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Comprehensive Study on Bituminous Coal Oxidation by TGA–DTA–FTIR Experiment

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Abstract

The spontaneous combustion of coal can have serious consequences. Bituminous coal is especially problematic as it produces a large amount of smoke comparative to other coals. Variable heating rate thermogravimetry analysis–differential thermal analysis–Fourier transform infrared spectroscopy experiments (TGA–DTA–FTIR) were conducted on three kinds of bituminous coals to study the change rule of weight, heat, and generated gas during the entire oxidation process from slow self-heating to burn out. Experimental results indicate that weight, heat, and gas release are in mutual correspondence at stages 1-4 in the oxidation process. However, change in generated gas lags behind weight and heat changes in the last stage. The main gas products of the oxidation process are CO, CO_2, H_2O, and CH_4.The process of gas release depends on the reaction characteristics of related active structures. The concentration of generated gas from the same coal is CO_2>H_2O>CO>CH_4. CO_2 accounts for about 90% of the total amount of gas. The relationships between absorbance and temperature of generated gases in the rapid generation stage are linear or binomial, R^2 are higher than 0.95. A comparison of the experimental results on different bituminous coals shows that when volatile matter is high, the characteristic temperatures are low and the concentration of generated gas and rate of heat release are high.

Keywords: TGA–DTA–FTIR; Oxidation Process; Volatile matter; Characteristic Temperature

1. Introduction

The spontaneous combustion of coal can trigger a major coal mine disaster. Once it happens, it will seriously affect coal production, cause significant economic and resource loss, pollute the environment, and can even cause explosions and casualties. Thus, studying the process and mechanism of spontaneous combustion is a common concern of coal-producing countries. Burning bituminous coal produces a substantial amount of smoke. Therefore, the spontaneous combustion of bituminous coal will have more serious effects than that of other coals.

The occurrence and development of spontaneous combustion of coal—which includes a chemical kinetic process, heat transfer, weight change, and emission of various harmful gases—is a complicated physical and chemical process. In recent years, scholars have used several research methods to study these aspects. Online Fourier transform infrared spectroscopy (FTIR) is used to study the change in index gas to determine the stage of coal oxidation [1, 2]. FTIR is also used to study the change in various functional groups [3–7] to reveal the oxidation mechanism [3–7]. A special chamber or oven is used to study gas emission from low-temperature oxidation and spontaneous combustion [8, 9]. Experimental furnaces for spontaneous combustion of coal were constructed to study the change in temperature, gases, and heat intensity [10]. Low temperature oxidation experiment, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and other methods are used to study low temperature features and influence factors [11–13]. Most of these studies focused on a certain aspect of coal oxidation. Although the experimental furnaces of spontaneous combustion can perform multi-angle studies [10], the process uses large quantities of coal and is time consuming and difficult to replicate. Recently, the

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Figure 1: Actual picture of the experimental system

combination of a temperature-programmed heating device and detection instrument are applied in scientific research. TGA–differential thermal analysis–FTIR (TGA–DTA–FTIR) is one of the most advanced thermal analysis techniques currently available. The technique has several advantages, such as small sample weight, ease of operation and replication. The most important advantage is that it obtains weight, heat and generated gas data simultaneously. At present, studies on spontaneous combustion of coal are mostly limited to low and moderate temperature stages. Limited research has been conducted about the stage after ignition. The rule of the change in weight, heat, and gas emission from coal self-heating until burn out is investigated using TGA–DTA–FTIR. This research can provide a scientific basis for accurate determination of coal spontaneous combustion stage, timely forecasting and effective governance.

2. TGA–DTA–FTIR experiment of bitumious coal

2.1. Experimental system

The experiment was performed in the Institute for Thermal Power Engineering at Zhejiang University. The experimental system includes a TGA/SDTA851^e thermal analyzer produced by Mettler–Toledo and a Nexus 670 FTIR produced by Thermo Nicolet Corporation. The two devices were connected together, and TGA, DTA, and FTIR data were obtained simultaneously. Fig. 1 shows the experiment system.

A schematic diagram of the experiment principle is shown in Fig. 2. The thermal analyzer performs TGA and DTA simultaneously by thermo-balance and thermocouple. With the increase in temperature, coal produces chemical reactions and emits gases. These gases are deposited into a sample cell of FTIR. Radiation is initially changed from an infrared source into parallel light. The light then goes into a Michelson interferometer where the parallel light is changed into a fluctuating light. The fluctuating light leaves the interferometer and casts on Oscillating Mirror B, which enables the light to pass alternately through the sample and the reference. Then the light goes through Oscillating Mirror C and focuses on the detector. The detector collects the interference image, which is changed into FTIR spectrum by performing a fast Fourier transform in a computer. Then, the spectrum can be used to study the molecular structure and chemical composition of the sample.

Thermal analyzer conditions include temperature measurement ranging from 0..1,600°C, maximum heating rate of 100°C/min, and maximum gas flow of 100 ml/min. Infrared spectrometer conditions include infrared spectrum in the range of 450..4,000 cm^{-1}, spectrum resolution better than 0.09 cm^{-1}, scanning rate of 65 charts per second, minimum scanning resolution at 16 cm^{-1}, and wavenumber accuracy of 0.01 cm^{-1}.

2.2. Bituminous coal samples

The bituminous coal samples were obtained from Jinzhengtai Coal Mine in Ordos, Inner Mongolia, Suncun Coal Mine in Tai'an, Shandong, and Xuandong No.2 Coal Mine in Zhangjiakou, Hebei. The Jinzhengtai Mine is an open-pit mine, which was reconstructed based on an underground coal mine. The coal sample was taken from No. 6 coal seam. The average ignition point of the sample is 317..320°C. The ignition point of the oxidation sample is 283..299°C, and the ignition point of the reduced sample is 343..349°C, ΔT is 29..74°C. Therefore, the coal sample is spontaneous combustion coal. The mining depth of Suncun Coal Mine has a maximum depth of 1,400 meters, which makes it the deepest mine in Asia. With the increase in mining depth, spontaneous combustion accidents occur more frequently. Based on experimental coal samples taken from No. 15 Coal Seam, the quantity of absorbing oxygen is 0.41 cm^3/g. Hence the coal is type II spontaneous combustion coal. Xuandong No.2 Coal Mine is currently working the III3 coal seam. The oxygen absorption features of III3 coal seam were assessed by the chromatographic method, which showed that the coal is type II spontaneous combustion. To perform the TGA–DTA–FTIR experiment, sufficient coal was first collected from the coal mine sites and sent to the laboratory where the oxidation surface layers were stripped off. Then, the coal core is broken, grounded, and screened to obtain the coal powder used for the experiment, which measures 60..80 mesh (0.18..0.25 mm). The industrial and elemental analyses of the coal samples were conducted in the In-

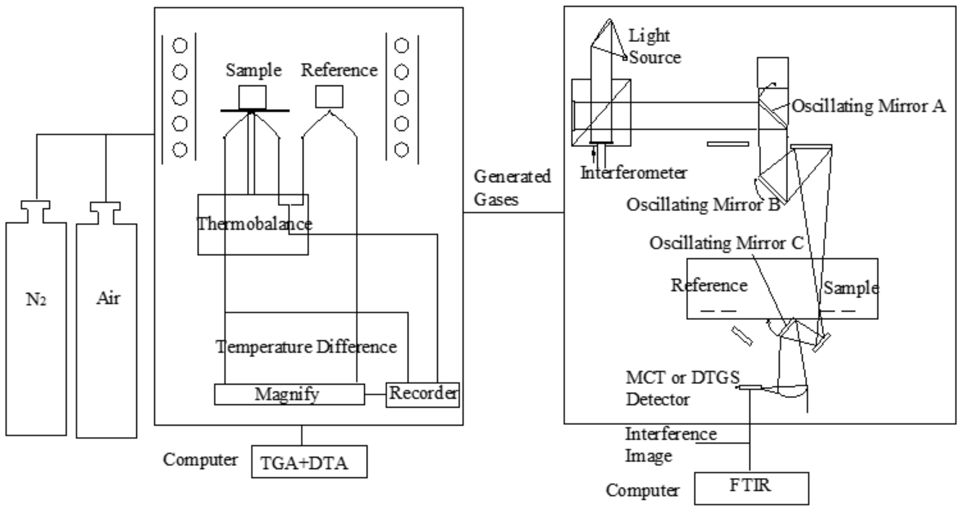

Figure 2: Schematic diagram of the experiment principle

Table 1: Industrial and elemental analyses of coal samples

Mine name	Mad, %	Vad, %	Aad, %	Nad, %	Cad, %	Sad, %	Had, %	Oad, %
Suncun	2.17	33.49	7.86	1.3	74.21	0.62	4.99	8.85
Jinzhengtai	6.28	27.04	11.26	0.82	65.14	0.73	3.8	11.97
Xuandong No.2	1.59	20.98	19.3	0.59	66.93	0.45	3.53	7.61

stitute for Thermal Power Engineering at Zhejiang University. The results are shown in Tab. 1.

2.3. Experimental conditions

No obvious difference was observed in the oxidation reaction at the same temperature when the intrinsic factors of the coal sample, such as physical and chemical structure and inherent moisture remain unchanged under the same oxygen concentration, regardless of whether the heat comes from the oxidation of coal itself or from environmental heating. Therefore, the characteristics of coal oxidation can be studied by using a temperature programmed experiment. The experiment adopts a variable heating rate, namely, the heating rate is low when the temperature is low and the heating rate is high when the temperature is high. The test is used to simulate the entire process from slow self-heating to burn out. Heating rate at 20..200°C is 3°C/min, 10°C/min at 200..800°C, and 20°C/min at 800..1000°C. The coal samples have natural water content with a weight of 10 mg. The experiment atmosphere is composed of air with a gasflow of 80 mL/min. The protective gas is N_2 with a gasflow rate of 20 mL/min.

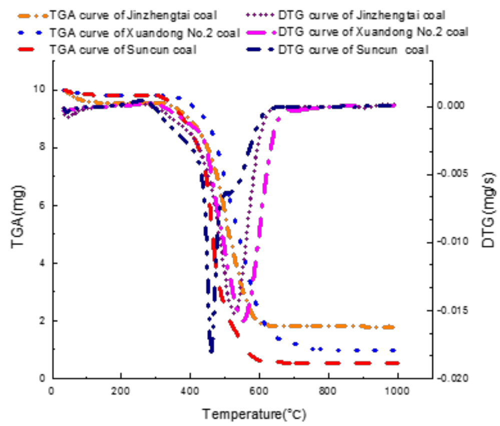

Figure 3: TGA–DTG curves of the entire oxidation process

3. Experimental results and analysis

3.1. Results and analysis of the TGA–DTA experiment

The TGA–DTG (differential thermogravimetry graph) and TGA–DTA curves obtained from the TGA–DTA–FTIR experiments of three kinds of bituminous coal are shown in Fig. 3 and Fig. 4. The TGA curves and corresponding DTA curves can be divided into five stages.

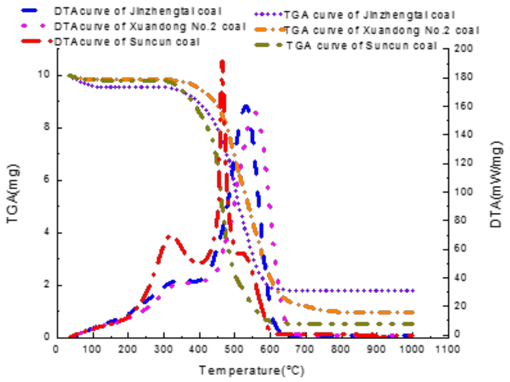

Figure 4: TGA–DTA curves of the entire oxidation process

Table 2: Characteristic temperatures of the stages of coal oxidation process

Mine name	T_1, °C	T_2, °C	T_3, °C	T_4, °C
Suncun	84	303	420	620
Jinzhengtai	94	320	428	650
Xuandong No.2	98	322	443	700

The first stage is moisture evaporation and gas desorption, where through the internal energy of molecules, water evaporation and gas desorption gradually accelerate with temperature. Therefore, the weights of coals gradually fall. The end temperature of this stage is denoted as T_1, the values of which are listed in Tab. 2. The TGA curves show that the biggest weight loss of the bituminous coal obtained from Jinzhengtai Mine at this stage is about 5%, whereas those of Suncun Mine and Xuandong No.2 Mine are only about 1%. The DTG curves indicate that weight change rate of the bituminous coal from Jinzhengtai Mine is the fastest. Those of Xuandong No.2 Mine and Suncun Mine are slower. These results are all related to the moisture contents of coals. The DTA curves show that micro heat absorption is caused by water evaporation. So moisture content plays a decisive role at this stage.

The second stage reflects an increase in weight because of oxygen absorption. Water evaporation and gas desorption caused an increase in the number of pores and free surfaces. The chemical reaction accelerates and the rate of oxygen absorption increases. Thus, the weight of coal gradually increases. When the weight reaches its peak, the corresponding temperature is denoted as T_2, the values of which are listed in Tab. 2. A fast exothermic reaction at this stage is indicated in the DTA curve. It is the first exothermic peak in the oxidation process. The peak height and peak area of the bituminous coal obtained from Suncun Coal Mine is the largest, which means the rate of heat release and heat output is the largest. Those of bituminous coals from Jinzhengtai Mine and Xuandong No.2 Mine are the second and the third, respectively. The order is the same as the order of volatile matters of coal samples.

T_3 denotes the burning point and T_4 denotes the temperature when coal burns out. Values of T_3, T_4 are listed in Tab. 2. T_2–T_3 is the thermal decomposition stage. T_3–T_4 is the combustion stage. When the temperature is higher than T_4, the oxidation process has entered the burn out stage. When temperature is higher than T_2, rapid weight loss and rapid heat release begin. When temperature is higher than T_3, substantial amounts of heat and gases are emitted from coal. When the tempertature is higher than T_4, the weight and heat of coals no longer change.

Tab. 2 shows that the characteristic temperatures of bituminous coal from Suncun Coal Mine is the lowest. Those of Jinzhengtai Coal Mine and Xuandong No.2 Coal Mine are second and third, respectively. The order is the same as that of the volatile matter of coals.

In summary, experimental results indicate that weight and heat changes are in mutual correspondence during the five stages of oxidation. The oxidation process curves of different coals depend on the industrial analysis results. Moisture content plays a decisive role in the first stage. Volatile matter content plays a decisive role during the whole process.

3.2. *Results and analysis of the FTIR experiment*

A large amount of toxic and harmful gases are generated from coal during oxidation. The air outlet of the thermal analyzer is connected to an infrared analyzer in the TGA–DTA–FTIR technology. Hence, the infrared spectrum of generated gases at different setting times can be obtained. An absorption peak appears at the position of the wavelength or wavenumber of the absorbed light on the infrared spectrum. When more light of a certain wavelength is absorbed, transmittance is lower and the absorption peak is higher. The longitudinal coordinate of the infrared spectrum can choose from transmittance and absorbance, corresponding spectrum is called the transmittance spectrum or absorbance spectrum. The transmittance spectrum can directly reflect the absorption of infrared light of different wavenumbers, but has no quantitative relationship with concentration. The absorbance value of the absorbance spectrum is proportional to the concentration of the sample, which can be used for quantitative analysis. According to the positions of characteristic peaks and the values of absorbance on the spec-

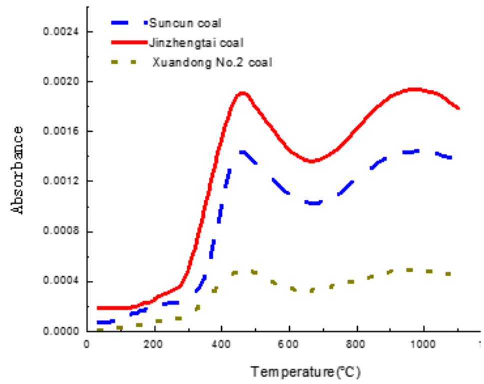

Figure 6: Relation between absorbance and temperature of CH_4

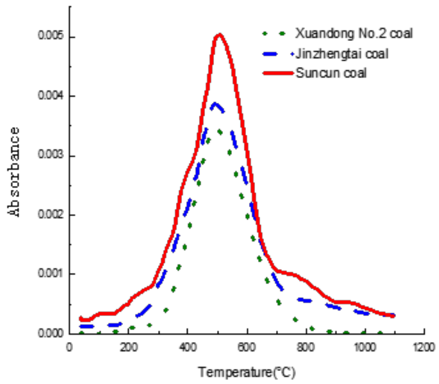

Figure 7: Relation between absorbance and temperature of CO

trum, qualitative and quantitative studies can be conducted on the change rule in concentrations of various generated gases that vary with temperature.

The change rule of wavenumber–time–absorbance of the sample obtained from Jinzhengtai Mine is reflected in Fig. 5. The spectrum of the other two samples is similar. The infrared spectrum of various generated gases under different temperatures can be obtained by splitting Fig. 5. The main products of coal oxidation are CO_2, CO, CH_4, and H_2O. The wavenumber ranges of infrared absorption characteristic peaks of these gases are: CO_2 at 2400 cm^{-1}–2100 cm^{-1}; CO at 2,100..1,900 cm^{-1}, CH_4 at 3,100..2,800 cm^{-1}, and H_2O at 3,500..3,800 cm^{-1}. According to the infrared spectrums of the samples, CO_2, H_2O, CO, and a small amount of CH_4 are detected at the beginning of the programmed temperature. The concentration of water increases with temperature and a small peak appears at about 100°C. As the oxidation reaction develops, a large amount of these gases are detected at about 300°C. Concentrations of gases increase quickly with temperature. Concentrations of CO, CO_2, and CH_4 reach their peak values at about 500°C. Then the concentration of CH_4 vibrates down, whereas the concentration of CO falls sharply and the concentration of CO_2 remains almost stable till 900 °C. The concentration of H_2O increases slowly after the first peak, then enters the second peak from 300°C to 1,100°C.

3.2.1. Concentration variation of CH_4 during bituminous coal oxidation

The change curve of CH_4 absorbance over temperature is shown in Fig. 6. The amount of CH_4 is very small from room temperature to 300°C. Coal molecules are oxidized to emit CH_4. At this stage, oxygen molecules attack the carbon atom in the middle of the propyl of the benzene ring side chain, (–CH_2–COOH) and CH_4 are generated. When the temperature is higher than 300°C, side chains or branch chains of aliphatic hydrocarbons are broken and several alkyl branch chains are split; both of the reactions produce CH_4. Therefore, the amount of CH_4 increases sharply with the increase in temperature. When the temperature is about 500 °C, the amount of CH_4 reaches the maximum value, and then vibrates down. The relationship between absorbance and the temperature of CH_4 at the rapid generation stage of 300..500°C is linear, R^2 is greater than 0.96.

3.2.2. Concentration variation of CO during bituminous coal oxidation

The change curve of CO absorbance over temperature is shown in Fig. 7. CO is slowly released from coal at low temperatures. Large amounts of CO are generated at 300..700°C. The amount of CO reaches the maximum value at about 500°C before decreasing quickly. Coal molecules are oxidized to emit CO at low temperatures, where oxygen molecules attack the carbon atom at the end of the propyl of benzene ring side chain, (–CH_2–CH_2–COH) and water are generated. (–CH_2–CH_2–COH) continues to decompose to emit CO. From 350°C to 500°C, the removal of hydroxyl groups from coal molecules becomes a source of CO. When temperature is higher than 500°C, water is reduced by semi-coke to emit CO. In addition, oxygenous heterocyclic compounds possibly split to emit CO. Thus, CO has four sources. The relationship between absorbance and temperature of CO at the rapid generation stage 300..500°C is binomial, and R^2 is greater than 0.99.

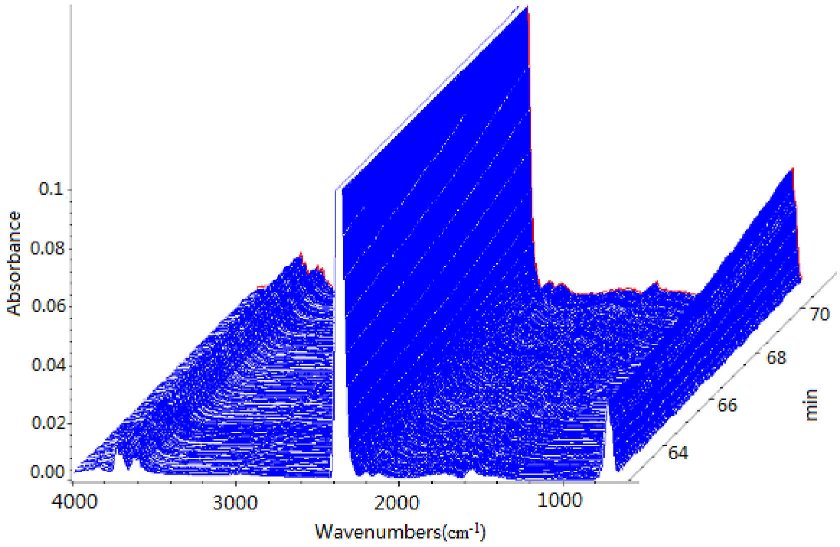

Figure 5: Infrared 3D spectrum of generated gases of bituminous coal from Jinzhengtai Coal Mine

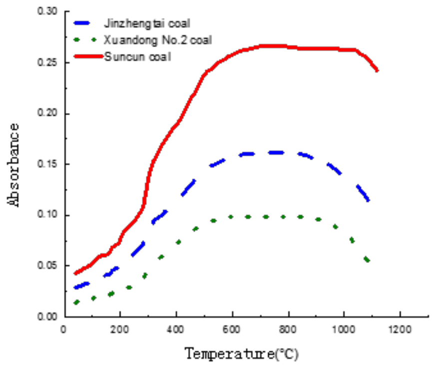

Figure 8: Relation between absorbance and temperature of CO_2

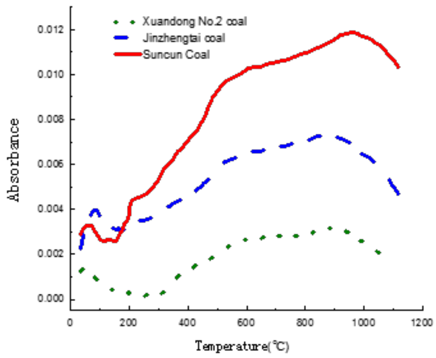

Figure 9: Relation between absorbance and temperature of H_2O

3.2.3. *Concentration variation of CO_2during bituminous coal oxidation*

The change curve of CO_2 absorbance over temperature is shown in Fig. 8. CO_2 is emitted from coal at low temperatures. When the temperature reaches 300°C, the generated speed of CO_2 increases. The amount of CO_2 reaches the maximum value at 500°C, and remains stable till 900°C, then starts to decline. At low temperatures, oxygen molecules attack the carbon atom of the benzene ring side chain, (–CH_2–CH_2–COOH) and water are generated. (–CH_2–CH_2–COOH) continues to decompose to emit CO_2. With the increase in temperature, a large number of carboxyl is split to generate CO_2, and the amount of CO_2 quickly increases. When temperature is above 500°C, almost all the carboxyl in coal has been split [14]. But some stable compounds which contain carboxyl undergo a decarboxylation reaction to produce CO_2. Thus, the amount of CO_2 is relatively stable from 500°C to 900°C. The relationship between absorbance and the temperature of CO_2 in the rapid generation phase of 300°C–500°C is linear, and R^2 is greater than 0.96.

3.2.4. *Concentration variation of H_2O during bituminous coal oxidation*

The change curve of H_2O absorbance over temperature is shown in Fig. 9. There are two peaks in the figure. A small peak appears at about 100°C. A big peak covers 300..1,100°C. The first peak reflects the emission of inherent moisture and external moisture. As temperature rises, oxygen-containing functional groups of coals are decomposed to generate H_2O. The second peak covers a large temperature range because the chemical bond strength of oxygen-containing groups C–OH and C–O are different [15]. The order of peak height and peak area of the first peak are the same as the order of water content of samples: Jinzhengtai Mine bituminous coal>Suncun Mine bituminous coal>Xuandong No.2 Mine bituminous coal.The order of peak height and the peak area of the second peak is: Suncun Mine bituminous coal>Jinzhengtai Mine bituminous coal>Xuandong No.2 Mine bituminous coal. This order is the same as that of the volatile matter of coals. The relationship between absorbance and temperature of the second peak 300..1,100°C is binomial, and R^2 is greater than 0.95.

In summary, the gas release process depends on the reaction characteristics of related active structures such as side chains, branch chains and functional groups. Different active structures are activated at certain temperatures to form free radicals. The free radicals are combined with other free radicals to emit certain gases. The number of active structures in coal is the key factor in coal oxidation, and volatile matter can reflect the number of active structures. In the experiment the order of concentration of generated gases is the same as that of the volatile matter of coals: Suncun Mine bituminous coal>Jinzhengtai Coal Mine bituminous coal>Xuandong No.2 Coal Mine bituminous coal.

A comparison of the TGA-DTA-FTIR experiment shows that weight, heat, and gas are in mutual correspondence at stages 1-4. Weight and heat do not change anymore in the last stage. But concentrations of various gases need a longer time to decrease, which indicates hysteresis characteristics.

The concentrations of generated gas from high to low are CO_2>H_2O>CO>CH_4. For example, the absorbance of CO_2, H_2O, CO, and CH_4 of Suncun Coal Mine bituminous coal at 500°C are 0.25, 0.01, 0.005, and 0.002, respectively. The proportional relation of gases at other temperatures does not have apparent differences. Carbon dioxide accounts for about 90% of the gases.

4. Conclusion

Weight, heat, and gas release are in mutual correspondence at stages 1..4 in the oxidation process. However, the change in generated gas lags behind weight and heat changes in the last stage.

The volatile matter of bituminous coal has a significant impact on characteristic temperatures, concentrations of generated gas and heat release rates. When volatile matter is high, the characteristic temperatures are low and the concentration of generated gas and rate of heat release are high. This is mainly because volatile matter reflects the number of active structures on the surface of the coal. It is a symptom of the degree of difficulty and reaction speed of coal oxidation.

The concentrations of generated gas from the same coal are CO_2>H_2O>CO>CH_4. CO_2accounts for about 90% of the total amount of gas.

The relationships between absorbance and temperature of generated gases at rapid generation stage are linear or binomial, R^2 are greater than 0.95.

Acknowledgments

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