The 6th International Conference on Mining Science & Technology

Experiment study of model compound oxidation on spontaneous combustion of coal

Li Zeng-hua*, Wang Ya-li, Song Na, Yang Yong-liang, Yang Yu-jing

School of Safety Engineering, China University of Mining & Technology, Xuzhou 221008, China

Abstract

Spontaneous combustion is one of the severest accidents in the process of coal production and transportation. Therefore it is significant to study the mechanism of coal spontaneous combustion. Based on theoretical analysis, 7 kinds of model compounds have been chosen in this paper, which are hyacinthin, anisole, diphenylmethane, phenetole, benzyl alcohol, benzhydrol, and α-phenylpropanol. And they contain respectively active groups such as aldehyde group, methoxyl group, hypomethyl bond, hypomethyl ether bond, hypomethyl bond of α-carbon atom with hydroxyl, hypoalkyl bond of α-carbon atom with hydroxyl, and so on. According to the theory of free radical reactions, taking the model compound of coal above as research object, chemical reaction kinetic parameters, thermodynamic parameters, and products from normal temperature to 150 ℃ have been quantitatively studied by oxidation device and analytical instrument, then the oxidation course can be deduced. The results show that all the model compounds consumed oxygen and produced CO and CO2 at different degrees after temperature programmed to 150 ℃. The oxidation characteristic of the active groups in coal and the effect of them on spontaneous combustion can be recognized, and spontaneous combustion mechanism can be expositied systematically in chemistry by means of studying the oxidation of model compound.

Keywords: coal spontaneous combustion; model compound; active group; oxygen consumption rate

Coal spontaneous combustion is one of the severest disasters in coal mines. Coal is organic macromolecule composed of various functional groups and chemical bonds, so spontaneous combustion of it is a complex physical and chemical process. For a long time, people make a lot of researches [1] about coal spontaneous combustion mechanism. Theories of coal spontaneous combustion such as the doctrine that bacteria is a cause of spontaneous combustion, the doctrine that pyrite is a cause of spontaneous combustion, the doctrine that pyrite is a cause of spontaneous combustion, action theory of phenolic group, coal oxygen complex action theory[2] and mechanism of free radical reactions [3] were put forth.

The modern theory of coal molecular structure [4] holds that the main structure units of coal are condensed aromatic nucleus and heterocyclic aromatic nucleus, and these structure units are linked by methylene bond, ether bond and aldehyde group bond. Relevant study [5] shows that side chain group and low molecular weight compound in coal are the matters inducing coal spontaneous combustion. It is a common method to study chemical reaction of complex system using model compound, such as liquefaction, cracking and desulfurization of coal and petroleum refining. Benjamin [6] once studied cracking of bridge bond in liquefaction of coal using more than 50 kinds of model...
compound. Therefore in this paper model compound is used replacing coal molecules to study chemical properties of coal, through measuring chemical reaction kinetic parameters and thermodynamic parameters in oxidation process from normal temperature to 150 °C, and spontaneous combustion mechanism could be exposited systematically in chemistry by means of studying the oxidation of model compound.

1. Selecting model compound

This paper is studying the spontaneous combustion process of coal from normal temperature to 150 °C. So model compound selected should be liquid or solid, and their boiling points should be above 100 °C, which shows that molecular weight of model compound selected is not low so as to conduct heating oxidation experiment. Therefore principles of selecting model compound are as follows:

(1) Model compound selected must contain only one oxidative active group of coal;
(2) These oxidative active groups should be representative, the oxidation activity of them should be high, and they should be common structures of coal.

Xu Jingcai and Shi Ting et al from Xi’an University of Science and Technology [7,8,9] put forth chemical structure schematic model of surface molecules of self-ignition coal, based on Wiser’s coal macromolecular structure model. According to theoretical analysis, the oxidative active groups of coal which are oxidized at ambient temperature and pressure are aldehyde group, methoxyl group, hypomethyl bond, hypomethyl ether bond, hypomethyl bond of α-carbon atom with hydroxyl, hypoalkyl bond of α-carbon atom with hydroxyl and so on. They are shown in Table 1.

### Table 1. Oxidative active group at surface of coal

<table>
<thead>
<tr>
<th>Names</th>
<th>Molecular formula</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldehyde group</td>
<td>−CHO</td>
<td>It only existed in peat and soft brown coal, and its content is decreased with coalification degree increasing</td>
</tr>
<tr>
<td>Methoxyl group</td>
<td>−O−CH3</td>
<td></td>
</tr>
<tr>
<td>Alkyl group of α-carbon atom with hydroxyl</td>
<td>−HCOH−CH3</td>
<td>They are all bridge bond in coal, not hyperdispersion in coal; there are many bridge bond such as long hypomethyl bond and hypomethyl ether bond in low coalification degree coal; amount of bridge bond in middle coalification degree coal is the least, such as mainly −CH2− and −O− in bituminite stage bridge bond increases</td>
</tr>
<tr>
<td>Hypomethylether bond</td>
<td>−CH2−O−</td>
<td></td>
</tr>
<tr>
<td>Hypoalkyl bond with hydroxyl</td>
<td>−HCOH−</td>
<td></td>
</tr>
<tr>
<td>Hypoalkyl bond with branched chain</td>
<td>−HCR−CH2−</td>
<td></td>
</tr>
<tr>
<td>Hypoalkyl bond of α-carbon atom with hydroxyl</td>
<td>−CHOH−CH2−</td>
<td></td>
</tr>
</tbody>
</table>

Shi Ting and Deng Jun in Xi’an University of Science and Technology [10] proved that activity of carbon atom and hydrogen atom in active group doesn’t change with the number of aromatic ring. So model compound combined by aromatic ring and oxidative active group of coal is chosen in this paper, which are shown in Table 2.

### Table 2. Model compound of coal molecules

<table>
<thead>
<tr>
<th>Oxidative active group</th>
<th>Model compound</th>
<th>Molecular formula of model compound</th>
<th>Property of model compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>−CHO</td>
<td>Hyacinthin</td>
<td><img src="image" alt="Hyacinthin" /></td>
<td>Colorless transparent liquid; boiling point is 195 °C; flash point is 87 °C</td>
</tr>
<tr>
<td>−O−CH3</td>
<td>Anisole</td>
<td><img src="image" alt="Anisole" /></td>
<td>Colorless liquid; melting point is -37.8 °C; boiling point is 155 °C</td>
</tr>
<tr>
<td>−CH2−O−</td>
<td>Phenetole</td>
<td><img src="image" alt="Phenetole" /></td>
<td>Colorless aromatic liquid; boiling point is 171~173 °C</td>
</tr>
<tr>
<td>−HCOH−</td>
<td>Benzyl alcohol</td>
<td><img src="image" alt="Benzyl alcohol" /></td>
<td>Colorless transparent liquid; melting point is -15.3 °C; boiling point is 205.35 °C</td>
</tr>
</tbody>
</table>
2. Experimental device

The experimental device is divided into two parts, which are temperature programming oxidation reaction device and gas testing device. It is shown in Fig. 1.

![Experimental device diagram](image)

Gas chromatograph | Mass flow controller | Temperature programming furnace | Pressure reducing valve | Dry air
---|---|---|---|---
Model compound | Sample tank | Glass wool | PC | Temperature sensor

In the experimental device, dry air is provided by high-pressure air cylinder, in which oxygen concentration is 20.9%. Mass flow controlling system consists of pressure maintaining valve, steady flow valve and rotameter, in which air flow rate is 20 mL/min. Glass wool prevents 6201 supporter particles from blocking pipeline. Temperature programming furnace heats to corresponding temperature and keeps constant temperature in a certain time in order to collect and test gas.

Gas testing device consists of SP501N gas chromatograph 5A molecular sieve, N2000 chromatography workstation, gas detector tube and so on.

Oxygen concentration is measured by gas chromatograph, while model compound in sample tank being oxidized at different temperature. Temperature sensor is embedded in the center of model compound to monitor temperature using PC in real time. CO and CO\(_2\) concentration at different temperature is measured by CO and CO\(_2\) detector tube.

3. Experimental procedure

Model compound and acetone solution are mixed uniformly in the ratio 1:4. Then 6201 supporter is added into the mixed solution, while being stirred by glass rod. After they mixed uniformly, 6201 supporter is tiled on ceramic tray. When acetone solution is volatilized completely, model compound would adhere to 6201 supporter uniformly.
4. Experimental results and analysis

Model compound chosen in this experiment is respectively hyacinthin, anisole, diphenylmethane, phenetole, benzyl alcohol, benzhydrol and α-phenylpropanol. Concentration of O₂, CO, and CO₂ measured after oxidation at different temperature is respectively shown in Fig. 2, Fig. 3 and Fig. 4.

In Fig. 2, oxygen consumption of hyacinthin is the highest. After the temperature of 100 °C, oxygen concentration in sample tank begins rising, which shows that hyacinthin has already basically oxidized completely. So oxygen concentration gradually rises with air pumped in unceasingly. Otherwise oxygen consumption of phenetole and anisole is higher than other model compound. Because of the highest oxygen consumption of hyacinthin, concentration of CO and CO₂ is much higher than other model compound in oxidation process. In Fig. 3, CO concentration of phenetole oxidation products is the highest expect that of hyacinthin. And CO₂ concentration of phenetole oxidation products is also the highest expect that of hyacinthin, which of other model compound is close.

Oxygen consumption rate expresses oxygen consumption of model compound per unit volume in unit time. In order to be convenient for study, temperature of model compound in sample tank is approximately equal, and air at inlet is in standard condition, with effects of molecular diffusion and non-steady state ignored, when calculating oxygen consumption rate. Then average oxygen consumption rate of model compound per unit volume in fresh air could be derived, which can be expressed as:
\[ V_{O_2}(T) = \frac{(C_0 - C_{O_2}(T)) \times Q}{60 \times G} \times \frac{M}{22.4 \times 10^3 \times 10^2} \]  

(1)

Where \( V_{O_2}(T) \) is the oxygen consumption rate of model compound at the temperature of \( T \), which expresses \( O_2 \) that unit mole model compound consumes in unit time, \( \text{mol/(mol} \cdot \text{s)} \); \( C_0 \) the \( O_2 \) concentration at inlet, \( C_0 = 20.9 \% \); \( C_{O_2}(T) \) the \( O_2 \) concentration at inlet at the temperature of \( T \), \( \% \); \( G \) the mass of model compound, \( G = 2.5 \text{ g} \); \( Q \) the flow rate of dry air, \( Q = 20 \text{ mL/min} \). and \( M \) the molecular weight of model compound.

CO producing rate expresses CO production of model compound per unit volume in unit time, which can be expressed as:

\[ V_{CO}(T) = \frac{C_{CO}(T) \times Q}{60 \times G} \times \frac{M}{22.4 \times 10^3 \times 10^6} \]  

(2)

Where \( V_{CO}(T) \) is the CO producing rate of model compound at the temperature of \( T \), \( \text{mol/(mol} \cdot \text{s)} \); \( C_{CO}(T) \) the CO concentration in sample tank at the temperature of \( T \), \( \text{ppm} \).

CO₂ producing rate expresses CO₂ production of model compound per unit volume in unit time, which can be expressed as:

\[ V_{CO_2}(T) = \frac{C_{CO_2}(T) \times Q}{60 \times G} \times \frac{M}{22.4 \times 10^3 \times 10^2} \]  

(3)

Where \( V_{CO_2}(T) \) is the CO₂ producing rate of model compound at the temperature of \( T \), \( \text{mol} / \text{(mol} \cdot \text{s)} \); \( C_{CO_2} \) the CO₂ concentration in sample tank at the temperature of \( T \), \( \text{ppm} \).

Oxygen consumption rate, CO producing rate and CO₂ producing rate of 7 kinds of model compound are calculated respectively before comprehensive comparison. The results are shown in Fig. 5, Fig. 6 and Fig. 7.

![Fig. 5. Curve of oxygen consumption rate in model compound oxidation process](image)

![Fig. 6. Curve of CO producing rate in model compound oxidation process](image)

![Fig. 7. Curve of CO₂ producing rate in model compound oxidation process](image)
In Fig. 5, oxygen consumption rate of 7 kinds of model compound can be divided into 3 gradients. Oxygen consumption rate of hyacinthin is the highest, which begins decreasing after 100 °C because of oxidization completely. Then oxygen consumption rate of phenetole and anisole is higher than that of other 4 kinds of matter except hyacinthin. Oxygen consumption rate of benzhydrol, diphenylmethane, α-phenylpropanol and benzyl alcohol are the lowest, of which oxygen consumption rate of the first three is slightly higher.

In Fig. 6, CO producing rate of hyacinthin is the highest, which begins decreasing after 100 °C because of oxidization completely. So there is a downward trend in curve after 100 °C. Then CO producing rate of phenetole is higher than that of diphenylmethane, α-phenylpropanol and benzhydrol except hyacinthin, which of other model compound is close. In Fig. 7, CO2 producing rate of hyacinthin is the highest, and phenetole is the second, which of other model compound is close.

Above analysis of experimental result and calculation result show that oxygen consumption, oxygen consumption rate, CO product concentration and CO producing rate of hyacinthin is the highest. So hyacinthin is the most active of 7 kinds of model compound, and phenetole is the second. Therefore aldehyde group and hypomethylether bond which hyacinthin and phenetole contain are more active.

5. Conclusion

Coal is a complicated macromolecular compound, so model compound can be used to simulate simple coal molecule. The paper has selected seven kinds of coal model compounds, and then carried out oxidation reaction experiments separately. In the experimental process, the oxygen consumption, CO and CO2 concentration of model compound oxidation products were measured, and then their rates of oxidation reaction were calculated respectively. Through comparative analysis, the following conclusions have been obtained.

1) In the oxidation process, the oxygen consumption rate, CO and CO2 producing rate of hyacinthin are the highest, and are two orders of magnitude higher than those of the other model compound. And hyacinthin has been completely oxidized basically in 100 °C. Oxygen concentration in the sample tank begins increasing. At the same time, CO and CO2 producing rate decrease gradually. So the oxidation reaction rate of hyacinthin is faster than that of the other model compound, and hyacinthin is the most active. Therefore aldehyde group which hyacinthin contains has the highest activity. Except phenyl acetaldehyde, in the oxidation progress, phenetole has the highest oxygen consumption, CO and CO2 concentration of oxidation products, and its reaction rate is the fastest. So hypomethyl ether bond has higher activity.

2) In addition, in the experimental process, all the coal model compound have obvious oxygen consumption after 80 °C, accompanied by a certain amount of CO and CO2 products, such as anisole, diphenylmethane, benzhydrol and α-phenylpropanol besides hyacinthin. So the activity of methoxyl group, hypomethyl bond, hypoalkyl bond with hydroxyl and hypoalkyl bond of α-carbon atom with hydroxyl are higher.

Among the active groups of the coal molecules, aldehyde group is the most active. Therefore, in the future study of mechanism of coal spontaneous combustion, the new direction of the prevention and treatment of coal spontaneous combustion can be proposed by measuring the aldehyde group of the coal qualitatively and quantitatively.

References


