

Low-Temperature Oxidation of Aldehyde and Alcohol by Model Compounds on Spontaneous Combustion of Coal

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The model compounds which involve representational functional group (aldehyde and alcohol) of coal molecule were oxidized from 293 to 423 K by temperature-programmed. The FTIR and GC-MS were adopted to qualitatively measure the change of the active structure and the ingredients of oxidation product in model compounds. Acetophenone, benzyl alcohol and benzaldehyde *etc.*, were detected in oxidation product of the hyacinthin. Meantime, propiophenone and benzaldehyde were found in the oxidation product of the 1-phenylpropanol. Furthermore, the hyacinthin and 1-phenylpropanol both produce CO₂ and CO in low-temperature oxidation stage. The experimental results demonstrated that the hyacinthin achieves maximum oxidative activity at 368 K. By comparison, the oxidizing intensity of 1-phenylpropanol was slightly grew with the increase of temperature form 293 to 423 K. It indicated that the oxidation of aldehyde in coal may play a significant role in heat production during the initial stage of the spontaneous combustion of coal.

Key Words: Spontaneous combustion of coal, Model compound, Low-temperature oxidation, FTIR, GC-MS.

INTRODUCTION

Spontaneous combustion of coal leads to serious disasters during coal-related industry¹, which common occurs in underground coal mining, long-term storage and transportation of coal. For centuries, people try to study the mechanism of spontaneous combustion of coal²⁻⁴. The traditional method for elaborating spontaneous combustion of coal always focus on the change of thermodynamic parameters in low-temperature oxidation of coal^{5,6}. Currently, many significant research achievements are proposed and elements (such as coal rank, particle size of coal, moisture content of coal and oxygen absorption of coal *etc.*) have been widely recognized as important influencing factors^{7,8}. Inorganics associated in the coal is also considered a key factor which effects on self-heating^{9,10}. In spite of that, with the development of analytical chemistry, researchers increasing pay attention to study spontaneous combustion of coal by chemical view¹¹⁻¹³.

It is necessary to detect the variation of coal molecular structure before and after the low-temperature in order to reveal the mechanism of spontaneous combustion of coal comprehensively. Infrared spectroscopy was employed for providing reference on the transform of functional groups in coal after self-heating of coal^{14,15}. Deng *et al.*¹⁶ also explained the generation of gaseous products during the spontaneous combustion of coal by computational chemistry¹⁶. However, it is difficult

to assure the accuracy of these results due to the fact that the coal molecular structure is extremely complex and erratic.

In the petroleum refining area, Isao *et al.*¹⁷ investigate some target structures for the modification of paraffinic petroleum residues by model compounds. For simplifying the complex molecular structure of coal, we selected mode compounds to research some special structure in coal on the low-temperature oxidation. The main structural units of the coal are condensation aromatic and heterocyclic aromatic and these structural units are connected by several active groups and bridge bonds¹⁸. The structures of hydroxyl, carbonyl, carboxyl and methyl are widespread existing in coal with different coal rank¹⁹. Chemical properties of condensation aromatic and heterocyclic aromatic are relatively stable. Therefore, the active groups and bridge bonds are preferential oxidized in process of low-temperature oxidation of coal²⁰. It is significant to detect the oxidizing intensity and reaction pathway of active structures in coal. As a result, the aromatic compound (hyacinthin and 1-phenylpropanol) which includes single active group, such as aldehyde or alcohol, was selected as the model compound.

EXPERIMENTAL

The schematic diagram of the experimental apparatus was shown in Fig. 1. In experimental system, 0.02 L/m dry air uniformly passes through the pipeline. The temperature control

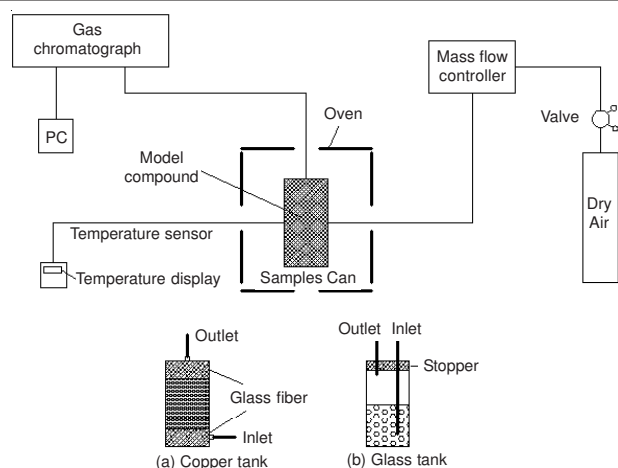


Fig. 1. Experimental set-up

system assures that the sample can enable to be conducted by temperature programming and stabilized at setting temperature.

The inert supporter with the particle size of 0.180 mm was employed to simulate particle state of coal in order to simulate coal particles and create "gas-solid reaction" condition similar with self-heating oxidation of coal from the physical perspective. Firstly, take 0.01 mol model compound and 10 g acetone with electronic balance and then uniformly mix them. Next, we poured 40 g supporter into mixture and stir it with glass rod so as to make acetone and model compound evenly attached to supporter surface. Then the mixture were dried under vacuum for 24 h to make acetone volatilize absolutely. After acetone fully volatilizes, model compound would be attached to the supporter evenly. After that, the supporter was place into the sample can. At each setting temperature, gaseous products of reaction need to be collected. In addition, concentration variation of reaction products would be analyzed quantitatively by making use of the gas chromatograph. Furthermore, 0.1 mol liquid model compound was pour into glass bottle and pass into the air continuously for oxidation (airflow for 2 L/m). Keep oxidizing under setting temperature. Afterwards, product constituents were qualitatively analyzed via GC-MS.

RESULTS AND DISCUSSION

The infrared spectroscopy is a kind of test method which could effectively reflect the changes of functional groups in organics. As shown in Fig. 2(a), the activity structures in model compounds were oxidized continuously with the ceaseless temperature increase. When the reaction temperature reached 373 K, absorption peak representing flexural vibration of C-H (1485 cm^{-1}) and stretching vibration of C=O (1729 cm^{-1}) weakened after low-temperature oxidation for 4 h, which indicated that the alkanes and carbonyl in hyacinthin were gradually decreased. Meanwhile, a small adsorption peak representing -OH also emerged at 3391 cm^{-1} . As shown in Fig. 2(b), the main characteristic peaks at 3385 cm^{-1} was obviously declined, which suggested that the -OH structure in 1-phenylpropanol was damaged. Specifically, a new absorption peak which stands for C=O occurred around 1732 cm^{-1} . In addition, there were fewer changes among other adsorption peaks.

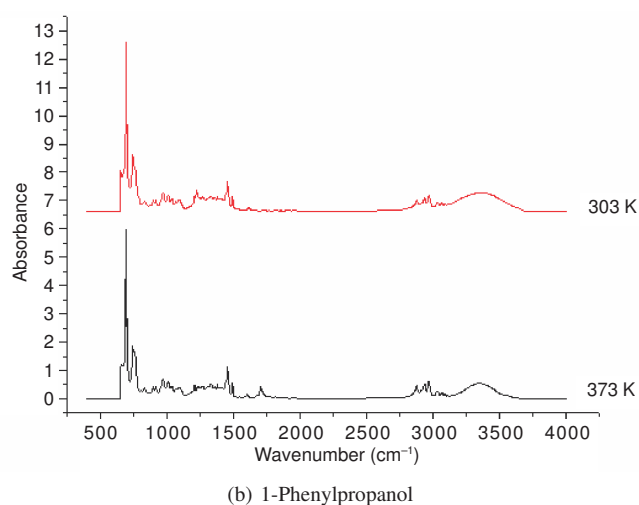
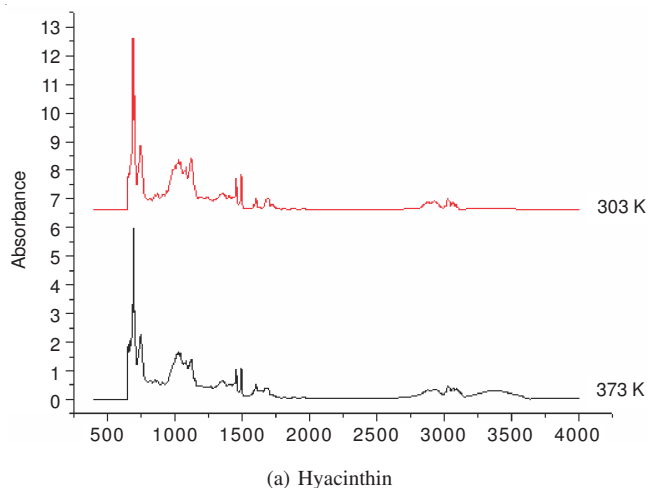


Fig. 2. Infrared spectra of the oxidation products

Fig. 3 showed that the oxidation products of hyacinthin involve acetophenone, benzaldehyde, benzyl alcohol and 1-methyl-benzenemethanol. This phenomenon demonstrates that the aldehyde has active chemical characters, which makes it prone to be oxidized, also can easily be restored at the same time. By contrast, the propiophenone and benzaldehyde were measured in the oxidation products of 1-phenylpropanol. In addition, it's worth noting that the CO and CO₂ were discovered in gaseous products of both hyacinthin and 1-phenylpropanol (Fig. 4). The pathway of the low-temperature oxidation of model compounds can be inferred as follows:

It is evident from the Fig. 5(a) that hyacinthin is easy to be oxidized by oxygen. The oxygen concentration from the outlet of experimental set-up was dramatically dipped to minimum (1.48 %) from 293 to 368 K, sharply climbed to 7.94 % until 393 K and then gradually rose to 13.01 % by 423 K. Fig. 6(a) showed that the concentration of CO₂ produced by hyacinthin was rapidly increased from 0.1 to 1.65 % between 308-368 K, then slightly dropped to 1.51 % by 383 K and fluctuated around 1.5 % on different temperature until 423 K. This variation demonstrated that the activity of hyacinthin reached to the maximum once the temperature increased to 368 K, as well as indicated that the aldehyde in hyacinthin tended to be oxidized under low-temperature.

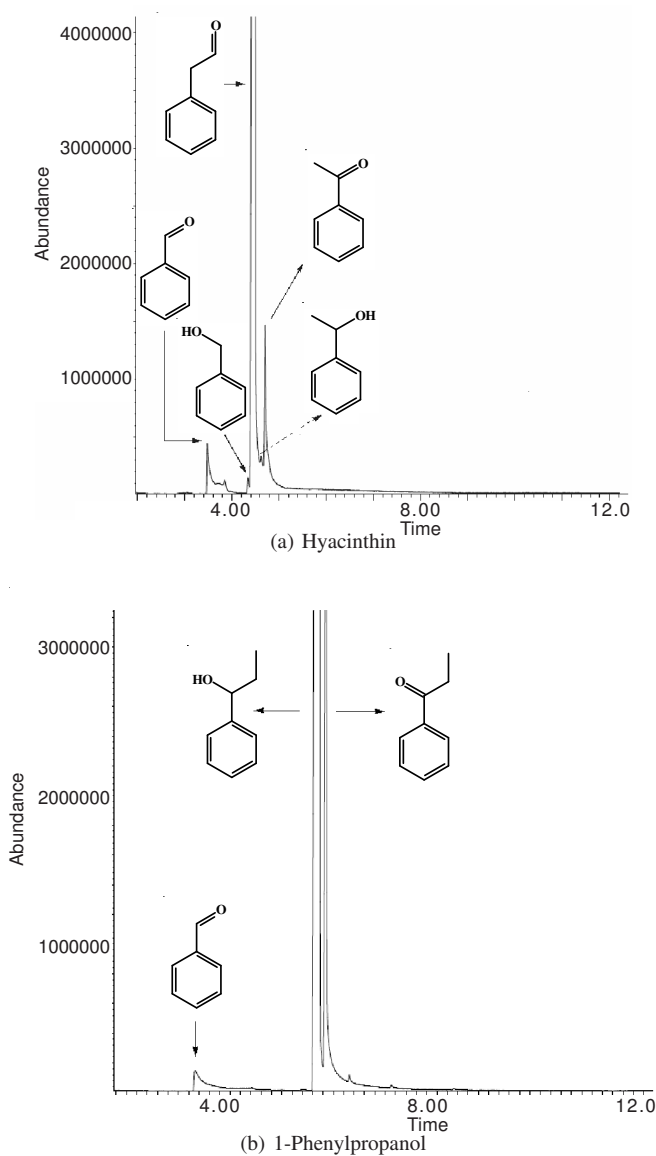


Fig. 3. Chromatograms for composition of oxidation products from model compounds, 373 K

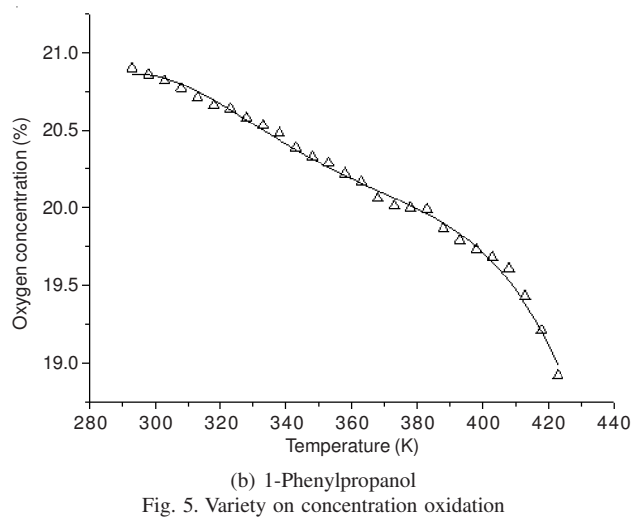
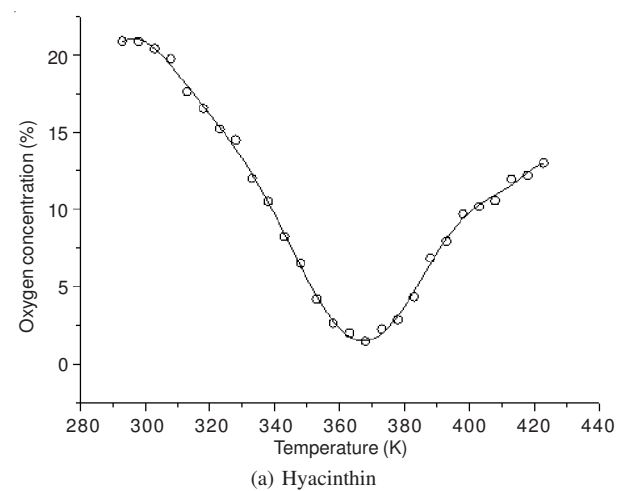
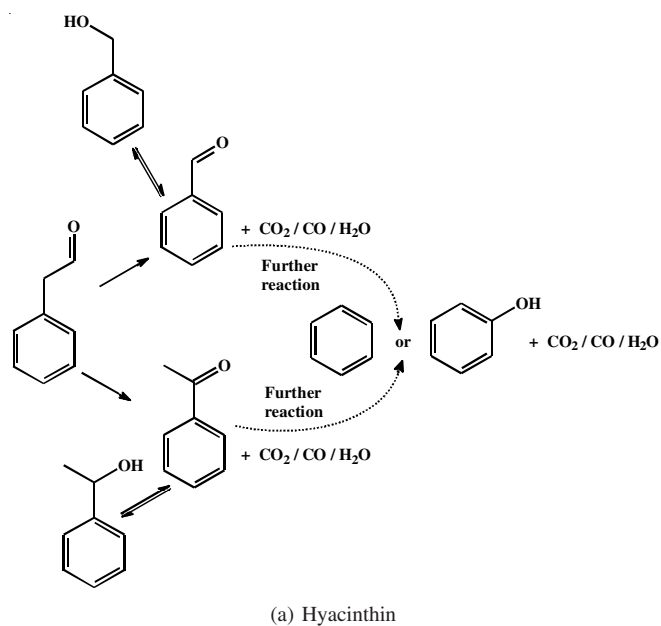
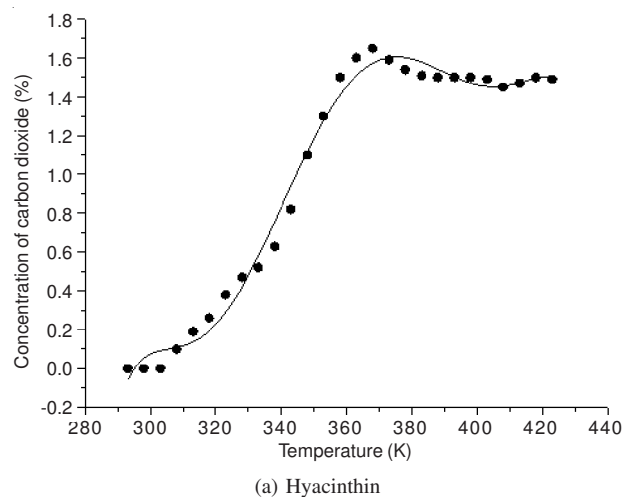
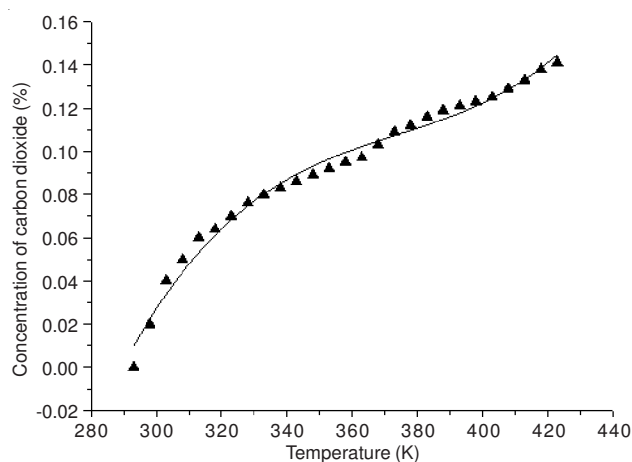


Fig. 5. Variety on concentration oxidation





(b) 1-Phenylpropanol

Fig. 6. Variety on concentration of carbon dioxide

Conclusion

A laboratory investigation into the oxidizing property of coal functional group on spontaneous combustion was carried out. Gas products of the model compound oxidized at different temperatures were measured by the chromatographic apparatus. We could learn from the experiments that the aldehyde is a highly-activity functional group of coal can be oxidized since room temperature. The oxidative activity of hyacinthin achieves crest value once temperature reach 368 K. Notably, the exothermic from oxidation of aldehyde may be a critical incentive on heat production during self-heating of coal. In contrast, the low-temperature oxidation of 1-phenylpropanol is a gentle reaction. Over all, this research gives the oxidation properties of hydroxyl and carbonyl in coal, especially provides guide for explaining spontaneous combustion of coal.

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