Study on the Combustion and Kinetic Characteristics of Pulverized Coal in Low-pressure Environment

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ABSTRACT

Combustion characteristics of two Chinese pulverized coals have been investigated using TG/DTG/DSC in the low-pressure environment. The changes of combustion characteristic parameters of pulverized coals under the different low-pressure environment are analyzed and the kinetic parameters of pulverized coals of each condition are calculated. In the low-pressure environment, a series of characteristic parameters such as ignition temperature, burnout temperature, the temperature corresponding to maximum burning rate, $\text{DTG}_{\text{max}}$, combustion characteristics index S, the combustion characteristics of the experiments coal was researched. Also the thermal analysis kinetics (Coats-Redfern) method were investigated on the activation energy in three different absolute pressures (80kPa, 70kPa, 60kPa) to reveal the effects of the pressures on coal combustion. The results indicate that: when the pressure decreased, the $T_V$, $T_m$, $T_h$ increased, and simultaneously the activation energy ($E$) increased, the combustion characteristics became much bad, indicated that need more energy from external.

INTRODUCTION

The combustion of pulverized coal is widely used as fuel in China and elsewhere in the world, such as in electric power boilers and metallurgical furnaces.
In the foreseeable future, coal will continue to be a major fuel for power generation in China [1].

In China, the coal reserves 20% for the total account of the world. Furthermore, coal resources in western provinces accounted for a large proportion. Considering that the western regions of China area with high altitude, and the pressure is much lower than the Plain area in the east, the combustion of coal is low efficiency. The study of dynamic and combustion characteristics of coal in low pressure environment have great significances for the efficient use of energy in plateau section.

Depending on different properties and characteristics, such as particle size, rank, maceral composition, and composition of mineral matter, coal undergoes a series of complex physical and chemical changes during combustion [2].

Thermal gravimetric analysis (TG) has been widely used in combustion and pyrolysis of coal [3-5]. However, there were few researches on the combustion characteristics of pulverized coal in the low pressure environment by using the thermal gravimetric method, whether in China or abroad.

At present, only few works are concerned with the combustion in the low-pressure environment. Feng Liu and Peifang Fu applied the reaction kinetic model based on Simple Collision Theory (SCT) which was developed by Prof. Peifang Fu analysis the activation energy (E) of the combustion process in the low-pressure environment [6], indicated that the combustible dynamic of coal at low pressure conditions was worse than at normal atmospheric.

The thermogravimetric analysis method was used to study the influence of atmosphere pressure variation on the bituminous coal and lignite combustion characteristics. The bituminous coal and lignite were chosen as the experiment material. The objective of this study is to obtain an overall understanding of the combustion mechanism of pulverized coal in low-pressure environment. It can provide some references about the coal combustion in boiler at low-pressure area.

**EXPERIMENTAL**

**Materials**

Two kinds of coals were used in the experiments for this study. The samples were bituminous coal and lignite obtained from Yunnan province, China. It is commonly exploited in thermal power stations. The bituminous coal and lignite was milled and sieved in less than 200 μm. The samples were dried at 105 °C for 8 h before the experiment. The proximate and ultimate analyses were given in Table 1.
Table 1. The proximate and ultimate analyses of the coal, wt. ad %.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>M_ad</th>
<th>V_ad</th>
<th>A_ad</th>
<th>FC_ad</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous</td>
<td>64.34</td>
<td>2.01</td>
<td>1.38</td>
<td>0.43</td>
<td>6.91</td>
<td>1.93</td>
<td>9.22</td>
<td>33.27</td>
<td>55.58</td>
</tr>
<tr>
<td>Lignite</td>
<td>44.59</td>
<td>2.51</td>
<td>0.93</td>
<td>0.79</td>
<td>15.98</td>
<td>1.81</td>
<td>16.75</td>
<td>38.25</td>
<td>43.19</td>
</tr>
</tbody>
</table>

Thermogravimetry Analysis

The equipment used in this study was a NETZSCH STA 409 F3 simultaneous analyzer capable of simultaneous determination of the Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG) profiles of samples. In order to compare the samples, factors such as sample mass, heating rate and gas flow rate were well established to ensure good repeatability between each runs. Sample (10±0.5 mg) was placed in an Al2O3 ceramic pan. Each sample was heated at 10K/min from ambient temperature up to 800°C under artificial air with a flow rate of 50 mL/min. To simulate the combustion and pyrolysis processes, three different absolute pressures were selected (80kPa, 70kPa, 60kPa). In order to compare the different activation energy (E) in the low-pressure, two samples were heated from ambient temperature to 800°C at heating rates of 10K/min under artificial air with a flow rate of 50 mL/min in three different low-pressures. Argon is used as protective gas with a flow rate of 20 mL/min in all experiments.

RESULTS AND DISCUSSION

TG/DTG Analysis

As shown in Figure 1 and Figure 2 (TG profile), either bituminous coal or lignite, with decreasing pressure, TG curve gradually move to the high temperature zone, exhibit hysteresis. The combustion process can be divided into three stages.

The first stage corresponded to loss of moisture and very light volatile compounds. The bituminous coal was from ambient temperature to about 450°C, and the lignite was from ambient temperature to about 300°C. In these stages, TG and DTG curves for the bituminous coal and lignite have no obvious change. The second stage (the bituminous coals was 450°C-700°C, the lignite was 300°C-650°C) is the main stage of coal combustion, a significant drop in mass was observed. At this stage, as the temperature increases, fixed carbon and a large number of organic volatile combusted. The third stage (the bituminous coals was 700°C-800°C, the lignite was 650°C-800°C). In these stages, a slight continued loss of weight is shown in the weight loss curve, caused by the second stage’s product continue to pyrolysis.
Less the mass loss mean the fixed carbon combustion is exhausted, mainly ash in samples. And with decrease of the pressure, the residue yield of the samples increased.

Derivative thermogravimetric (DTG) was the sample mass change rate with the program-controlled temperature. DTG profiles make possible to know the mass loss which is taking place at a temperature during the bituminous coal and lignite combustion process. The characteristics of the TG experiments for combustion of the bituminous coal and lignite are summarized in Figure 4 and Figure 5 (DTG profile).

It can be seen from the DTG curve that the DTG curve also moved to the high temperature area with the gradual decrease of the pressure. The pressure was greater, combustion reaction can start at the low temperature, and the combustion activity is lower in the low pressure conditions than that in normal atmosphere conditions. The pre heating conditions effect on the combustion of fixed carbon in the later stage from bituminous coal of DTG curve. It appeared obvious sufficient that the peaks of pulverized coal and lignite volatile were combustion stage, volatile and fixed carbon. The peak value of fixed carbon decreases gradually with the pressure decreasing.

The characteristics of the TG experiments for combustion of the bituminous coal and lignite are summarized in Figure 3 and Figure 4 (DTG profile). It can be seen from the DTG curve, when the DTG curve also moved to the high temperature area, that the peak was lower with the gradual decrease of the pressure.

The DTG curves of bituminous coal and lignite shows one peak comprised between 300°C and 650°C. The peak is a maximum mass loss rate. The maximum mass loss rate corresponds to the temperature increased with decrease of the pressure. The value of the DTG curve peak gradually also decreased. Feng Liu [3] in his study explained that the diffusion resistance of the oxygen molecules into the pore size of the coal is larger than that of the normal pressure in the low pressure environment.
Characteristic Parameters

Several methods can be used to determine the ignition temperature of sample. In this paper, TG/DTG thermal analysis method was employed, as shown in Fig.5. The first peak valley was defined as point A of the DTG curve. The line perpendicular to the horizontal axis through the point A can define the point B by crossing the TG curve. The point C is the cross point of the tangent line of point B and the base line of TG curve, the temperature of point C was defined as the ignition temperature. The combustion ending temperature is defined as the value at which the weight loss of sample is 99% [7]. The characteristic parameters of bituminous coal and lignite combustion are shown in Table 2. Ti is onset temperature for volatile release and weight loss. Ignition temperature reflects the ignition performance of coal or levels of activation energy of coal. The smaller of Ti indicates that the coal was fired easier. Tm is temperature of maximum weight loss rate. Th is final combustion temperature detected as weight stabilization. Burnout temperature is the temperature of the fixed carbon and volatile burn out. The higher of the burning temperature shows that burning time was longer and coal was burned out hardly. The remaining amount of fuel was more in the residual carbon. DTGmax is the maximum weight loss rate.

Table 2 shows that the Ti, Tm, Th increased with decreasing of the pressure for the same coal. It indicated that pulverized coal ignition is more difficult in the pressure of 60 kPa than the pressure of 80 kPa. Because the low-pressure suppressed the activity of the coal, the maximum burning rate lower significantly in low pressure(70 kPa, 60kPa) than in the pressure of 80kPa. It was easy to know that the initial temperature increases gradually with the decrease of the pressure from table 2, which shows that the low pressure hampered ignition of coal. The combustion characteristic is tendency also. Burnout temperature is gradually increased with the decreasing pressure. In a word, the lower pressure decreased of the combustion activity.
Table 2. Characteristic parameters of the coal.

<table>
<thead>
<tr>
<th>Sample parameters</th>
<th>$T_i$ (°C)</th>
<th>$T_{mi}$ (°C)</th>
<th>$T_h$ (°C)</th>
<th>$DTG_{max}$ (%/S$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous coal (80kPa)</td>
<td>480</td>
<td>582</td>
<td>708</td>
<td>-4.29</td>
</tr>
<tr>
<td>Bituminous coal (70kPa)</td>
<td>497</td>
<td>594</td>
<td>735</td>
<td>-4.16</td>
</tr>
<tr>
<td>Bituminous coal (60kPa)</td>
<td>502</td>
<td>610</td>
<td>751</td>
<td>-3.37</td>
</tr>
<tr>
<td>Lignite (80kPa)</td>
<td>410</td>
<td>548</td>
<td>632</td>
<td>-3.87</td>
</tr>
<tr>
<td>Lignite (70kPa)</td>
<td>422</td>
<td>560</td>
<td>648</td>
<td>-3.75</td>
</tr>
<tr>
<td>Lignite (60kPa)</td>
<td>432</td>
<td>566</td>
<td>656</td>
<td>-3.47</td>
</tr>
</tbody>
</table>

DSC measures the difference in energy inputs into a substance and a reference material as they are subjected to a controlled temperature programmer [8]. The characteristics of the DSC experiments for combustion of the bituminous coal and lignite are summarized in Figure 6 and Figure 7.

It can be seen that the heat release increases gradually from the DSC curve with the increase of the pressure. Because pressure conditions will change the burning rate, the curve of bituminous coal has only one obvious exothermic peak, but the curve of lignite present two distinct exothermic peaks. Exothermic peak produced in
the low-temperature section by combustion of volatile. High-temperature exothermic peak corresponding produced by the combustion of fixed carbon. It can be seen from the DSC curve, lignite in 300 °C~ 400 °C curve upward, exothermic, indicating that is more intense with the temperature increases by the volatile combustion. Corresponding DSC curves have a significant exothermal peak. When the bituminous coal and the lignite were at around 600 °C and 550 °C respectively, heat of coal released up to the maximum. The combustion phenomenon occurs in the role of oxygen about fixed carbon, fixed carbon combustion accompanied by the generation of heat. Heat release is gradually reduced with the reduction in mass of the sample. When the quality does not change, it means the end of the combustion process.

The Combustibility Index S

The index S was a better index to reflect the ignition of these pulverized coals. The index S is summarized as follow.

\[
S = \frac{(dw/dt)_{\text{max}}(dw/dt)_{\text{mean}}}{T_v T_a}
\]

(1)

\((dw/dt)_{\text{max}}\) is the maximum rate of combustion. \((dw/dt)_{\text{mean}}\) is the average rate of weight loss. \(T_v\) is the ignition temperature; obtain from the TG–DTG thermal analysis method. \(T_a\) is the burnout temperature.

The value of index S showed the combustion performance. The index S includes the main characteristics of coal combustion from ignition through volatile matter and char combustion to burnout. It overall reflected the combustion characteristics of coal [9]. The relations of the index S with low pressure for the bituminous coal and lignite were shown in Figure 8.

It can be seen in Figure 8 that the pressure increased from 60kPa to 70kPa, 80kPa, bituminous coal combustion characteristics index (S) increased from 1.65 to 2.11 and 2.62, and lignite combustion characteristic index (S) increased from 2.21 to 2.56 and 3.13. Thus, increased pressure can effectively improve combustion of pulverized coal ignition and burnout characteristics. At the same time, combustion characteristic index for different kinds of coal also have certain difference. When the pressure increased from 60 kPa to 70 kPa, 80 kPa, the combustion index (S) of bituminous coal respectively increased by 27.8% and 24.1%, the lignite respectively increased by 15.8% and 22.3%. Thus, the increasing of pressure has more effect on combustion characteristics of bituminous coal than the combustion characteristics of lignite.

Isoconversional Kinetic Analysis

The Coats-Redfern method was selected in the calculation of the bituminous coal and lignite combustion process. TG and DTG curves were used to analyze
dynamics kinetics. In this study, burning profiles of the coal samples were used to calculate the activation energy values of the coal samples by the method of Coats-Redfern [10-12]. According to the definition of the Coats-Redfern method, the activation energy (E) could be calculate from the line’s slope (-EP/R). The results were shown in Table 3 and there exist line relationship during the different combustion stages for the bituminous coal and lignite under different low-pressure environment.

Activation energies of the different stage of combustion cannot describe the reactivity of the coal. Then, Cumming [13] has described the reactivity or combustibility of combustion with the mean activation energy (Em) in the overall processes. The method is shown as Eq. (2)

\[ E_m = E_1F_1 + E_2F_2 + \ldots + E_nF_n \]  

(2)

Where E1~En are the activation energies of the different stages, F1~Fn are the mass loss fraction of the different stages. The mean activation energy was calculated and shown in the Table 3.

![Figure 8. Relation of the integrated combustion index S with low pressure.](image)

The mean activation energy can also reflect the difficulty of the chemical reaction. Table 3 showed that the combustion of the bituminous coal and lignite with the pressure decreasing. The combustion reaction was more difficult with activation energy (Em) increasing. Compare with combustion in 80kPa, the low pressure (60 kPa, 70 kPa) combustion need more energy.
Table 3. Activation Energies and Pre-exponential Factors of Coal in Low-pressure Environment.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature (℃)</th>
<th>Activation energies $E_p$(kJ/mol)</th>
<th>Pre-exponential $A$(min$^{-1}$)</th>
<th>Mass loss fraction(%)</th>
<th>Correlated coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite (80kPa)</td>
<td>430-548</td>
<td>58.91</td>
<td>1.077×10$^{11}$</td>
<td>34.48</td>
<td>0.99937</td>
</tr>
<tr>
<td></td>
<td>548-610</td>
<td>64.34</td>
<td>1.215×10$^{11}$</td>
<td>25.01</td>
<td>0.9674</td>
</tr>
<tr>
<td>Lignite (70kPa)</td>
<td>442-560</td>
<td>59.37</td>
<td>1.031×10$^{11}$</td>
<td>30.96</td>
<td>0.99894</td>
</tr>
<tr>
<td></td>
<td>560-620</td>
<td>63.86</td>
<td>1.209×10$^{11}$</td>
<td>32.85</td>
<td>0.98666</td>
</tr>
<tr>
<td>Lignite (60kPa)</td>
<td>450-566</td>
<td>59.61</td>
<td>1.051×10$^{11}$</td>
<td>34.59</td>
<td>0.9982</td>
</tr>
<tr>
<td></td>
<td>566-626</td>
<td>64.06</td>
<td>1.227×10$^{11}$</td>
<td>30.82</td>
<td>0.97516</td>
</tr>
<tr>
<td>Bituminous coal(80kPa)</td>
<td>480-582</td>
<td>55.09</td>
<td>9.17×10$^{10}$</td>
<td>30.82</td>
<td>0.99037</td>
</tr>
<tr>
<td></td>
<td>582-708</td>
<td>70.82</td>
<td>1.57×10$^{11}$</td>
<td>37.98</td>
<td>0.97099</td>
</tr>
<tr>
<td>Bituminous coal(70kPa)</td>
<td>497-594</td>
<td>55.87</td>
<td>9.58×10$^{10}$</td>
<td>29.14</td>
<td>0.99688</td>
</tr>
<tr>
<td></td>
<td>594-735</td>
<td>75.78</td>
<td>1.89×10$^{11}$</td>
<td>47.99</td>
<td>0.97995</td>
</tr>
<tr>
<td>Bituminous coal(60kPa)</td>
<td>502-610</td>
<td>56.04</td>
<td>9.81×10$^{10}$</td>
<td>38.01</td>
<td>0.99681</td>
</tr>
<tr>
<td></td>
<td>610-751</td>
<td>78.75</td>
<td>2.11×10$^{11}$</td>
<td>45.65</td>
<td>0.96957</td>
</tr>
</tbody>
</table>

From table 4 knowable, activation energy increases gradually with decreasing pressure, which the burning need additional energy more. Because the pressure decreases, the combustion is not sufficient. With the decrease of the oxygen concentration, ignition temperature, burnout temperatures are increased, which means that ignition characteristics and Burnout Characteristics getting worse.

**CONCLUSIONS**

The combustion characteristics and kinetic behaviors of the bituminous coal and lignite were studied at the different low-pressure.

A first-order parallel reactions model is fitted for the bituminous coal and lignite combustion in different low-pressures.

With the low-pressure decreased, TG, DTG and DSC curves move to the higher temperature zone, the average reaction rate of coal combustion decreased.

According to the DTG profiles of the bituminous coal and lignite, the Ti, Tm, Th increased with the low-pressure decreased. Because the low-pressure suppressed the activity of the coal, the heat cumulative time increased. The bituminous coal
combustion characteristics become well compare with the bituminous coal and lignite from the index S.

The average values of activation energy (E), the bituminous coal were 43.87, 52.46, and 53.88 kJ/mol in the low-pressure 80 kPa, 70kPa, and 60 kPa. The lignite was 36.57, 39.35, 40.36 kJ/mol respectively. It is obvious that the average values of activation energy (E) increased with the increasing pressure.

However, the combustion characteristics and mechanisms of the bituminous coal and lignite under low-pressure environments need further examination.

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