Pyrolysis Characteristics of Jet Coal and Oxidation of Residues in Zhundong Coalfield Fires

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ABSTRACT: Coalfield fire area reburning is one of the serious disasters in fire prevention and safety production. In this study, a synchronous thermal analyzer was used to conduct isothermal pyrolysis of jet coal at different temperatures, and the reaction characteristic parameters of different pyrolysis residual structures were analyzed. FTIR was used to measure group contents in raw coal and different pyrolysis residues. Programmed oxidation thermogravimetric experiments were carried out on the residues to obtain their oxidation characteristic parameters. The results demonstrated that the reaction characteristic parameters of the residual structures changed at 450 °C. The pyrolysis reaction mainly affected the variation of hydroxyl, aliphatic hydrocarbon, and aromatic hydrocarbon groups. The increase in pyrolysis temperature resulted in the decline in hydroxyl and aliphatic hydrocarbon groups as well as the increase in the aromatic hydrocarbon group. After pyrolysis, the ignition point temperature of the coal sample decreased, which causes the coal more likely to spontaneously ignite. It indicated that the pyrolysis residue at 450 °C is most likely to reburn. Compared with raw coal, the maximum combustion intensity of the pyrolysis residue was greatly increased, which reached the peak at 500 °C.

1. INTRODUCTION

China is one of the countries most affected by coalfield fires.1−3 The area of the Zhundong Coalfield is 13,000 km² with an estimated resource amount of about 390 billion tons, accounting for 17.8% from Xinjiang and 7% from the whole nation.4−7 The fire area of the Zhundong Coalfield is reburning seriously. Coalfield fires not only burn a large amount of coal but also cause a large amount of coal to not be mined, which has become a significant problem for the sustainable development of China’s coal resources and mining.8 The combustion of the coal seam produces a large number of greenhouse gases and toxic substances (carcinogens such as poly-hydroxy-alkanoates (PHAs), formaldehyde, and phenol), which damage the local ecological environment and groundwater resource.9 The oxidation of coal in the fire zone is different from natural oxidation. In the fire zone, most of the coal is smoldered under low-oxygen conditions, and it is pyrolyzed under the influence of high temperature. Pyrolysis changes the structure of macromolecules in coal and produces small molecules that are easily oxidized. The quality characteristics of coal pyrolysis and the oxidation of pyrolysis residues are the key factors affecting the occurrence and development of the coal reburning phenomenon.

Pyrolysis and oxidation are important coal-utilization methods. A large number of previous studies have been carried out on the characteristic of coal pyrolysis and oxidation. Liu et al.10 adopted TGA to investigate the oxidation characteristics of coal in a low-oxygen environment and explained the reaction mechanism of coal in a methane atmosphere. Xi and Sun11 studied the delaying and inhibiting effects of thermoplastic powder on the spontaneous combustion of coal by the thermogravimetric method. Onifade et al.12 researched coal and coal—shale undergoing spontaneous combustion between coal seams when exposed to oxygen in the air. Du et al.13 applied thermogravimetric analysis to explore the thermal degradation of bituminous coal at various heating rates in both nitrogen and air atmospheres. Liu et al.14 performed TG/FTIR to analyze the gas release rule in the process of bituminous coal combustion under different oxygen concentrations. Zhang et al.15 used a synchronous...
thermal analyzer to study the critical temperature, maximum peak temperature, ignition temperature, and burnout temperature of coal samples. Zhang et al.16 adopted TG/DSC-FTIR to analyze the macroscopic characteristics of functional groups in the process of coal spontaneous combustion, which indicates that −OH is the most active group in coal spontaneous combustion. Wang et al.17 investigated the influence of pre-pyrolysis temperatures on the spontaneous combustion characteristics of wetting coal. Xu et al.18 studied the combustion (secondary oxidation) characteristics of jet coal after oxidation and water immersion, and the results showed that water immersion had both inhibition and promotion effects on spontaneous combustion. Xu et al.19 analyzed the effects of particle size and temperature on the secondary oxidation characteristics of coal, and the results showed that the coal secondary oxidation activity was improved by reducing the particle size of pulverized coal. Zhang et al.20 studied the influence of nitrogen on the secondary oxidation combustion of coal and extinguishing ability. With the increase in nitrogen concentration, the combustion characteristic temperature was delayed and the activation energy of secondary oxidation increased. When the nitrogen concentration increased to 50%, the cooling time of coal decreased greatly. Wang et al.21 studied the effect of pre-oxidation temperature on the secondary oxidation characteristics of coal. After pre-oxidation, the heat absorption of coal was obviously reduced and the methyl, hydroxyl, and carboxyl groups were reduced.

FTIR has become the main technical means to characterize the distribution of groups in coal.22–26 Zhao et al.27 performed FTIR to study the microscopic characteristics of coal spontaneous combustion at different oxygen concentrations and heating rates, and four types of active functional groups were observed. Wang et al.28 analyzed the effect of N,N-dibenzylhydroxylamine (DBHA) on the change in the active groups during coal oxidation at different temperatures by in situ FTIR. Wang et al.29 adopted in situ infrared spectroscopy to appraise the evolution of low-temperature (<200 °C) oxidation of aromatic hydrocarbons, aliphatic hydrocarbons, and oxygen-containing functional groups on the surfaces of the coal samples. Shi et al.30 performed FTIR to characterize the chemical structure characteristics of coal and investigated the effect of igneous intrusions on the structure and combustion characteristics of coal. Niu et al.31 performed in situ FTIR to analyze the evolution of six main functional groups of two different grades of coking coal during non-isothermal pyrolysis under N2.

The effects of coal rank, reaction atmosphere, coal sample size, heating rate, and pyrolysis temperature on the reaction characteristics of coal pyrolysis and combustion have been studied by a large number of researchers using thermal analysis.32–34 but there is little research on the reburning characteristics of coal in fire areas. Research on the reburning of fire areas is mainly on the secondary oxidation of coal as well as fire prevention and extinguishing technology.35 Due to the influence of high temperature and exothermic heat, the coal has pyrolyzed in goaf, and its reburning characteristics have not been studied yet. In this paper, TG and FTIR were performed to analyze the structural characteristics and oxidation characteristics of pyrolysis residues of jet coal in the Zhundong Coalfield. The influence mechanism of pyrolysis on coal oxidation characteristics was obtained, and then the reburning characteristics of the residual structure during jet coal pyrolysis were analyzed. This study on the quality characteristics of coal pyrolysis and the oxidation of pyrolysis residues can provide theoretical support for the prevention and control of rapid reburning in the fire area, which is of great significance for the safe mining of the Zhundong Coalfield.

2. EXPERIMENTAL SECTION

2.1. Coal Samples. China’s low-middle rank coal is prone to spontaneous combustion. We selected the jet coal from the LiuHuanggou mine (LHG) in the Zhundong Coalfield of Xinjiang Province. After taking coal samples at the coal mine site, the coal sample was vacuum-sealed and sent to the laboratory. The surface of the coal sample was peeled off, and the center was crushed. After further grinding in an agate mortar, the samples with particle sizes of 100–160 and 200–300 mesh were obtained by sieving. Coal sample proximate analysis and ultimate analysis are shown in Table 1.

2.2. Thermogravimetric Experiments. Thermogravimetric analysis (TG) is a method for measuring the change in weight and heat flux of a substance under programmed temperature control. In this paper, a TA-Q600 simultaneous thermal analyzer (USA), which is equipped with an Alicat Scientific mass flow controller, was used for coal sample pyrolysis and oxidation thermogravimetric experiments. The reburning characteristics of coal pyrolysis residues were studied.

Coal samples with a particle size of 200–300 mesh were selected for pyrolysis. High-purity nitrogen with the gas flow rate at 100 mL/min was selected as the purge gas of the simultaneous thermal analyzer. The coal samples were heated to 350, 400, 450, and 500 °C at a rate of 10 °C/min in a nitrogen environment and were kept at those temperatures for 30 min to obtain coal pyrolysis residues.

The reoxidation of raw coal and pyrolysis residues was carried out using the synchronous thermal analyzer. The pyrolysis residue was cooled to room temperature in a nitrogen environment. Dry air was selected as the reaction gas, and a mass flow controller was used to stabilize the gas flow rate at 100 mL/min. In a dry air environment, the pyrolysis residue and raw coal were heated from room temperature to 900 °C at a heating rate of 5 °C/min to obtain the oxidation curve.

2.3. Infrared Spectrum Experiments. Fourier transform infrared spectroscopy (FTIR) is a common method for testing the types, positions, and quantities of the functional groups on the coal surface. In this experiment, a Nicolet 6700 FTIR instrument with an in situ reaction cell was selected. The instrument includes a main engine, operating software, and
infrared accessories, which record the infrared spectra of raw coal and pyrolysis residues at different pyrolysis temperatures.

Jet coal with a particle size of 200–300 mesh was selected as the experimental coal sample. The infrared spectrometer was turned on to warm up the system. The real-time acquisition software was opened, the temperature was set at 30–600 °C, the wavenumber range was from 650 to 4000 cm\(^{-1}\), the acquisition resolution was 4 cm\(^{-1}\), the number of scans was 64, the acquisition time interval was 30 s, and the acquisition time was 60 min. The KBr powder was put into an infrared reaction chamber for base vector collection. After the collection, the infrared in situ cell was cleaned and put into a special metal pad, and a layer of coal powder was spread. Then, the gas circuit was opened and the gas flow rate was set to 30 mL/min. When the set temperature was reached, the coal samples were collected for infrared spectroscopy.

3. RESULTS AND DISCUSSION

3.1. Reaction Characteristics at Different Pyrolysis Temperatures. From the constant temperature pyrolysis curve of jet coal, the characteristic parameters of the pyrolysis were obtained. The quality characteristics of coal samples were analyzed to reveal the stage change rule of the reaction, which provides a reference for evaluating the oxidation characteristics of pyrolysis residues.

Figure 1 shows the TG-DTG curve of the pyrolysis of LHG jet coal and the oxidation of raw coal. The pyrolysis process of coal includes three rapid weight loss stages. The temperature range of thermal condensation polymerization is 550–1000 °C. The maximum temperature was 500 °C in this experiment, hence, the weight loss stage of thermal condensation was not shown in this TG-DTG curve.

To characterize the quality and stage characteristics of residues at different pyrolysis temperatures, five eigenvalues were found to quantitively characterize the quality characteristics of pyrolysis residues.

The weight of the initial separation residue of volatile components \(W_v\) is the weight of coal when it begins to lose weight in the thermal decomposition stage. This is the value of the y-coordinate when the TG curve starts to fall. The maximum precipitation rate of volatile matter \(V_{\text{max}}\) represents the speed of volatile precipitation, generally taking the peak value of the DTG curve. The coal sample residual weight at the constant temperature starting point \(W_c\) refers to the weight of the coal sample at the beginning of constant temperature pyrolysis. The coal sample weight at the end of pyrolysis \(W_p\) is the remaining coal sample weight at the end of pyrolysis. The weight of the coal sample at the end of oxidation \(W_o\) refers to the weight of the residue when the temperature is increased to 900 °C. The selection of \(W_o\) is shown in Figure 1. As shown in Figure 2, the pyrolysis curve at 500 °C was taken as an example to illustrate the selection of characteristic parameters of the coal pyrolysis reaction.

The pyrolysis characteristic parameters of coal at different temperatures are shown in Table 2.

When the pyrolysis temperature increases, the maximum precipitation rate of volatile matter \(V_{\text{max}}\) gradually increases, reaching the maximum at 500 °C. The coal sample residual weight at the constant temperature starting point \(W_c\) and the coal sample weight at the end of pyrolysis \(W_p\) are both gradually decreasing. When the pyrolysis temperature increases, a large number of active molecules in coal are activated and participate in the reaction, resulting in the decline in the residual weight of the coal sample.

In order to study the changing trend of characteristic parameters at different pyrolysis temperatures and analyze the reaction content and residue composition, three variables, \(W_{vp}\), \(W_{cp}\), and \(W_{po}\), were defined and calculated, as shown in Figure 3. Their definition and calculation methods are as follows.
Table 2. Pyrolysis Eigenvalues of Coal at Different Temperatures

| coal type          | $T_o$, °C | $V_{max}$ %/min | $W_{cp}$, % | $W_{ct}$, % | $W_{po}$, % | $W_{co}$, % |
|--------------------|-----------|------------------|-------------|-------------|-------------|-------------|
| LHG jet coal       | 350.00    | 0.23             | 87.93       | 88.41       | 86.65       | 7.86        |
|                    | 400.00    | 0.51             | 86.00       | 80.95       | 76.12       | 23.88       |
|                    | 450.00    | 1.31             | 80.93       | 75.12       | 69.25       | 30.75       |
|                    | 500.00    | 1.37             | 74.83       | 71.25       | 65.75       | 34.25       |

*$T_o$: constant temperature; $V_{max}$: maximum precipitation rate of volatile matter; $W_{cp}$: weight of the initial separation residue of volatile components; $W_{ct}$: coal sample residual weight at the constant temperature starting point; $W_{po}$: coal sample weight at the end of pyrolysis; and $W_{co}$: weight of the coal sample at the end of oxidation.

![Graph](image-url)

**Figure 3.** Changes in coal pyrolysis characteristic parameters: (a) $W_{vp}$, $W_{cp}$, and $V_{max}$ and (b) $W_{po}$.

1. The variation of pyrolysis residual weight $W_{vp}$ (%) is defined as $\Delta W_{vp} = W_v - W_{vp}$ which indicates the amount of change in the weight of the coal sample during thermal decomposition.

2. The variation of constant temperature residual weight $W_{cp}$ (%) is defined as $\Delta W_{cp} = W_c - W_{cp}$ which represents the weight loss of the coal sample during constant temperature pyrolysis.

3. The pyrolysis residual combustible component weight $W_{po}$ (%) is defined as $\Delta W_{po} = W_{po} - W_{vp}$ which indicates the amount of combustible material present in the residual structure of the coal sample after the end of pyrolysis.

As shown in Figure 3, $V_{max}$ slowly increases as the pyrolysis temperature increases, which reaches the maximum at 500 °C.

For the overall growth trend, the growth rate between 350 and 400 °C is slow, and it is accelerated between 400 and 450 °C and shows a slight increase after 450–500 °C (from 1.306 to 1.368). It indicates that LHG jet coal entered the early stage of pyrolysis at 350 °C with a slow decomposition rate. The growth rate of $V_{max}$ in the range of 350–400 °C is slow, indicating that coal samples are still in the early stage of pyrolysis in this temperature range. The $V_{max}$ between 400 and 450 °C becomes larger, suggesting that it has entered the rapid stage of thermal decomposition. At that moment, the thermal decomposition reaction proceeds rapidly, producing tar, gas, and other volatiles. Although $V_{max}$ still does not reach the maximum at 450 °C, it has a small difference from the $V_{max}$ value at 500 °C, in which the $V_{max}$ approaches the maximum.

In the 450–500 °C range, the reaction spans the early stage of thermal decomposition and enters the late stage of thermal decomposition at 500 °C. The colloidal body begins to solidify and becomes semi-coke. At 500 °C isothermal pyrolysis temperature, the critical temperature is the maximum precipitation temperature of 446 °C.

The variation of pyrolysis residual weight $W_{vp}$ (%) increases rapidly between 350 and 450 °C, with a slow growth rate between 450 and 500 °C, indicating that the reaction proceeds faster with the increase in temperature in the early stage of thermal decomposition. The amount of material generated increases rapidly. After entering the late stage of thermal decomposition, the reaction content begins to change, and the reaction translates a coal-colloidal body to form a semi-coke. The variation of constant temperature residual weight $W_{cp}$ first increases and then decreases, reaching peaks at 450 °C. It indicates that with the increase in temperature, the number of substances that can be pyrolyzed in coal increases gradually. The number of molecules participating in the reaction reaches the maximum at 450 °C, which consumes a large amount of decomposable macromolecules in coal. At 500 °C, the substances during the pyrolysis reaction change. The number of molecules undergoing the decomposition reaction becomes small, and the $W_{vp}$ value decreases.

In the pyrolysis residue at 500 °C, the $W_{po}$ is as high as 63.391%, which is related to the nature of the coal sample body. LHG coal has a long chain branch, which easily generates tar after thermal decomposition. At 350–450 °C, $W_{po}$ decreases rapidly. With the increase in pyrolysis temperature, the active substances in the coal are continuously activated, the rate of volatilization precipitation becomes faster and faster, and the residual weight of the coal sample decreases rapidly. At 450–500 °C, $W_{po}$ decreases slowly. In this temperature range, the active material has reacted completely, the formed coal colloid begins to decompose, the release rate of volatiles slows down, and hence, the residual weight change is not obvious.

### 3.2. Functional Group Distribution Characteristics of Pyrolysis Residues

In this section, we have obtained the infrared spectra of raw coal and residues from pyrolysis at 350, 400, 450, and 500 °C. The contents of functional groups in the coal are calculated and analyzed. According to the distribution of groups, the characteristic structural parameters of raw coal and different pyrolysis residues are calculated.
The peak area of the infrared absorption spectrum is less affected by samples and instruments, and the value obtained by quantitative calculation is more accurate. To analyze the results more accurately, the infrared spectrum was optimized by the peak fitting method, and the interference peaks were separated. By integrating the separated spectrum, the peak area $A(v)$ was obtained, and then the ratio of the peak area $A(v)$ to the group vibration intensity $f$ was obtained, as shown in Table 3.

The composition and structure of the groups are different, and the absorption coefficients of the groups vary greatly. The vibration intensity of the associated hydroxyl group is the largest followed by the carbonyl group and the benzene ring double bond, and that of the hydroxyl group is the smallest. It can be seen from the theoretical analysis and the structural characteristics of coal that the revised results can more accurately reflect the contents of various functional groups in the coal. According to the data in Table 3, the functional group contents of raw coal and pyrolysis products were obtained by employing quantum chemical calculation. Figure 4 shows the change in groups with pyrolysis temperature and quantitatively characterizes the evolution of the structural characteristics of coal.

Figure 4 shows that the largest proportion of the raw coal structural components was the aromatic structure, up to 61.97%, followed by the aliphatic hydrocarbons, with the content being 24.95%, and the hydroxyl group content was 8.15%. The oxygen-containing functional groups in the LHG coal structure account for about 5%. With the increase in pyrolysis temperature, the content of hydroxyl and aliphatic hydrocarbons decreased gradually, the content of the aromatic skeleton structure became higher, and the change in oxygen-containing groups was smaller.

As shown in Figure 4, pyrolysis makes the hydroxyl content vary greatly. The coal has undergone drying and dehydration in the initial stage of pyrolysis, and the weak chemical bonds are broken to form colloids. The content of water-associated hydroxyl decreases rapidly. After 350 °C, the pyrolysis temperature has little effect on the hydroxyl group. The associated hydroxyl group has been completely consumed at 350 °C, while the free hydroxyl group still has certain content. At 350 °C, the chemical bonds are broken in the coal structure, the macromolecular structure is decomposed to produce volatile small molecular substances, and the carbonyl group decreases significantly. The carboxyl and benzoyl groups were very small in raw coal and were mainly converted from other functional groups. Carboxyl groups were the direct source of carbon dioxide. The formation of carboxyl groups was limited by low oxygen, and hence, pyrolysis has little effect on carboxyl groups.

The aliphatic hydrocarbon content was also affected by high-temperature pyrolysis. The increase in pyrolysis temperature, the aliphatic hydrocarbon branched chains with weak molecular interaction force were broken and formed volatile gas and tar. As a result, the aliphatic hydrocarbon content of coal was reduced.

The content of the benzene ring was significantly affected by high-temperature pyrolysis. The benzene ring content of raw coal before pyrolysis was 61.97%. When heated to 350 °C, the content of the benzene ring in the coal skeleton structure reached 75.17%, and the content reached 78.44% at 500 °C. The pyrolysis reaction leads to the breakage of weak bonds in coal. The higher the temperature is, the higher the reaction level that can be achieved and the more chemical bonds are involved in pyrolysis. The fracture of a large number of weak chemical bonds makes the aromatization of the coal structure increase. At the same time, the coal-colloidal body begins to pyrolyze at the late stage of thermal decomposition, and the intermolecular condensation produces coal semi-coke, which leads to an increase in the content of aromatic hydrocarbons in the coal.

### 3.3. Structural Parameters Changing in Coal Pyrolysis

In this section, the characteristic structural parameters of raw coal and different pyrolysis products were calculated based on the functional groups corrected by quantum chemistry. $A_{CH}/A_{a}$ has been proposed and applied by many researchers. $A_{CH}/A_{a}$ was selected to represent the capacity of hydrocarbon production in coal. The ratio of CH$_2$/CH$_3$ can describe the aliphatic chain length and polymerization of the side chain into a bridged bond. H$_d$/H represents the proportion of hydrogen in aliphatic hydrocarbon in total hydrogen in coal.

Figure 5 shows the changes in the H$_d$/H, CH$_2$/CH$_3$, and A$_{CH}$/A$_d$ parameters of pyrolysis residuals. It can be seen that A$_{CH}$/A$_d$ increases with the increase in pyrolysis temperature and accelerates after 450 °C. At the late stage of thermal decomposition (between 450 and 500 °C), the coal structure begins to transform from colloid to semi-coke, and the degree of aromatization increases. CH$_2$/CH$_3$ fluctuates with the increase in pyrolysis temperature. The ratio of CH$_2$/CH$_3$ decreases from 5.66 to 3.33 at 400 °C and then increases rapidly. The value of CH$_2$/CH$_3$ in jet coal is related to the pyrolysis characteristics. During pyrolysis at 400 °C, the weak chemical bonds in the jet coal are broken, the volatile small molecules are not lost, and there is a large amount of CH$_3$ in coal. As shown in Table 3, in the 400 °C pyrolysis residue, the content of CH$_3$ is the largest, while the CH$_2$ content is less.

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| Table 3. Original Peak Areas and Corrected Values of Functional Groups in Coal |
|-------------------------------|------------|------------|------------|------------|-----------|-------------|
|                               | O−H       | −CH$_3$    | −CH$_2$=  | −COOH      | −C=O      | benzene (C=C) |
|-------------------------------|------------|------------|------------|------------|-----------|-------------|
|                               | 3200−3600 cm$^{-1}$ | 2965 cm$^{-1}$ | 2924 cm$^{-1}$ | 2854 cm$^{-1}$ | 1700 cm$^{-1}$ | 1660 cm$^{-1}$ | 1620−1490 cm$^{-1}$ |
| raw coal                      | A($v$)    | 7184.45    | 569.57     | 1518.17    | 866.30     | 461.18      | 786.25      | 3724.95      |
|                               | A($v$)/f  | 11.37      | 7.37       | 27.45      | 5.01       | 3.01        | 1.47        | 86.47        |
| 350 °C pyrolysis residue      | A($v$)    | 1039.35    | 430.65     | 1961.90    | 744.49     | 518.80      | 492.27      | 5734.06      |
|                               | A($v$)/f  | 1.64       | 5.57       | 31.50      | 2.11       | 3.14        | 133.10      | 586.35       |
| 400 °C pyrolysis residue      | A($v$)    | 765.31     | 658.02     | 1807.08    | 659.79     | 592.79      | 572.76      | 5862.35      |
|                               | A($v$)/f  | 1.21       | 8.52       | 28.39      | 2.41       | 3.65        | 136.08      | 106.08       |
| 450 °C pyrolysis residue      | A($v$)    | 1093.73    | 438.80     | 1968.03    | 853.39     | 649.65      | 617.44      | 5976.75      |
|                               | A($v$)/f  | 1.73       | 5.68       | 32.47      | 2.64       | 3.93        | 138.74      | 6707.79      |
| 500 °C pyrolysis residue      | A($v$)    | 920.63     | 422.75     | 1638.32    | 856.45     | 733.49      | 652.66      | 6707.79      |
|                               | A($v$)/f  | 1.46       | 5.47       | 28.72      | 2.98       | 4.16        | 155.71      | 6707.79      |
Therefore, the CH₂/CH₃ ratio is the smallest. At 450 °C, the colloid begins to decompose rapidly and solidify into semi-coke. The CH₂ content in coal increases greatly, and the CH₂/CH₃ ratio increases.

The H_d/H decreases with increasing temperature and drops to a minimum at 500 °C, which is 0.07. The side chains, weak chemical bonds, and oxygen-containing heterocycles in the coal are broken and decompose under the influence of high temperature. These substances separate from the coal skeleton to generate light hydrocarbons and tar. The higher the pyrolysis temperature, the greater the energy provided by the outside and the more fatty chains would be broken.

3.4. Pyrolysis Residue Reoxidation. In order to analyze the effect of pyrolysis temperature on the reoxidation characteristics of the residue, ignition point temperature Tᵢ, burnout temperature Tₑ, maximum speed of weight loss dW_max, and maximum weight loss temperature TW_max were selected as the four characteristic parameters on the reoxidation curve. In this paper, the TG-DTG method was selected to determine the Tᵢ and Tₑ. The dW_max and TW_max are, respectively, the weightlessness rate and temperature when the oxidation reaction is the most intense. They reflect the combustion intensity of coal, and the value is the point of the weightlessness peak of the DTG curve.

The raw coal and the residue formed under different pyrolysis temperatures were selected as experimental coal samples. The oxidative thermogravimetric experiments under programmed temperature were carried out in a dry air atmosphere. The TG-DTG curves were compared and analyzed, as shown in Figure 6a,b.

Figure 5. Structural parameter curves of pyrolysis residues: (a) A_ar/A_al and CH₂/CH₃ and (b) H_d/H.
It can be seen from Figure 6 that there is the same changing trend between the reoxidation curves of raw coal and different pyrolysis residues. The raw coal has a low degree of structural polymerization and more active groups. Hence, the weight consumed by the reaction exceeds the increase by oxygen absorption. The weight gain of coal by oxygen absorption is not obvious. Pyrolysis changes the microstructure and composition of coal. Pyrolysis causes a large number of volatiles to separate from the jet coal. Some closed pores in coal are transformed into open pores or semi-open pores, which provide a large number of adsorption sites for oxygen. The coal matrix and inorganic minerals are affected by high temperature, and the expansion has an effect on the pores in the coal. The content of inorganic minerals in jet coal is low, and the expansion is not obvious. Therefore, the precipitation of volatiles is the main cause of the pore increase and oxygen absorption weight gain in coal. With the increase in pyrolysis temperature, the precipitation rate of volatiles increases gradually, the oxygen absorption process of the residue is gradually obvious, and the oxygen absorption process of the pyrolysis residue at 450 °C is the most obvious. After 450 °C, the precipitation rate of volatiles slows down. The pore in coal collapses at high temperature, and the aromaticity of the coal structure increases. The adsorption sites of oxygen become less, and the maximum oxygen absorption point becomes smaller.

The reoxidation characteristics of pyrolyzed coal and raw coal were quite different. The change rule of the residual oxidation characteristics of the coal samples can be obtained. The reoxidation characteristic parameters of raw coal and pyrolysis residues are shown in Figure 7.

Figure 6. Thermogravimetric curves (a) and Deriv. weight curves (b) under different coal oxidation conditions.

Figure 7. Changes in the trends of coal sample pyrolysis characteristic parameters: (a) $dW_{\text{max}}$ and (b) $T_{\text{i}}$, $T_{\text{r}}$, $T_{W_{\text{max}}}$.
temperature increases, the burnout temperature increases slightly, indicating that the pyrolysis temperature has little effect on the $T_i$.

$dW_{\text{max}}$ is related to the maximum combustion intensity. With the increase in pyrolysis temperature, the $dW_{\text{max}}$ of jet coal gradually increases. With the increase in pyrolysis temperature, there are more and more small molecular structures in coal. At 500 $^\circ$C, the thermal decomposition rate reached the maximum, and the amount of tar remaining in the coal sample was the largest. At that moment, the combustion intensity of the residual structure of the coal reached the maximum, and $dW_{\text{max}}$ also reached the maximum. The $TW_{\text{max}}$ of jet coal shows a slight upward trend with the increase in pyrolysis temperature, which shows that the pyrolysis has little effect on the maximum weight loss temperature of coal samples.

4. CONCLUSIONS

In this paper, the jet coal was pyrolyzed using a synchronous thermal analyzer (TA-Q600), and the reoxidation experiments were carried out based on the residues of different pyrolysis degrees. The influence of pyrolysis on coal oxidation characteristics was analyzed, and the reburning characteristics of pyrolysis residual structures were obtained. The influence of pyrolysis on the functional groups and structural parameters of coal was analyzed by FTIR. The conclusions are as follows:

(1) The results demonstrate that the increase in the isothermal temperature in pyrolysis leads to the increase in $V_{\text{max}}$ as well as $W_{\text{op}}$. In addition, $W_{\text{op}}$ increases before 450 $^\circ$C and gradually decreases during 450−500 $^\circ$C, and $W_{\text{pu}}$ decreases gradually. Jet coal pyrolysis is divided into two stages, early pyrolysis and late pyrolysis, at 350 to 500 $^\circ$C. The components contained in the residue are different in each pyrolysis stage of coal.

(2) Aromatic hydrocarbon, aliphatic hydrocarbon, and hydroxyl groups are very sensitive to pyrolysis temperature. The increase in isothermal temperature in pyrolysis leads to the decrease in aromatic hydrocarbon and hydroxyl groups. Compared with the raw coal, the hydroxyl content decreases by 7.19% in the pyrolysis residue at 350 $^\circ$C. In the range of 350−500 $^\circ$C, the change in the hydroxyl group in the pyrolysis residue is only 0.2%.

Pyrolysis breaks a large number of weak chemical bonds and increases the aromatization of the coal structure. At 350 $^\circ$C, the content of the benzene ring (C=C) in coal has reached 75.17%, and at 500 $^\circ$C, it has reached 78.44%. Pyrolysis has little effect on $-C=O$ and $-\text{COOH}$. Under the influence of pyrolysis, $-C=O$ decreases by 1.49% and $-\text{COOH}$ increases by 0.16%. The ratio of $\text{CH}_2/\text{CH}_3$ decreases from 5.66 to 3.33 at 400 $^\circ$C and then increases rapidly. The $A_h/A_d$ decreases with increased temperature and drops to a minimum at 500 $^\circ$C. $A_{\text{lu}}/A_d$ increases with the increase in pyrolysis temperature.

(3) With the increase in isothermal temperature in pyrolysis, the $T_i$ decreases gradually and then increases. The $T_i$ is the lowest at 450 $^\circ$C, which is 266 $^\circ$C. $T_{\text{lu}}$ and $TW_{\text{max}}$ are less affected by pyrolysis, and the change is not obvious. Although a large number of combustible components are lost in the pyrolysis process, the oxidation of coal has been greatly improved, and it is more likely to spontaneously ignite with higher combustion intensity.

The $dW_{\text{max}}$ of jet coal increases gradually with the increase in pyrolysis temperature and reaches the maximum rate of thermal decomposition at 500 $^\circ$C.

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Notes

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