Characteristic Temperatures of Coal Chars Combustion in O$_2$/N$_2$ and O$_2$/CO$_2$ Atmospheres

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oxy-fuel combustion technology

- Oxy-fuel combustion is currently technology used to reduce the CO$_2$ emission from coal-fired power plants, and also is used in coal gasification.
- Differences between oxy-fuel combustion and conventional air combustion are gas properties such as density, heat capacity, diffusivity and gas emissivity, subsequently, affecting the heat transfer, flame ignition, coal burnout, emissions, and ash properties.
1. Introduction

- Liu et al. indicated that replacing N2 in the air with CO2 results in significant decreases in gas temperatures and the char burnouts due to the larger specific heat of CO2 compared to N2.

- Maffei et al. observed that the presence of CO2 in the atmosphere reduces the overall coal reactivity because of the higher CO2 heat capacity reducing the surrounding gas temperature and the lower oxygen binary molecular diffusion in CO2, in respect of that in N2, reducing the O2 flux to and inside the particle.
1. Introduction

TGA techniques have been widely employed to determine the characteristic temperatures: ignition temperature, peak temperature and burnout temperature.

- Cloke pointed out that the ignition temperature was defined as the temperature at which the combustion rate rises to 1 wt% min⁻¹, the burnout temperature (BT) was defined as the temperature at which the rate of combustion (dW/dt) falls to 1 wt% min⁻¹.

- Yong Chen proposed the turning point on the TG curve where the TG combustion curve was separated from TG pyrolysis curve was defined as the ignition temperature.
1. Introduction

- The ignition behavior and reactivity of coal particles is of considerable importance for designing the boiler, and controlling flame stability, the formation and emission of pollutants, and flame extinction during the combustion process.
1. Introduction

The methods for measuring the ignition temperature of coal particles:

In fixed bed such as TGA, TG–DTA, Electrodynamic Thermogravimetric Analyzer (EDTGA); various cylinder-shaped beds [5], mesh reactor and chain furnace;

The entrained flow pulverized coals are heated such as in drop-tube furnace, isothermal flow reactor or one-dimensional furnace, coal-fired suspended boiler and circulating fluidized bed.
1. Introduction

- Whether do those ignition temperatures have an intrinsic relationship or not?
- Can we measure the ignition temperature of coal particles by using TG-DSC to predict that of coal particles in entrained flow reactor?
- This work endeavors to develop a simple and effective method, in order to measure and understand the ignition energy, heat acceleration and characteristic temperatures during coal char combustion.
2 Heat flow model

Fig. 1. Schematic diagram of simplified heat network with burning heat flow rate.
2 Heat flow model

\[ \dot{Q}_s = \frac{T_w - T_s}{R_s} + \dot{Q}_{re} - C_s \frac{dT_s}{dt} \]  

(1)

\[ \dot{Q}_r = \frac{T_w - T_r}{R_r} - C_r \frac{dT_r}{dt} \]  

(2)

In which, \( \dot{Q}_{re} = \dot{Q}_{ox} - \dot{Q}_{pyr} - \dot{Q}_{ev} \). The enthalpy of coal pyrolysis \( Q_{pyr} \) per unit time within \( T < 300° C \) can be neglected, due to the small contribution to the total heat \( (< 4\%) \) [23]. The enthalpy of water increases with temperature per unit time.
2 Heat flow model

In general, two same crucibles are used in experiment, so the factors of radiation adsorption, convection and conduction heat transfer between the crucibles and furnace wall are same, and the ratio of sample mass to crucible mass is very small,

\[
\phi = \phi_{re} - \left( c_{ash} \eta_{ash} + (1 - \eta_{ash})(1 - \alpha)c_{cm} \right) \theta - k(T_s - T_r)
\]  

(5)
2 Heat flow model

- At the initial stage, the evaporation of water, the oxidation and pyrolysis of coal samples can be negligible in a range of temperature less than 50°C, i.e., $\phi_{re} \rightarrow 0$. The function relation between heat flow rate and temperature is almost linear, as shown in Fig. 2. The heat capacities of ash and combustible matter are calculated on the paper published [24].

$$\phi = - \left( (c_{ash} \eta_{ash} + (1 - \eta_{ash}) c_{cm}) \right) \theta$$  \hspace{1cm} (6)
Fig. 2. The rate of heat adsorbed by heat capacity of coal char samples with the increase of temperature.
2 Heat flow model

- At the mid stage from the point b to d shown in Fig. 4b, the last two terms are very small, the ratio is less than 2% relative to heat of char oxidation in the right side of formula (5), and water vaporization is over, pyrolysis heat can be neglected, so the calorimetric results is approximately equal to the heat of coal/char oxidation,

\[ q \approx q_{ox} \quad (7) \]
2 Heat flow model

Fig. 4. Analysis curves of characteristic temperatures of ZCY coal char combustion in air atmosphere
2 Heat flow model

- At the end of stage, the combustion of coal/char is over, and \( \alpha \approx 1 \), therefore,

\[
\phi = -c_{\text{ash}} \eta_{\text{ash}} \theta
\]  

(8)
2. Experimental

2.1 Coal prepared

- **Coals used**: JWY anthracite, ZCY bituminous coal, SLH lignite.
- **Particle size**: 37-74μm.

Table 1. Proximate and ultimate analyses of parent coals

<table>
<thead>
<tr>
<th>Rank</th>
<th>Proximate analysis (ad, wt%)</th>
<th>Ultimate analysis (daf, wt%)</th>
<th>Q_{daf, gw}(MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>V_{daf}</td>
<td>A</td>
</tr>
<tr>
<td>JWY</td>
<td>3.03</td>
<td>12.33</td>
<td>12.54</td>
</tr>
<tr>
<td>ZCY</td>
<td>1.37</td>
<td>26.21</td>
<td>19.31</td>
</tr>
<tr>
<td>SLH</td>
<td>7.32</td>
<td>50.63</td>
<td>15.45</td>
</tr>
</tbody>
</table>
2. Experimental

2.2 Char prepared

- The char samples were produced by the quartz tube furnace in an isothermal procedure. The temperature was 900°C.

<table>
<thead>
<tr>
<th>Rank</th>
<th>M</th>
<th>V&lt;sub&gt;daf&lt;/sub&gt;</th>
<th>A</th>
<th>FC</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>Q&lt;sub&gt;daf,gw&lt;/sub&gt;/MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>JWW900</td>
<td>4.71</td>
<td>8.26</td>
<td>10.68</td>
<td>77.62</td>
<td>96.04</td>
<td>0.85</td>
<td>0.78</td>
<td>1.32</td>
<td>1.36</td>
<td>34.05</td>
</tr>
<tr>
<td>ZCY900</td>
<td>1.66</td>
<td>10.77</td>
<td>38.25</td>
<td>53.62</td>
<td>95.86</td>
<td>1.24</td>
<td>0.43</td>
<td>1.82</td>
<td>0.65</td>
<td>34.38</td>
</tr>
<tr>
<td>SLH900</td>
<td>5.87</td>
<td>14.02</td>
<td>24.39</td>
<td>59.96</td>
<td>94.61</td>
<td>1.29</td>
<td>0.53</td>
<td>2.36</td>
<td>1.21</td>
<td>34.11</td>
</tr>
</tbody>
</table>
2.3 Situations of TG-DSC tests

(1) STA 449F3 Jupiter (NETZSCH, Germany), which has a precision of measurements of 1μg.

(2) Sample mass: 5 ± 0.2mg

(3) Heating rate: 10℃/min

(4) Final temperature: 1000℃

(5) Atmosphere: 21%O2/79%N2, 21%O2/79%CO2, 30%O2/70%CO2, 40%O2/60%CO2, 100%O2.
3. Results and discussion

- After the point a, the rate of char oxidation starts to be further accelerated, it means that there are more combustible matter activated with the increase of temperature. Until the temperature rises up to the point b, \( T_b = 530^\circ C \), and \( \& = 0 \), substitute it into the formula (5), it is shown that the heat release rate of carbon oxidation is equal to the rate of heat absorbed. If let \( \& = (C_s - C_r)\frac{dT}{dt} \), the formula (5) have an identical equation with the Semenov thermal explosion theory, i.e., the ignition conditions of \( \frac{dT}{d\tau} = 0 \) and \( \frac{d^2T}{d\tau^2} = 0 \) are also found, therefore, the temperature of the point b is the ignition temperature \( (T_i) \). As the heat rate of \( \theta \) is very small and keeps a constant, then the \( T_s \approx T_r \), the ignition temperature can be only determined by the following formula,

\[
k_0 (1-\alpha) Q_{daf} P x_{o_2} \exp\left(-\frac{E}{RT_s}\right) = \&_{pyr} + \&_{ev} + \left(c_{ash} \eta_{ash} + (1-\eta_{ash})(1-\alpha)c_{cm}\right)\theta
\]
3. Results and discussion

- If taking into account the heat loss by heat transfer with the surrounding boundary, then the formula (9) is changed as follow,

\[
k_0(1 - \alpha)Q_{daf}P_xo_2 \exp\left(-\frac{E}{RT_s}\right) = Q_{pyr} + Q_{ev} + \left(c_{ash} \eta_{ash} + (1 - \eta_{ash})(1 - \alpha)c_{cm}\right) \theta + k_1(T_s - T_\infty)
\]  

(10)

In which \( k_1 \) is coefficient of heat transfer, as the ambient temperature \( T_\infty < T_s \), it is corresponding to the **self-ignition** in spontaneous combustion system; and the ambient temperature \( T_\infty > T_s \), it is corresponding to the **forced ignition** in industrial combustion installation.
3. Results and discussion

In the formula (10), the ignition temperature is controlled by many of factors:

- first, the properties of pyrolysis and combustion of char, including high-rank coal char, high activation energy $E$, low heat value $Q_{daf}$, and high content of ash in char will make the ignition temperature rising;

- second, the physical properties, such as high specific heat capacity and water evaporation will make the ignition temperature rising;

- and third, the properties of combustion system, such as pressure, temperature, heating rate, oxygen concentration and diffusion, primary air ratio and heat transfer. High pressure and high oxygen concentration can make the ignition temperature drop.
3. Results and discussion

2.3 Ignition and intensive ignition temperature

When oxidation heat of the coal char is greater than the sum of heat absorption and heat loss at point $a$, which is the ignition temperature $T_i$, char is ignited.

But the burning is unstable at the point $a$, only supply enough oxidants to hold the char burning acceleration until to $b$, the inflection point of DSC curve, the corresponding temperature is defined as the intensive ignition temperature, $T_{ig}$.

Then the heat release rate reaches the maximum value, corresponding to the point $c$, defined as the maximum heat release temperature $T_{DSCmax}$.
Coal/char releases heat after ignition, in this procedure, there is a concerning about the acceleration of heat release. We define the heat release acceleration $a$ as follows:

$$a = \frac{d^2q}{dt^2} \quad J/ (s^2 \cdot mg)$$

The acceleration $a$ can be calculated though the first derivate of DSC curve.
3. Results and discussion

TG-DTG curves analysis

With increasing the oxygen concentration, the maximum rates of mass loss increase and the temperature corresponding to the maximum value of DTG, $T_{DTG_{max}}$, decrease.

Fig.2. TG-DTG curves of different chars, a. JWY, b. ZCY, c. SLH.
DSC curves analysis

With increasing the oxygen concentration, all DSC curves show the trend of more tall and slim, the maximum heat releases increase, and $T_{DSCmax}$ decrease.

At the same oxygen concentration, as the coal rank increases, the reactivity of char decreases, results in $T_{DSCmax}$ increasing.
With increasing the oxygen concentration, the maximum heat release acceleration ($a_{max}$) increases. From the aspect of heat release acceleration, char sample burns more faster and fiercer under higher oxygen concentration.

Fig.3 Heat release acceleration of coal char
3. Results and discussion

Table 3. Intensive ignition temperature of coal chars under different oxygen concentration

<table>
<thead>
<tr>
<th></th>
<th>21%O₂/79%N₂</th>
<th>21%O₂/79%CO₂</th>
<th>30%O₂/70%C</th>
<th>40%O₂/60%C</th>
<th>100%O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>JWY</td>
<td>530.6*</td>
<td>586</td>
<td>573</td>
<td>562</td>
<td>538</td>
</tr>
<tr>
<td>ZCY</td>
<td>477*</td>
<td>568</td>
<td>564</td>
<td>555</td>
<td>531</td>
</tr>
<tr>
<td>SLH</td>
<td>372.8*</td>
<td>501</td>
<td>494</td>
<td>488</td>
<td>466</td>
</tr>
</tbody>
</table>

Table 4. Maximum heat release acceleration of coal chars under different oxygen concentration

<table>
<thead>
<tr>
<th></th>
<th>21%O₂/79%CO₂</th>
<th>30%O₂/70%CO₂</th>
<th>40%O₂/60%CO₂</th>
<th>100%O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>JWY</td>
<td>1.8</td>
<td>2.1</td>
<td>3.0</td>
<td>4.8</td>
</tr>
<tr>
<td>ZCY</td>
<td>2.0</td>
<td>2.9</td>
<td>3.7</td>
<td>8.5</td>
</tr>
<tr>
<td>SLH</td>
<td>2.8</td>
<td>4.1</td>
<td>5.1</td>
<td>7.0</td>
</tr>
</tbody>
</table>
4. Conclusion

1. The goal of this study was to propose a new method for determining the intensive ignition temperature according to the DSC curves.

2. The intensive ignition temperature $T_{ig}$ increases with the coal rank, and decreases with increasing oxygen concentration.

3. Heat release rate increases with increasing oxygen concentration, while $T_{DSCmax}$ decreases. At the same oxygen concentration, as the coal rank increases, results in $T_{DSCmax}$ increasing.

4. With increasing the oxygen concentration, the maximum heat release acceleration ($a_{max}$) increases.
Acknowledgments

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Thank for your attention!