their blends under non-isothermal conditions and isothermal conditions. A higher blending amount of WC or CH under non-isothermal conditions resulted in a lower ignition temperature, burnout temperature, and a greater comprehensive combustion characteristic index. Meanwhile, the co-combustion of BC, WC, and CH all showed inhibiting effects. The inhibition effect was prominent when the blending ratio of WC was below 30%. Under isothermal conditions, with the increase of oxygen concentration and blending amount, the combustion performance of BC improved gradually. The synergistic effect between BC and biomass dominated, and the interaction was more distinct when WC content exceeded 50%. Under both non-isothermal and isothermal conditions, the interaction between CH and BC did not vary at diverse blending ratios. The dynamic results suggested that the chemical reaction model O1 was suitable for stage 1 of the co-combustion of WC and BC, the model diffusion controlled D4 controlled the co-combustion of CH and BC and stage 2 of the co-combustion of WC and BC. The blending ratio of WC or CH with the lowest activation energy was 50%.

Keywords: Biomass; Bituminous coal; Co-combustion; Thermogravimetric analysis; Isothermal conditions

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INTRODUCTION

China is a major energy consumer. According to statistics from 2019, China’s coal consumption exceeded 4 billion tons, accounting for more than 50% of the global total. A large amount of CO2, SO2, PM2.5, and other pollutants will be generated during the combustion of coal. Since 2010, China has become the world’s largest CO2 emitter (Zhao et al. 2015), and therefore, pollutant emission reduction is an urgent problem to be resolved. Simultaneously, China is a large agricultural country, and it produces high quantities of agricultural waste each year. Biomass contains a large quantity of chemical energy, and if half of this energy was used as fuel, it would be equivalent to 400 million tons of standard coal (Wang et al. 2016b). As a type of renewable energy, biomass has the benefits of abundance, ease of access, less pollutant emissions, etc., and has remarkable environmental and economic benefits. However, there are problems such as widespread distribution and difficult collection. Hence, currently, it has not been effectively utilized in China. Co-combustion of biomass and coal is the cheapest and most valid way to make use
of biomass (Pang et al. 2013). It not only maximizes the utilization of agricultural waste but also reduces the dependence on fossil energy, such as coal, which lowers emissions and possesses important practical significance.

Compared with coal, the structure and properties of biomass are both distinct. The analysis showed that biomass contains higher moisture and volatiles, and less fixed carbon. Elemental analysis has demonstrated that the oxygen content of biomass is much higher than that of coal, but the content of sulfur and nitrogen is lower. Because of the remarkable differences in combustion materials, it is essential to study the thermodynamic properties of the combined combustion of biomass and coal. Thermogravimetric analysis (TGA) has the advantages of fast speed, high efficiency, and convenient measurement of small mass samples in comparison to other analysis methods (Idris et al. 2012).

Most of the current combustion experiments have been carried out under isothermal conditions. However, in actual coal-fired power plants, the cost of non-isothermal combustion is higher, so isothermal combustion was often used. Studying the combustion characteristics and interaction of BC and WC/CH under two temperature conditions could further discover the advantages and disadvantages of each, which can provide certain guidance for practical applications (Wang et al. 2016a). There is a great difference in the combustion of biomass and coal. Biomass possesses two distinct combustion peaks, while coal has only one peak. The biomass ignition temperature and burnout temperature are lower, and the weight loss rate is higher in contrast to coal (Li et al. 2014; Gai et al. 2015). Hence, synergistic effects may impact the co-firing of biomass and coal. Guo et al. (2020) studied the combustion behavior of biomass pellets (BP), bituminous coal (BC), and lignite (XL). The mixture of BP and BC possessed three combustion stages, while there were only two evident combustion stages in the mixture of BP and XL. Meanwhile, with the increase of BP, the combustion performance was improved, and there was a clear synergistic effect in the combustion process. Li et al. (2016) found that the addition of distillation slag could ameliorate the combustion performance of coal. There was a synergy between distillation slag and coal, which increased at first and then decreased with the increase of distillation slag. However, diverse outcomes had been reported by some scholars. Zhou et al. (2014) found that there was no obvious promoting effect in the process of co-firing peanut shells or wheat straw with coal, and the slight differences calculated in the experiment were within the error range. Moreover, Wang et al. (2016b) observed that blending rice husk or pine wood chips in bituminous coal might improve the ignition performance, while it had no remarkable impact on the composite combustion characteristic of coal. The activation energy of biomass was slightly higher than coal, and it firstly decreased and then increased with the increase of biomass. Jayaraman et al. (2017) found that with the increase of the content of poplar or hazelnut shells, the reactivity of the sample was enhanced. The activation energy of biomass was higher than that of coal, which was connected with the temperature dependence of the pore structure. In contrast, diverse opinions were put forward by Wang et al. (2012). In the process of co-firing coal with sawdust or straw, kinetic studies made it clear that a higher biomass content resulted in lower activation energy of the mixture. From these reports, the effect of the blending ratio on the interaction and kinetics has not been fully studied during the combined combustion of biomass and coal, thus there is a need for further research.

In this experiment, the combustion characteristics at different biomass blending ratios were analyzed under non-isothermal and isothermal conditions. Furthermore, combining the experimental results at both low heating rate, high heating rate, and kinetic
analysis, the co-firing characteristics of biomass and coal were confirmed.

EXPERIMENTAL

Materials
Wood chips (WC) and Chaff (CH), two common agricultural wastes with remarkable difference in their volatiles and ash content, are available in a wide range of sources and low prices. The WC and CH were collected from Wuhan, Hubei Province (China), and the bituminous coal (BC) was collected from Shanxi Province (Datong, China). The raw materials were dried at 105 °C, passed through 60- to 200-mesh sieves, and then stored in a drying vessel. Proximate analysis and ultimate analysis of WC, CH, and BC were conducted. The results are shown in Table 1.

Table 1. Proximate Analysis and Ultimate Analysis of Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate Analysis (wt%.ad)</th>
<th>Ultimate Analysis (wt%.daf)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>V</td>
</tr>
<tr>
<td>BC</td>
<td>5.27</td>
<td>32.29</td>
</tr>
<tr>
<td>WC</td>
<td>8.87</td>
<td>77.29</td>
</tr>
<tr>
<td>CH</td>
<td>8.79</td>
<td>64.10</td>
</tr>
</tbody>
</table>

<sup>1</sup>: Calculated by the difference method
Note: ad- air-dry basis; daf- dry ash-free basis

Methods

Thermogravimetric analysis
The thermogravimetric method was adopted to analyze the combustion characteristics of coal and biomass, and thermogravimetric experiments were performed using a heating furnace (SK1250-8, Yingshan Jianli Electric Furnace Manufacturing Co., Ltd., Yingshan, China). Under non-isothermal conditions, the experiment process was as follows: 200 ± 0.2 mg of the sample was placed in the electric furnace hearth and heated from room temperature to 800 °C at a rate of 20 °C/min. Under isothermal conditions, the experiment process was as follows: the temperature was raised to 800 °C and held for 5 min to stabilize the temperature in the furnace. Then, the sample basket was placed into the furnace. The atmosphere in the furnace was 21% O<sub>2</sub>/79% N<sub>2</sub> and the gas flow rate was 100 mL/min. Repeated thermogravimetric experiments were carried out (Wielinski et al. 2018), and the number of repetitions for the same sample was 3 times.

The thermodynamic curve was made and the characteristic parameters of combustion were analyzed. The peak temperature and the maximum burning rate corresponding to the two stages of non-isothermal combustion were \( T_1, DTG_1, T_2, \) and \( DTG_2 \), respectively. Composite combustion characteristic index S was a comprehensive index reflecting ignition and burnout. The calculation formula of S is shown in Eq. 1,

\[
S = \frac{DTG_{\text{max}} \times DTG_a}{T_1 \times T_b}
\]
where $DTG_{\text{max}}$ (°C/min) is the maximum rate of weight loss, $DTG_{a}$ (°C/min) is the average rate of weight loss between the ignition point and the burnout point, $T_{i}$ (°C) is the ignition temperature, and $T_{b}$ (°C) is the burnout temperature. A higher value of $S$ meant it was easier for the biomass fuel to catch fire, burn out more fully, and possess better combustion characteristics (Vamvuka and Sfakiotakis 2011).

In the isothermal experiment, the stability factor was used to measure the combustion status. The stability factor is the ratio of burnout time $t_{f}$ to the maximum combustion share $\varepsilon_{m}$, and the calculation formula of the stability factor is shown in Eq. 2,

$$\text{Stability factor} = \frac{t_{f}}{\varepsilon_{m}}$$

where $t_{f}$ (s) and $\varepsilon_{m}$ (%) represent the burnout time and the maximum combustion share, respectively. The parameter $\varepsilon_{m}$ is the difference between the assumed average weight loss curve (the assumed average weight loss curve is a curve that takes the average weight loss rate of the sample from ignition to burnout as the assumed weight loss rate) and the actual weight loss curve. The larger the stability factor was, the closer the overall weight loss of the sample was to the average weight loss curve, and the more stable the overall combustion process.

**Kinetics analysis methods**

The kinetic parameters can be obtained according to Eq. 3,

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}f(\alpha)$$

where $\alpha$, $t$ (min), $A$ (min$^{-1}$), $E$ (KJ/mol), $R$ (8.314 J • mol$^{-1}$ • K$^{-1}$), and $T$ (°C) represent mass conversion rate, time, pre-exponential, activation energy, gas constant, and temperature, respectively. $f(\alpha)$ depends on the mechanism, and when the heating rate ($w = \frac{dT}{dt}$) is constant, it could be transformed into Eq. 4,

$$g(\alpha) = \int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{w} \int_{T_{0}}^{T} e^{-\frac{E}{RT}}dT$$

where $g(\alpha)$ is a function of $\alpha$, $w$ (°C/min) is the heating rate, and $T_{0}$ (°C) is the initial temperature. Diverse forms correspond to different reaction mechanisms (Gil et al. 2010). The specific formulas are shown in Table 2.

**Table 2. Reaction Models and the Corresponding $G(\alpha)$ Functions**

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Model</th>
<th>$G(\alpha)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Controlled chemical reaction order</td>
<td>O1</td>
<td>-ln(1 - $\alpha$)</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>$(1 - \alpha)^{1}$</td>
</tr>
<tr>
<td></td>
<td>O3</td>
<td>$(1 - \alpha)^{2}$</td>
</tr>
<tr>
<td>Controlled phase boundary</td>
<td>R2</td>
<td>1 - $(1 - \alpha)^{1/2}$</td>
</tr>
<tr>
<td></td>
<td>R3</td>
<td>1 - $(1 - \alpha)^{1/3}$</td>
</tr>
<tr>
<td>Controlled diffusion</td>
<td>D1</td>
<td>$\alpha^{2}$</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>$(1 - \alpha) \cdot \ln(1 - \alpha) + \alpha$</td>
</tr>
<tr>
<td></td>
<td>D3</td>
<td>$[1 - (1 - \alpha)^{1/3}]^{2}$</td>
</tr>
<tr>
<td></td>
<td>D4</td>
<td>$1 - 2\alpha / 3 - (1 - \alpha)^{2/3}$</td>
</tr>
</tbody>
</table>
Equation 4 was integrated by Coats-Redfern (Magalhães et al. 2017), and the following Eq. 5 was available:

\[
\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left[ \frac{AR}{wE} \left( 1 - \frac{2RE}{T} \right) \right] - \frac{E}{RT} \tag{5}
\]

For the combined combustion of coal and biomass, \( E/RT \geq 1 \) and \( 1 \sim 2 \cdot RT/E \approx 1 \). Therefore, \( \ln(AR/wE) \) can be regarded as a constant. The origin software is used to fit the kinetic data. The values of \( g(\alpha) \) corresponding to different models in Table 2 were substituted into Eq. 5 one by one, making it possible to plot the curve of \( \ln[g(\alpha)/T^2] \) and \( 1/T \). The line with the highest degree of the fitting can be obtained, as well as the corresponding model and kinetic parameters (\( E \) and \( A \)).

**RESULTS AND DISCUSSION**

**Non-isothermal Experiment**

*Thermogravimetric analysis of coal and biomass*

It was observed from Fig. 1 that the thermal behaviors of WC, CH, and BC were different. There were three stages in the combustion process of WC and CH. It could be seen from the TG curve that the slight reduction in quality before combustion was the first stage, namely dehydration. Combined with the DTG curve, there were two peaks in the combustion process. These two processes corresponded to the second and third stages, namely volatiles analysis and combustion, and char combustion. Moreover, in the combustion of BC, the boundary of combustion between volatiles and char was not prominent. Hence, it could be divided into two stages: dehydration and the combustion of volatiles and char.

![Fig. 1. The TG and DTG curves of coal and biomass: (a): TG curve; (b): DTG curve](image)

The dehydration range of BC, WC, and CH was between 80 °C and 240 °C, corresponding to the percentage of residual combustion mass decreased from 99.7% to 99.0%, and the order of weight loss was WC > CH > BC, which was consistent with the results of moisture content in proximate analysis. For WC, the temperature range of stage
2 and stage 3 was from 240 to 400 °C and from 400 to 510 °C, corresponding to the maximum weight loss rate of 20 %/min (1.00 %/°C) and 6.6%/min (0.33 %/°C), respectively. For CH, the temperature range of stage 2 and stage 3 was from 250 to 420 °C and from 420 to 590 °C, which corresponded to the maximum weight loss rate of 17.2 %/min (0.86 %/°C) and 4.2 %/min (0.21 %/°C), respectively. In contrast with CH, WC possessed more volatiles, lower ash, and a higher calorific value, hence giving it a higher chance to catch fire. There was one weight loss peak in the combustion process of BC, mainly occurring between 280 and 750 °C, and the maximum weight loss rate at 560 °C was 7.8 %/min (0.39 %/°C), which was caused by the simultaneous burning of volatiles and char. It was obvious that the decomposition of WC and CH was faster than BC. The polymers of cellulose, hemicellulose, and lignin were linked together with relatively weak bonds (Xie and Ma 2013). Therefore, WC and CH, which were rich in substances such as cellulose, decomposed more easily.

**Co-combustion of coal and biomass**

As shown in Fig. 2, the DTG curves could be divided into two stages. The temperature range of stage 1 was between 270 and 430 °C, which corresponded mainly to the release of volatiles and combustion of biomass. The range of stage 2 was between 430 and 730 °C, which was primarily BC combustion and char combustion in biomass. The thermodynamic curve of stage 2 had some wiggles, which might be due to the instability of the gas flow caused by the decomposition of corresponding substances, so the change of the combustion rate fluctuated.

![Fig. 2. DTG curves of co-combustion under non-isothermal conditions: (a): BC and WC; (b): BC and CH](image)

As the WC or CH blending ratio increased, the maximum combustion rate in stage 1 increased and stage 2 gradually fell off, corresponding to the increase in volatile compounds and the decrease in char, respectively. In addition, the temperature at which the maximum rate of mass loss occurred decreased, demonstrating that the addition of WC or CH facilitated combustion. The promoting in stage 2 was more obvious. When the ratio of WC was 90%, the peak value in stage 2 increased slightly. It was because the time at which the peak rate occurred was the smallest, the sample was more reactive, and the
maximum combustion rate grew. The volatiles weight loss peak of WC changed remarkably when the blending ratio was between 30 and 90%, which indicated that when a blend of WC and CH combusted, volatiles combustion was more affected under high blending ratio. There were differences in the influence of the volatiles weight loss peak of CH and WC at diverse blending ratios, which might be caused by the differences in the properties of the two biomasses.

The combustion characteristic parameters and their variation trends are shown in Table 3 and Fig. 3 respectively. It was observed that both $T_i$ and $T_b$ decreased with the increase of the content of WC or CH, which showed that with the addition of biomass, the temperature of ignition and burnout decreased. Since the heating rate of the furnace was constant, the time for fuel to start and end combustion was reduced, and the combustion reaction was advanced. The range of variation was greater when the blending ratio exceeded 30%, indicating that the impact on the combustion process was more pronounced and the advance of reactions was more remarkable at a higher blending rate.

Table 3. Combustion Characteristic Parameters of Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_i$</th>
<th>$T_b$</th>
<th>$T_1$</th>
<th>$T_2$</th>
<th>DTG1</th>
<th>DTG2</th>
<th>S (10^-8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC/CH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/0</td>
<td>444.57</td>
<td>728.07</td>
<td>/</td>
<td>/</td>
<td>557.38</td>
<td>0.389</td>
<td>0.199</td>
</tr>
<tr>
<td>9/1</td>
<td>463.03</td>
<td>715.22</td>
<td>382.46</td>
<td>0.136</td>
<td>587.47</td>
<td>0.408</td>
<td>0.208</td>
</tr>
<tr>
<td>8/2</td>
<td>432.56</td>
<td>725.57</td>
<td>367.11</td>
<td>0.225</td>
<td>590.48</td>
<td>0.369</td>
<td>0.183</td>
</tr>
<tr>
<td>7/3</td>
<td>413.53</td>
<td>700.08</td>
<td>360.94</td>
<td>0.280</td>
<td>542.77</td>
<td>0.344</td>
<td>0.197</td>
</tr>
<tr>
<td>6/4</td>
<td>340.48</td>
<td>693.72</td>
<td>384.12</td>
<td>0.518</td>
<td>513.41</td>
<td>0.299</td>
<td>0.211</td>
</tr>
<tr>
<td>5/5</td>
<td>343.97</td>
<td>680.27</td>
<td>377.95</td>
<td>0.686</td>
<td>513.41</td>
<td>0.280</td>
<td>0.206</td>
</tr>
<tr>
<td>4/6</td>
<td>337.41</td>
<td>631.17</td>
<td>370.12</td>
<td>0.929</td>
<td>467.21</td>
<td>0.339</td>
<td>0.250</td>
</tr>
<tr>
<td>3/7</td>
<td>300.97</td>
<td>533.22</td>
<td>333.87</td>
<td>1.013</td>
<td>457.10</td>
<td>0.330</td>
<td>0.275</td>
</tr>
<tr>
<td>2/8</td>
<td>298.66</td>
<td>594.32</td>
<td>328.03</td>
<td>0.850</td>
<td>478.36</td>
<td>0.221</td>
<td>0.242</td>
</tr>
</tbody>
</table>

$T_i$: the ignition temperature
$T_b$: the burnout temperature
$T_1$, $T_2$: the peak temperature corresponding to the two stages of non-isothermal combustion
DTG1, DTG2: the maximum burning rate corresponding to the two stages of non-isothermal combustion
$S$: the composite combustion characteristic index

When the blending ratio was above 30%, the ignition temperature of CH was invariably lower than WC, and hence, it was easier to take fire. As the amount of WC or CH increased, DTG1 increased constantly and DTG2 gradually decreased. The reasons could be that under high blending ratio, there were more volatiles and the burning rate of stage 1 was faster, leading to a small amount of residual char and a low peak rate in stage 2. It could be seen that in two stages of combustion, the DTG curve of blended WC was above of that of blended CH. This might be due to WC possessing more volatiles than CH,
and therefore the reactivity of WC was higher (Vamvuka et al. 2003). The combustion rate in the whole process was faster. Moreover, DTG<sub>a</sub> and S gradually increased, which indicated that the addition of WC or CH could improve the combustion performance. When the blending ratio was less than 50%, the change of DTG<sub>a</sub> was not obvious, which may have been because there was less biomass, and the uniformity of blending was not guaranteed, resulting in an obscure rule. When the blending ratio of WC and CH exceeded 70% and 30%, respectively, DTG<sub>a</sub> and S increased remarkably, the DTG<sub>a</sub> and S of WC were always greater than CH, indicating that the combustion performance of WC was superior to CH at a high blending ratio. Assuming that adding WC/CH to BC to make fuel ignite at a lower temperature were pure mixing effects, then, since the burning rate of WC/CH was much greater than that of BC, the peak value of DTG curves in stage 1 should change regularly. The magnitude of this change depended on the ratio of WC/CH in the mixture. However, the experimental results in Table 3 showed that this was not the case, which indicated that there was an interaction between BC and WC/CH. This will be discussed in the next section.

![Graphs showing the relationship between combustion characteristic parameters and WC or CH blending ratio.](image)

**Fig. 3.** The relationship between combustion characteristic parameters and WC or CH blending ratio: (a): \( T_i, T_b \); (b): DTG<sub>1</sub>, DTG<sub>2</sub>; (c): DTG<sub>a</sub>, S

**Isothermal Experiment**

*Co-combustion of coal and biomass*

Isothermal conditions were in accordance with the combustion conditions of the boiler (Wang et al. 2016a). The TG curves of WC or CH blended with BC in different
proportions at 800 °C are shown in Fig. 4. In a specific position, the non-isothermal experiment was a batch reaction process in which the furnace temperature changed with time, while the isothermal experiment was a continuous reaction process in which the furnace temperature was constant with time changing. There was a difference in the combustion behavior between non-isothermal and isothermal conditions. Compared with Fig. 1, the weight loss under isothermal conditions was much faster. The weight loss curve of BC was smooth and had no inflection point, demonstrating that there was no distinct stage in the combustion process, and the reaction ended at 650 s. The combustion process of WC and CH was similar, which could be divided into two stages. The stage 1 was a rapid response area. At this time, moisture and volatiles were devolatilized simultaneously, the volatiles and part of the char rapidly burned with a mass loss of more than 80% within 22 s and 32 s, respectively. Then, there was the burnout of char, which took a long time and had little weight loss, the reaction reached the end at 190 s for WC and 210 s for CH. When the amount of WC or CH was small, the weight loss curve resembled that of BC. With the increase of the amount of WC or CH, the inflection point gradually increased earlier, the combustion behavior was closer to that of biomass, and the weight loss accelerated slowly. It proved that WC or CH promoted the combustion of BC. Similarly, assuming that the co-combustion of BC and WC/CH under isothermal conditions were just pure mixing effects, since the burning rate of WC/CH was much greater than that of BC, the combustion parameters should be regularly changed as the mixing ratio increased. However, the trend of \( t_f \) in Fig. 5 showed that this was not the case. This showed that there was an interaction between BC and WC/CH. It was consistent with the results of the non-isothermal experiment and was discussed in the next section.

As shown in Fig. 5, with the increase of biomass the value of \( t_f \) was shortened, which made clear that it was conducive to raise the overall combustion rate when adding WC or CH, possibly because there was a facilitating effect of the heat released by the volatiles’ combustion on the subsequent reaction to some extent. When the blending ratio was less than 50%, there was a decrease of \( t_f \), showing that when the blending ratio was relatively low, the combustion rate was impervious to the biomass content. When the blending ratio was between 10% and 90%, the \( t_f \) of WC was always greater than that of
CH, probably because the ash content of WC was lower and there was less combustion residue. Hence, it took longer to burn out. Furthermore, the stability factor diminished constantly, demonstrating that the weight loss distribution of mixtures was unevenly distributed throughout the combustion process and the weight loss rate was rapid, which may have been caused by the large difference in weight loss rate between biomass and BC. When the blending ratio was less than 50%, the stability factor of CH exceeded that of WC, while it was distinct that the stability factor of WC was larger than that of CH when the blending ratio surpassed 50%. It was clear that under a low blending ratio, WC lost more weight in the rapid reaction zone, and as the blending ratio increased, there was more weight loss in the rapid reaction zone of CH.

![Figure 5](image_url)

**Fig. 5.** The relationship between combustion characteristic parameters for blending of WC and CH

**Co-combustion of coal and biomass at different oxygen concentration atmospheres**

The $S$ values of the co-combustion of WC and BC at different oxygen concentration atmospheres are shown in Fig. 6. As the content of WC increased, it could be seen that the corresponding $S$ value increased significantly. It is known that $S$ is a comprehensive parameter that reflects the combustion characteristics of the sample. The larger the $S$, the better the combustion characteristics. Therefore, as the blending ratio of WC increased, the combustion characteristics improved. Under the condition of low oxygen and air combustion, there was a small difference in the combustion performance when the blending ratio was below 70%. With further increase of the blending ratio, there was a remarkable improvement of combustion performance, and the turning point was advanced to 50% at a higher oxygen concentration (30%). Raising the oxygen concentration from 5 to 30% at the same blending ratio made the combustion performance improve, while the enhancement was not obvious when the blending ratio was below 50%. This may be because the biomass content was lower, the BC content in the form of graphitization was more, and there were less volatiles of the mixture, so the impact on the combustion by oxygen was less. With the increase of BC, $S$ was enhanced, and increased most in the oxygen concentration range of between 21 and 30%. Therefore, both the increase of oxygen and the blending of WC could improve the combustion performance of BC. The higher the oxygen concentration was and the higher the WC blending amount, the more remarkable the improvement.
Fig. 6. The S curves of co-combustion of BC and WC under different oxygen concentrations

Interaction between BC, WC, and CH

To investigate the interaction between biomass and BC under isothermal and non-isothermal conditions, the thermodynamic behavior of mixtures was calculated by Eq. 6,

\[ TG = X_1 \times TG_1 + X_2 \times TG_2 \]  \hspace{1cm} (6)

where \( TG \) (%) represents the weight-loss and \( X \) (%) represents the mass percentage (Peng et al. 2015). The deviation curves represent the possible interaction between BC and biomass (subtract calculated TG from experimental TG), as described in Figs. 7 and 8. Parts (a)-(f) of the figures are TG curves of blending WC, and parts (g)-(l) of the figures are TG curves of blending CH. The circular symbol indicates the experimental data, and the triangle symbol indicates the calculated data.

The results illustrated that under non-isothermal conditions, TG curves preceding 260 °C were similar, while there was a difference above 260 °C, which gradually disappeared when temperature exceeded 700 °C. The co-combustion of BC, WC, and CH all manifested as inhibition, which may be the result of more heat dissipation in the non-isothermal conditions, and hence, it was impossible to rapidly burn volatiles in a short time. There were two distinct peaks of deviation curves. The temperature ranges were between 260 and 410 °C, and between 410 and 700 °C, respectively, corresponding to the two stages of combustion. The maximum deviation of combusting a blend of WC and BC was prominently larger than that of a blend of CH and BC. When blending WC and BC, the inhibiting effect was stronger between 260 and 410 °C, and the deviation reached up to 41.6% when the blending ratio was 90%. However, the deviations of two stages when blending CH and BC were relatively close. The maximum deviation was 15.74% at the ratio of 10%. Simultaneously, it was observed that the interaction was not proportional to the blending ratio, which was consistent with previous conclusions (Chen et al. 2019).

There were larger inhibiting effects when the blending ratio of WC was smaller than 30%, and with the blending ratio greater than 30%, the inhibiting effect was relatively small. Nevertheless, the inhibiting effect of CH at different blending ratios was not much different, probably because the density of CH was close to BC, so the interaction was uniformly affected by blending amounts. It was revealed that when blending WC and BC, the deviation in stage 1 increased with increased blending ratios, and the overall variation trend of stage 2 was that the higher the blending amount, the smaller the deviation would be. There was not much difference in the general trend of blending BC and CH, in contrast with WC, the change range was small, and the experimental data was slightly irregular. Because the blending ratio was above 70%, the co-combustion of WC or CH and coal would cause remarkable change in ash properties. Reaction occurred between alkaline substances in biomass and minerals in coal, giving rise to slagging, agglomeration, and reducing combustion reactivity (Priyanto et al. 2016). Therefore, the inhibiting effect in stage 2 was enhanced.
Fig. 8. Under isothermal conditions: (a) to (l): experimental and calculated TG curves; (m) to (n): deviations curves (exp represents the data obtained from the experiment, cal represents the calculated value)

Isothermal experiments can be viewed as non-isothermal experiments with high heating rates. Compared with non-isothermal conditions, weight loss at isothermal conditions was markedly different. There was only one peak of the deviation curve, and the maximum deviation of CH was noticeable earlier than that of WC. The reaction between WC and BC mainly occurred within 100 s, while the reaction of CH and BC mostly occurred within 70 s, and the difference of TG curves faded away after 70 s. There was a sudden reduction in the deviation around 20 s. This may have been due to the abrupt increase in the weight loss rate when reaching 20 s under isothermal conditions, resulting in the rapid decrease in the experimental TG value. When WC blending ratios surpassed 50%, the interaction was more overt, while the interaction of CH with different blending ratios had little change. This was consistent with the rule under non-isothermal conditions. There was the largest deviation when the blending ratio of WC and CH was 70% and 50%,
respectively. Blending 30% WC, 20% CH, and 90% CH showed inhibiting effects. Blending 30% and 70% CH had no obvious interaction. The co-combustion of WC or CH with BC was synergistic. Under isothermal conditions, the volatiles in WC or CH burned rapidly at short notice, releasing more heat, and meanwhile, the carbon produced after biomass volatiles analysis and combustion catalyzed the degradation of coal (Xie and Ma 2013), thus promoting the combustion of BC. The promotion of combustion caused by the non-mixing effect could be used to indicate that there was a synergy between biomass and coal. The interaction between biomass and coal under two temperature conditions showed that compared with the inhibition effect between BC and WC/CH under non-isothermal conditions, the co-combustion of BC and WC/CH under isothermal conditions mostly showed synergistic effects. Therefore, in this experiment, combustion characteristics of fuel under isothermal conditions would be better, and there was some advantages in practical applications. Zhu et al. (2018) researched that under different blending ratios, the interaction between biomass (cattle manure) and two coals showed the same trend under isothermal and non-isothermal conditions. This may be due to the large difference in properties between cattle manure with agricultural and forest residues (WC and CH).

**Kinetics**

It was observed that under non-isothermal conditions, the combustion of BC was concentrated in one stage. The combustion of biomass and the mixture of biomass and coal were divided into two stages, so diverse stages should be analyzed separately. Kinetic parameters are shown in Table 4. The results illustrated that the model O1 fitted WC and the mixture of WC and BC was best in stage 1 ($R^2$ between 0.975 and 0.990), indicating that the rate-controlling step was the chemical reaction. The model D4 had the best fit for stage 2 ($R^2$ between 0.971 and 0.998), showing that the diffusion mechanism played a decisive role at this stage. Differing from WC, the two combustion stages of CH, BC, and the mixture of CH and BC were controlled by the D4 model ($R_1^2$ between 0.896 and 0.998, $R_2^2$ between 0.973 and 0.998), indicating that the combustion of these two stages were all based on a diffusion-controlled mechanism. It is known that the greater the activation energy, the more difficult the reaction will be. The activation energy of BC was remarkably greater than that of WC and CH. As the content of WC or CH increased, the activation energy of stage 1 decreased first and then increased. The transition ratio of WC and CH was 20% and 30%, respectively. This was probably because volatile contents were higher at larger blending ratios, and the rapid release of oxygen for a short time hindered the diffusion of oxygen, giving rise to combat combustion. The activation energy of stage 2 diminished constantly, which was the same as the change rule of $S$ in the previous thermogravimetric analysis. In this study, there was a difference from previous research results in the activation energy of the co-combustion of biomass and coal (Magalhães et al. 2017). This may have been due to the difference in sample properties and heating rate. When the ratio of WC or CH was greater than 50%, the activation energy of stage 2 changed slightly. Therefore, based on two stages, it is recommended that the blending ratio of WC or CH should be 50%. 

Table 4. Kinetic Parameters of All Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stage 1</th>
<th></th>
<th>Stage 2</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>E (KJ/mol)</td>
<td>Model</td>
<td>R²</td>
<td>E (KJ/mol)</td>
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<tr>
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<td>/</td>
<td>/</td>
<td>/</td>
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<tr>
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<td>O1</td>
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<td>O1</td>
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<tr>
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<td>25.404</td>
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<td>6.875</td>
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</tbody>
</table>

E: activation energy

CONCLUSIONS

1. As the blending ratio of biomass increased, the ignition temperature and burnout temperature decreased, the comprehensive combustion characteristic index increased, and the combustion performance was improved. Meanwhile, under isothermal conditions, the increase in oxygen concentration and the addition of biomass improved the combustion performance.

2. In a specific position, the non-isothermal experiment was a batch reaction process in which the furnace temperature changed with time, while the isothermal experiment was a continuous reaction process in which the furnace temperature was constant with time changing. Under non-isothermal conditions, the co-combustion of coal and biomass all showed inhibiting effects. When the blending ratio of WC was below 30%, the inhibition effect was greater, while the inhibition effect of CH under different blending ratios was not much different. Under isothermal conditions, the synergistic effect was dominant. The interaction was distinct when WC content was above 50%, while the interaction of CH under different blending ratios was not much different. It can be seen that the fuel in this experiment had better combustion characteristics under isothermal conditions and has some advantages in practical applications.

3. The kinetic results indicated that the model O1 controlled stage 1 of the co-combustion of WC and BC, and the model D4 controlled the co-combustion of CH and BC, and the stage 2 of the co-combustion of WC and BC. The blending ratio of WC or CH with the lowest activation energy was 50%.
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