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Thermal and kinetic characteristics of combustion of coal sludge

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Abstract The combustion characteristics of coal sludge were investigated with thermogravimetric analysis at different heating rates (10, 20, 30, 40 °C min^{-1}). The influences of heating rates on the combustion behavior of coal sludge were studied. The research found that the value of general combustion parameters for Taiyuan coal sludge (TY) is the lowest, for Shuozhou coal sludge (SZ) is the highest, and for Jincheng coal sludge (JC) is in middle at any heating rate. The experimental results indicated that a higher heating rate is useful for the combustion performance of coal sludge in this study. Kinetic parameters of the coal sludge samples were evaluated with the Ozawa–Flynn–Wall (OFW) and distributed activation energy model (DAEM) method. The activation energy values obtained from the DAEM method are a little lower than the ones obtained from the OFW method for every kind of coal sludge. The activation energy values of JC were 119.62 and 113.63 kJ mol^{-1} obtained by OFW and DAEM methods, respectively, and were lower than corresponding values of TY and SZ. Higher amounts of alkaline metal (Na and K), alkaline earth metals (Ca and Mg), Fe and Ti in JC may play a major role in lowering the activation energy values. The present results have important significance for understanding the characteristics of combustion of coal sludge.

Keywords Coal sludge · Thermal analysis · Kinetics · Combustion

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Introduction

Coal sludge is the by-product of coal washing and selecting process, and its production is about 10–20% of raw coal [1]. With the development of coal industry and the improvement of the coal mechanized mining technology, the quantity of coal sludge has been increasing. And the more coal production, the more coal sludge to be generated. A large amount of coal sludge occupies land and causes serious environmental pollution of air, water and soil. However, coal sludge utilization is inefficient due to its inherent disadvantages such as high ash content, high moisture and so on. Hence, how to dispose coal sludge is still a rigorous problem for coal industry. Coal sludge combustion is one of important ways of its utilization right now. Therefore, research on combustion behavior of coal sludge should be conducted comprehensively for increasing its combustion efficiency and decreasing fuel gas emission.

Thermogravimetric analysis is a traditional and one of the most widespread techniques and has been broadly used for studying the combustion behavior of coal. The advantages of thermogravimetric analysis are its rapid assessment of combustion parameters such as ignition temperature, burnout temperature, maximum rate of mass loss, the general combustion parameter and so on. And thermogravimetric analysis is useful for studying the kinetics of combustion processes. Kok [2] used differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG) to obtained information on the temperature-controlled combustion characteristics of seventeen coals. And the activation energies of the samples were varied in the range of 54–92 kJ mol^{-1}. Elbeyli et al. [3] studied the thermal characteristics and kinetic parameters of cleaned Tunçbilek lignite. They concluded that activation energy values of combustion and pyrolysis reactions were 34.53 and 29.24 kJ mol^{-1}, respectively. Özbas and Kök [4] investigated the effect of heating rate of the thermal properties and kinetics of raw and cleaned coal samples basing on thermogravimetry (TG/DTG) at different heating rates (5, 10, 15 and 20 °C min^{-1}). And for all of the coal samples, higher peak and burnout temperatures were measured with an increasing heating rate. The activation energies of all of the samples were affected inversely as the heating rate was increased. Altun et al. [5] investigated the combustion properties of the lignite, and different binders were analyzed by thermogravimetric (TG/DTG) methods. It was observed that molasses and carboxyl methylcellulose may decrease the residue content at the end of the combustion period. Ren et al. [6] studied combustion characteristics of coal gangue under different atmosphere using TG and tube reactor tests. The results showed that ignition temperature, burnout temperature and peak temperature increase, while the maximum and average combustion rates decrease with decreasing O_2 concentrations and the activation energy values of coal gangue combustion varied from 117.6 to 137.4 kJ mol^{-1} under different atmospheres.

Nevertheless, previous studies have been used the application of thermal analysis to evaluate combustion properties and kinetic of lignite, bituminous, anthracite, coal gangue and their blends [7–12], there are very little studies in the literature on coal sludge combustion characteristics.

In this study, three different types of coal sludge with various volatile contents, ash contents and fixed carbon were chosen to perform TG experiments. And combustion characteristic parameters like ignition temperature, burnout temperature and maximum mass loss rate were deduced from the TG–DTG curves. Furthermore, by performing TG analysis at different heating rates, a kinetic estimate of the coal sludge combustion process using Ozawa–Flynn–Wall (OFW) and distributed activation energy model (DAEM) iso-conversional methods was carried out to calculate the activation energy of the coal sludge. The results can provide a useful basis for further utilizing coal sludge with high efficiency.

Materials and methods

Coal sludge samples

Three kinds of coal sludge from different places were selected for this study, including Taiyuan coal sludge (TY), Jincheng coal sludge (JC) and Shuozhou coal sludge (SZ). All these coals are typical in Shanxi in North China. The coal sludge samples were dried in air, then were grinded and sieved to obtain particle with size smaller than 74 μm for experiments. The data for the corresponding proximate and ultimate analysis are listed in Table 1. The ash composition analysis of the coal sludge samples is shown in Table 2.

The ash yield of TY (53.71 mass%) is higher than that of JC (28.9 mass%) and SZ (27.08 mass%). Furthermore, SZ yields higher amount of volatiles (26.98 mass%) than TY (18.93 mass%) and JC (18.78 mass%). However, the fixed carbon of JC (51.31 mass%) is higher than that of SZ (44.87 mass%) and, especially, than that of TY (26.33 mass%).

TG analysis

The combustion characteristics of coal sludge were studied in a thermogravimetric analyzer (Pyris1, PerkinElmer Co). Coal sludge sample was placed in a Pt crucible and was burned under an air atmosphere, with an air flow rate of 60 mL min^{-1}, the furnace temperature was increased from the ambient temperature to 1000 °C. Each coal sludge sample was tested at four different heating rates of 10, 20, 30 and 40 °C min^{-1}. In every test, about (6 ± 0.1) mg sample was loaded into the silver crucible. At these conditions, the residues left in the crucible after combustion were formed by loose particles, which indicate that there was no sign of melting behavior caused by mass and heat transfer limitation [13]. The corresponding thermogravimetric (TG) and the differential thermogravimetric (DTG) combustion curves were recorded continuously as a function of temperature and time during the heating run. The experiments were performed at least three times under identical conditions in order to assure reproducibility of the results for each sample of each heating rate. And the error was acceptable.

Determination of characteristic parameters

Several characteristic parameters were used in this work to evaluate the combustion properties of the coal sludge samples. These characteristic parameters including the ignition temperature (T_i); the burnout temperature (T_b); the maximum mass loss temperature (T_{max}); and the maximum mass loss rate (DTG_{max}).

The ignition temperature (T_i) is described in Fig. 1, and it is identified as following way [14, 15].

Through the DTG peak point A, a vertical line was made upward to meet the TG curve at point B. Then, a tangent line of TG curve was made at point B, which met the extended TG initial level line at point C. Finally, another vertical line was made downwards through point C, which met the cross axle at point D. And the corresponding temperature of point D was the ignition temperature, T_i.

Table 1 Properties of coal sludge

Sample	Proximate analysis/mass% (air dried basis)				Ultimate analysis/mass% (air dried basis)					HHV/MJ kg^{-1}
	M_{ad}	V_{ad}	A_{ad}	FC_{ad}	C	H	O	N	S	
TY	1.03	18.93	53.71	26.33	29.95	2.90	9.88	1.64	0.89	11.32
JC	1.01	18.78	28.9	51.31	58.07	3.44	6.28	1.01	1.29	28.38
SZ	1.07	26.98	27.08	44.87	52.75	3.7	12.71	1.49	1.20	22.55

M moisture content, *V* volatile matters, *A* ash, *FC* fixed carbon, *HHV* high heat value

Table 2 Ash composition of coal sludge samples/mass%

Sample	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	P_2O_5	TiO_2	SiO_2
TY	32.49	2.49	3.03	1.42	0.58	0.16	0.21	1.1	55.92
JC	28.45	3.58	7.48	1.95	0.65	0.19	0.08	1.53	53.24
SZ	36.99	2.58	5.01	0.89	0.60	0.15	0.27	1.02	45.77

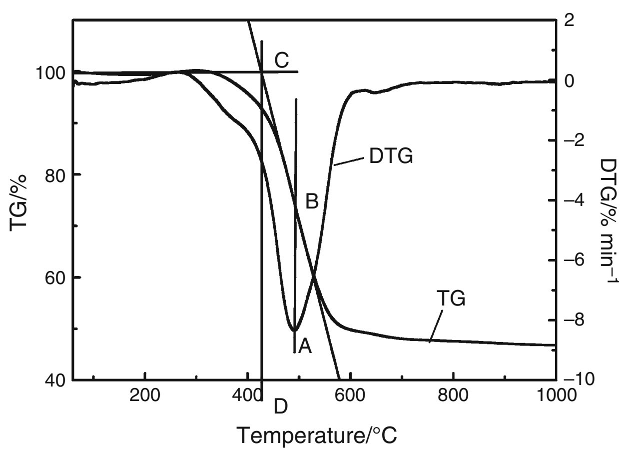

Fig. 1 Ignition temperature (T_i) definition sketch

The burnout temperature (T_f) was defined as the temperature at which the DTG curve reaches a 1% combustion rate at the end of the curve [16].

The maximum mass loss rate (DTG_{max}) was the mass loss rate of the DTG peak point, and the maximum mass loss temperature (T_{max}) was the corresponding temperature.

Furthermore, there was integration parameter, the general combustion parameter S.

The general combustion parameter S was used to reflect combustion reactivity of the whole combustion process. It was calculated by Eq. (1).

$$S = \frac{DTG_{max} \times DTG_{mean}}{T_i^2 \times T_f} \quad (1)$$

where DTG_{max} and DTG_{mean} were the maximum and mean combustion rates, T_i was the ignition temperature, and T_f was the burnout temperature.

The coal sludge with higher value of S has better combustion performance [17].

Kinetic methods

Coal sludge combustion is greatly complex processes.

The rate of heterogeneous solid- state reaction can be expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

where α is the conversion degree, *t* is the time, *T* is the temperature, *k*(*T*) is the temperature dependent constant, and *f*(α) is a function that depends on the reaction model. α could be calculated from data obtained in the TG analysis, according to Eq. (3)

$$\alpha = \frac{m_o - m}{m_o - m_\infty} \quad (3)$$

where m_o and m_∞ are the mass at the beginning and at the end of the combustion, respectively. While *m* is the mass at temperature *T*.

The explicit temperature dependence of the rate constant is introduced by replacing *k*(*T*) with the Arrhenius equation which gives

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \quad (4)$$

where *A* is the pre-exponential factor, *E* is the activation energy, and they are Arrhenius parameters. *R* is ideal gas constant, and $R = 8.314$ J mol^{-1} K^{-1}. When the heating rate $\beta(\beta = dT/dt)$ remains constant, the above expression can be transformed into the following equation with a constant β inserted:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{5}$$

The integral form of the non-isothermal rate law is produced by integrating the differential non-isothermal rate law:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta}\int_{T_0}^{T} e^{-\frac{E}{RT}} dT \tag{6}$$

where $g(\alpha)$ is the integral function of conversion and T_o is the initial temperature of the combustion reaction.

The kinetics of combustion reactions can be determined by single-scan methods (model-fitting methods) and multiple-scan methods (iso-conversional methods). Compared to model-fitting methods, using iso-conversional methods, the influence from mass transfer is reduced by using different heating rates, and the mechanism is allowed to be changed during the course of the reaction [18, 19]. The OFW method and the DAEM method are both the representatives of the iso-conversional methods.

According to non-isothermal iso-conversional methods applied by Ozawa [20], Wall and Flynn [21] using the Doyle's approximation of *p(x)* [22],the activation energy can be determined by measure the temperature corresponding to fixed values of α from experiments at different heating rates.

The equation for OFW model is showed in following:

$$\ln\beta = \ln\left[\frac{AE}{g(\alpha)R}\right] - 5.331 - 1.052\frac{E}{RT} \tag{7}$$

From this equation, we know that the activation energy can be obtained from the slope of the resulting straight line without specifically knowing reaction mechanism by plotting $\ln\beta$ versus $1/T$.

The equation for DAEM model is showed in following [23]:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) + 0.6075 - \frac{E}{RT} \tag{8}$$

From this equation, both the activation energy can be estimated from the slope of the resulting straight line by plotting $\ln\left(\frac{\beta}{T^2}\right)$ versus $1/T$.

In order to calculate reaction order, Avrami theory [24–26] is employed so as to describe the non-isothermal data where the variation of the degree of conversion with temperature and heating rate can be described as

$$\alpha(T) = 1 - \exp\left[-\frac{k(T)}{\beta^n}\right]. \tag{9}$$

Taking double logarithm of both sides of Eq. (2) with $k(T) = Ae^{-E/RT}$, gives

$$\ln[-\ln(1-\alpha(T))] = \ln A - \frac{E}{RT} - n\ln\beta \tag{10}$$

At the same temperature, by plotting $\ln[-\ln(1-\alpha(T))]$ versus $\ln\beta$ at different heating rates, the reaction order can be determined from the slope of the straight line.

Result and discussion

Combustion characteristics of coal sludge

Thermogravimetric analysis of coal sludge

The TG and DTG curves obtained from the temperature-programmed combustion of three kinds of coal sludge at the heating rate of 20 °C min^{-1} are shown in Fig. 2.

As shown in Fig. 2a, with the rise of temperature, combustion of coal sludge samples accompany with mass

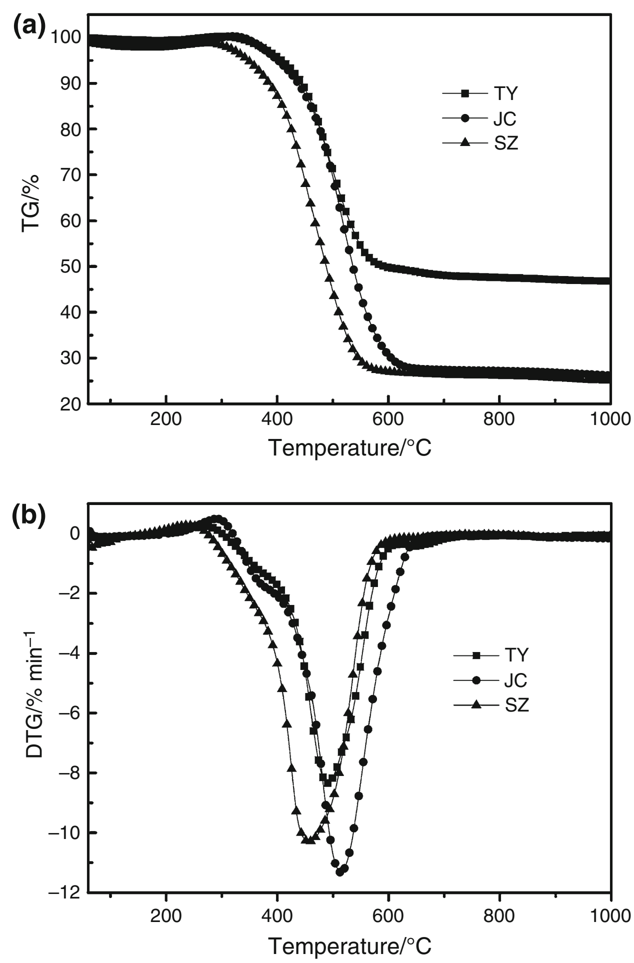

Fig. 2 Comparison of the TG–DTG curves of three kinds of coal sludge at the heating rate of 20 °C min^{-1}: TG curve (**a**); DTG curve (**b**)

loss. From TG curves given in Fig. 2a, the TG curves are different obviously, there is a small mass loss before 200 °C for each coal sludge, which indicates evaporation process. And after the temperature of 200 °C, as the different nature of different kinds of coal sludge, the mass losses observed from the TG profiles are different. The results showed that the major mass losses for TY, JC and SZ occurred at 320–570, 320–620 and 280–560 °C, respectively. The temperatures of mass started to loss for TY and JC were similar, and it for SZ was a little earlier. That because SZ had higher volatile and lower ash, its devolatilization required lower temperature. So the higher the volatile content in the coal sludge, the lower the devolatilization temperature and vice versa. From Fig. 2a, the residual mass of TY, JC and SZ at the end of the combustion process is 48.04, 28.06 and 26.88%, respectively, which are largely consistent with their ash content.

The DTG curves of coal sludge are shown in Fig. 2b. As can be seen from Fig. 2b, the three kinds of coal sludge exhibit unique DTG profiles. However, three kinds of coal sludge are all displayed only one prominent peak over a wide temperature distribution, respectively. And that means there was no obvious boundary for the combustion of volatile and carbon, which was the same to the literature [12].

The peak temperature which shows the maximum combustion rate has been reached at 455.75 °C for SZ, 489.97 °C for TY and 512.81 °C for JC, respectively. The temperature of maximum combustion rate is the lowest for SZ, and this maybe attributed by the higher volatile content in SZ which is shown in Table 1.

The values of the maximum combustion rate for TY, JC and SZ were 8.33, 11.32 and 10.29% min^{-1}, respectively. The value for JC was the highest, for TY was the lowest, for SZ was a litter lower than that for JC and higher than that for TY. Peak temperature and its corresponding rate can be used as the measure of combustibility and reactivity, respectively [27]. SZ had higher combustibility, and JC had higher reactivity.

Characteristic parameters of coal sludge combustion

Several characteristic parameters deduced from TG–DTG curves are listed in Table 3. These parameters could evaluate the coal sludge combustion properties.

As can be seen from Table 3, at the heating rate of 20 °C min^{-1}, the most easily ignited coal sludge is SZ, and the ignition temperature of SZ is 388.92 °C. The next easily ignited coal sludge is TY and then comes JC with ignition temperature is 434.80 and 443.33 °C, respectively. This order was consistent with that of content of volatile in three kinds of coal sludge. And the same time, the orders of burning temperature and the maximum mass loss temperature for the three kinds of coal sludge were same to the order of ignition temperature. The general combustion parameters (S) also are listed in Table 3. It can be found from Table 3 that value of S for TY coal sludge is the lowest, for SZ is the highest and for JC is in middle. For TY coal sludge, its lowest value of S may largely attribute to its too high content of ash to impact heat and mass transfer in combustion process.

What is more, it can be seen from Table 3 that the change trends of these characteristic parameters of this three kinds of coal sludge at other different heating rates were the same as what happened at the heating rate of 20 °C min^{-1}.

The effect of heating rate on combustion process

The thermogravimetric (TG) and the differential thermogravimetric (DTG) results of TY, JC and SZ coal sludge samples of different heating rates (10, 20, 30 and

Table 3 Characteristics parameters of three kinds of coal sludge

Sample	β/ °C min^{-1}	DTG_{max}/% min^{-1}	T_{max}/°C	T_i/°C	T_f/°C	$S \times 10^{-7}$
TY	10	4.56	480.05	424.33	546.49	0.69
	20	8.33	489.97	434.80	584.27	2.02
	30	11.05	505.67	442.61	615.09	3.2
	40	12.41	515.23	446.67	650.26	4.03
JC	10	6.94	497.85	442.16	571.24	0.84
	20	11.32	512.81	444.33	625.01	2.24
	30	13.45	529.37	446.42	660.04	3.35
	40	15.09	553.73	452.10	700.28	4.33
SZ	10	5.86	458.01	386.83	536.52	0.99
	20	10.29	455.75	388.92	568.36	2.57
	30	13.23	474.22	401.42	600.98	4.14
	40	14.82	484.87	406.26	635.59	5.13

40 °C min^{-1}) are shown in Fig. 3. Because the change trends of TG and DTG profiles with the heating rates of three different kinds of coal sludge were similar, we take TY coal sludge as example to analysis. As can be seen in Fig. 3a, although the different heating rates are, the curves of TG are similar. However, the combustion process is found in a wider temperature range with the heating rate increase. The percentage of mass loss is all about 52% at heating rate 10 °C min^{-1} and at heating rate 40 °C min^{-1}. It can be known that the residue yield could not been affected by heating rate obviously. Their onset temperature for volatile release and mass loss is about 350 °C, and final combustion temperature detects as mass stabilization is about 650 °C.

As can be seen in Fig. 3b, the temperature of maximum mass loss rate of TY is 480.05 °C at a heating rate of 10 °C min^{-1}, while it is 489.97 °C at 20 °C min^{-1}, 505.67 °C at 30 °C min^{-1}, 515.23 °C at 40 °C min^{-1}. As the heating rate increases, the DTG curves are translated to higher temperatures, which means that coal sludge combustion happens in a higher temperature zone, but the heating rate could not affect the temperature of maximum mass loss rate obviously. However, the maximum mass loss rate of TY coal sludge increases from 4.56 to 12.41% min^{-1}; therefore, the heating rate could affect the maximum mass loss rate obviously. It shows that the coal sludge has higher reactivity with increasing the heating rate. That may be because it was difficult for the difficult-flammable component in the coal sludge sample to be ignited only using the heat released from the reactivity, and much more heat from external environment was needed to supply for continued combustion. So, a higher heating rate provides the advantageous condition for coal sludge to continue to combust.

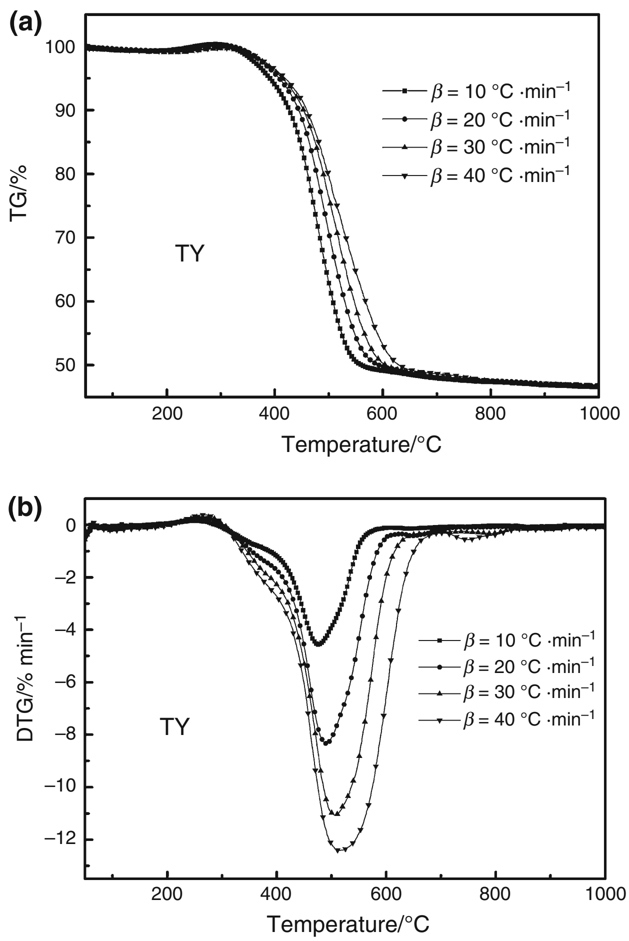

Fig. 3 TG and DTG curves for TY at different heating rates: TG curves (**a**); DTG curves (**b**)

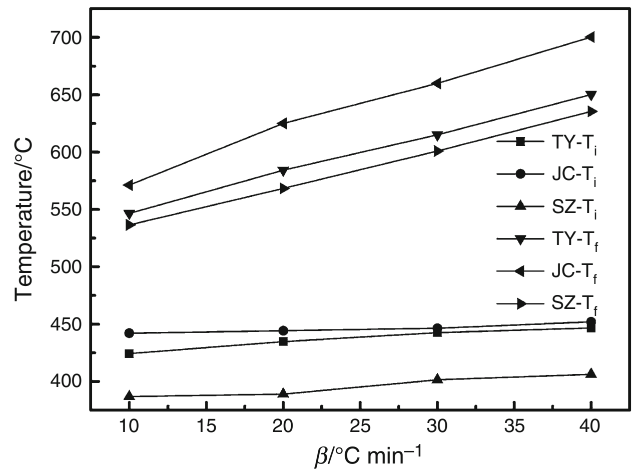

Fig. 4 Effect of heating rate on the combustion characteristic temperatures

Figure 4 shows the effect of heating rate on the ignition temperature, burnout temperature of the three kinds of coal sludge. It can be seen from Fig. 4 that the ignition

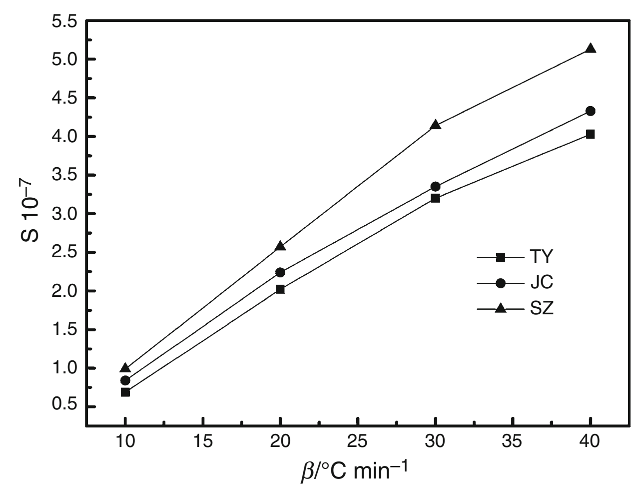

Fig. 5 Effect of heating rate on the general combustion parameter S

temperature and the burnout temperature tend to increase with increasing the heating rates. Furthermore, the ignition temperature is affected slightly by the heating rate, while the burnout temperature is affected strongly. That may be because the increasing heating rate induced the large temperature gradient between internal and external surfaces of the coal sludge particle, which was adversed to the release of volatile. And the ignition temperature and burnout temperature were further affected [8].

Figure 5 shows the effect of heating rate on general combustion parameter S of the three kinds of coal sludge. And it can be found from Fig. 5 that the general combustion parameter S of three kinds of coal sludge increases with the increase of the heating rate from 10 to 40 °C min^{-1}, and the effect of heating rate on S of SZ is

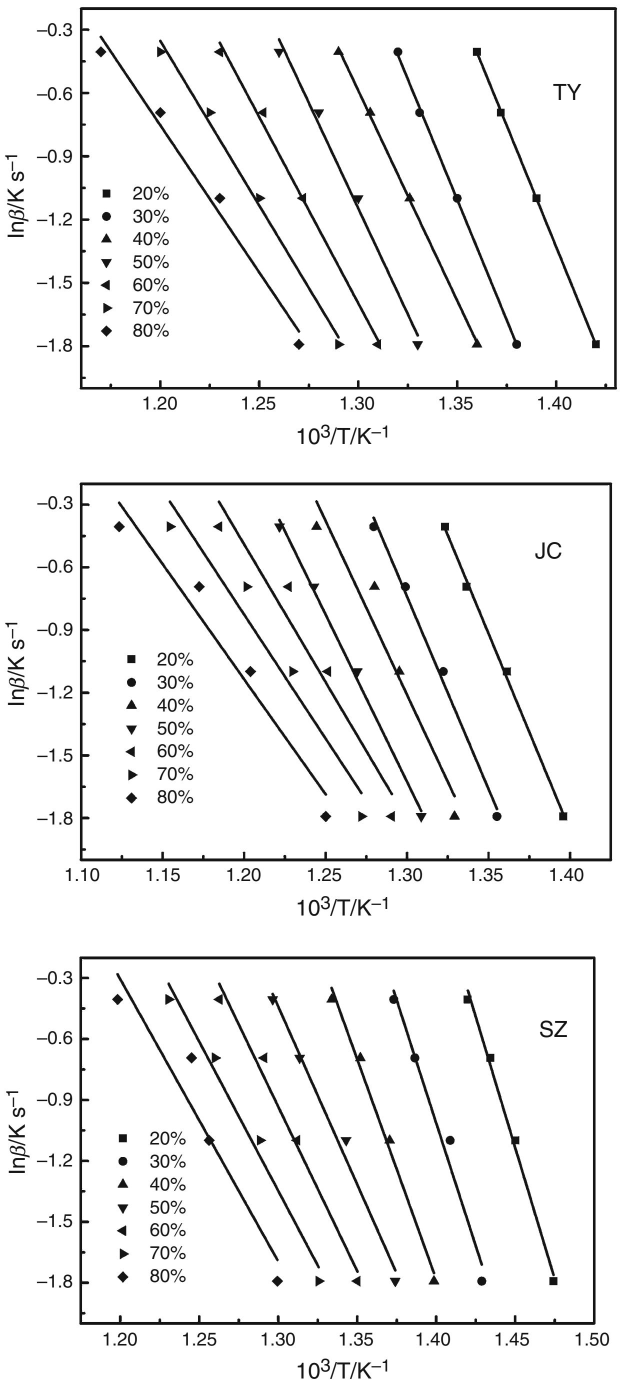

Fig. 6 Curves of fitting to kinetic model proposed by Ozawa–Flynn–Wall to various conversion degrees (α) corresponding to the combustion of TY, JC and SZ at different heating rates

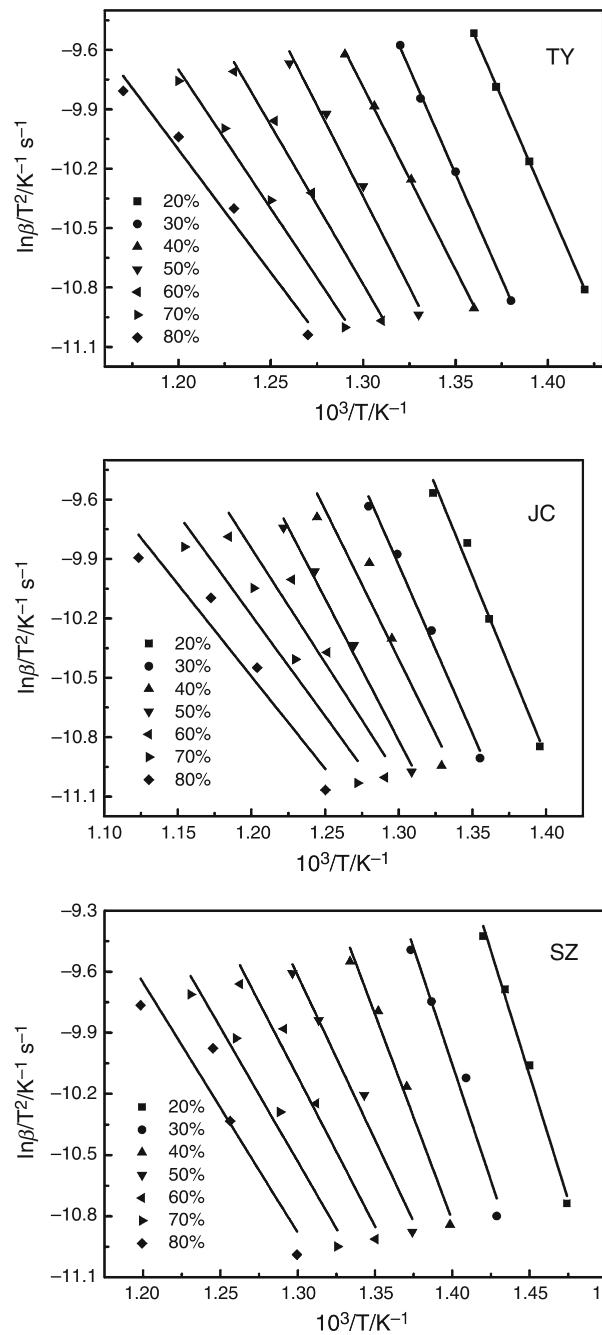

Fig. 7 Curves of fitting to kinetic model proposed by DAEM to various conversion degrees (α) corresponding to the combustion of TY, JC and SZ at different heating rates

Table 4 Activation energy values obtained from OFW and DAEM method for TY, JC and SZ coal sludge

Sample	Conversion/%	OFW			DAEM		
		slope	E/kJ mol^{-1}	R^2	slope	E/kJ mol^{-1}	R^2
TY	20	23.04	182.08	0.9999	21.49	178.66	0.9998
	30	22.87	180.74	0.9989	21.25	176.67	0.9988
	40	20.03	158.29	0.9992	18.42	153.14	0.9987
	50	19.92	157.42	0.9852	18.33	152.39	0.9818
	60	17.65	139.48	0.9924	16.04	133.35	0.9899
	70	15.61	123.36	0.9894	14.03	116.64	0.9840
	80	13.95	110.24	0.9753	12.42	103.25	0.9653
	Average		150.23			144.88	
JC	20	18.83	148.81	0.9969	18.17	151.06	0.9749
	30	18.41	145.49	0.9910	16.97	141.08	0.9876
	40	16.64	131.50	0.9187	15.09	125.45	0.9116
	50	16.01	126.52	0.9951	14.33	119.13	0.9899
	60	13.19	104.24	0.9235	11.57	96.19	0.9909
	70	11.86	93.73	0.9229	10.22	84.96	0.9111
	80	11.01	87.01	0.9509	9.32	77.48	0.9039
	Average		119.62			113.63	
SZ	20	25.82	204.05	0.9923	24.42	203.02	0.9888
	30	24.18	191.09	0.9649	22.78	189.39	0.9554
	40	21.65	171.10	0.9870	20.21	168.02	0.9778
	50	17.52	138.46	0.9824	16.11	133.93	0.9729
	60	16.19	127.95	0.9752	14.66	121.88	0.9585
	70	14.69	116.09	0.9706	13.14	109.24	0.9597
	80	13.90	109.85	0.8841	12.26	101.92	0.8730
	Average		151.23			146.78	

Slopes and correlation coefficients (R^2) corresponding to linear fittings together with the resultant activation energy values using OFW method and DAEM method

the greatest. The experimental results indicate that a higher heating rate is useful for the combustion performance of coal sludge under the experimental conditions in this study.

Kinetic analysis

The iso-conversional method is considered as a good approach for the study of combustion kinetics of carbonaceous material. In this study, the combustion activation energy values were obtained by Ozawa–Flynn–Wall (OFW) method and distributed activation energy model (DAEM) method. According to Eqs. (7) and (8), activation energy values were calculated adopting heating rates of 10, 20, 30, 40 °C min^{-1}. The curves of fitting to kinetic model proposed by OFW and DAEM to various conversion degrees (α) corresponding to the combustion of TY, JC and SZ at different heating rates are shown in Figs. 6 and 7, respectively. From the slope of line, the apparent activation energy (E) of the dynamic combustion at various conversion degrees (α) could be estimated. And the activation energy values obtained by the OFW method and the DAEM method are listed in Table 4. It can be seen from Table 4 that the activation energy values have good correlation coefficients (R^2) in the range of 0.8730–0.9999, and most of them are larger than 0.9500, showing acceptable accuracy of results. As the data outside the range of 20–80% had poor correlation coefficient, only the conversion values in this range were considered. Table 4 shows the activation energy values corresponding to each conversion value, and the average value of E was obtained as arithmetic mean of several values. Furthermore, there were significant variations of activation energy with conversion values, as conversion values increase, the values of activation energy reduce, which indicated that the combustion processes of three kinds of coal sludge were all kinetically complex, and should be considered as multi-step processes. And the change trends were similar to the literature for lignite coal [28].

The slopes of linear fittings, the value of E calculated by the OFW method and DAEM method are shown in

Table 4. The activation energy values during combustion process of TY are 150.23 and 144.88 kJ mol^{-1}, estimated through OFW and DAEM methods, respectively. The activation energy values of JC are 119.62 and 113.63 kJ mol^{-1}, and the corresponding values are 151.23 and 146.78 kJ mol^{-1} for SZ. The activation energy values obtained from the DAEM method are lower than that obtained from the OFW method. However, the change trends are similar between values calculated by OFW method and DAEM method. From Table 4, it is obvious that TY possessed relatively similar activation energy values to that of SZ, and the values of them both are higher than the corresponding values of JC coal sludge. This may be related to the different amounts of alkaline metal (Na and K), alkaline earth metals (Ca and Mg), Fe and Ti in each kind of coal sludge. As seen in Table 2, JC contains significantly higher amounts of alkaline metal, alkaline earth metals, Fe and Ti compared with TY and SZ, and these metal may play a catalytic role during combustion of coal sludge, which resulted in lower activation energy value. However, the interactions of coal sludge component may be a reason, too.

Anyway, the activation energy values of the three kinds of coal sludge were higher than values of coal, when compared to the data in the literature [29, 30].

Figure 8 shows the curves of activation energy versus the conversion rate of coal sludge combustion. It can be seen that within the $\alpha = 20$–80% range, the curves corresponding to the different coal sludge from OFW and DAEM method are similar. So, we choose the activation energy versus the conversion rate by OFW method to analysis. The activation energy value on each conversion is lowest for JC coal sludge. And the values for SZ coal sludge are higher than that of TY when the conversation rate $\alpha \leq 40$, while the results are opposite for $\alpha \geq 50$. Furthermore, the activation energy values are almost the same for TY and SZ coal sludge when the conversation rate is 80%. Moreover, the activation energy values decrease with the increasing conversation rates. This result agreed with the results reported in previous research on coal [29].

The relationship between the apparent activation energy E and the pre-exponential factor A can be written in the following formula [31, 32]:

$$\ln A = aE + b,$$

where a and b are the compensation coefficients.

Figure 9 shows the compensation effect analysis curves of TY, JC and SZ coal sludge combustion. The linear fitting of lnA and E was carried out based on the calculated kinetic parameters through DAEM method. It can be observed from Fig. 9 that the pre-exponential factor A increases with increasing values of E, the three kinds of coal

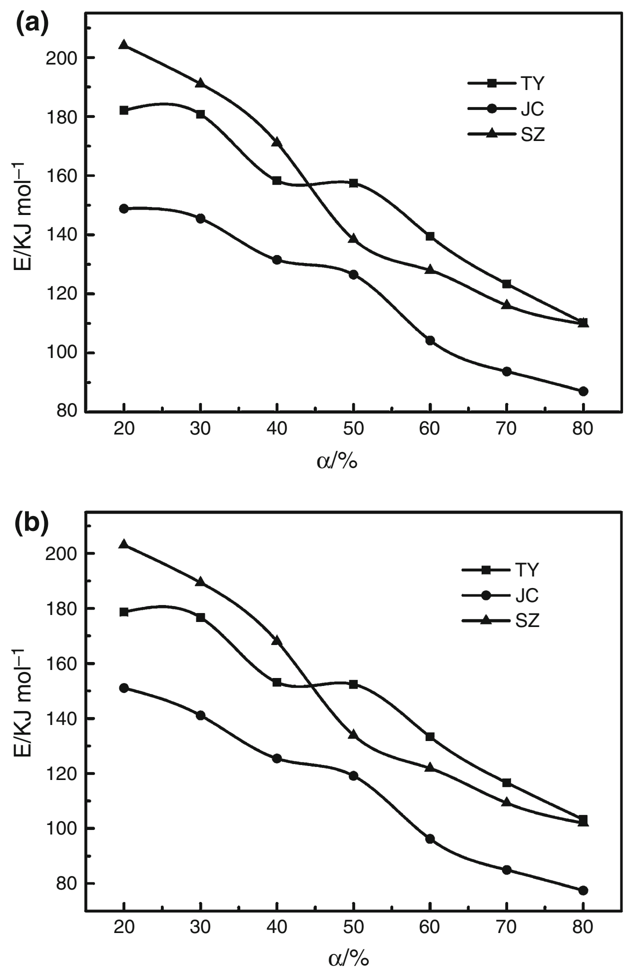

Fig. 8 Activation energy versus the conversion rate of coal sludge combustion **a** by OFW method; **b** by DAEM method

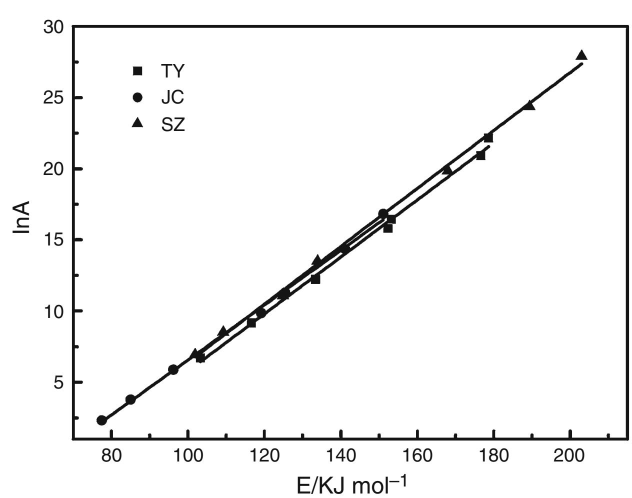

Fig. 9 Compensation effect analysis curves of TY, JC and SZ coal sludge combustion

Table 5 Reaction order versus temperature

Temperature/ °C	TY	JC	SZ
430	0.60	0.53	0.39
480	0.64	0.64	0.54
530	0.67	0.68	0.62
Average n	0.64	0.62	0.51

sludge show linearity, which indicates that the linear correlation between ln*A* and *E* is quite good.

Reaction order is also a kinetic parameter to describe combustion mechanism. It is calculated based on Eq. (10) by plotting $\ln[-\ln(1-\alpha(T))]$ versus $\ln\beta$. The reaction order (*n*) as a function of temperature for TY, JC and SZ coal sludge combustion is shown in Table 5. Reaction orders were evaluated at three different values of temperature (430, 480 and 530 °C). The values are in the range of 0.39–0.68 and are dependent on the extent of the reaction and on the type of the coal sludge. It is not constant during the combustion, which also indicates that the complexity of the multiple step process. TY and JC coal sludge had comparable reaction order values and higher than that of SZ coal sludge.

Conclusions

This research provided the thermal and kinetic behavior of TY, JC and SZ coal sludge from Shanxi in northwestern China, and the following conclusion was obtained:

1. The value of general combustion parameters (S) for TY coal sludge is the lowest, for SZ is the highest, and for JC is in middle at any heating rate. It was observed that the residue yield and the ignition temperature could not been affected by heating rate obviously. However, the heating rate could affect the maximum mass loss rate and the burnout temperature obviously and strongly. Furthermore, the value of general combustion parameters (S) of three kinds of coal sludge increases with increased heating rate. The experimental results indicate that a higher heating rate is useful for the combustion performance of coal sludge in this study.
2. The activation energy values obtained from the DAEM method are a little lower than the ones obtained from the OFW method for every kind of coal sludge. OFW and DAEM methods showed that the activation energy values of JC coal sludge are minimum, with the value of 119.62 kJ mol^{-1} using OFW method and 113.63 kJ mol^{-1} using DAEM method.

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References

1. Duan LB, Liu DY, Chen XP, Zhao CS. Fly ash recirculation by bottom feeding on a circulating fluidized bed boiler co-burning coal sludge and coal. Appl Energy. 2012;95:295–9.
2. Kök MV. Temperature-controlled combustion and kinetics of different rank coal samples. J Therm Anal Calorim. 2005;79(1):175–80.
3. Elbeyli İY, Pişkin S. Combustion and pyrolysis characteristics of tunçblek lignite. J Therm Anal Calorim. 2006;83(3):721–6.
4. Özbas KE, Kök MV. Effect of heating rate on thermal properties and kinetics of raw and cleaned coal samples. Energy Sour. 2003;25(1):33–42.
5. Altun NE, Hicyilmaz C, Kök MV. Effect of Different binders on the combustion properties of lignite part I. Effect on thermal properties. J Therm Anal Calorim. 2001;65(3):787–95.
6. Ren J, Xie CJ, Guo X, Qin ZF, Lin JY, Li Z. Combustion characteristics of coal gangue under an atmosphere of coal mine methane. Energy Fuels. 2014;28(6):3688–95.
7. Wang HY, Zhang JL, Wang GW, Xu RS, Zhang PC, Liu SY, et al. Characteristics and kinetic analysis of co-combustion of brown coal and anthracite. J Therm Anal Calorim. 2016;126(2):447–54.
8. Zou C, Zhang L, Cao SY, Zheng CG. A study of combustion characteristics of pulverized coal in O_2/H_2O atmosphere. Fuel. 2014;115:312–20.
9. Xu Y, Zhang YF, Zhang GJ, Guo YF, Zhang J, Li GQ. Pyrolysis characteristics and kinetics of two Chinese low-rank coals. J Therm Anal Calorim. 2015;122(2):975–84.
10. Zhang YY, Nakano J, Liu LL, Wang XD, Zhang ZT. Co-combustion and emission characteristics of coal gangue and low-quality coal. J Therm Anal Calorim. 2015;120(3):1883–92.
11. Wang CA, Liu YH, Zhang XM, Che DF. A study on coal properties and combustion characteristics of blended coals in Northwestern China. Energy Fuels. 2011;25(8):3634–45.
12. Niu SL, Lu CM, Han KH, Zhao JL. Thermogravimetric analysis of combustion characteristics and kinetic parameters of pulverized coals in oxy-fuel atmosphere. J Therm Anal Calorim. 2009;98(1):267–74.
13. Zhang KH, Zhang K, Cao Y, Pan WP. Co-combustion characteristics and blending optimization of tobacco stem and high-sulfur bituminous coal based on thermogravimetric and mass spectrometry analyses. Bioresour Technol. 2013;131:325–32.
14. Nie QH, Sun SZ, Li ZQ, Zhang XJ, Wu SH, Qin YK. Thermogravimetric analysis on the combustion characteristics of brown coal blends. J Combust Sci Technol. 2001;7(1):72–6.
15. Li XG, Ma BG, Xu L, Hu ZW, Wang XG. Thermogravimetric analysis of the co-combustion of the blends with high ash coal and waste tyres. Thermochim Acta. 2006;441(1):79–83.
16. Li QZ, Zhao CS, Chen XP, Wu WF, Li YJ. Comparison of pulverized coal combustion in air and in O_2/CO_2 mixtures by thermogravimetric analysis. J Anal Appl Pyrolysis. 2009;85(1–2):521–8.
17. Cheng JY, Sun XX. Determination of the devolatilization index and combustion characteristic index of pulverized coals. Power Eng. 1987;7(5):33–6.

18. Sima-Ella E, Mays TJ. Analysis of the oxidation reactivity of carbonaceous materials using thermogravimetric analysis. J Therm Anal Calorim. 2005;80(1):109–13.
19. Sanchez ME, Otero M, Gómez X, Morán A. Thermogravimetric kinetic analysis of the combustion of biowastes. Renew Energy. 2009;34(6):1622–7.
20. Ozawa T. A new method of analyzing thermodynamic data. Bull Chem Soc Jpn. 1965;38:1881–6.
21. Flynn JH, Wall LA. A quick, direct method for the determination of activation energy from thermogravimetric data. Polym Lett. 1966;4:323–8.
22. Cd D. Kinetic analysis of thermogravimetric data. J Appl Polym Sci. 1961;5(15):285–92.
23. Miura K, Maki T. A simple method for estimating f(E) and ko(E) in the distributed activation energy model. Energy Fuels. 1998;12(5):864–9.
24. Avrami MJ. Kinetics of phase change. I General theory. Chem Phys. 1939;7:1103–12.
25. Mj A. Kinetics of phase change II. Transformation-time relations for random distribution of nuclei. Chem Phys. 1940;8:212–24.
26. Mj A. Kinetics of phase change III. Granulation, phase change, and microstructure. Chem Phys. 1941;9:177–84.
27. Idris SS, Rahman NA, Ismail K. Combustion characteristics of Malaysian oil palm biomass, sub-bituminous coal and their respective blends via thermogravimetric analysis (TGA). Bioresour Technol. 2012;123:581–91.
28. Zhou ZJ, Hu X, You Z, Wang ZH, Zhou JH, Cen KF. Oxy-fuel combustion characteristics and kinetic parameters of lignite coal from thermo-gravimetric data. Thermochim Acta. 2013;553:54–9.
29. Buratti C, Barbanera M, Bartocci P, Fantozzi F. Thermogravimetric analysis of the behavior of sub-bituminous coal and cellulosic ethanol residue during co-combustion. Bioresour Technol. 2015;186:154–62.
30. Kok MV. Simultaneous thermogravimetry–calorimetry study on the combustion of coal samples: effect of heating rate. Energy Convers Manag. 2012;53(1):40–4.
31. Koga N, Šesták J. Kinetic compensation effect as a mathematical consequence of the exponential rate-constant. Thermochim Acta. 1991;182(2):201–8.
32. Wang CA, Zhang XM, Liu YH, Che DF. Pyrolysis and combustion characteristics of coals in oxyfuel combustion. Appl Energy. 2012;97:264–73.