Thermal analysis was used to study the oxidation and thermal degradation reaction of Yangquan coal. One method is that the coal was heated to a certain temperature and held at that temperature for 45 min; Another method is that coal was heated to a temperature and held for 45 min, then it was taken out and the new coal sample was re-put with other temperature’s experiments. Two different experiments and their dynamic characterizes were compared, showing that the change degree of TG curve is different from each other. The process of coal oxygenolysis belongs to the first-order of chemical reaction. The activation energy increases along with the reaction process. Moreover, the oxidation of coal is a process that contains lots of reaction steps which mutually promote and connect.

**Keywords:** coal; thermal analysis; reaction kinetics;
respectively, and held at that temperature for 45 min, then the TG curves under these temperatures were got (it was called continuous experiment). Another method is that samples were heated to 100 and held on for 45 minutes, then it were taken out and the new coal sample were put in and heated to 140 experiment (separated experiments), in this way the four TG curves were got. The curves and the conversion rate of two experiments are respectively shown in Table 1 and Figure1.

Table 1. The conversion rate of two methods experiments

<table>
<thead>
<tr>
<th>Coal</th>
<th>Temperature range ( )</th>
<th>Conversion rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous</td>
<td>100</td>
<td>60.45</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>48.03</td>
</tr>
<tr>
<td>Separation</td>
<td>180</td>
<td>42.80</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>42.51</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>39.08</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>37.09</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>27.72</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>24.90</td>
</tr>
</tbody>
</table>

Fig. 1. TG curves of two experiments

(1) From Table1, conversion rate of the coal samples change greater between 100 and 140 under the two methods, which indicates the coal may have the moisture removed at this stage. Between 180 and 220, the quality of coal has increased significantly, which indicate the reaction got into the phase of weight gaining after 180. There are different change characteristics with different experimental methods. Under certain temperature, the active ingredients of coal sample has been involved in some oxidation in continuous experiment and some unstable oxygen compounds were produced which existed in the coal molecules, therefore the mass changes slowly in the continuous experiment.

(2) There are different change degrees in the TG curves of two experiments. A reasonable explanation is that the diffusion resistance and the temperature gradient in the specimen have major influence on it. The reaction of samples endotherm or exotherm will deviate from the linear temperature of process. The greater the gas diffusion resistance is, the more significant changes degrees of TG curves are. The resistance of separated experiment is larger than the continuous experiment, so the degree of TG curve has more significant changes in the separated experiment.

(3) Along with temperature increasing, the most of coal samples will usually produce the phenomenon of weight gain on the oxygen condition, with an upward trend in the beginning of the TG curve, which shown coal samples had a reaction with oxygen. According to the theory of coal combustion, the product after the loss of volatile is called the residual carbon or carbon. As carbon combined with oxygen in pattern of chemical absorption, the gas molecules dissolved in the carbon lattice form a solid solution, which provide conditions for the combustion reaction
of carbon[3].

2.2. Kinetic model

The rate of heterogeneous solid-state reactions can be generally described by

$$\frac{da}{dt} = Ae^{-\frac{E}{RT}} f(a)$$

(1)

The conversion rate \(a\) can be obtained from TG curves as

$$a = \frac{(w_0 - w)}{(w - w_\infty)}$$

(2)

Where \(a\) is the conversion degree or fraction of material combusted; \(t\) the time; \(w_0\) the initial mass; \(w_\infty\) the final mass; \(w\) the residual mass of the coal at time \(t\); \(T\) the temperature; \(A\) the Arrhenius parameter; \(E\) the activation energy; \(f(a)\) a function called the reaction model, which describes the dependence of the reaction rate on the extent of reaction; And \(g(a)\) the integral function of TG curves. As temperature changes at a constant positive rate, \(\beta \frac{dT}{dt}\). When \(\beta\) is put into Eq. (1), the Eq. (3) can be obtained as follows:

$$\frac{da}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(a)$$

(3)

Integrating up to the conversion rate \(a\), Eq. (3) can be changed as follows:

$$\int_0^a \frac{da}{f(a)} = \frac{A}{\beta} \int_{T_0}^T e^{-\frac{E}{RT}} dT$$

(4)

A problem with Eq. (4) is that it is not analytically solved. The function \(g(a)\), however, can be expressed by some approximate equations. As many approximate results have been derived and still discussed[4-5], the numerical analysis method is used to get the solution, and Eq.(4) is integrated by using Coats-Redfen formula.

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

(5)

For different reaction mechanisms, the dynamics of integral function \(g(a)\) can be written as:

$$g(a) = -\ln(1-a), \quad n = 1$$

$$g(a) = \frac{1 - (1-a)^{1-n}}{1 - n}, \quad n \neq 1$$

Where \(n\) is the reaction order. The dates of \(a\) and \(T\) were selected in different temperature ranges. For each value of conversion \(a\), the term of \(\ln \left[\frac{g(a)}{T^2}\right]\) varies linearly with \(\frac{1}{T}\) as slope of the line is \(\frac{E}{R}\), which is plotted in Fig.3. Subsequently, values of \(E\) may be estimated from the slope of a plot of \(\ln \left[\frac{g(a)}{T^2}\right]\) versus \(\frac{1}{T}\) [6-9].
2.3. Kinetic calculation and analysis

According to the decomposition process, the oxygen will be consumed and a small amount of gas was generated with the continuous reaction. The instability solid-state carbon-oxygen products were generated at the beginning, which performed the phase of weight increasing in the TG curve. With gradually reactants decrease, lots of gaseous oxidation products were released and the energy increased with the burning completely. The dates of $a$ and $T$ were selected from different temperature ranges and the different function mechanisms were applied to analysis, then the plots of $\ln \left( \frac{g(a)}{T^2} \right)$ versus $\frac{1}{T}$ were got. Here $n=1$, $n=0$, $n=2$ were selected to analysis its function mechanism. The following are the plots of $\ln \left( \frac{g(a)}{T^2} \right)$ versus $\frac{1}{T}$:

(a) The temperature of 100

(b) The temperature of 140

(c) The temperature of 180
The temperature of 220

Fig. 3. The plot of $\ln \left[ \frac{g(a)}{T^2} \right]$ versus $\frac{1}{T}$

From Fig. 3, the better linear correlation is at $n = 1$ in the two types of experiment at different temperatures. Through $n = 1$, the plots of $\ln \left[ \frac{g(a)}{T^2} \right]$ versus $\frac{1}{T}$ are got. The activation energy and correlation coefficient of two experiments were calculated, which was shown in Table 2.

Table 2. Kinetic parameters of two type’s oxidation experiments

<table>
<thead>
<tr>
<th>Coal</th>
<th>Temperature</th>
<th>Activation energy</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous experiment</td>
<td>100°</td>
<td>121.741</td>
<td>0.9804</td>
</tr>
<tr>
<td></td>
<td>140°</td>
<td>185.718</td>
<td>0.9961</td>
</tr>
<tr>
<td></td>
<td>180°</td>
<td>259.987</td>
<td>0.9889</td>
</tr>
<tr>
<td></td>
<td>220°</td>
<td>276.681</td>
<td>0.9897</td>
</tr>
<tr>
<td>Separation experiment</td>
<td>100°</td>
<td>152.362</td>
<td>0.9912</td>
</tr>
<tr>
<td></td>
<td>140°</td>
<td>209.762</td>
<td>0.9973</td>
</tr>
<tr>
<td></td>
<td>180°</td>
<td>223.854</td>
<td>0.9936</td>
</tr>
<tr>
<td></td>
<td>220°</td>
<td>264.659</td>
<td>0.9900</td>
</tr>
</tbody>
</table>

It was known that:

1. The reactions are all the first-order in two types experiment at different temperatures and the correlation coefficient are greater than 0.98. Along with the increasing, of oxidation degree, the activation energy with which coal continues to oxidation also increases.

2. Table 2 indicates that the activation energy of continuous experiment is larger than the other after 180°. A reasonable explanation is reported that Yangquan coal has a process of water losing before 140°. Because coal samples have been contacted with oxygen, the process of oxygen adsorption and desorption takes place, and adsorption is in a larger proportion (Figure 1). The active ingredients can be involved in partial oxidation with the previous temperature of the continuous experiment, so it requires very little energy to go on the follow-up process. However, the oxygen reaction has a larger proportion after the 180°. Along with the early lost of moisture, the external hole had opened, and then oxygen is adsorbed by reactive molecules. With the temperature increasing, oxygen diffusion and chemical reactions take place. For continuous experiments, there is a constant temperature stage after water losing. It is a failure to timely contact with oxygen, or the coal-hole may be blocked by residual water condensation.

3. When coal contacted with oxygen, it has a adsorption and desorption process on the surface, but in different stages it has different weights. With temperature increasing and reaching a certain value of energy, the coal goes on the follow-up process. So the oxidation of coal is a multi-step, and it may be accompanied by oxygen absorption and
desorption and mutual promote process. By means of studying on the mechanism of coal oxidation, it can be clearly identified to the oxidation process, and the ways to prevent spontaneous combustion can be obtained.

3. Conclusions

(1) There are different quality change ranges in different experimental methods. The consecutive experiments change smaller, which illustrate that the active ingredients of coal sample has been involved in some oxidation at certain temperature and unstable oxygen compounds were produced which existed in the coal molecules.

(2) There are different change degrees in TG curves of two types experiment. The reaction of samples endotherm or exotherm will deviate from the linear temperature of process. The greater the gas diffusion resistance is, the more significant changes of the TG curves are.

(3) The coal oxygenolysis belongs to the first-order of chemical reaction, and the activation energy of coal increases along with the process of coal reaction.

(4) The reaction of coal is a very complex process, which is along with the oxygen adsorption and desorption. When the heat released from adsorption and chemical reaction exceeds the required, the reaction enters into the first-order in two types experiment at different temperatures and the correlation coefficient are greater than 0.98. Along with the increasing, of oxidation degree, the activation energy with which follow-up stage. Based on the kinetic analysis, the oxidation reaction is a process which mutual promote and connect.

Acknowledgements

Financial supports for this work, provided by NSFC (50274061), PCSIRT (IRT0618), Basic and Advanced Technology Research Program of Henan Province (072300420180, 082300463205) and the Program for New Century Excellent Talents in University of Henan Province (2005HANCET-05), is gratefully acknowledged.

References