Experiment analysis of relationship between oxygen concentration and coal oxidation characteristics

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Abstract
This paper had experiments on lignite and bituminous coal, respectively. The characteristic temperature points were obtained at the oxygen concentration of 5%、10%、15%、17%、21% and 30% when the heating rate was 10K/min, respectively. The coal ignition decreased as oxygen concentration increased. Coats-Redfern integral formula was utilized to calculate the activation energy from ignition temperature to end temperature of the combustion. It revealed that the activation energy increased along with oxygen concentration increasing. And the activation energy of lignite was less than bituminous coal, and spontaneous combustion of lignite occurred more easily. For the same coal sample, TG curve drifted to the left with the increase of oxygen concentration. It indicated that within a certain range the increase of the oxygen concentration shorted the reaction time, the coal sample was more likely to catch fire.
Key words: TG, TG-CURVE, OXYGEN CONCENTRATION, ACTIVATION ENERGY, COAL SPONTANEOUS COMBUSTION

Introduction

Coal resources is an important source of energy in China. At the same time mine fire is one of the major natural disasters in coal mines. According to statistics, more than 90% of coal mine fires are caused by coal spontaneous combustion [1].Therefore, analysis of mechanism and prevention measures of coal spontaneous combustion is very important. Spontaneous combustion of coal is affected by internal and external factors. Some scholars have analyzed the relationship of absorbed oxygen with moisture, ash, volatile, relative density and total sulfur, and found that coal spontaneous combustion tendency was related to absorbed oxygen [2]. Hanwen Huang et al. [3] utilized the lead adiabatic simulation method to determine ignition point of coal spontaneous combustion, analyzed the relationship of ignition point with oxygen concentration, drying desorption, inhibition process coal types. They also put forwards spontaneous combustion temperature point as an index for the tendency of coal spontaneous combustion. Some scholars [4] used adiabatic oxidation experiments, ultimate analysis experiments and proximate analysis experiments to analyze the relationship of C, H, O, N and S with critical points of spontaneous combustion, obtained that the lower *Tr0.05*, the faster coal was heated up. Coal was getting spontaneous combustion more easily. Some other scholars obtained the conclusion that oxygen consumption rate of coal was affected by oxygen concentration through program heating experiments when loose coal was supplied different oxygen concentration. But the oxygen concentration had no obvious effect on the trend of oxygen consumption rate as it varied with temperature [5]. Since the activation energy can be used as indicators for coal spontaneous combustion tendency and spontaneous combustion of coal is a complex process of physical and chemical reactions, there are many factors which affect the reaction of coal with oxygen. Nowadays the domestic and foreign scholars have got some achievements in scientific research about the relationship of coal spontaneous combustion tendency and various factors [6-9], but the effect of oxygen concentration on coal spontaneous combustion is not very deep. In this paper, TGA method was utilized to product the kinetic experiments of lignite and bituminous coal in different oxygen concentrations, and then activation energy was calculated to analysis the effect of oxygen concentration on coal spontaneous.

Preparation of coal sample and TG experiments

The coal samples of experiments are lignite and bituminous coal, respectively. A large lump was crushed to become coal particles with a grain size of 180 μm (80 mesh). The proximate analysis is shown in table 1. The mass of coal sample for each experiment is about 10 mg. The test equipment is STA449F3 thermal analyzer. The experimental temperature range is from room temperature to 1000 ℃. The heating rate is 10 K/min. The gas atmosphere of reaction is a mixture of nitrogen and oxygen, in which the oxygen concentration (volume fraction) is 5%, 10%, 15%, 17 %, 21% and 30%, respectively. The aeration rate is 20 ml/min.

Table 1. Proximate analysis of coal samples

Coal sample	moisture	Volatile matter	Ash	Fixed carbon
Lignite	5.7	30.23	11.34	52.68
Bituminous coal	1.26	12.95	8.07	77.72

Results and discussion

Characteristic temperature and oxygen concentration

Fig.1 shows the TG-DTG curves of lignite when the heating rate is 10 K/min and the oxygen concentration is 21%. In Fig.1, T_1 is the critical temperature. At T_1, DTG curve reaches the first maximum weight loss rate. T_2 is the dry temperature of coal sample. At this temperature the weight loss of coal sample reaches a minimum value before the ignition temperature. T_3 is the active temperature, at which the coal sample starts to gain weight as the coal weight keeps constant from dry temperature (T_2). T_4 is the growth rate temperature of coal. At T_4, the weight loss rate reaches the minimum value while the weight gain rate reaches the maximum value. T_5 is devolatilization temperature where coal mass ratio reaches a maximum value. T_6 is the ignition temperature of coal and coal begins to burn. T_7 is the temperature of maximum weight loss rate of coal in the whole process of combustion. T_8 is end temperature and the process of coal combustion terminates.

According to the experimental results, the shape of TG-DTG curves of bituminous coal is basically similar with the lignite. But the slope of the curves is different. Thus the characteristic temperature (T1-T8) is different. The characteristic temperature values of the two coal samples at heating rate of 10 K/min with oxygen concentration of 5%, 10%, 15%, 17%, 21% and 30%, respectively, are shown in Table 2.

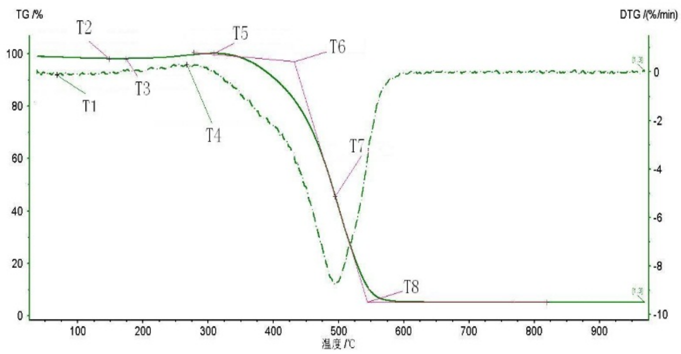

Figure 1. TG-DTG curves of lignite coal sample

Table 2. Characteristic temperatures of coal at different oxygen concentrations

Coal sample	Oxygen concentration (%)	Characteristic temperatures (℃)							
		T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8
Lignite	5	76	179	189	221	294	460.7	584.7	666.9
	10	105	164	180	243	301	444.3	542.7	596.3
	15	108	160	183	245	295	440.0	524.2	565.8
	17	107	159	174	260	284	434.4	506.0	554.0
	21	87	160	175	249	289	432.1	502.4	541.5
	30	107	152	174	239	288	417.6	459.9	525.1
Bituminous coal	5	175	188	203	328	369	537.5	617.5	738.3
	10	75	95	114	331	367	517.9	581.9	654.5
	15	125	128	146	316	359	504	551.6	618.5
	17	131	170	178	311	356	499.8	542.0	604.7
	21	102	122	127	310	356	493.4	532.9	587.3
	30	101	159	175	295	352	480.8	512.3	561.0

Table 2 shows that at the same oxygen concentration, ignition temperature T_6 of bituminous coal is higher than lignite. Combined with Table 1, the volatile matter of lignite is 30.23%, which is 17.28% higher than bituminous coal, thus the ignition of lignite is lower than bituminous coal. It conforms the laws that coal with higher volatile matter are more prone to spontaneous combustion [10]. For one same sample, with the increase of oxygen concentration, the ignition of coal shows a decreasing trend. It is because the physical and chemical oxygen adsorption and reaction are getting faster, the reaction time is shortened. So the higher the oxygen concentration, the lower the ignition point of coal.

Activation energy and oxygen concentration

The minimum energy required by coal oxidation reaction is called activation energy, and the value of activation energy decides the reaction rate of coal oxidation [11]. It indicates the tendency of coal spontaneous combustion. Coal oxidation decomposition is a typical gas-solid reaction. In this paper, the carbon conversion rate of coal gasification process can be expressed as:

$$\alpha = \frac{(m_0 - m)}{(m_0 - m_\infty)} \qquad (1)$$

Where m_0 is the initial mass of coal sample, mg; m is mass of coal sample at T(t), mg; m_∞ is coal sample mass when the reaction is over, mg.

Thermogravimetric dynamic is utilized to calculate the activation energy of coal, according to Coats-Renfern integral formula:

$$\ln\left|\frac{g(\alpha)}{T^2}\right| = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (2)$$

Where $g(\alpha)$ is a integral function concerning the mechanism of coal oxidation [12]; T is temperature, K; A is pre-exponential factor, K/s; β is the heating rate, in this paper it is 10 K/min. E is activation energy, J/mol; R is gas constant, 8.314 J/(K·mol).

As the reaction of coal with oxygen belongs to a first order reaction, $g(\alpha)$=-ln(1-α), then equ.2 can be expressed:

$$\ln\left|\frac{-\ln(1-\alpha)}{T^2}\right| = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RE}{E}\right)\right] - \frac{E}{RT} \qquad (3)$$

For general reaction zone and most of E values, $\frac{E}{RT}$ is much larger than 1, so $\left(1 - \frac{2RT}{E}\right) \approx 1$, therefore equ.3 can be simplified as:

$$\ln\left|\frac{-\ln(1-\alpha)}{T^2}\right| = \ln\frac{AR}{\beta E} - \frac{E}{RT} \qquad (4)$$

Data is plotted when $\ln\left|\frac{-\ln(1-\alpha)}{T^2}\right|$ is the ordinate and $\frac{1}{T}$ is the abscissa. In this paper, the activation energy of lignite coal sample at oxygen concentration of 21% is taken as an example to save paper space, shown in Fig. 2. The activation energy of 2 coal samples at different oxygen concentrations can be obtained through calculation, shown in Table 3.

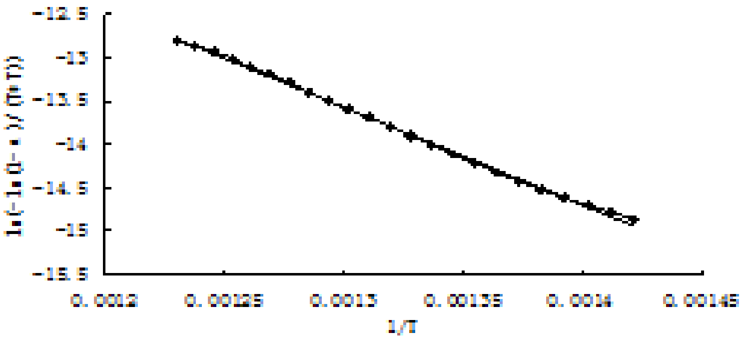

Figure 2. Kinetic linear correlation analysis of lignite at oxygen concentration of 21%

Table 3. Activation energy of coal samples at different oxygen concentrations

Oxygen concentration (%)	Activation energy E (KJ·mol-1)	
	Lignite	Bituminous coal
5	58.2047	85.8254
10	73.2937	111.9563
15	84.3289	127.0213
17	88.4194	131.6771
21	93.3247	141.8701
30	100.0174	155.5716

Combined with Table 1 and Table 3, it indicates that at the same oxygen concentration, the activation energy of lignite is smaller than bituminous coal. This is because that the content of volatile matter in lignite is higher than in bituminous coal while the fixed carbon content is lower in lignite. The lower the volatile matter content in coal, the activation energy of coal is larger. Vice versa. Table 2 and Table 3 indicate that for one coal sample, the ignition temperature T6, the maximum combustion rate temperature T7 and the end temperature T8 decrease with the oxygen concentration increasing from 5% to 30%. At high temperature, the reactive groups in coal are more readily activated to react with oxygen. Thus the activation energy of coal oxidation at high temperature is less. Taking lignite as an example in this paper, the activation energy calculated when the oxygen concentration is 5% is 41.8127 KJ/mol less than the value calculated when the oxygen concentration is 30%. As a result, for one coal sample, the activation energy increases along with the oxygen concentration increasing.

Coal oxidation and oxygen concentration

Fig.3 and Fig.4 shows the TG curve of two coal samples at different oxygen concentrations, respectively. Before the weight loss of coal begins, the effect of oxygen concentration on TG curves is very small. 6 TG curves substantially coincide together. When the temperature reaches the ignition and coal starts to burn, the weight of coal lost fast and TG curve starts to move to the left. This is because with the increase of oxygen concentration, coal can absorb oxygen to react adequately. The reaction rate increases, thus shortens the time of coal oxidation. Finally TG curves appear leftward drift phenomenon.

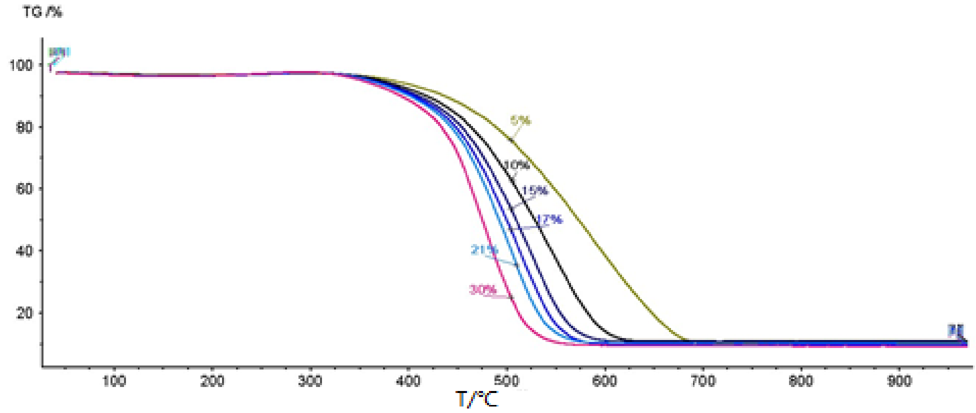

Figure 3. TG curves of lignite at different oxygen concentrations

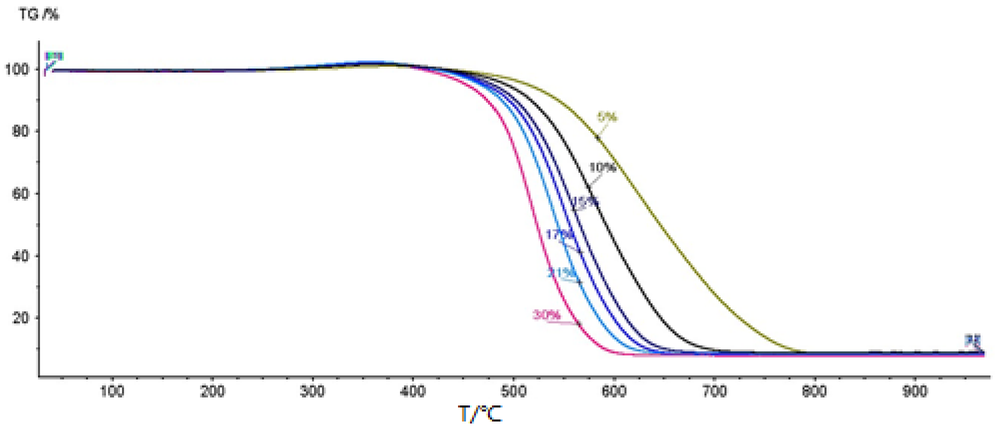

Figure 4. TG curves of bituminous coal at different oxygen concentrations

Conclusion

Characteristic temperatures of the two coal samples are found out in this paper. Ignition of bituminous coal is higher than lignite when the 2 coal samples are at the same oxygen concentration. The reason is that the content of volatile matter in lignite is higher. Lignite starts to burn more easily than bituminous coal. For one coal sample, T_5-T_8 decrease with oxygen concentration increasing but there is no obvious change in T_1-T_4.

The activation energy of coal are calculated by Coats-Renfern integral formula. Through comparison of the 2 coal samples, it indicates that activation energy of lignite is smaller than the activation energy of bituminous coal. That is lignite is more prone to spontaneous combustion. For one coal sample, the activation energy increases along with the increases of oxygen concentration. In a certain range of oxygen concentration, the activation energy is getting larger when the oxygen concentration increases.

At the heating rate of 10 K/min, with the increase of oxygen concentration from 5% to 30%, TG curves of coal samples shift to the left and the combustion time is shortened. But with the increase of oxygen concentration, the ignition of coal, the maximum combustion rate and the end temperature of combustion decrease, respectively, while the activation energy increases instead of decrease. Therefore, in order to suppress spontaneous combustion of coal, simply reducing the oxygen content of the surrounding environment cannot play a role. It should be considered synthetically.

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