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Study on the Pyrolysis Kinetics of Blended Coal in the Fluidized-Bed Reactor

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Abstract

The micro fluidized bed reaction analyzer (MFBRA) was employed to investigate the emission characteristics and the formation kinetics of methane which was released from different kinds of coal and the blended coal during the coal pyrolysis. The results show that under the same pyrolysis condition, the initial release temperature of methane and the pyrolysis activation energy (E) decreases with increasing volatile content of the coal, while the maximum releasing rate and the total volatilization amount of methane increased, indicating that the higher the volatile content of coal, the easier the pyrolysis reaction. Coal blending can change the quality parameters of the single coal. The water content, volatile content and ash content of the blended coal were equal to the weighted average of corresponding single coal, while the activation energy (E) of blended coal was not equal to the weighted average of corresponding single coal.

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Keywords: fluidized-bed; pyrolysis; blended coal; activation energy; methane

1. Introduction

Coal is the primary energy in China. It accounts for about 70 percent in the primary energy consumption structure and 50 percent of coal is used for power generation.\textsuperscript{[1]} There are some problems in coal utilization and processing...
including high energy consumption, low efficiency and high pollution, which are caused by the coal’s unavailability of meeting boiler requirements. As a result, the coal-blending technique has been adopted by many enterprises, especially power plants. Different kinds of coal are blended in a certain proportion to modify the quality parameters, thus the technical requirements of boiler can be met. Coal pyrolysis is not only a necessary process for coal combustion, gasification and liquefaction, but also an important approach to utilize coal. In recent years, numerous researchers had implemented thermo-gravimetric analysis (TGA) to study pyrolysis kinetics of coal (blended coal), from which great progress has been made \cite{2-9}. Since the TGA can only simply reflect change of coal’s mass during the process, while the compositions and the corresponding yields of pyrolysis products remain unknown due to the complexity of pyrolysis, there are several research conclusions \cite{10} which are contrary to the realities of coal pyrolysis. Having considered the reasons above and the current status of utilization of blended coal in most of plants, micro fluidized bed reaction analyzer (MFBRA) was employed to explore the emission characteristics of gaseous products (CH\textsubscript{4}) during the process of pyrolysis of blended coal and then its emission activation energy would be calculated by Coats-Redfern integration according to Arrhenius law \cite{11}. This study has important significance for the establishment of basic theory of power coal blending and the improvement of combustion efficiency of blended coal.

2. Experimental

2.1. Experimental coal samples

The types of coal used in this investigation were Shenhua coal (SH), Jincheng coal (JCH) and Xiaolongtan coal (XLT). According to the China national standards of coal classification (GB5751—86), they belong to bitumite, anthracite and lignite, respectively. Proximate and ultimate analysis of experimental coal samples are shown in table 1. The coal samples used in the investigation were firstly dried in the air and then pulverized into powder samples with an average size of 52\(\mu\)m, in which the largest size was 0.01mm and the percentage of size that less than 74\(\mu\)m was 70%~74%. The blended coals used in the investigation are composed of XLT coal and JCH coal with the respective proportion of 1:3 (25%XLT+75%JCH), 1:1 (50%XLT+50%JCH) and 3:1 (75%XLT+25%JCH). As shown in the table 1, the water content, volatile content and ash content of the blended coal were equal to the weighted average of corresponding single coal.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate analysis/%\textsuperscript{1}</th>
<th>(Q_{\text{net,ad}})/ (MJ·kg\textsuperscript{-1})</th>
<th>Ultimate analysis/%\textsuperscript{1}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(M_{\text{ad}})</td>
<td>(A_{\text{ad}})</td>
<td>(V_{\text{ad}})</td>
</tr>
<tr>
<td>JCH</td>
<td>2.48</td>
<td>8.23</td>
<td>8.15</td>
</tr>
<tr>
<td>SH</td>
<td>9.36</td>
<td>7.60</td>
<td>33.21</td>
</tr>
<tr>
<td>XLT</td>
<td>22.65</td>
<td>7.92</td>
<td>52.73</td>
</tr>
<tr>
<td>25%XLT+75%JCH</td>
<td>7.52</td>
<td>8.15</td>
<td>19.29</td>
</tr>
<tr>
<td>50%XLT+50%JCH</td>
<td>12.56</td>
<td>8.07</td>
<td>30.44</td>
</tr>
<tr>
<td>75%XLT+25%JCH</td>
<td>17.61</td>
<td>7.99</td>
<td>42.36</td>
</tr>
</tbody>
</table>

\textsuperscript{1} Percentage of weight

2.2. Apparatus and methods

The micro fluidized bed reaction analyzer \cite{12,13} (MFBRA) jointly developed by Institute of Process Engineering of Chinese Academy of Sciences and Beijing Henven Scientific Instrument Factory was employed in the
investigation. The instrument mainly consisted of a fluidized bed reactor and a residual gas analyzer. The product gases produced from the fluidized bed reactor, such as CH\textsubscript{4}, CO, CO\textsubscript{2}, H\textsubscript{2}, etc., can be detected by the on-line residual gas analyzer. To ensure that the coal powders were in fluidized state during the process of reaction, quartz sand was used as fluidizing medium and nitrogen was used as fluidizing gas with a flow rate of 300mL/min. 20mg of coal powder was carried into the MFBRA by flow gas when the temperature had risen to the set-point, and the heating rate was 10°C/min. The termination of product gas volatilization marked the completion of pyrolysis reaction. The components and masses of the pyrolysis gas were determined by the on-line residual gas analyzer, and the activation energies of the coal pyrolysis reactions in the fluidized bed could be extrapolated from the methane yields at various temperatures.

2.3. Calculation of activation energy of coal pyrolysis

Coal pyrolysis, also known as thermal decomposition or carbonization of coal, refers to heating the coal at changing temperature in the absence of air, there are a series of complex physical changes and chemical reactions during the process\textsuperscript{[14]}. The chemical equation of overall reaction of coal pyrolysis is given as follows:

$$\text{Coal} \xrightarrow{400\degree C - 900\degree C} \text{Gas(CH}_4, \text{CO, H}_2, \text{etc.} + \text{Liquid(tar)} + \text{Solid(semi-coke or coke)}$$

During the coal pyrolysis, the formation of product gas, such as methane, is in conformity with the first-order kinetic model\textsuperscript{[15, 16]}. The dynamics equation is as follows:

$$\frac{dx}{dT} = \frac{A}{\phi} \cdot e^{-\frac{E}{RT}} \cdot (1-x) \quad (1)$$

Integrating equation (1) gives:

$$\ln\left(-\frac{\ln(1-x)}{T^2}\right) = \ln\left(\frac{AR}{\phi E}(1-\frac{2RT}{E})\right) - \frac{E}{RT} \quad (2)$$

where x means methane formation fraction, \%; \(\phi\) is heating rate, °C·s\textsuperscript{-1}, \(\phi = \frac{dT}{dt}\); E refers to activation energy, KJ/mol; R is gas law constant, \(R=8.315 \times 10^{-3}\)kJ/(mol·°C); A is frequency factor, s\textsuperscript{-1}. And in equation (2), \(\frac{E}{RT} \gg 1\),

$$(1-\frac{2RT}{E}) \approx 1$$, hence equation (2) can be simplified into:

$$\ln\left(-\frac{\ln(1-x)}{T^2}\right) = \ln\left(\frac{AR}{\phi E}\right) - \frac{E}{RT} \quad (3)$$

Let \(y = \ln\left(-\frac{\ln(1-x)}{T^2}\right), a = \ln\left(\frac{AR}{\phi E}\right), b = -\frac{E}{R}, x = \frac{1}{T}\), then equation (3) can be converted into an linear equation: \(y=a+bx\). The slope and intercept of the plot of the linear equation can be used to obtain E and A in equation (1).
3. Results and discussion

3.1. Methane release characteristics and coal pyrolysis kinetics during single-coal pyrolysis

As shown in the figure 1 and the table 2, during the single-coal pyrolysis, the pyrolysis experiments of different coal samples under the same conditions exhibit varying methane release characteristics and pyrolysis kinetics. In the table 2, $T_0$ is the initial releasing temperature, °C; $T_{\text{max}}$ refers to the temperature of the maximum releasing rate, °C; $T_{\infty}$ is the temperature corresponding to the termination of gas release, °C; $(dV/dT)_{\text{max}}$ is the maximum releasing rate, cm$^3$/°C; E means the activation energy of methane release, kJ/mol.

We can conclude from the figure 1 and the able 2 that the initial release temperature of methane and the activation energy of coal-pyrolysis depend on coal type under the same conditions. They are negatively correlated with the volatile contents of coal samples. It’s also found that the maximum releasing rate and the total amount of methane are varied with coal types under the same thermal conditions. They are positively correlated with the volatile contents of coal samples. The results demonstrate that the higher the volatile content of coal, the easier its pyrolysis reaction.

![Figure 1](image)

**Table 2** Characteristic parameters of the release of methane during single coal pyrolysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_0$/°C</th>
<th>$T_{\text{max}}$/°C</th>
<th>$T_{\infty}$/°C</th>
<th>$(dV/dT)_{\text{max}}$/×10$^{-10}$cm$^3$/°C$^{-1}$</th>
<th>E/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>XLT</td>
<td>326</td>
<td>521</td>
<td>755</td>
<td>0.97</td>
<td>104</td>
</tr>
<tr>
<td>SH</td>
<td>372</td>
<td>552</td>
<td>829</td>
<td>0.91</td>
<td>125</td>
</tr>
<tr>
<td>JCH</td>
<td>500</td>
<td>626</td>
<td>742</td>
<td>0.82</td>
<td>372</td>
</tr>
</tbody>
</table>

3.2. Methane Release Characteristics and Coal pyrolysis Kinetics during Blended-coal pyrolysis

Under the same thermal conditions, the release characteristics of methane and the pyrolysis kinetics of blend-coal composed by XLT coal and JCH coal with particular proportions have been shown in the figure 2 and the table 3. The meaning of $T_0$, $T_{\text{max}}$, $T_{\infty}$, $(dV/dT)_{\text{max}}$, and E in the table 3 are identical to those in the table 2. As shown in figure 2 and the table 3 that the higher proportion of XLT coal, which has relative higher volatile content than JCH coal, would result in decreases of initial releasing temperature and activation energy as well as increases of maximum releasing rate and the total output of methane. It can be summarized that the activation energy of blended coal is not equal to the weighted average value of corresponding data from single-coal. These results indicate that the quality characteristics of coal have been modified by coal blending. The water content, the volatile content and the ash
content of the blended coal are identical with the weighted average values of corresponding data from single-coal samples. However, due to the fact that pyrolysis characteristics and the combustion characteristics of blended-coal are not consistent with the weighted average values of corresponding data from single-coal samples, special attention must be paid to prevent combustion instability and flameout accidents.

These results should be considered from two aspects. Firstly, the low-volatile coal may have an adsorption effect on the methane released by the high-volatile coal, thus the methane releasing properties including methane yield, initial releasing temperature would be changed. Secondly, some metallic components such as iron pyrite could serve as catalyst to promote or inhibit the methane release process. The detailed mechanism needs to be further investigated.

![Fig 2 Relation between releasing rate of methane and temperature during blended coal pyrolysis](image)

Table 3 Characteristic parameters of the release of methane during blended coal pyrolysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_0/°C</th>
<th>T_max/°C</th>
<th>T_G/°C</th>
<th>(dV/dT)_max/×10^-10cm^3°C^-1</th>
<th>E/kJ mol^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>25%XL+75%JCH</td>
<td>428</td>
<td>597</td>
<td>743</td>
<td>0.85</td>
<td>341</td>
</tr>
<tr>
<td>50%XL+50%JCH</td>
<td>345</td>
<td>573</td>
<td>746</td>
<td>0.89</td>
<td>269</td>
</tr>
<tr>
<td>75%XL+25%JCH</td>
<td>336</td>
<td>549</td>
<td>752</td>
<td>0.91</td>
<td>167</td>
</tr>
</tbody>
</table>

4. Conclusions

1) Under the same pyrolysis conditions, the initial temperature of methane release is negatively correlated with the volatile content of coal. Moreover, the maximum releasing rate and the total amount of methane are positively correlated with the volatile content of coal.

2) The activation energy of coal-pyrolysis and the pyrolysis kinetics of coal are varied with coal types. As the volatile content of coal increased, the activation energy of coal-pyrolysis decreased, which means that the higher the volatile content of coal, the easier the pyrolysis reaction.

3) The quality characteristics of coal have been modified by coal blending. The water content, the volatile content and the ash content of the blended coal are equal to the weighted average values of corresponding data from single-coals, but the activation energy of blended-coal is different from the corresponding weighted average value, which indicates that some changes occur in terms of the pyrolysis characteristics and the combustion characteristics of
blended-coal. In addition, special attention must be paid for preventing combustion instability and flameout accidents.

4) Two assumptions are proposed including the adsorption effect of low-volatile coal and the catalytic effect of metallic component to explain that the activation energy of blended-coal is different from the corresponding weighted average value.

Acknowledgements

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References