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Oxidation Experiment of Coal Spontaneous Combustion Model Compounds

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Theories on coal spontaneous combustion were proposed by several scholars since the 17th century. The coal-oxygen complex effect theory is widely accepted by researchers at present. However, this theory still can not detailed explains the mechanism of the coal-oxygen combination. The coal is different from the other general polymer or compound. The molecular structure and composition of coal is extremely complex and irregular, which causes the disturbance in experimental test of coal spontaneous combustion. In order to solve this problem, the study applies the small-molecule model compound oxidation to simulate the coal macromolecular structure oxidation. Seven kinds of model compounds were selected to study coal spontaneous combustion according to the theories of coal spontaneous combustion and the molecule structure of coal. Oxidation products of model compounds were qualitative and quantitative tested by test devices and gas chromatographs. The results show that model compounds oxidation produce carbon monoxide, carbon dioxide, benzene and phenol, *etc*. Furthermore, the experiments of coal samples as the same experimental condition as the model compounds were implemented for comparison of the oxidation products. The concentration of benzene and phenol in model compounds oxidation products is calculated by external reference method. It is demonstrated that the oxidation processes and properties of the model compounds are consistent with the coal, which provides references for explaining the mechanism of coal spontaneous combustion in chemical view.

Key Words: Coal spontaneous combustion, Active groups, Model compound, Oxidation product.

INTRODUCTION

Coal spontaneous combustion causes huge losses in the process of coal mining and transportation[1-3]. It is significant to research the mechanism of coal spontaneous combustion. Researchers have proposed theories about coal spontaneous combustion such as the bacterium-effect theory, pyrite-effect theory, phenyl-effect theory[4], coal-oxygen complex effect theory[5] and free radical reactions theory[6], *etc*. Among all the theories, the coal-oxygen complex effect theory is widely agreed. However, its detail mechanism needs further studying.

The model compounds are widely adopted for studying chemical reaction of complex system, such as the petroleum refining and the coal liquefaction. Benjamin[7] once used more than 50 kinds of model compounds to study the bridge bonds crack in the coal liquefaction. Liu *et al*.[8] selected methanol as model compound to study the effect of activator in bio-oil process.

Because the molecule structures of the coal are complex and irregular, the experimental tests of spontaneous combustion are usually be disturbed and the existing research results of coal spontaneous combustion can not exactly describe the oxidation process of coal-surface-activate-groups. In order to solve the problem, the model compounds are used to replace the coal molecules to study the chemical properties of coal spontaneous combustion.

Base on the free radical reactions theory[6], this paper small-molecule model compounds are used to simulate large-molecule structure by experiments. Compounds, which both containing the representative active groups of coal and aromatic ring are chosen as model compounds to study the oxidation of model compounds[9]. Through measuring the oxidative and thermodynamic parameters of model compounds in oxidation progress, the mechanism of spontaneous combustion is revealed from chemical perspective. This study provides a new approach to inhibit coal spontaneous combustion.

EXPERIMENTAL

According to the modern theory of molecule structure [10,11], the coal molecule is consists of three parts, which are the kernel structure, functional groups out of kernel and bridge bonds.

Wang *et al*.[12] believed that bridge bond and oxygen-containing functional groups out of kernel are firstly oxidize in oxidation of coal molecule, which suggest that low-weight-molecular compounds and side chain groups of organic macromolecule are the chief factors of spontaneous combustion[13,14].

According to the coal structure model propose by Xu *et al.*,[15,16] and the analysis by Li *et al.*[9], the active groups of coal, which can oxidize in normal temperature and pressure are shown in Table-1.

TABLE-1
ACTIVE GROUPS OF COAL

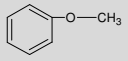
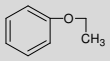
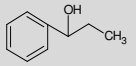
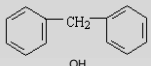
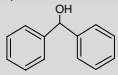
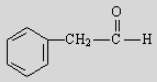
Group	Distribution
—O—CH_3	It only exist in peat and soft brown coal
—CH_2— —CH_2—O— —CH(OH)—CH_2— —CH(OH) — ——CHO —CH_2—OH	They inequality exist in the lignite, bituminous coal and anthracite.

Shi *et al.*[17] believe that the activity of hydrogen atom and carbon atom in active group does not change with the number of aromatic rings. In addition, aromatic ring does not tend to attend reaction in the initial period of coal oxidation due to the research by Shi *et al.*[17]. So compound of aromatic ring and oxidative active groups of coal can be selected as the model compound. The formulae for choosing model compounds are as follows[9].

(1) The model compound selected should contain single oxidative active group of coal; (2) The oxidative active group of model compound is the representative construct in coal molecule; (3) The construct in the model compound should not impact the oxidative properties of the active group.

By the previous analysis, the model compounds chosen in this work are shown in Table-2.

TABLE-2
MODEL COMPOUNDS OF COAL SPONTANEOUS COMBUSTION

Name	Active group	Molecular formula of the model compound
Anisole	—O—CH_3	
Phenetidine	—CH_2—O—	
Benzyl alcohol	—CH_2—OH	
α-Phenylpropanol	—CH(OH)—CH_2—	
Diphenyl methane	—CH_2—	
Diphenyl methanol	—CH(OH) —	
Phenylacetaldehyde	——CHO	

According to corresponding theory of organic chemistry [18,19], the oxidation process of model compounds, different from the simple chemical reaction, is a complex multi-step reaction. This process can divide into three steps *i.e.*, chemical adsorption, decomposition and further decomposition. Oxidation processes of 7 kinds of model compounds are supposed in Table-3.

TABLE-3
ANALYSIS OF THE MODEL COMPOUND OXIDATION PROCESS

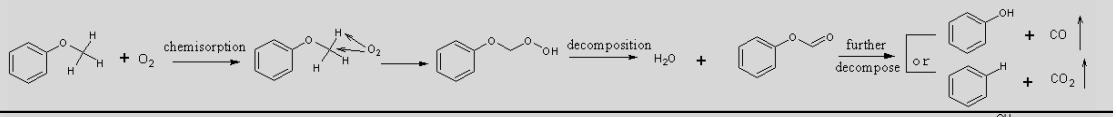
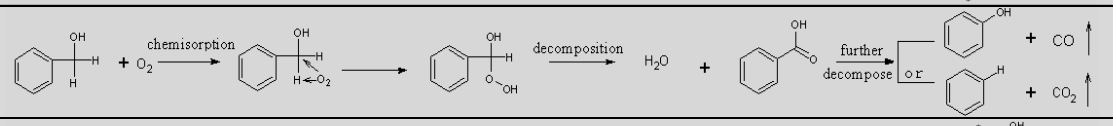
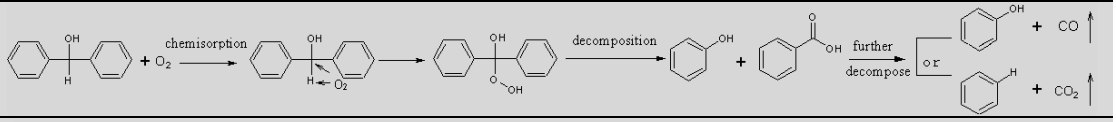
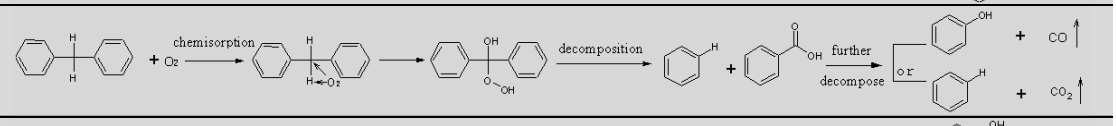
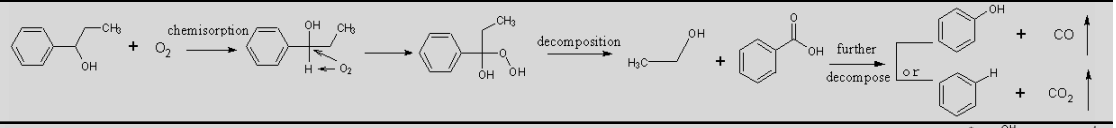
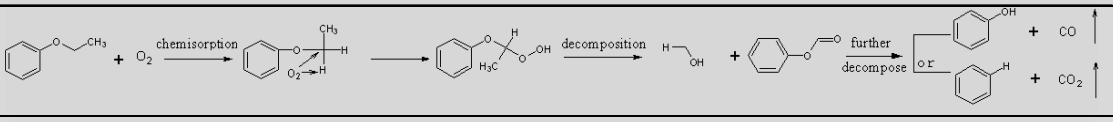
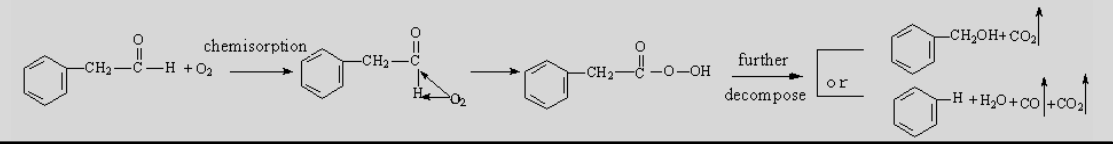
Name	Model compound oxidation process
Anisole	
Benzyl alcohol	
Diphenyl methanol	
Diphenyl methane	
α-Phenylpropanol	
Phenetidine	
Phenylacetaldehyde	

Fig. 1 shows the experimental devices for the model compounds' oxidation experiments, which consist of reaction component and test component.

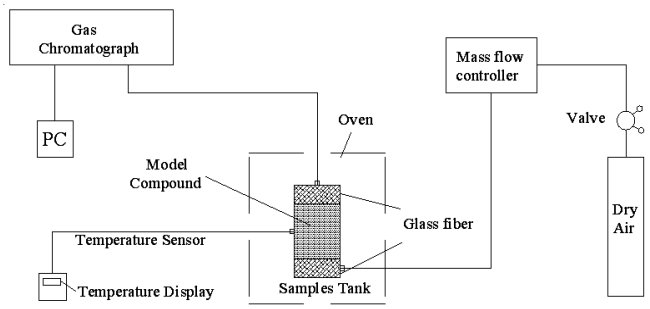


Fig. 1. Schematic diagram of experimental apparatus

Regulator valve, steady flow valve and rotameter constitute are make up of the mass flow regulate facility, which ensure the air flow rate is 20 mL/min. The glass fiber is used to prevent model compounds particles from clogging the pipeline.

Temperature-programmed oven makes temperature rise to the setting temperature and keep the temperature remain stable within a certain time to facilitate collection and testing of oxidation products.

Test devices of oxidation products include GC-4000A gas chromatograph, GC9890A gas chromatograph (capillary column, detector temperature 260 ºC, injector temperature 250 ºC and FID detector). The oxidation products of model compound in the sample tank can be measured by gas chromatograph.

The coal is solid at normal temperature and atmospheric pressure, whereas the model compounds used for experiments are most liquid. A kind of solid particle, non-participate in the reaction, is used to experiment for simulating the solid-gas thermal oxidation conditions of coal particles. The 6201 supporter, 80-mesh, a type of red diatomite inert particle, is used for replacing the coal particles to experiment.

The model compounds and acetone were mixed with the ratio 1:4 and then 6201 supporters were added into the mixture and the mixture is stirred with a glass rod. The 6201 supporters were tiled on the ceramic tray after mixed sufficiently. The model compounds will be attached to the body of the 6201 supporters uniformly when the acetone is completely evaporates and then the mixture of the 6201 supporter and the model compounds were put into the samples tank which placed at temperature-program oven. Dry air through the sample tank (20 mL/min) is controlled by the mass flow regulate facility. Temperature-program oven heats from room temperature and PC collects temperature of the model compounds by the sensor placed at the center of samples tank.

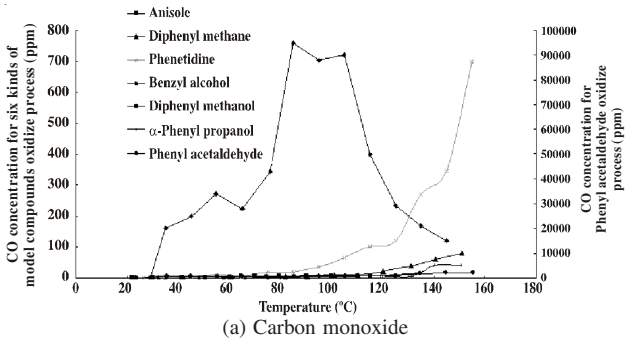
When the temperature reaches the specific setting temperature, keep the temperature steady for 15 min and acquire gaseous oxidation products of model compounds. Following this, the 6201 supporters were removed to extract with acetone for acquiring liquid oxidation product of model compounds. Meanwhile, 8 kinds of coal samples (Table-4) were experimented on the same experimental conditions for comparing the oxidation products.

TABLE-4
PARAMETERS OF EXPERIMENTAL COAL SAMPLES

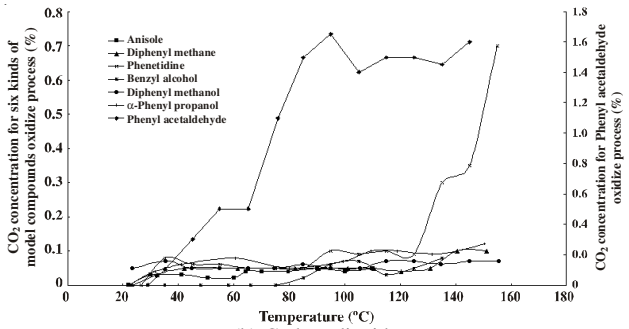
Name	Coal quality
3# Coal seam (Xutuan coal mine)	Coking coal
8# Coal seam (Zhuxianzhuang coal mine)	Gas coal
10# Coal seam (Zhuxianzhuang coal mine)	Gas coal
6# Coal seam (Yuanzhuang coal mine)	Fat coal
16# Coal seam (Zhaopo coal mine)	Fat coal
3# Coal seam (Shitanjing coal mine)	Coking coal
5# Coal seam of Shitanjing coal mine	Coking coal
6# Coal seam of Zhuzhuang coal mine	Lean coal

RESULTS AND DISCUSSION

Analysis of CO and CO_2: Fig. 2 shows the concentrations of carbon monoxide and carbon dioxide have various trends at different temperatures.



(a) Carbon monoxide



(b) Carbon dioxide

Fig. 2. Curve of product concentration in model compounds oxidation process

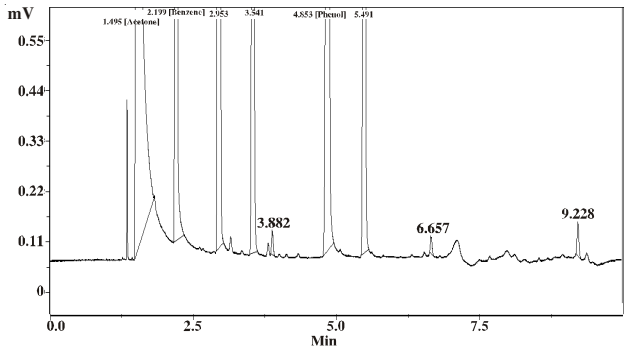
As shown in the Fig. 2(a), phenylacetaldehyde generate the highest concentration of carbon monoxide, which is much higher than that produce by the other model compounds. However, the corresponding data of phenylacetaldehyde reach a peak at 100 ºC and then plummet. In contrast, corresponding figures of other six kinds of model compounds slightly increase from 20 to 150 ºC.

Similarly, Fig. 2(b) illustrates that the generate rate for carbon dioxide of phenylacetaldehyde is the maximum among the seven kinds model compounds and then followed by the data of phenetidine. The data of the remaining five kinds of model compounds are shown with a slightly upward trend from 30 to 150 ºC.

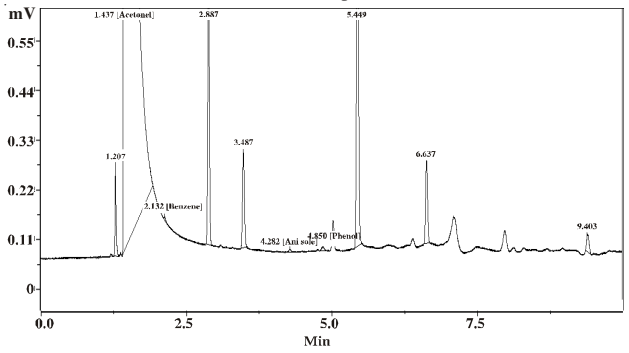
Analysis of other oxidations: It is supposed that the model compounds oxidation generate benzene and phenol through analyzing oxidation processes of the model compounds. This assumption is confirmed by measuring oxidation products of the model compounds in external-reference-

method. Acetone, benzene, phenol are mix at mass ratio of 50:2:1 as benzene-phenol standard samples in this experiment. Micro-injector is used to take 0.4 μL acetone-benzene-phenol mixture into the gas chromatograph and the chromatogram is shown in Fig. 3(a).

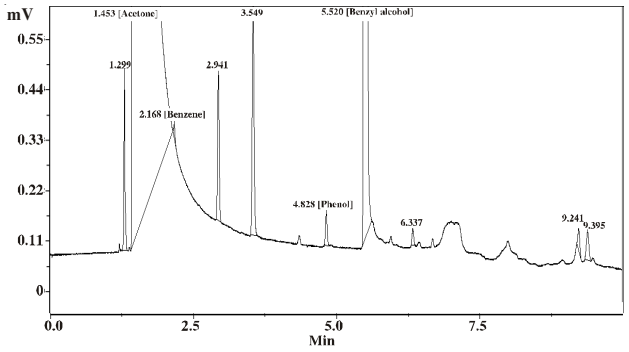
The model compound oxidation products at 40, 60, 80, 100 and 120 ºC were tested by the chromatograph. By comparing the chromatograms of each temperature, the retention time of peak in different temperatures is approximately the same. Therefore, chromatograms of model compounds oxidation products in 80 ºC are used for example, as shown in Fig. 3(b)- 3(h).



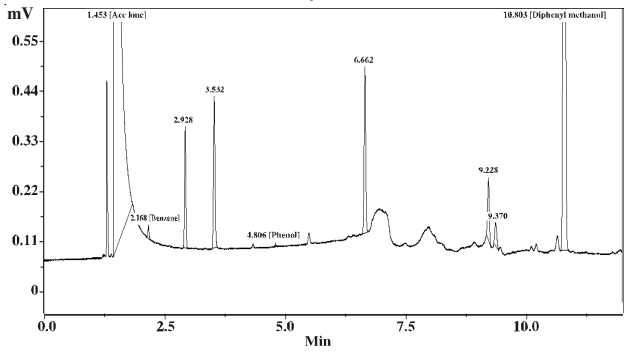
(a) Acetone-benzene-phenol mixture



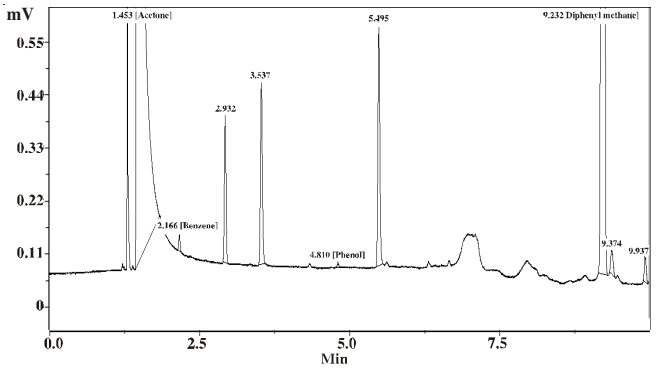
(b) Anisole



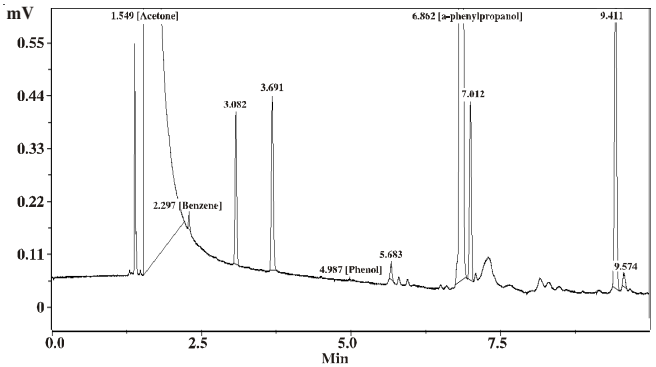
(c) Benzyl alcohol



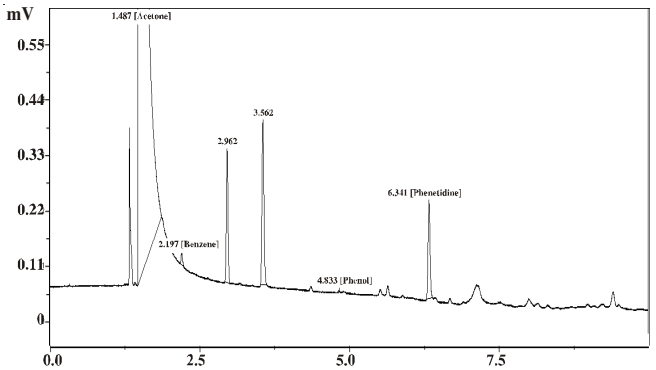
(d) Diphenyl methanol



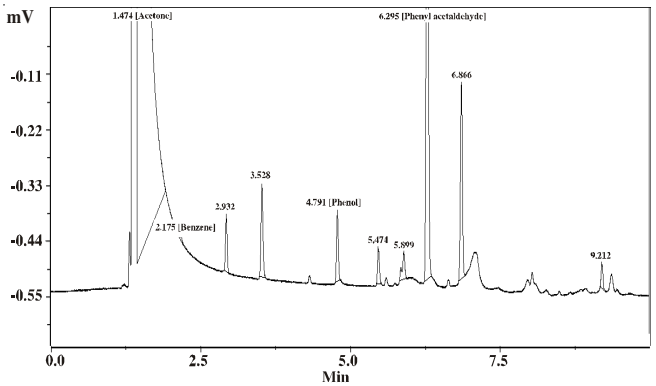
(e) Diphenyl methane



(f) α-Phenylpropanol



(g) Phenetidine



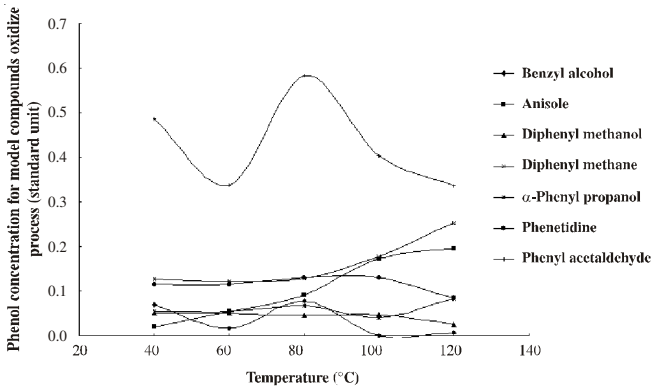
(h) Phenylacetaldehyde

Fig. 3. Chromatograms of the acetone-benzene-phenol mixture and the model compounds' oxidation products

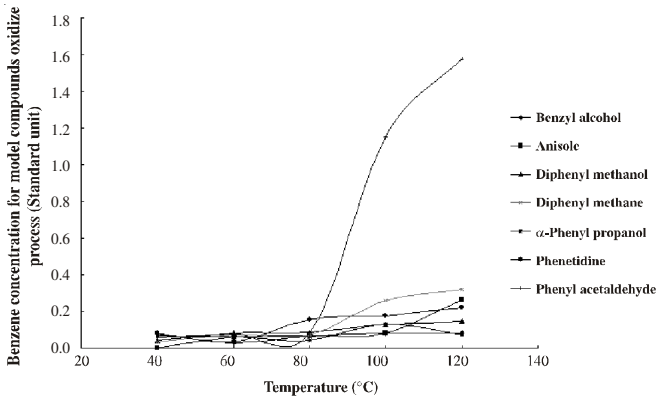
Fig. 3(a) shows, the peak around 2.199 min corresponds to the composition of benzene, the peak around 4.853 min corresponds to the composition of phenol, the peak around

1.495 min corresponds to the composition of acetone. The rest peaks correspond to the impurities of the acetone and model compound samples.

It is apparent from the Fig. 3(a)-3(g) that benzene and phenol peaks all show in the chromatograms of 7 kinds model compounds and those figures indicate that 7 kinds of model compounds all generate benzene and phenol by oxidation. As the model compounds are rarely used in those experiments, concentration of oxidation products is relatively low. It is difficult to analyze the concentration variation of benzene and phenol if results according to the actual concentration of oxidation products. To solve this problem, the methodology to enlarged concentration of benzene and phenol is used. To define the benzene concentration in the benzene and phenol standard samples as 200 standard units and the phenol concentration as 100 standard units, the concentration of benzene, phenol in model compounds oxidation products are shown in Fig. 4.



(a) Benzene

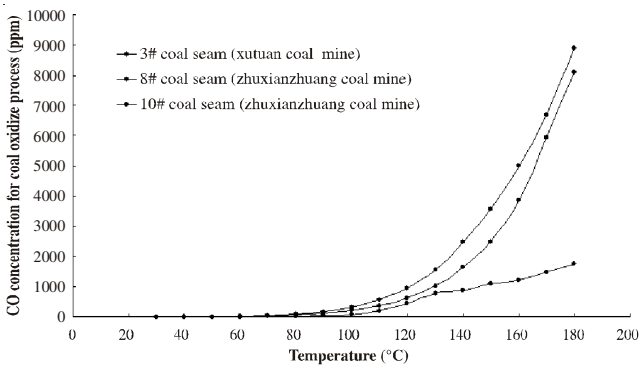


(b) Phenol

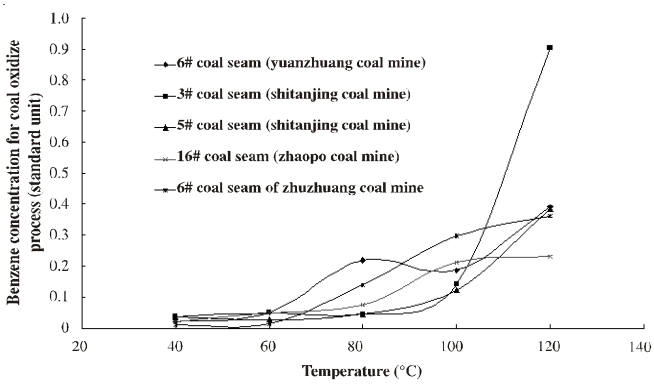
Fig. 4. Oxidation products concentration of model compounds

According to the Fig. 4 that the benzene and phenol concentrations generated by phenylacetaldehyde are much higher than that of other model compounds in the oxidation process, while the other model compounds are similar. It is suggested that activity of phenylacetaldehyde is maximum among 7 kinds of model compounds.

Analysis of oxidations for coal samples experiments: Eight kinds of coal samples were tested under the same experimental condition as model compounds for measuring production of the carbon monoxide and benzene. It is shown that vary with the increase of temperatures (Fig. 5).



(a) Carbon monoxide



(b) Benzene

Fig. 5. Oxidation products concentration of coal samples

Fig. 5(a) shows that, the data do not rise obviously until 100 ℃ in oxidation process. However, a considerable increase occurred from 100 to 180 ℃. Fig. 5(b) reveals that the five kinds of coal samples are all generated benzene by the oxidation from 40 to 120 ℃. Furthermore, the concentration of benzene is increased with the temperature going up. Those confirmed the assumption for oxidation process of 7 kinds of model compound before.

Conclusion

The oxidation process of the coal spontaneous combustion's model compounds is supposed with the organic chemistry theory. The model compounds of coal spontaneous combustion were experimented by oxidation device. Gas and liquid products of model compounds oxidized at different temperatures were measured by gas chromatographs. The main conclusions are as follows:

(1) The process of model compound oxidation is a complex multi-step reaction, which can divide into three parts: chemical adsorption, decomposition and further decomposition. Finally, carbon monoxide, carbon dioxide, benzene and phenol are generated by oxidation of the model compounds.

(2) The suppositions for oxidation process of model compounds are confirmed through the experiments of seven kind model compounds and eight kind coal samples. It's suggested that oxidation characteristics and processes of the coal are approximately the same as the model compounds by comparing the coal and the model compounds' oxidation process and products. Through experiment, it is confirmed that the oxidation and properties of model compounds are similar to the coal. So it is feasible to use oxidation of the model compounds for simulating the coal spontaneous

combustion. The study provides experimental references for describing the mechanism of spontaneous combustion in chemical view by studying the oxidation properties of model compounds.

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