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Ignition and Kinetics Analysis of Coal Combustion in Low Oxygen Concentration

Y. LIU,1 C. WANG,1 and D. CHE1

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Abstract The combustion of coals in low oxygen concentration, which exists widely in industry combustion, was investigated by the use of thermogravimetry. Experimental results show that thermogravity/differential thermogravity/differential scanning calorimetry curves of four studied coals shift to a higher temperature zone in lower oxygen concentration. The ignition temperature is almost constant for each coal and increases with the increased coal rank. The burnout temperature and peak temperature increase with the decreased oxygen concentration. The kinetic parameters were calculated using the Coats-Redfern method for coal combustion in low oxygen concentration. The apparent activation energy increases linearly with oxygen concentration, and high rank coal has a high apparent activation energy. An intensive compensation effect exists between the apparent activation energy E and pre-exponential factor A, and the corresponding compensation coefficients are obtained.

Keywords ignition, kinetic parameters, low oxygen concentration, thermogravimetric analysis

1. Introduction

Coal or char combustion in low oxygen concentration exists widely in industry combustion because oxygen concentration decreases from an initial 21% in fresh air to 3–4% at the furnace outlet. For many advanced swirl burners, an intense recirculation of hot combustion products to the primary reaction zone fast dilutes the oxygen significantly to form a low oxygen concentration and the corresponding ignition and burning actually occur in low oxygen concentration. Even in the new developing technologies, such as oxygen-enriched combustion and pure oxygen combustion, burn-off process also occurs in low oxygen concentration. The previous studies on coal combustion characteristics with thermogravimetry analysis (TGA) were mainly carried out under air conditions (Kok, 2005), high oxygen concentration (Fan et al., 2008) or just a little lower than 21% oxygen concentration. What’s more, it has already been shown experimentally that NOx emissions of coal combustion could be significantly reduced with a burner design (Stadler et al., 2009a, 2009b) using flameless combustion technology, which is under low oxygen concentration.

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Thermogravimetry using isothermal and non-isothermal methods for the determination of the combustion characteristics, especially the kinetics for the conversion of coal/coal-chars and other solids have been reported extensively in the literature (Hu et al., 2008; Otero et al., 2008; Sanchez et al., 2009; Sutcu and Piskin, 2009). In the present article, experimental studies of coal combustion were carried out in low oxygen concentration by use of non-isothermal thermogravimetry for understanding of the coal combustion under low oxygen concentration in order to better organize the furnace combustion and effectively improve the efficiency of coal combustion.

2. Experimental

2.1. Proximate and Ultimate Analyses of Coal

Fushun bituminous (abbreviated as FS, hereinafter), Shenmu coal (SM), Huangling bituminous (HL), and high rank anthracite Jiaozuo (JZ) were selected for this study. Each sample is ground and sieved to a size \(<280 \mu m\), dried at 105°C, and kept airproof in a glass container at room temperature before being combusted. The ultimate and proximate analyses of coal samples are listed in Table 1, in which all of the coals are represented as the corresponding code names. The elements in the coal samples were measured with a conventional, combustion-type elemental analyzer. Fuel ratio is the ratio of fixed carbon content to volatile content \(\frac{FC_{daf}}{V_{daf}}\) and can be used as an indicator of coal rank.

2.2. Experimental Method

Non-isothermal thermogravimetry is used in the present experiments. The experimental procedure of the thermogravimetry/differential thermogravimetry/differential scanning calorimetry (TG/DTG/DSC) includes preparing of the sample, setting the heating and gas flow rates, and commencing the experiments. About 15 ± 0.1 mg of coal sample, which is weighed by a Sartorius MC5-type electronic balance of microgram level, is charged into an \(Al_2O_3\) container that is then placed on the NETZSCH simultaneous thermal analyzer STA 409 PC Luxx. All the experiments are carried out at a constant heating rate of 20

<table>
<thead>
<tr>
<th>Coal code</th>
<th>Fuel ratio</th>
<th>(w(FC))</th>
<th>(w(V))</th>
<th>(w(A))</th>
<th>(w(C))</th>
<th>(w(H))</th>
<th>(w(O)^*)</th>
<th>(w(N))</th>
<th>(w(S))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FS</td>
<td>1.24</td>
<td>52.59</td>
<td>42.58</td>
<td>4.83</td>
<td>72.57</td>
<td>5.21</td>
<td>13.8</td>
<td>2.42</td>
<td>1.18</td>
</tr>
<tr>
<td>SM</td>
<td>1.44</td>
<td>53.52</td>
<td>37.18</td>
<td>9.3</td>
<td>71.83</td>
<td>4.29</td>
<td>12.69</td>
<td>1.14</td>
<td>0.81</td>
</tr>
<tr>
<td>HL</td>
<td>1.74</td>
<td>52.71</td>
<td>30.31</td>
<td>16.98</td>
<td>69.5</td>
<td>3.77</td>
<td>8.06</td>
<td>1.14</td>
<td>0.64</td>
</tr>
<tr>
<td>JZ</td>
<td>14.75</td>
<td>75.82</td>
<td>5.14</td>
<td>19.04</td>
<td>75.61</td>
<td>2.25</td>
<td>1.64</td>
<td>0.73</td>
<td>0.73</td>
</tr>
</tbody>
</table>

\(^*w(O) = 100 - w(C) - w(H) - w(N) - w(S) - w(A)\).
K/min in a temperature range of 20 to 1200°C with a preset O2-N2 gas flow rate of 150 mL/min. Prior to the experiments, the thermogravimetry instrument is calibrated for temperature readings, using indium as the reference material. The balance is calibrated for the buoyancy effect, allowing the quantitative estimation of weight changes. Thermal properties of the samples are found from the TG/DTG curves. Six oxygen concentrations of 3.3 to 21% are adopted for Shenmu coal, and only three oxygen concentrations of 3.3 to 13.3% are adopted for the other three coals.

3. Experimental Results and Discussion

3.1. Ignition and Combustion Characteristics of Coal in Low Oxygen Concentration

TG/DTG/DSC curves of Shenmu bituminous combustion using non-isothermal thermogravimetry in different oxygen concentrations under N2 atmosphere are shown in Figure 1. The TG/DTG/DSC graph of the Shenmu coal clearly indicates that combustion occurs in three main stages: (1) The first stage generally involves drying process in lower than 300°C; however, the TG curves in Figure 1 are very flat due to the pre-drying of the coal. (2) The second stage involves devolatilization and the ignition of coal. (3) The third stage is the burn-off of coal. Some small peaks exist around 800°C, which may be caused by the minerals decomposition, especially for carbonates in parent Shenmu coal.

As shown in Figure 1, with the decrease of oxygen concentration, TG and DTG curves of Shenmu coal combustion shift to a high temperature zone, and the process of coal combustion is prolonged. Both the peak temperature at which the TG curve reaches maximum weight loss rate and the burnout temperature increase. For the other three coals, the changes of combustion TG and DTG curves follow the same rules. In the actual industrial coal combustion process, the oxygen concentration decreases gradually. Therefore, the effects of oxygen concentration change on burnout time should be considered in boiler design and operation.

The ignition temperature \( T_i \), burnout temperature \( T_b \), and peak temperature \( T_{\text{max}} \) are three characteristic temperatures that represent combustion characteristics of coal (Kok, 2005). In this article, the ignition temperature \( T_i \) and burnout temperature \( T_b \) are determined by using the TG-DTG measurements. The ignition temperature \( T_i \) is the extrapolated onset temperature calculated from the partial peak that results from the

![Figure 1. TG/DTG/DSC curves of SM bituminous combustion in different oxygen concentrations.](image-url)
coal combustion. This value indicates the inception of the coal combustion. The peak temperatures ($T_{\text{max}}$) are the corresponding temperature to the maximum of the mass loss rate. $T_{\text{max}}$ is the characteristic of the combustion of the coal. $T_b$ is the extrapolated offset temperature of the DTG curves. This value indicates the end of the coal combustion. $T_i$, $T_b$, and $T_{\text{max}}$, varying with oxygen concentration for Shenmu bituminous coal, are shown in the left side of Figure 2.

As shown in Figure 2, ignition temperatures in low oxygen concentration for Shenmu bituminous coal do not change as oxygen concentration decreases from 21 to 3.3%. It is interesting that the ignition temperature from TGA is kept almost constant even in high oxygen concentration (Fan et al., 2008), which is consistent with the present experimental results. This is due to the fact that heterogeneous ignition can occur at low particle temperatures by the direct attack of oxygen on the coal, which can be seen from the onset of heat release from DSC curves in Figure 1. Therefore, the ignition temperature is independent of the oxygen concentration. In addition, the oxidation of coal particle before ignition is in a kinetic controlled region. This ignition might be extinguished when the volatile matter is evolved at higher temperatures at an extremely high heating rate.

As shown in the left side of Figure 2, with the decrease of oxygen concentration, the burnout temperature increases. The lower the oxygen concentration, the greater the burnout temperature increases. It shows that the oxygen concentration has a large effect on the burnout temperature. On the other hand, the burnout temperature changes much bigger compared with the ignition and peak temperatures. The burnout temperature decreases 311.1°C with the increase of oxygen concentration from 3.3 to 21%, while the ignition temperature and the peak temperature decrease only 13.3 and 90.3°C, respectively. As shown in Figure 2, the peak temperature for Shenmu coal also increases with the decrease of oxygen concentration because the burning rate is controlled by both kinetic and diffusion limitation after ignition. For the other three coals studied, those characteristic temperatures show the same trend for different O$_2$ concentrations. As an example, ignition temperatures are given in the right side of Figure 2 for the four coals. Ignition temperature increases with the increase of coal rank. Thus, the following conclusions can be drawn: changes in oxygen concentration show a great influence on the burnout characteristics, and it needs a longer time and higher temperature for coal to burn out in the lower oxygen concentration.

![Figure 2. The curves of characteristic temperatures of coal combustion in different oxygen concentrations.](image-url)
3.2. Kinetic Analysis of Coal Combustion in Low Oxygen Concentration

3.2.1. Kinetic Analysis Theory. It is necessary to provide some preliminary interpretation of the activation energies obtained from the data analysis procedure. Coal combustion is quite complex and involves a range of chemical and physical processes, generally including a number of interrelated stages, namely devolatilization, combustion of volatiles, and char burnout. These concurrent processes contribute to the overall empirical weight loss in TG/TGA analysis. Therefore, the kinetic parameters derived from the relevant TG/DTG curve should be considered as apparent values, which are not precisely related to any one particular mechanistic step (Kok, 2003).

According to Arrhenius law,

\[ \frac{d\alpha}{dt} = A \cdot e^{-E/(RT)} \cdot f(\alpha), \]  

(1)

\[ f(\alpha) = (1 - \alpha)^n, \]  

(2)

where \( \alpha = \frac{m_0 - m}{m_\infty - m} \) is the converted fraction obtained from TG/DTG curves, of which \( m_0 \), \( m_\infty \), and \( m \) represent the initial, ultimate, and the instant weight of a sample, respectively. Also, \( t \) is the time, \( E \) is the apparent activation energy, \( T \) is the temperature, \( A \) is the pre-exponential factor that includes the heating rate and the partial pressure of oxygen, which is assumed to be constant, and \( n \) is the reaction order.

In the TGA experiment, using a linear heating ramp, \( \beta = \frac{dT}{dt} \) represents heating rate. Therefore, Eq. (1) can be transformed as follows:

\[ \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \cdot e^{-E/(RT)} dT. \]  

(3)

The Coats-Redfern integral method is used widely to analyze the kinetic parameters of the non-isothermal combustion process (Kok, 2007; Li and Suzuki, 2009; Sutcu and Piskin, 2009; Yorulmaz and Atimtay, 2009) and was adopted in the present investigation. According to the Coats-Redfern equation (Coats and Redfern, 1964):

\[ \ln \left[ \frac{1 - (1 - a)^{(1-n)}}{T^2(1-n)} \right] = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT}, \]  

if \( n \neq 1 \),

(4)

\[ \ln \left( \frac{\ln(1-a)}{T^2} \right) = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT}, \]  

if \( n = 1 \),

(5)

In order to obtain kinetic parameters, coal combustion is assumed as first-order reaction, using the above Coats-Redfern equation to calculate the activation energy \( E \) and frequency factor \( A \). Thus, a plot of \( \ln \left[ \frac{\ln(1-a)}{T^2} \right] \) versus \( \frac{1}{T} \) should result in a straight line with the slope equal to \( -\frac{E}{RT} \) for the first-order kinetics.

3.2.2. Kinetic Parameters and Compensation Effect. The kinetic analysis with the Coats-Redfern method is shown in Figures 3 and 4 for four coals in different oxygen concentrations. As shown in Figures 3 and 4, analysis curves of kinetic parameters of different coals in low oxygen concentration show a very good linearity between \( \ln \left[ \frac{\ln(1-a)}{T^2} \right] \) and \( \frac{1}{T} \). The linear correlation of experimental curves become better with the increase of the
oxygen concentration, which shows that coal combustion is closer to first-order reaction in the high oxygen concentration.

The activation energy is plotted in Figure 5 where coal rank is used as abscissa. The apparent activation energy increases with the increase of coal rank in low oxygen concentration. At the same time, the gap of activation energy for different coal rank decreases as the oxygen concentration reduces, which suggests that the impact of coal rank on combustion declines with decreased oxygen concentration decreases.

The relationship between the apparent kinetic parameters and oxygen concentration for Shenmu coal combustion is shown in Figure 6. As shown in Figure 6, in low oxygen concentration, the apparent activation energy seems to increase linearly with the increase of oxygen concentration, while the pre-exponential factor of coal combustion increases exponentially with the increase of oxygen concentration. This means that the compensation effect (Brown and Galwey, 2002) exists between $E$ and $A$ of coal combustion. The increase of activation energy seems to attenuate the increase of the reaction rate constant caused by an increase of pre-exponential with the increase of
Figure 5. Effect of coal rank on the activation energy.

Figure 6. Effect of oxygen concentration on the kinetics parameters for Shenmu coal.

Oxygen concentration. Plenty of research has been reported about compensation effect between the apparent activation energy $E$ and pre-exponential $A$ for pyrolysis (Wang et al., 2007), gasification (Xie, 2002) and combustion (Cuesta et al., 1993; Wu et al., 2005; Toniolo et al., 2008; Jankovic et al., 2009). In the usual presentation and discussion of the theoretical foundations for the Arrhenius equation, no feature connecting the magnitudes of the frequency of occurrence of the reaction situation ($A$) and the energy barrier to reaction ($E$) has been identified. The detailed mechanism remains to be further studied.

Compensation effect makes it more complicated for coal combustion in low oxygen concentration, because decrease of the activation energy and decrease of the pre-exponential factor play opposite roles for burning rate: the former is in favor of chemical reaction, while the latter causes the combustion rate to decline. Therefore, it is not reasonable to determine the reactivity of a chemical reaction with compensation effect just by simply using the pre-exponential factor or apparent activation energy.
It is found that the relationship between the activation energy $E$ and the pre-exponential factor $A$ can be governed by the following formula (Koga and Sestak, 1991; Zsako, 1996):

$$\ln A = aE + b,$$

(6)

where $a$ and $b$ are the compensation coefficients. In the present experimental study of coal combustion in low oxygen concentration, the relationship between the apparent activation energy $E$ and the pre-exponential factor $A$ in different oxygen concentration can also be described as Eq. (6).

Figure 7 shows the relationship between kinetic parameters $E$ and $A$ for studied coals combustion in different oxygen concentrations. As shown in Figure 7, the linear correlation between $\ln A$ and $E$ is good enough with all correlation coefficients ($R > 0.999$) over 2.

Influence of coal rank on kinetics of coal combustion in low oxygen concentration could be described by the compensation coefficients $a$ and $b$ as listed in Table 2. As shown in Table 2, with the increase in coal rank, the compensation coefficient $a$ decreased slightly, while the absolute value of compensation coefficient $b$ increased slightly. For the three studied bituminous coals, the compensation coefficients $a$ and $b$ can be the average values of 0.202 and −5.07, respectively.

| Table 2 |

| Compensation coefficients for different coals |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Coal type       | FS              | SM              | HL              | JZ              |
| Compensation coefficient $a$ | 0.21204         | 0.19989         | 0.19529         | 0.16744         |
| Compensation coefficient $b$  | −5.01558        | −5.08469        | −5.12224        | −5.38761        |
4. Conclusions

The combustion characteristics for four coals in low oxygen concentrations have been investigated using the non-isothermal TG/DTG method. The apparent kinetic parameters have been examined by the first-order Coats-Redfern equation, and the following conclusions can be drawn:

1. With the decrease of oxygen concentration, TG/DTG/DSC curves shift to a high temperature zone, and the burnout temperature and the peak temperature both increase. The ignition temperature increases with the increase of coal rank, but almost keeps constant for each coal at different oxygen concentrations.
2. The kinetic parameters were calculated using the Coats-Redfern method for coal combustion in low oxygen concentration. The apparent activation energy increases linearly with oxygen concentration for each coal. High rank coal has a high apparent activation energy at a given oxygen concentration.
3. The compensation effect exists between the apparent activation energy $E_a$ and pre-exponential factor $A$ for coal combustion in low oxygen concentration, and the corresponding compensation coefficients are obtained.

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