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Article

Study on spontaneous combustion tendency of coals with different metamorphic grade at low moisture content based on TPO-DSC

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Abstract: In the environments of all kinds open coal storage sites , mining-affected coalbeds, and goafs, parts of coal body at low moisture content (≤8%) are prone to spontaneous combustion under the influence of some external environmental factors. In order to examine the influence effect of low moisture content on the spontaneous combustion tendency of coals with different metamorphic grade, we conducted temperature programmed oxidation (TPO) experiment and differential scanning calorimetry (DSC) experiment to study the spontaneous combustion characteristics of coals with different metamorphic grade at four different low moisture content, and comparatively analyzed the change laws of the characteristic parameters of four different metamorphic grade coals at four different low moisture content. The experimental results indicate that: 1) Compared other low moisture content, anthracite and fat coal at low moisture content of 1.2% show stronger tendency to undergo spontaneous combustion, long flame coal and lignite at low moisture content of 3.4% and 5.6% are more prone to spontaneous combustion. 2) Four different metamorphic grade coals at low moisture content of 7.8% are less prone to spontaneous combustion; 3) Coals with different metamorphic grade have different tendency to undergo spontaneous combustion.

Keywords: low moisture content; metamorphic grade; temperature-programmed oxidation; differential scanning calorimetry; spontaneous combustion tendency

1. Introduction

It is well known that moisture in many influencing factors plays an important role in the spontaneous combustion of coal [1-4]. From the increased probability of spontaneous combustion of coals after damping or flooding, some scholars realized that coal with different moisture content have different thermal reaction characteristics [5-6]. In the all kinds open coal storage sites, coal washing plants, coal bunkers, power plants, etc, long-term open-air piles of static coal piles are piled up, and under the influence of sunlight or atmospheric wind, the moisture in the coal piles is continuously evaporated [7]. In the underground, moisture in ore body and surrounding rock seepage channels could be evaporated due to roadway ventilation, airflow or geological factors, especially under the influence of mining. After the coal in the goaf is immersed in moisture, coal may gradually reduce the moisture due to the influence of long-term air leakage. In these environments, some coals will be in the low moisture content state [8] (low moisture content of coal, $M_t \le 8.0\%$, according to China Coal Water Classification Industry Standards, MT/T 850-2000) due to the external environment, once spontaneous combustion of coal occurs, it not only will inevitably cause coal resources waste, environmental pollution, and severe economic losses, but also directly endangers the safety of field workers [9-14].

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In recent years, researchers have extensively studied the influence of moisture on coal's spontaneous combustion characteristics [15]. From the view of moisture content's effects on coal's spontaneous combustion and its characteristic parameters, Arisoy and Beamish [16] found that high moisture content could slow down the process of coal's spontaneous combustion and make it unable to reach thermal runaway status. Xuyao et al. [17] found that high moisture content could postpone coal's self-heating process. Arisoy et al. [18] constructed a mathematical model for spontaneous combustion of moisture-bearing coals and concluded that moisture helps slow down the process of coal's spontaneous combustion. Kadioğlu and Varamaz [19] study the spontaneous combustion characteristics of Turkish moisture-bearing coal samples at different drying conditions using the cross-point method and found that with increasing drying time and gradual decreasing moisture content, moisture-bearing coals are more reactive and prone to spontaneous combustion. Beamish and Hamilton [20] studied the effect of moisture on the R70 self-heating rate of coal using adiabatic experiments and found that when coal's moisture content increased from dry state to 6%, its R70 self-heating rate decreased by 50%; when coal's moisture content is between 17% and 18.6%, its R70 self-heating rate becomes zero; and when coal's moisture content reaches 40-50% of its moisture-holding capacity, its self-heating rate begins to increase significantly, thus, ensuring coal' actual moisture content above this critical level can greatly delay its spontaneous combustion cycle. Deng [21] found coals from Mengba Coal Mine are most sensitive to spontaneous combustion at moisture content of 14.27%. Song et al. [22] found that after water immersion, a large number of closed pores in long flame coal are unclogged, leading to enhanced ability to adsorb oxygen, reduced cross-point temperature and increased concentration of index gases due to oxidation and high risk of spontaneous combustion. Wang et al. [23] showed that the threshold of coal's moisture content depends on its maximum oxygen consumption. When coal's moisture content exceeds the threshold, excessive water will form a multi-layer structure that hinders the diffusion of oxygen into pores and cracks in the coal, resulting in a slower chemical adsorption reaction between coal and oxygen. Zhang et al. [24] found that the swelling degree of the lignite matrix enhances at moisture content in the range of 10%-30%, which is favorable for the transportation or migration of oxygen in the coal. Li et al. [25] explored the effect of moisture content on lignite's characteristic temperature using a coal oxidation simulation device and concluded that at critical moisture content of 15%, heat released by lignite during the oxidation process reaches its peak. Chen and Stott [26] found that at moisture content of 7%-17%, oxygen adsorption by coals with low metamorphic grade from New Zealand reached the maximum. In this critical range, the coal exhibits specific oxidation features, that is, the reaction points inside coal pores can fully access to oxygen, and the residual moisture content optimally enhances the chemical reaction. Zhao et al. [27] oxidized Indonesian coal using a double-fixed quartz reactor, examined the effect of moisture content on the characteristics of coal under the low-temperature oxidation and found that the separation point temperature (SPT) as the starting point of self-heating of the coal in the oxidation process is greatly affected by the coal's moisture content and is the lowest when the moisture content is in the range of 6%-13%, indicating that the coal has the rapid oxidation rate in this critical moisture content range. From the point view of influence of moisture content on the spontaneous combustion characteristics of coals with different metamorphic grade, Wang et al. [28] found that lignite is prone to spontaneous combustion at moisture content of 35%, above this critical value, its tendency to spontaneous combustion is not obvious, when its moisture content is only 30%, the spontaneous combustion is unlikely to occur. Xu et al. [29] tested the exothermic characteristics of lignite, gas coal, fat coal, and anthracite at different moisture content (10%-25%, 20%-42%) in their oxidation processes by TA-DSC and showed that the influences of moisture content on coals with different metamorphic grade vary greatly, the critical moisture content of lignite and anthracite are 25% and 20%, in addition, for gas coal and fat coal, the lower their moisture content, the higher risk of spontaneous combustion.

The above researches on the effect of moisture content for spontaneous combustion tendency of coals mainly focus on the spontaneous combustion characteristics of coals with medium or high moisture content (medium or high moisture content of coal, Mt=8.0-40%, according to China Coal Water Classification Industry Standards, MT/T 850-2000) and low metamorphic grade, but rarely explored the spontaneous combustion tendency of coals with different metamorphic grade at low

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moisture content. Considering that some coals with different metamorphic grade at low moisture content could occur spontaneous combustion in the environments of all kinds open coal storage sites , mining-affected coalbeds, and goafs, etc. In this paper we utilized the temperature programmed oxidation (TPO) experiment and differential scanning calorimetry (DSC) experiment to examine the change law of spontaneous combustion tendency of anthracite, fat coal, long flame coal, and lignite at four different low moisture content, so as to further expand our understanding about the effect of low moisture content on spontaneous combustion tendency of coal. Thus, this study is of practical significance for the prevention of spontaneous combustion of coal with low moisture content.

2. Experiments and Methods

2.1. Coal samples

2.1.1. Collection and preparation

The different metamorphic grade of the collected coal samples is ranked in a descending order as follows: anthracite from Changcun Coal Mine, Shanxi Province, China; fat coal from Tangshan Fangezhuang Coal Mine, Hebei Province, China; long flame coal from Inner Mongolia, Inner Mongolia Autonomous Region; China, lignite from Tangshan Cuijiazhai Coal Mine, Hebei Province, China; Figure 1 shows the collected locations of these coal samples.

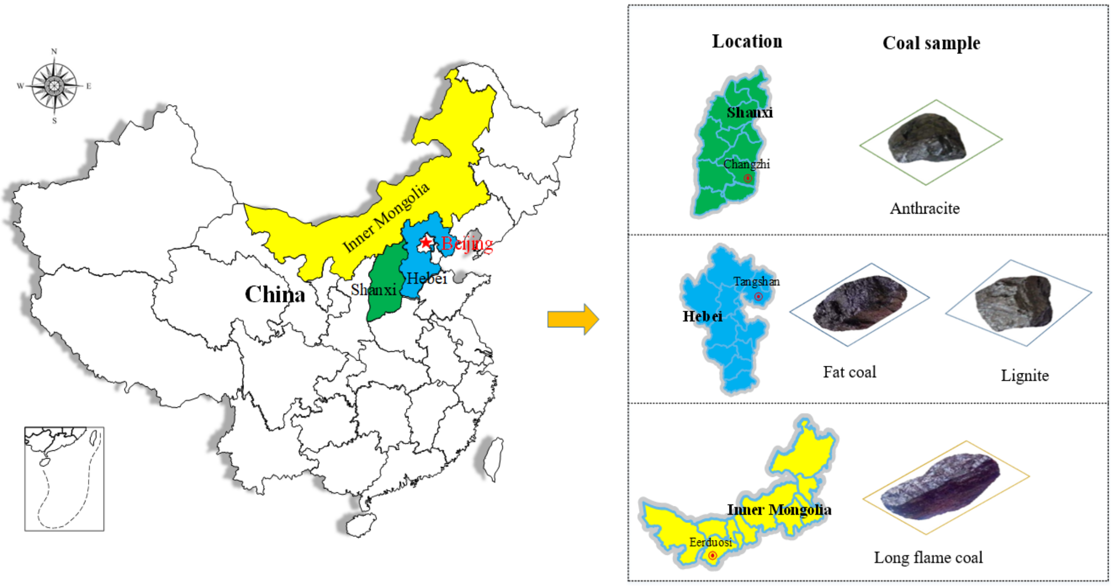

Figure 1. Location distribution of coal samples

These samples were processed as follows: 1) gather in situ fresh coal blocks from each coal mine, and seal and transport them back to the laboratory; 2) peel off the surface oxide layer from the raw coal block; 3) pulverize and sieve them into particles with size of 0.18-0.25 mm and 0.048-0.147 mm; and 4) store the coal samples in vacuum-sealed glass bottles. Table 1 lists the proximate analysis results for the different metamorphic grade coals.

Table 1. Proximate analysis of coal samples

Coal sample	Proximate analysis（%）			
	Misoture（M_{ad}）	Ash（A_{ad}）	Volatiles（V_{ad}）	Fixed carbon（FC_{ad}）
Changcun	0.845	11.795	11.190	76.170
Fangezhuang	1.995	8.960	26.615	62.430
Neimenggu	2.895	28.250	24.190	44.665
Cuijiazhai	12.145	8.990	33.550	45.315

2.1.2. Preparation of coal samples with different low moisture content

According to experimental requirements, we prepared four samples with low moisture contents of 1.2%, 3.4%, 5.6%, and 7.8% for each type of coals with the same particle size using the interlayer sprinkle method, the particle size is 0.18-0.25 mm for TPO and 0.048-0.147 mm for DSC. In brief, 1) place the treated coal samples with different metamorphic grade in a thermostatic drying chamber for drying; 2) the volume of moisture required to prepare for different low water content coal samples is calculated in advance, and at the same time, the coal samples of each metamorphic grade which are weighed, place them into the weighing bottles many times in equal quality; 3) the coal samples of equal quality was placed on the bottom of the bottle and use a tiny sprinkler to uniformly spray moisture on the coal samples according to the pre-designed moisture volume, then, on the sprayed coal sample, use again a tiny sprinkler to uniformly spray moisture on the coal samples for the same quality, and the cycle is continued until the pre-designed moisture content is uniformly sprayed on the coal samples; 4) repeat steps 3) until all designed coals and moisture were used up; 5) place the prepared coal samples into plastic bags, vacuum, and seal the bags; 6) store them in a shady and cool place for a period of time before using.

2.2. Experimental device and process

2.2.1. Temperature programmed oxidation experiment and process

Figure 2 shows the experimental device for temperature programmed oxidation of coal samples. The device consists of a TPO control system, a gas supply system, a standard gas cylinder, a control and filtration system, and a detection and analysis system. The TPO control system is a YI-2000 coal spontaneous combustion features tester; the standard gas is supplied by the standard gas pressure tank; the dry gas is provided by the QPT-300G series nitrogen-hydrogen-air-integrated device; the gas analysis system is a GC7820 gas chromatograph used for acquisition and analysis; and the temperature probe inside the coal sample tank is used to measure the temperature of coal samples.

The experimental steps for TPO of coal samples are as follows: 1) preheat the coal spontaneous combustion features tester to 30°C, put 80 mg coal sample into the sample tank, and uniformly cover the coal sample with a 2-3 mm thick asbestos layer; 2) filter air flow to avoid blocking gas path, closely fasten the two ends of the sample tank, and seal the joints between the end of the tank and the inlet/outlet of gas passages with high-temperature-resistant raw material tape; 3) place the sample tank in the coal spontaneous combustion features tester and turn on the TPO experimental system; 4) set the heating rate of 0.3°C/min and the gas flow of 50 ml/min, heat the coal sample and acquire data at every 10°C interval from 30°C to 160°C and at every 20°C interval from 160 °C to 260 °C; 5) repeat the above same experimental steps and obtain the various index gas concentrations of four different metamorphic grade coals at four different low moisture content; 6) in order to ensure the validity of the experimental datas, the same experiment is done at least twice, if the experimental error proves that the data is valid within 4%, take the average of the two results as the final result.

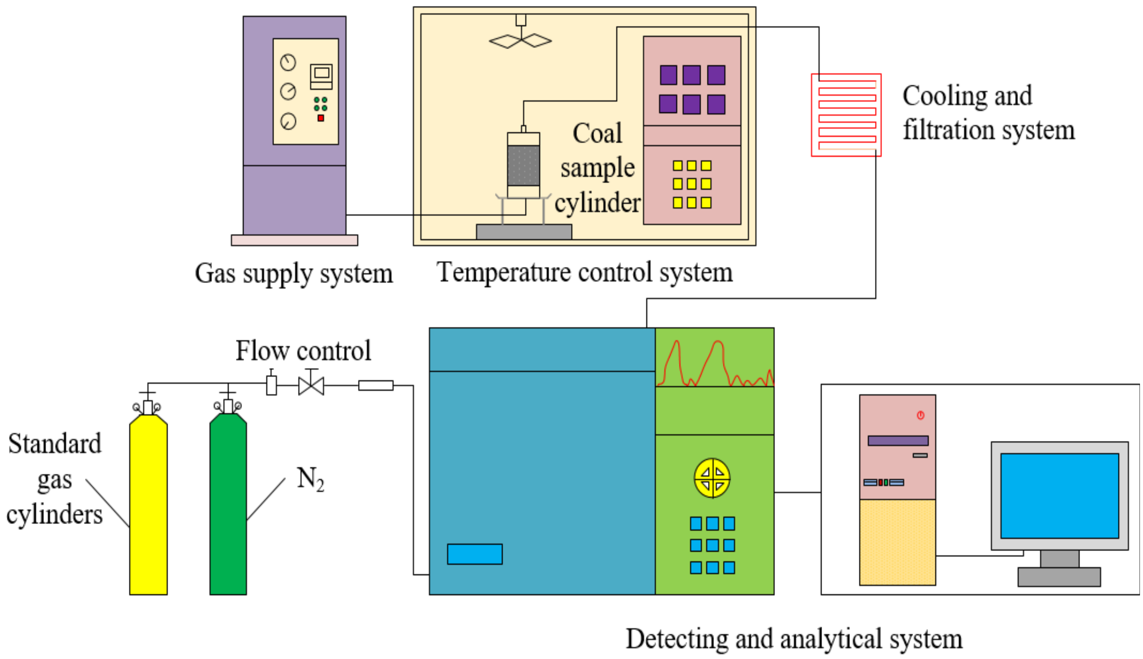

Figure 2. Schematic diagram of apparatus applied for temperature programmed oxidation of coal

2.2.2. Differential scanning calorimetric equipment and process

Figure 3 shows the experimental principle. Differential scanning calorimetric (DSC) experiment were performed using a DSC200F3 Maia® differential scanning calorimeter manufactured by NETZSCH. The device mainly consists of the "DSC200F3" basic module, cooler, and a computer control system.

The experimental steps for DSC of coal samples are as follows: 1) put 10 mg coal sample into the furnace chamber together with an reference empty crucible under the condition of satisfying the instrumental sensitivity; 2) turn on the computer control system to set the experimental parameters as the starting temperature of 25°C, the ending temperature of 400°C, the temperature accuracy of ±0.01°C, heating rate of 5°C/min, purge oxygen flow rate of 20 mL/min, and purge nitrogen flow rate of 80 mL/ min; 3) test the coal sample at a protection nitrogen flow rate of 70 mL/min; 4) draw the heat flow difference curves of four different metamorphic grade coals at four different low moisture content; 5) in order to ensure the validity of the experimental datas, the same experiment is done at least twice, if the experimental error proves that the data is valid within 4%, take the average of the two results as the final result.

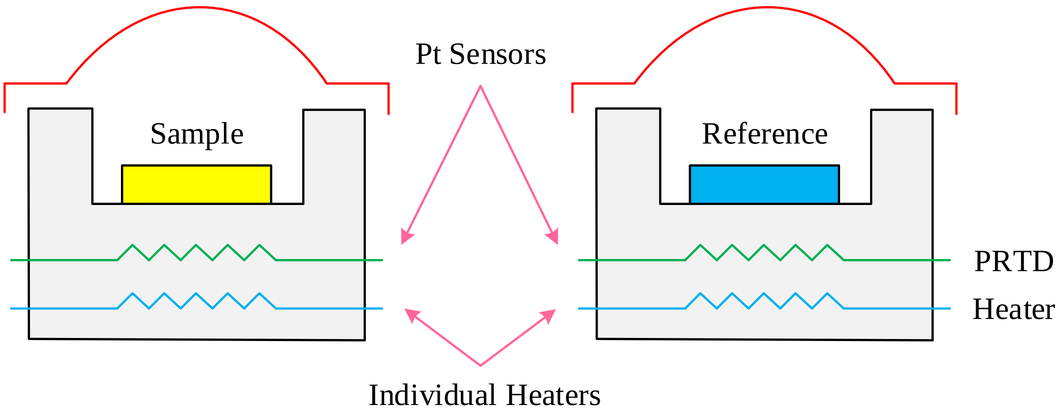

Figure 3. The schematic diagram of differential scanning calorimeter

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3. Results and Discussion

3.1. Analysis of temperature programmed oxidation experimental results

To study the effect of four different low moisture content on the spontaneous combustion characteristics of coals with different metamorphic grade, we conducted the temperature programmed oxidation experiment [30].

3.1.1. O_2 consumption concentration

Figure 4 shows the change of oxygen consumption of four different metamorphic grade coals at four different low moisture content during the temperature programmed oxidation process. It is clear from Fig.4 that the entire temperature programmed oxidation process of these coal samples has a typical staging characteristic and can be divided into three stages: the slow oxidation stage, the rapid oxidation stage, and the violent oxidation stage.

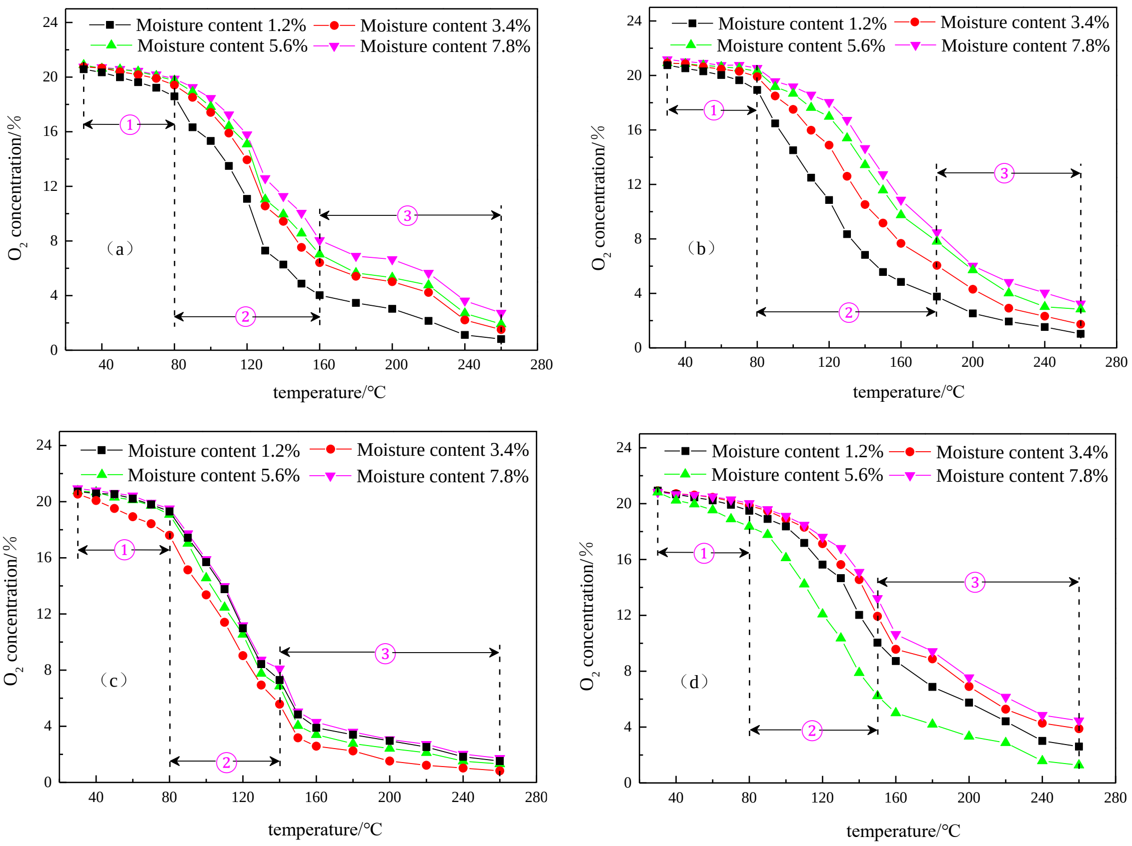

Figure 4. The curves of O_2 concentration consumption for anthracite（a）, fat coal（b）, long flame coal（c）, lignite（d）at four different low moisture content. ① indicates the slow oxidation stage, indicates the rapid oxidation stage, and ③ indicates the violent oxidation stage

In the slow oxidation stage, the temperature varying ranges of anthracite, fat coal, long flame coal, and lignite is 30-80 °C. In this range, the overall oxygen consumption of the four different metamorphic grade coals at four different low moisture content all decrease with the rise of temperature. The comparison of oxygen consumption concentration of four different metamorphic grade coals at four low moisture content before 80°C finds that their overall oxygen consumption display a slowly dropping tendency. When the coal at low moisture content begins to oxidize, the chemical reaction rate is slow and the oxygen consumption rate is low. Since coal is still in the early stage of oxidation reaction, although the rise of its internal moisture promotes the formation of coal-moisture-oxygen complex and increases the rate of oxygen consumption, but the excessive external moisture staying between coal molecules hinders oxygen flows, therefore, the change in oxygen

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consumption is not obvious. In the slow oxidation stage, for anthracite and fat coal, their oxygen consumption of coal samples at moisture content of 1.2% are the highest. In addition, oxygen consumption of coal samples at other low moisture content gradually decrease with the increase of moisture content. The higher the moisture content is, the longer the moisture evaporation time, the more the heat absorbed by evaporation, and the longer the oxygen adsorption is blocked, indicating that increase in moisture content inhibits their internal oxidation degree. For long flame coal and lignite, at moisture content of 3.4% and 5.6%, respectively, the oxygen consumption is the highest in the slow oxidation stage.

From Figure 4, it is clear that the rapid oxidation stages of anthracite, fat coal, long flame coal, and lignite are 80-160 °C, 80-180 °C, 80-140 °C, and 80-150 °C, showing significant differences. In this stage, the oxygen consumption of the four different metamorphic grade coals at four low moisture content significantly increase, illustrate that the degree of coal oxygen reaction is larger, the moisture in coal samples gradually evaporates completely and the flow of oxygen is increased, and thus the formation of moisture-oxygen complex is accelerated. The rapid oxidation of coal samples gradually turn physical and chemical adsorption to chemical reaction, leading to gradual increase in active groups on the surface of coal samples. For anthracite and fat coal, oxygen consumption gradually decreases with moisture content increasing, and oxygen consumption of coal samples at moisture content of 1.2% is still the maximum. This can be explained by that a small amount of moisture can immerse the coal with high or medium metamorphic grade and increase their internal pores, thereby facilitating the physical oxygen adsorption on coal samples. At the same time, moisture as a catalyst participates in the formation of moisture-oxygen complexes, which further promotes the chemical reaction of coal. However, with the increase of moisture content, fewer macropores and mesopores in coals with the high or medium metamorphic grade [31] are occupied by moisture, resulting in a drop in the ability of coal to adsorb oxygen. In addition, the evaporation of higher moisture content requires more heat, which is not conducive to the oxidation reaction of coal. For long flame coal and lignite, the oxygen consumption is the highest at moisture contents of 3.4% and 5.6%, respectively. For lignite, the oxygen adsorption increases with moisture content increases except moisture content at 5.6%. The reasons for the presence of inflexion moisture content in long flame coal and lignite to make oxygen consumption maximum may be that for coals with low metamorphic grade, the well development of macropores and mesopores [32], and leads to a weaker ability of coal to stop oxygen adsorption at low moisture content. Therefore, the presence of appropriate low moisture content in the coal will make its oxygen consumption reach the maximum.

Stage 3 is the violent oxidation stage. From the figure, obviously, the violent oxidation stages of anthracite, fat coal, long flame coal and lignite are 160-260 °C, 180-260 °C, 140-260 °C, and 150-260 °C, respectively. In this stage, as the moisture for the four different metamorphic grade coals at four low moisture content basically fully evaporates and its inhibition gradually disappear, the porosity of the coal sample increases, and the contact surface area of the coal-oxygen composite reaction increases, resulting in a more dramatic coal-oxygen reaction in this stage. Since the full evaporation of moisture inside coal will not affect the oxygen absorption of the coal, the effect of low moisture content on the oxygen consumption are the same of those at Stage 2.

3.1.2. Analysis of CO and CO_2 production

Figure 5 and Figure 6 show the index gases CO and CO_2 produced in the four different metamorphic grade coals at four different low moisture content in the temperature programmed oxidation process.

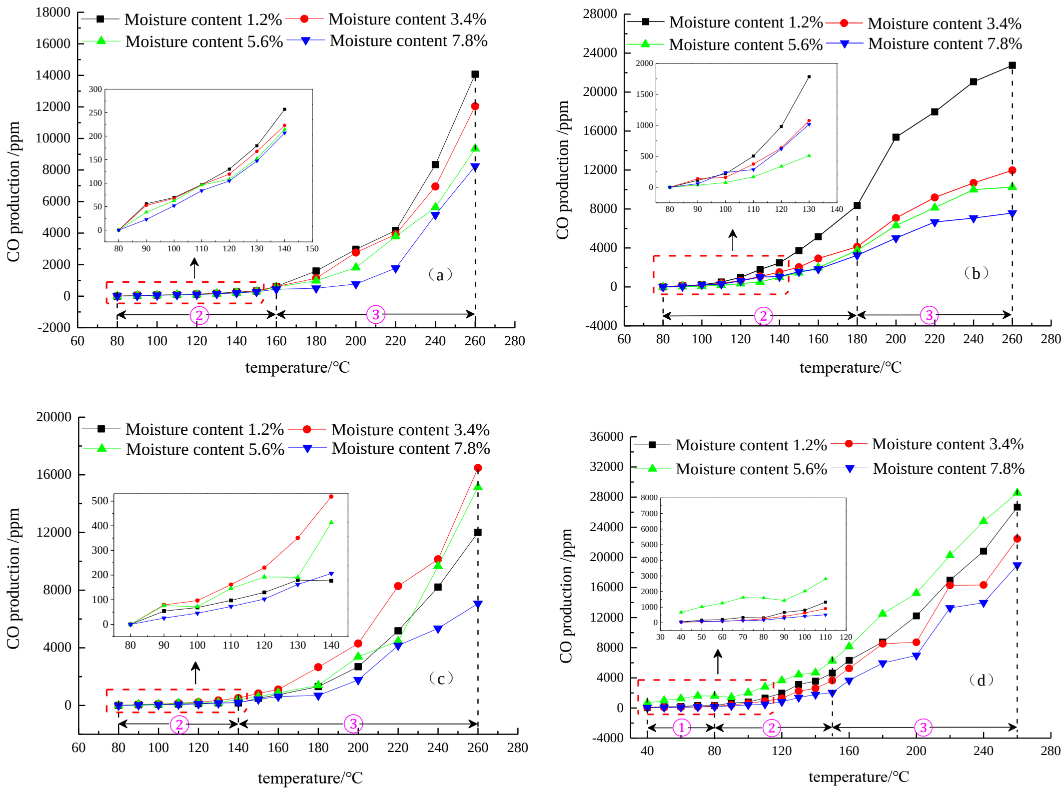

Figure 5. The curves of CO production for anthracite（a）, fat coal（b）, long flame coal（c）, lignite（d）at four different low moisture content. ① indicates the slow oxidation stage, ② indicates the rapid oxidation stage, and ③ indicates the violent oxidation stage

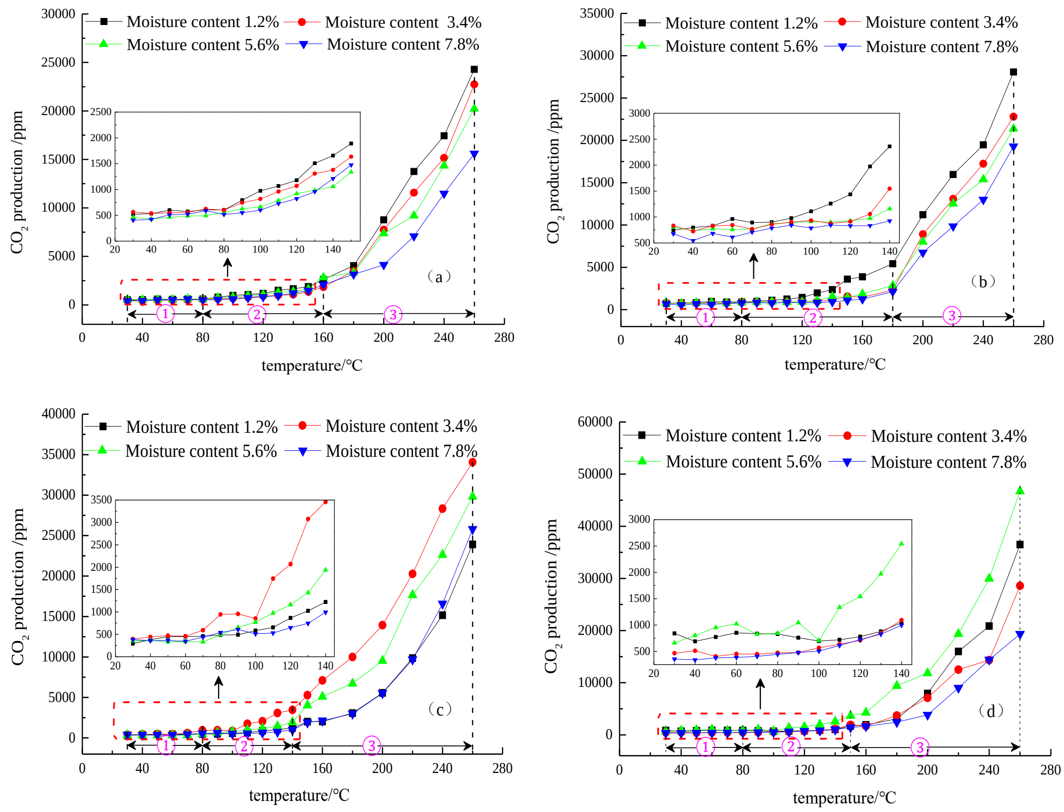

Figure 6. The curves of CO_2 production for anthracite (a), fat coal (b), long flame coal (c) and lignite (d) at four different low moisture content. ① indicates the slow oxidation stage, ② indicates the rapid oxidation stage, and ③ indicates the violent oxidation stage

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Figure 5 and Figure 6 clearly show that the productions of CO and CO_2 from the four different metamorphic grade coals at four different low moisture content have the same staging characteristics as their oxygen consumption in the same temperature ranges. But, anthracite, fat coal, and long flame coal did not produce CO in the slow oxidation stage until temperature rises to 80°C, while lignite to produce CO when temperature rises to 40°C. Overall, in the temperature programmed oxidation process, CO and CO_2 productions of the four different metamorphic grade coals with four different low moisture content always increase with the rise of temperature. In the slow oxidation stage, CO_2 production increases slowly, while in the rapid oxidation stage, CO and CO2 productions increase at a rapid speed, and in the violent oxidation stage, CO and CO_2 productions further increase without showing a slowdown trend. In the overall temperature programmed oxidation process, CO and CO_2 productions of anthracite and fat coal gradually decrease with the increase of their low moisture content and are the highest at moisture content of 1.2%. These results indicate that the two types of coal at moisture content of 1.2% undergo more violent oxidation reaction and show stronger self-ignition risks than other low moisture content coal samples. With moisture content increasing, CO and CO_2 productions from long flame coal and lignite at low moisture content does not show a single increase or decrease trend. At the inflection moisture content of 3.4% and 5.6%, respectively, long flame coal and lignite have the greatest spontaneous combustion risks than other low moisture content coal samples.

3.1.3. Maximum exothermic strength

The chemical bond energy method can be used to estimate the maximum exothermic strength, qmax(T) [33]:

$$q_{\max}(T)=\frac{V_{CO}^{0}(T)}{V_{CO}^{0}(T)+V_{CO_2}^{0}(T)}\cdot V_{O_2}^{0}(T)\cdot q_{co}+\frac{V_{CO_2}^{0}(T)}{V_{CO}^{0}(T)+V_{CO_2}^{0}(T)}\cdot V_{O_2}^{0}(T)\cdot q_{co_2} \tag{1}$$

Where $V_{co}^{0}(T)$ and $V_{co_2}^{0}(T)$ are the CO and CO_2 production rates at temperature T and oxygen concentration C_0, mol·cm^{-3}·s^{-1}; $V_{o_2}^{0}(T)$ is the oxygen consumption rate of the coal at the temperature T and oxygen concentration C_0, mol·cm^{-3}·s^{-1}; q_{co} is the average of heat released to produce one mol of CO, q_{co} =297.0KJ·mol^{-1}; q_{co_2} is the average of heat released to produce one mol of CO_2, q_{co_2} =446.7 KJ·mol^{-1}. And $V_{o_2}^{0}(T)$, $V_{co}^{0}(T)$ and $V_{co_2}^{0}(T)$ satisfy Eqs. (2), (3) and (4):

$$V_{O_2}^{0}(T)=\frac{Q\cdot C_0}{S\cdot L}\cdot\ln\frac{C_0}{C} \tag{2}$$

where Q is the input air flow rate, cm^3·s^{-1}; S is the cross-sectional area of the experimental furnace, cm^2; C_0 is the oxygen concentration at the inlet, 21%; C is the oxygen concentration at the outlet, %; L is the length of the test coal sample, cm; and C is the oxygen concentration, %.

$$V_{CO}^{0}(T)=\frac{V_{O_2}^{0}(T)\cdot C_{co}}{C_0\cdot\left(1-e^{-\frac{V_{O_2}^{0}(T)\cdot Vm}{Q\cdot C_0}}\right)} \tag{3}$$

$$V_{CO_2}^{0}(T)=\frac{V_{O_2}^{0}(T)\cdot C_{CO_2}}{C_0\cdot\left(1-e^{-\frac{V_{O_2}^{0}(T)\cdot Vm}{Q\cdot C_0}}\right)} \tag{4}$$

where C_{co} and C_{co_2} are CO and CO_2 concentrations at the outlet, ppm ; and V_m is the volume of the test coal sample, cm^3.

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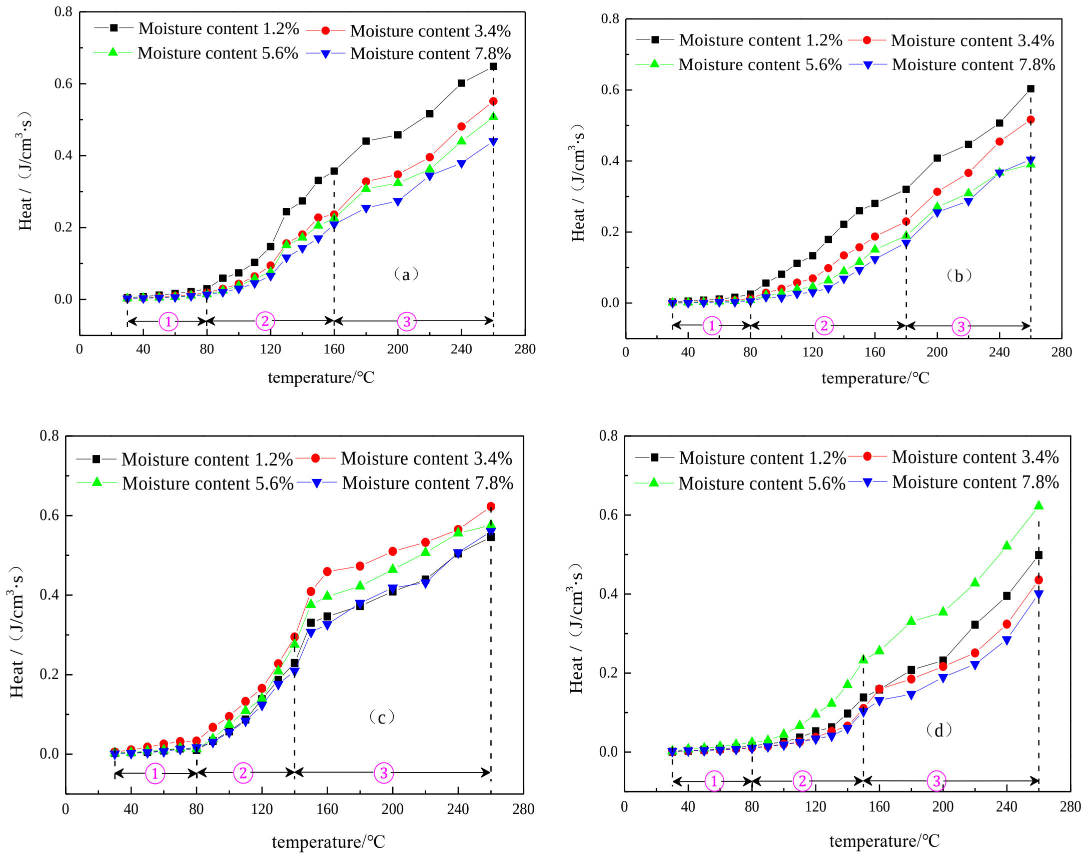

Figure 7. The curves of maximum exothermic strength for anthracite (a), fat coal (b), long flame coal (c) and lignite (d) at four different low moisture content. ① indicates the slow oxidation stage, ② indicates the rapid oxidation stage, and ③ indicates the violent oxidation stage

Figure 7 show the maximum exothermic strength calculated by inputting the data of four different metamorphic grade coals at four low moisture content measured in the temperature programmed oxidation process into Eqs. (1), (2), (3), and (4).

It is clear from Figure 7 that the maximum exothermic strength of the four different metamorphic grade coals at four low moisture content have the same staging temperature ranges as O_2, CO and CO_2 productions. In the slow oxidation stage, the maximum exothermic strength of coal samples differ slightly and barely affected by low moisture content. This phenomenon is caused by the fact that at a low temperature, both the physico-chemical adsorption of oxygen by coal and the wetting heat of moisture release heat, but this part of heat is relatively smaller. At the same time, at this stage, moisture in coal continuously undergoes slow evaporation and absorbs heat, the vapor pressure generated in the evaporation process will prevent oxygen from contacting coal to a certain extent [34], thereby reducing heat release. Subject to the joint effect of the above factors, although coal samples will release heat, its heat releasing is generally slower. In the rapid oxidation stage, the maximum exothermic strength from the four different metamorphic grade coals at four low moisture content show significant differences.

It is clear from Figure 7 that For anthracite and fat coal, their maximum exothermic strength gradually decrease with moisture content increasing, indicating that low moisture content hinders heat release from coal samples. The low moisture content of 1.2% facilitates the exothermic effect of coal. The lower the moisture content, the greater the exothermic intensity, and the stronger the promoting effect. Thus, a rise in coal sample temperature enhances the spontaneous combustion risk of coal. The reason is that on the one hand, it is related to the distribution of pores in coals with high or medium metamorphic grade. On the other hand, it may be the evaporation of moisture at this stage is large. Thus, the vapor pressure on the surface of the coal is high. As moisture evaporates, pores that are substantially exposed and the moisture-oxygen complex formed in the early stage also gradually exhibit an effect. Thus, under the influence of multiple factors, coal-oxygen composite reaction gradually slows down, leading to a drop in heat release. For long flame coal, its maximum exothermic strength shows a trend of increase before decrease with the increase of low moisture content, and at moisture content of 3.6%, its overall exothermic strength is the greatest. For lignite, its maximum exothermic strength displays a trend of decrease before increase then decrease again with the increase of low moisture content, and at moisture content of 5.4%, its overall exothermic strength is the highest. These phenomenons show that low moisture content have both hindrance and promotion effects on the heat released from coals with low metamorphic grade, the reason for which is related to the pore structure of coals with the low metamorphic grade. In the violent oxidation stage, with the complete evaporation of moisture in the coal, the inhibition gradually disappears and the porosity of the coal increases, resulting in an increase of the coal-oxygen contact area. Thus, as the reaction becomes violent, coal temperature further increases, the exothermic strength of the coal accordingly enhances, showing approximately an exponential growth trend. In this stage, the effects of different low moisture content on the maximum exothermic strength of each coal are the same as those in the previous stage.

3.2. The analysis for scanning calorimetric experiment results

Having studied the influence of four low moisture content on the spontaneous combustion characteristics of four different metamorphic grade coals in temperature programmed oxidation process, in order to further study the mechanism of this law, differential scanning calorimetry experiment was used for research [35].

3.2.1 The analyses of the zero point of heat flow difference and endothermic peak temperature

The DSC curves of the four different metamorphic grade coals at four low moisture content are shown in Figure 8. The DSC curve reflects the variation tendency of the heat flow difference with temperature during the temperature programmed oxidation process of coal. The curve abscissa represents the sample temperature and the ordinate represents the heat flow difference changes.

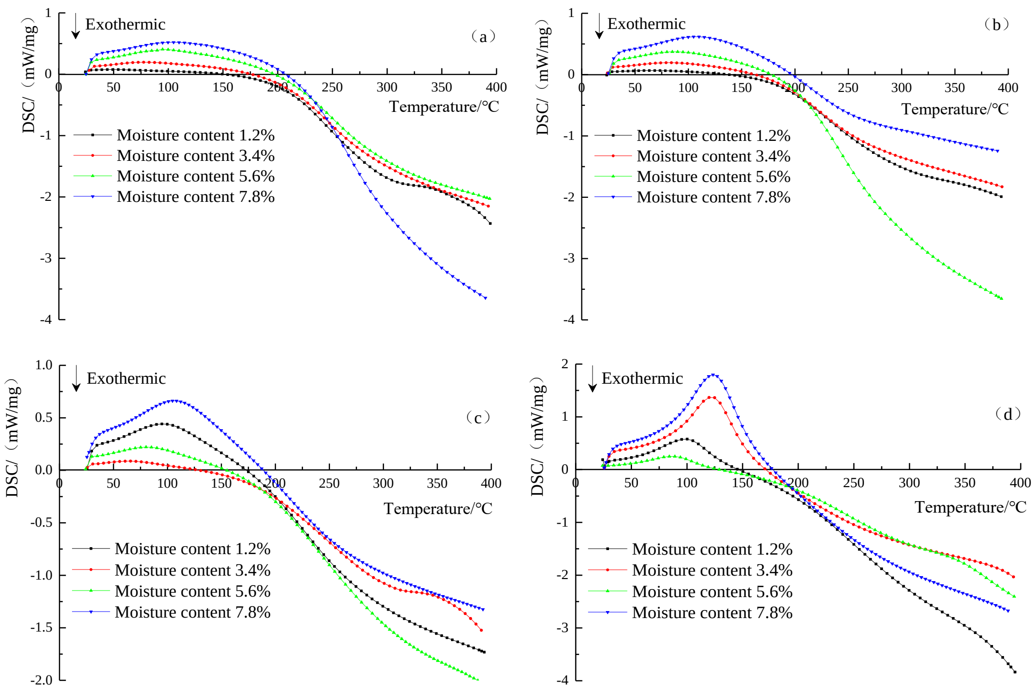

Figure 8. The DSC curves for anthracite (a), fat coal (b), long flame coal (c) and lignite (d) at four different low moisture content

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It is known from Figure 8 that the DSC curves of four different metamorphic grade coals at four low moisture content show a trend of gradually increasing to the peak before gradually decreasing. When the temperature gradually increases, the moisture in the coal gradually evaporates, and the coal absorbs heat. When the experimental temperature further increases, the degree of oxidation reaction of the coal is intensified, and the heat release is gradually increased. It can be clearly seen that the curve is divided into two main stages: namely the endothermic stage and the exothermic stage. The intersection of the curve and the abscissa is the zero point of the heat flow difference [36], that is, the corresponding temperature value when the heat absorption rate equals to the heat release rate. The zero point of heat flow difference is used as the critical point of the coal body between heat absorption and release. Before the zero point, the coal body is in an endothermic state, while after the zero point, the coal body is in an exothermic state. The zero point of heat flow difference and the endothermic peak temperature are important characteristic parameters for spontaneous combustion of coal. If the zero point of heat flow difference is in the stage of temperature oxidation of coal, its later appearance indicates that a longer time is needed for the coal body to reach the endothermic and exothermic transition stages, the heat release occurs in the later stage, the heat storage time is shortened, and the overall heat release of coal is reduced, which eventually cause coal to be less prone to spontaneous combustion. On the contrary, earlier appearance of the heat flow difference zero point means an earlier heat storage time and prolonged overall heat storage time. At this time, the coal is prone to spontaneous combustion. The endothermic peak temperature [37] is the inflection temperature that occurs when the heat flow difference of the coal heat absorption reaches the maximum value in the initial stage of the coal-oxygen compound reaction, and its value is related to the moisture evaporation and the exothermic reaction of the chemical reaction. According to Figure 8, the zero point of heat flow difference and the endothermic peak temperature of the four different metamorphic grade coals at four low moisture content are extracted, as shown in Figure 9.

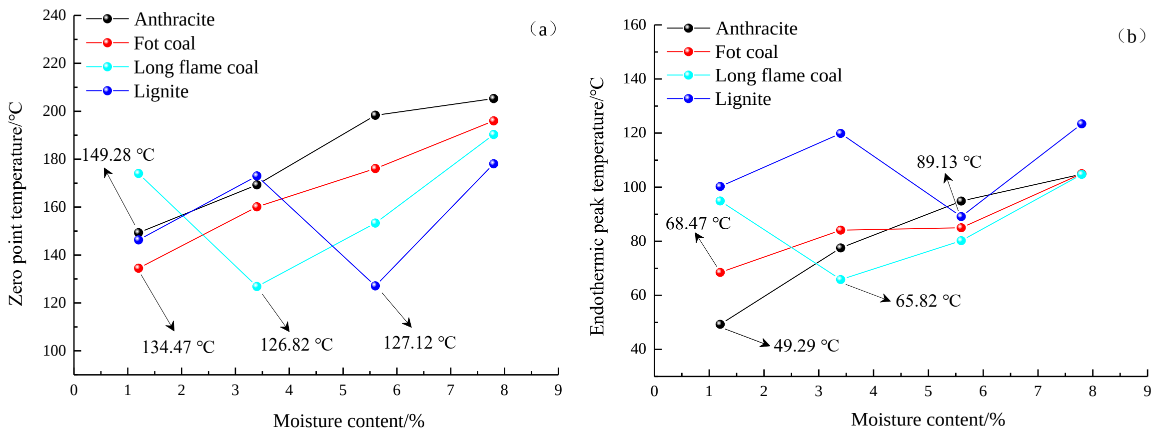

Figure 9. The curves of zero point temperature (a) and endothermic peak temperature (b) for anthracite, fat coal, long flame coal and lignite at four different low moisture content

It is known from Figure 9(a) and 9(b) that the zero point of heat flow difference and the endothermic peak temperature of anthracite and fat coal gradually increase with the increase of moisture content. At low moisture content of 1.2%, the zero point of heat flow difference and the endothermic peak temperature of anthracite and fat coal are the lowest, being 149.28°C and 134.47°C as well as 49.29°C and 68.47°C, respectively. As the moisture content increases, their zero point of heat flow difference appears later and later. At the same time, in combination with Figure 8 , it is known that the peak height and width corresponding to the endothermic peak temperature also increase, resulting in an increase in the endothermic peak area, an increase in total heat absorption, and a decrease in the overall heat release amount of the coal body. The results indicate that in the low moisture content stage, the higher the moisture content of the anthracite and fat coal, the more obvious the effect of inhibiting spontaneous combustion of the coal body. Compared with other low moisture content coal samples, anthracite and fat coal at moisture content of 1.2% is more likely to occur spontaneous combustion. The cause is that with the degree of coal's metamorphic grade increasing, the content of micropores greatly increases while the proportions of macropores and mesopores are relatively small. However, the macropores and mesopores in the coal body are the main channels for gas diffusing in and out of the coal particles. When the moisture content is low, water molecules occupy the porous surface of the coal, in favorable of oxygen absorption by coal. When the moisture content gradually increases, moisture occupies more macropores and mesopores in the coal body, which weakens the ability of coals to adsorb oxygen, reduces the internal surface area for coal and oxygen interaction, lowers the chemical burning rate, and hinders coal-oxygen composite reaction.

The zero point of heat flow difference and endothermic peak temperature of long flame coal show a trend of decreasing to the lowest value before increasing with the moisture content increasing. When moisture content increases, the zero point of heat flow difference and the endothermic peak temperature both have an inflection point, which is the lowest of 126.82°C and 65.82°C, at moisture content of 3.4%. The zero point of heat flow difference and endothermic peak temperature of lignite show a trend of increase to the peak value, followed by decrease to the lowest value and increase again with the moisture content increasing. When moisture content increases, the zero point of heat flow difference and the endothermic peak temperature also have an inflection point, which is the lowest of 127.12 °C and 89.13 °C, at moisture content of 5.6%. The results show that the effect of low moisture content on the spontaneous combustion characteristics of long flame coal and lignite does not show a single change trend. The optimal moisture content is 3.4% and 5.6%, respectively, which makes them prone to spontaneous combustion. The mechanism can be summarized as follows. For coals with low metamorphic grade, the proportions of macropores, mesopores and transition pores is relatively high, the average pore diameter is large, and the ability to adsorb oxygen is strong. At low moisture content, the pore surface of the coal occupied by water molecules is small. Thus, it is possible for the existence of specific moisture content, at which, oxygen adsorption is stronger than other low moisture content coal samples, so that the internal surface area for coal and oxygen interaction is greater. Thus, the chemical combustion rate increases. When the moisture content gradually increases, excess moisture will form a water film on the surface of the coal body to block oxygen. When a small amount of oxygen is adsorbed by the coal body, most of the released heat will be absorbed and consumed by the moisture, so that the heat around the coal body is difficult to accumulate, thereby delaying the temperature oxidation of the coal.

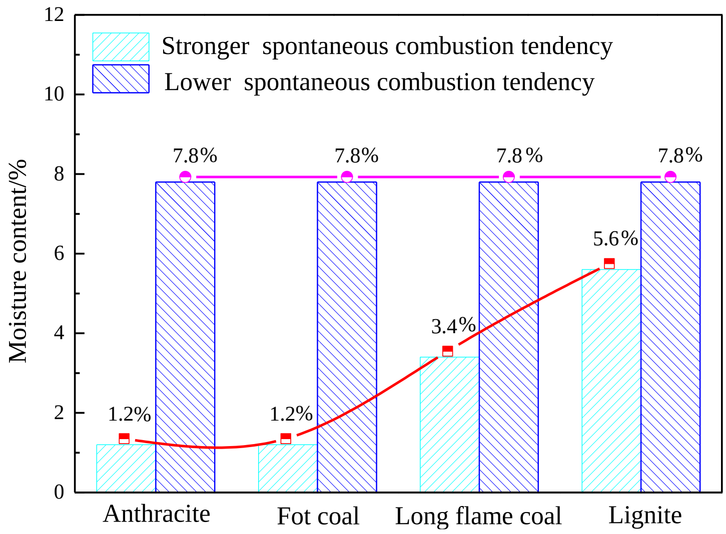

Figure 10. The curves of flammable moisture content and non-flammable moisture content for anthracite, fat coal, long flame coal, and lignite at four different low moisture content

As shown in Figure 10, anthracite, fat coal, long flame coal and lignite with low moisture content (1.2%, 3.4%, 5.6% and 7.8%) showed the strongest tendency to spontaneous combustion danger at moisture content of 1.2%, 1.2%, 3.4%, and 5.6%, and the lest tendency to spontaneous combustion danger at moisture of 7.8%. In other words, the moisture content of coals that are lest prone to spontaneous combustion danger is the highest among the four different low moisture content. This

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is because that water molecules occupy most pores on the surface of coals with the possible highest moisture content, forming an aqueous liquid film. This film together with the high vapor pressure in coal act as an oxygen barrier. In addition, most heat released by oxidation reaction of the coal body at low temperature will be absorbed by the water evaporation, which reduces the calorific value of the coal as a whole, making it difficult to accumulate the heat around the coal body, and prolonging the incubation period of coal spontaneous combustion.

3.2.2 The analyses of zero point of heat flow difference at the same low moisture content

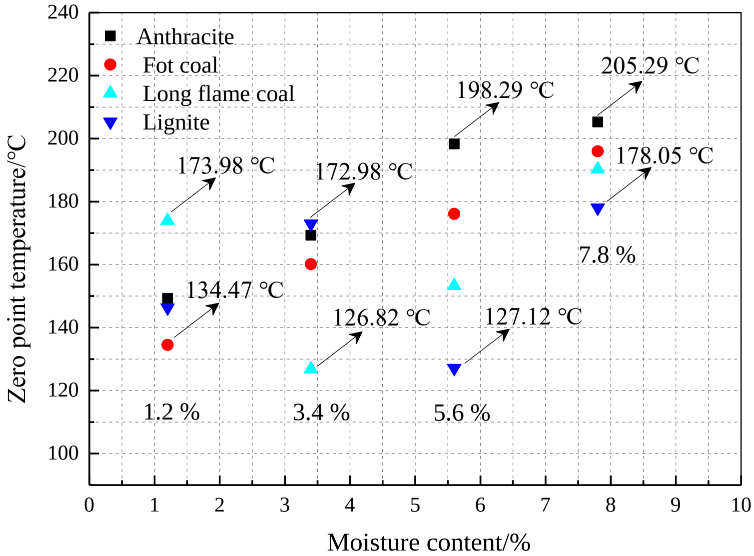

Figure 11. Comparison of the zero point of heat flow difference for anthracite, fat coal, long flame coal and lignite at the same low moisture content

Figure 11 compares the zero point of heat flow difference of the four different metamorphic grade coals at the same low moisture content. It can be seen from the figure that at moisture content of 1.2% and 3.4%, long flame coal and fat coal had the lowest zero point of heat flow difference of 134.47°C and 126.82°C, and anthracite and lignite had the highest zero point of heat flow difference of 173.98°C and 172.98°C, indicating that at the moisture content of 1.2% and 3.4%, the fat coal and the long flame coal show a stronger tendency to spontaneous combustion, and the long flame coal and lignite show the low spontaneous combustion tendency. Figure 11 also shows that at moisture content of 5.6% and 7.8%, lignite had the lowest zero point of heat flow difference of 127.12°C and 178.05°C, and anthracite had the highest zero point of heat flow difference of 198.29°C and 205.29°C, indicating that at moisture content of 5.6% and 7.8%, lignite was more prone to spontaneous combustion and anthracite was less spontaneous combustion. Overall, the above analyses showed that coals with different metamorphic grade had different spontaneous combustion tendency at the same low moisture content. In addition, the same coal body at different low moisture had different tendency to spontaneous combustion. Moreover, at the same low moisture content, with moisture gradually increasing, lignite was the most prone to spontaneous combustion [38] and anthracite was the least prone to spontaneous combustion.

4. Conclusions

The characteristics of spontaneous combustion of four different metamorphic grade coals at four low moisture content were studied in the temperature programmed oxidation experiment and differential scanning calorimetric experiment. The following conclusions are obtained.

At low moisture content, with moisture content increasing, the zero point of heat flow difference of anthracite and fat coals appears later, endothermic peak area increases, overall heat release decreases, and risk of spontaneous combustion weakens. When the moisture content is 1.2%, anthracite and fat coal show a stronger tendency of spontaneous combustion. By contrast, long flame

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coal and lignite are more prone to spontaneous combustion when the moisture content is 3.4% and 5.6%. When the moisture content is 7.8%, all of the four types of coals have low tendency of spontaneous combustion. In order to prevent the spontaneous combustion of coal, the moisture content of the coal should be kept at a high level.

At the same low moisture content, the coals with different metamorphic grade have different spontaneous combustion tendency and do not exhibit certain regular characteristics. At low moisture content, with moisture content increasing, of the four types of coals, lignite is most prone to spontaneous combustion and anthracite is least prone to spontaneous combustion.

The temperature programmed oxidation process of four different metamorphic grade coals at four low moisture content have experienced three similar stages: slow oxidation stage, rapid oxidation stage and violent oxidation stage, but at different temperature ranges. In the three different oxidation stages, the oxygen consumption of anthracite and fat coal decreased with the increase of low moisture content, and coal samples at moisture content of 1.2% consumed the most oxygen. By contrast, long flame coal and lignite at moisture content of 3.4% and 5.6%, consumed most oxygen consumption in the three stages.

During the overall temperature oxidation process, the production of CO and CO_2 and the maximum exothermic strength of anthracite and fat coal at low moisture content gradually decrease with moisture increasing. When the moisture content is 1.2%, the amount of CO and CO_2 production and the exothermic strength are higher than those at other low moisture content, showing a stronger risk of spontaneous combustion. Long flame coal and lignite at moisture content of 3.4% and 5.6%, produce more CO and CO_2 and possess higher exothermic strength than other low moisture content coal samples and are more prone to spontaneous combustion.

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