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Combustion Characteristics and Kinetics Study of Pulverized Coal and Semi-Coke

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Abstract: Combustion process of bituminous coal, steam coal, anthracite (AC) and semi-coke were investigated through thermogravimetric analysis method and influence of metamorphic grade as well as heating rate on combustion characteristics were analyzed. Results show that combustion performance could not be represented by single combustion characteristic parameter. Through analysis of comprehensive combustion characteristic indexes, with increase of metamorphic grade combustion performance of coal is lowered, and combustion performance of semi-coke and AC are close to each other. With increase of heating rate, combustion curves move into high temperature region and comprehensive combustion characteristic indexes are increased, which show that the combustion performance is improved. Random pore model (RPM), unreacted shrinking core model (URCM) and volume model were used to calculate kinetic parameters of combustion process. Results show that RPM has the best performance to represent combustion process of the four samples and through calculation by RPM kinetic energy of combustion process for all samples are between 43.08 and 99.43 kJ/mol, and there is compensation effect during combustion process.

Keywords: pulverized coal injection; thermogravimetric analysis; combustion characteristics; kinetics

Introduction

In traditional iron and steel making process energy consumed in iron making accounts for 70 % of total energy consumption and the ratio is the same for pollutant emission, so iron making process takes priority in energy conservation and emission reduction [1]. Coke in blast

furnace works as heat resource, reductant and carburizer, and at the same time in lower region of blast furnace coke is the only solid material serving as skeleton to guarantee gas permeability [2]. However, pollutant emission in the coking process is the most serious and the coking process also has disadvantages of high energy consumption and high capital expenditure, so to lower coke consumption is a continuous main goal for iron making process [3]. Pulverized coal injection is one of effective ways to lower energy consumption and pollutant emission in blast furnace iron making. For quite a long time, anthracite (AC) is the most common coal injected into blast furnace in China, but after decades of development the mixture of bituminous coal (BC) and AC is injected now to lower cost, and further for some enterprises and research units the injection of steam coal (SC) and semi coke is also proposed [4–7].

Thermogravimetric analysis method has been widely used in study of pulverized coal injection in blast furnace [8–11]. For thermogravimetric analysis the isothermal method focuses on reactivity for the whole combustion process and the non-isothermal method focuses on change of reactivity during combustion process. Compared with isothermal method, the non-isothermal method is program controlled heating and has advantages of less experiment work and more information [12]. He et al. [13] studied combustion characteristics and reactivity of blast furnace pulverized coal through thermogravimetric analysis method and came up with optimal proposal for Pansteel Company. Wang et al. [14] studied the combustion characteristics of brown coal, AC and their blends. It could be seen that adding brown coal could improve the combustion reactivity of coal blends, and meanwhile a double parallel reactions random pore model (RPM) provided a good prediction of the blends co-combustion process. Co-combustion of flash ash from coke dry quenching and pulverized coal were studied by Liu et al. [15] through thermogravimetric method and results showed that with increase of flash ash content in blends the ignition temperature and burn-out temperature both lowered and combustion properties were improved. It could be found from above research that the thermogravimetric analysis method is an effective way to study combustion process of pulverized coal.

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Four samples of normally used BC, SC, AC and semi-coke were selected from practical iron making plant, and through thermogravimetric analysis method the combustion of these samples and kinetics were investigated under different heating rate conditions. RPM [16, 17], unreacted shrinking core model (UCRM) [18], volume model (VM) [19, 20] were selected to calculate reaction kinetic parameters by linear fitting method, hoping to offer reference for blast furnace to inject more kinds of fuel.

Experimental

Raw materials

Four samples of BC, SC, AC and semi-coke (LC) were collected from work site of steel company. Before experiment samples were grinded and screened to make sure particle size smaller than 74 μm . Then samples were dried under 105°C for 4 h in drying oven to eliminate moisture. Contents of carbon, hydrogen and nitrogen were ascertained through LECO CHN600 elemental analyzer. Sulfur content was ascertained by sulfur determination device and content of oxygen was determined by subtraction method. Under standard heating rate and temperature condition contents of volatile, solid carbon and ash in samples were ascertained through LECO MAC500 coal analyzer. Proximate and ultimate analysis of different samples is shown in Table 1.

Combustion experiment

Combustion of samples was carried out through STA4009C thermogravimetric analyzer. For each experiment 5 mg sample was put into $\Phi 3\text{mm} \times 1.5\text{mm}$ alumina crucible and rested on balance pan, at the same time keeping minimum

distance between sample and thermal couple to make temperature tested with low deviation. During experiment pressed gas with flow of 100 ml/min was introduced into thermal balance. Compared with so small amount of sample the gas flow is excessive, and the aim of it is to reduce the influence of external diffusion into a very low level. Non-isothermal method was chosen to investigate combustion characteristics of samples and heating rates were set as 2.5°C/min, 5°C/min, 10°C/min and 20°C/min, respectively. Samples were heated from room temperature to 900°C then keeping constant for 10 min to make sure total combustion. To ensure accuracy of experiment data each test was repeated at least for three times until differences among three tests were less than 3°C.

During experiment weight loss curve was obtained automatically by computer with frequency 1s for one record and combustion rate curve was obtained through differentiation of weight loss data. In order to compare combustion characteristics and for kinetics analysis under different conditions the weight loss data was pre-treated to get conversion ratio curve. Conversion ratio α is calculated by formula (1):

$$\alpha = \frac{(m_0 - m_t)}{(m_0 - m_\infty)} \quad (1)$$

In the formula: m_0 is initial sample weight, mg; m_∞ is sample weight after total combustion, mg; m_t is sample weight at time t , mg.

Characteristic parameters of combustion

To quantitatively analyze combustion process of different samples, characteristic parameters of T_i , T_f , T_m , T_g and $R_{\max}$ were defined. The initial combustion temperature T_i , burn out temperature T_f , peak combustion rate $R_{\max}$ and peak combustion rate temperature (T_m) could be obtained from TG-DTG curves as shown in Figure 1. T_g is

Table 1: Proximate and ultimate analysis of different samples.

Sample	Proximate analysis, wt%			Ultimate analysis, wt%				
	V _d	FC _d	A _d	C _d	H _d	N _d	O _d	S _d
BC	31.17	61.25	7.58	79.32	4.72	0.8	5.76	0.16
SC	23.35	66.54	10.11	70.56	3.9	0.78	9.34	0.24
AC	7.91	81.15	10.94	83.37	1.69	1.55	2.02	0.43
LC	5.42	87.29	7.29	88.98	0.98	1.08	2.47	0.41

Notes: FC_d, V_d, A_d are mass fractions of fixed carbon, volatile content and ash, respectively; C_d, H_d, O_d, N_d, S_d are mass fractions of carbon, hydrogen, oxygen, nitrogen and sulfur of different samples, respectively.

Figure 1: Determine characterization parameter of combustion.

combustion time and it is defined as $T_g = T_f - T_i$. The comprehensive combustion characteristic index S is determined by the equation as follow [21]:

$$S = \frac{(da/dt)_{\max} \cdot (da/dt)_{\text{mean}}}{T_i^2 \cdot T_f}, \quad (2)$$

where $da/dt_{\max}$ is the maximum combustion rate; da/dt_{mean} represents mean value for combustion rate.

Results and discussion

Analysis of combustion curves

It could be concluded from Figure 2 that for different samples the conversion curves and conversion rate curves have similar trend, from which the total combustion process could be divided into three stages of preheating, quick combustion and burn out. In the first stage sample was heated and with temperature rising the weight of sample kept nearly constant. In the second stage, the sample weight lost quickly and the combustion of volatile and combustion of solid carbon overlapped with each other, so in conversion rate curve only one peak was presented though volatile content in different samples differed. In the third stage samples burned out. In thermogravimetric analysis device, compared with the sample amount the gas flow was surplus so it could be thought that all combustible matter like volatile and solid carbon was exhausted only with residue ash left. Through

comparison of initial weight loss temperature range for different samples it could be concluded that for BC and SC the range was 300–400 °C but for AC and semi-coke it was 400–500 °C, and with temperature further rising quick weight loss happened. From this aspect obvious difference was existed for different samples. In order to quantitatively analyze combustion characteristics for all samples the TG-DTG method was used to ascertain combustion characteristic parameters including ignition temperature (T_i), burn out temperature (T_f), peak combustion rate ($R_{\max}$), peak combustion rate temperature (T_m), mean combustion rate (R_{mean}), comprehensive combustion index (S), combustion time (t_g), and through comparison of these parameters the difference of combustion property for all samples could be obtained. Combustion characteristic parameters are shown in Table 2. From comparison of T_i for BC, SC and AC the T_i increases with increase of metamorphic grade. T_i is an important index to represent combustion property of coal and normally the lower is T_i the better is combustion property. In experiment two conditions are needed for ignition of coal, one is certain concentration of combustible matter at surface of coal particle, and the other is certain degree of superheat temperature. BC and SC has low metamorphic grade with fairly high content of volatile so in preheating process at relatively low temperature with volatilization of volatile content the concentration of combustible matter around particle surface could reach to high level and get ignition. For T_f of different samples, SC is the lowest, BC follows and AC is the highest, for which the order is different from that of T_i , and at the same time $R_{\max}$ and R_{mean} also have the same trend. Semi-coke is produced through middle temperature pyrolysis with

Figure 2: Conversion curves and conversion rate curves for different samples under different heating rates.

most of volatile content removed, so the combustion process of it is close to that of AC, which could also be concluded from combustion characteristic parameters. Combustion property of different samples could not be ascertained only through parameters of T_f , T_i , R_{max} and R_{mean} . According to

literature review the comprehensive combustion index S calculated based on above four parameters is used to represent combustion property of different samples. For S of different samples, BC has the highest value, SC follows and for AC and semi-coke the S of them are close to each other

Table 2: Combustion characteristic parameters of different samples under different heating rates.

Samples	β , °C/min	T_i , °C	T_m , °C	T_f , °C	R_{max} , s ⁻¹	R_{mean} , s ⁻¹	$S \times 10^{14}$	t_g , min
BC	2.5	319.80	467.02	519.67	0.53E-03	0.232E-03	0.04	62.35
	5	326.55	488.85	534.02	0.84E-03	0.323E-03	0.36	31.49
	10	349.62	519.67	590.32	1.58E-03	0.990E-03	0.41	16.87
	20	363.88	548.63	628.06	2.77E-03	1.030E-03	0.77	5.61
SC	2.5	337.32	426.00	475.66	0.60E-03	0.220E-03	0.24	55.34
	5	348.10	441.40	493.39	1.28E-03	0.430E-03	0.92	29.06
	10	368.16	463.96	520.64	1.98E-03	0.740E-03	2.07	15.25
	20	382.37	482.85	545.38	2.98E-03	1.180E-03	4.41	8.15
AC	2.5	722.20	796.44	839.67	6.60E-04	3.26E-04	0.05	46.99
	5	755.76	822.88	866.10	1.32E-03	5.48E-04	0.15	22.07
	10	772.54	842.19	882.88	2.36E-03	1.00E-03	0.45	11.03
	20	806.10	890.24	940.59	3.30E-03	1.41E-03	0.76	6.72
LC	2.5	724.12	796.44	839.82	5.70E-04	2.08E-04	0.03	46.28
	5	758.31	822.88	864.35	1.19E-03	5.08E-04	0.12	21.21
	10	772.23	842.20	881.99	2.49E-03	9.84E-04	0.47	10.98
	20	805.34	887.71	940.19	3.71E-03	1.57E-03	0.95	6.74

with the lowest value. This illustrates that combustion property of BC is the highest, SC follows and the combustion property of AC and semi-coke is the lowest.

For different samples through comparison of weight loss curves under different heating rates, with increase of heating rate the conversion curves and conversion rate curves all moved into high temperature range. The reason could be attributed to two aspects. One is that with increase of heating rate the combustion time in certain temperature range is shortened with less combustion weight loss and more sample remained for combustion in high temperature range. The other reason is that with increase of heating rate the temperature difference between the inside and surface of sample also increases. At the same time it could be found that with increase of heating rate the peak weight loss rate $R_{\max}$ and combustion comprehensive index S both increases, and combustion time is shortened. Take BC for example when heating rate is increased from $2.5^{\circ}\text{C}/\text{min}$ to $20^{\circ}\text{C}/\text{min}$, T_i is increased from 319.80°C to 363.88°C , $R_{\max}$ is increased from $0.53 \times 10^{-3} \text{ s}^{-1}$ to $2.77 \times 10^{-3} \text{ s}^{-1}$, combustion time t_g is shortened from 62.35 min to 5.61 min and comprehensive combustion index S is increased from 0.04×10^{-14} to 0.77×10^{-14} . So it could be ascertained that with increase of heating rate the combustion rate is increased and the combustion time is shortened, which showed that the combustion property of samples were improved.

Kinetic analysis

Kinetic study of combustion process has great meaning in selection of injection coal and design of combustion device. In order to illustrate kinetic combustion behaviors of coal under different heating rates different kinetic models were chosen to analyze combustion process through nonlinear fitting method. Pyrolysis, combustion and gasification of coal are typical gas-solid multi-phase reaction. Though combustion of coal is a complicated process including evaporation of water, volatilization of volatile and combustion of residue carbon, however through analysis of weight loss curve of different samples in this paper only one peak weight loss rate is existed, so the main reaction process could also be represented by typical gas-solid reaction formula:

$$\frac{d\alpha}{dt} = k(P_g, T)f(\alpha). \quad (3)$$

In the formula, k is apparent combustion rate constant, which is related with temperature and pressure; $f(\alpha)$ is kinetic mechanism function for combustion of coal.

During experiment the outlet of gas flow is open to atmosphere so gas pressure is constant during combustion process, so the apparent reaction rate constant k is determined by temperature, which could be performed according to Arrhenius formula:

$$k = k_0 e^{-E/RT} \quad (4)$$

In the formula, k_0 and E are pre-exponential factor and reaction activation energy, respectively.

For combustion of coal many kinetic models have been founded by former researchers and in this paper three models are chosen to analyze combustion process, and they are RPM, URCM and VM. In different models kinetic mechanism function $f(\alpha)$ is different. RPM is proposed by Bhatia and Perlmutter [16, 17] and has been widely applied in study of gas-solid reaction for porous carbonaceous materials. When reaction is controlled by interface reaction the model could be expressed as:

$$\frac{d\alpha}{dt} = k_{\text{RPM}}(1-\alpha)\sqrt{1-\psi \ln(1-\alpha)}. \quad (5)$$

In the formula: k_{RPM} is reaction rate constant; Ψ is parameter for particle size and shape, with expression $\Psi = 4\pi L_0(1-\varepsilon_0)/S_0^2$, S_0 representing specific reaction surface area, L_0 representing initial pore length in per unit volume, ε_0 representing initial porosity of particle.

URCM is proposed by Szekely and Evans [18], and during reaction process reaction starts from particle surface and gradually moves into inner particle. An unreacted core is existed and reaction could only happen at reaction interface. When particle is sphere and reaction is controlled by chemical reaction, the model could be expressed as:

$$\frac{d\alpha}{dt} = k_{\text{URCM}}(1-\alpha)^{2/3}. \quad (6)$$

In the formula: k_{URCM} is reaction rate constant.

In VM, the reaction process is independent of particle structure and reaction happens simultaneous across the particle, and during reaction process the reaction interface decreased with reaction progressing [19, 20]. The formula could be expressed as:

$$\frac{d\alpha}{dt} = k_{VM}(1 - \alpha). \quad (7)$$

In the formula, k_{VM} is reaction rate constant.

Under program controlled heating process combustion temperature T , heating rate β and reaction time t has the following relation:

$$T = T_0 + \beta t \quad (8)$$

In the formula, T_0 is room temperature, 25°C.

Put eq. (5) into eq. (8), and after integration the relation between conversion rate and reaction temperature could be obtained.

$$\alpha = 1 - \exp\left(-\frac{k_{RPM} C^n S_0}{1 - \varepsilon_0} \cdot \frac{(T - T_0)}{\beta}\right) \cdot \left(1 + \frac{4\pi L_0 k_{RPM} C^n}{S_0} \cdot \frac{(T - T_0)}{\beta}\right) \quad (9)$$

where C is concentration of reaction gas, and n is reaction order.

Put eq. (4) into eq. (9):

$$\alpha = 1 - \exp\left(-\left(k_0 \frac{(T - T_0)}{\beta} \exp\left(\frac{-E}{RT}\right)\right) \cdot \left(1 + k_0 \frac{\psi(T - T_0)}{4 \times \beta} \exp\left(\frac{-E}{RT}\right)\right)\right) \quad (10)$$

In the formula: $\psi = \frac{4\pi L_0(1 - \varepsilon_0)}{S_0^2}$.

The same could be obtained from eqs. (6) and (7):

$$\alpha = 1 - \left(1 - \frac{k_0(T - T_0)}{3\beta} \cdot \exp\left(\frac{-E}{RT}\right)\right)^3 \quad (11)$$

$$\alpha = 1 - \exp\left(-k_0 \frac{(T - T_0)}{\beta} \cdot \exp\left(\frac{-E}{RT}\right)\right) \quad (12)$$

Eqs. (10), (11) and (12) are integration form of RPM, URCM and VM, respectively. According to study of Miura and Silveston [22], when using program controlled heating method to study gasification kinetics arbitrary result could be obtained only through single heating rate, and at least three groups of experiment data under different heating rates could guarantee accurate and unique result. So in this study four different heating rates were chosen to calculate combustion kinetic parameters. Using the relation of α and T from eqs. (10), (11) and (12), the kinetic parameters k_0 and E can be calculated by nonlinear fitting method.

Different models are established based on different assumptions, and when different models are used to represent combustion process of different samples deviation between calculated value and experiment data are inevitable. In order to accurately determine the description of the coal char and biomass char combustion kinetics with different kinetic models eq. (13) can be used to calculate the deviation of the results for different models.

$$DEV(\alpha)(\%) = 100 \times \frac{\left(\sum_{i=1}^N (\alpha_{exp,i} - \alpha_{calc,i})^2 / N\right)^{1/2}}{\max(\alpha)_{exp}} \quad (13)$$

where $DEV(\alpha)(\%)$ is relative error, $\alpha_{exp,i}$, $\alpha_{calc,i}$ is the experimental data and calculated value by model. $\max(\alpha)_{exp}$ is maximum conversion rate of experiment, N is the number of experimental points.

Combustion kinetics of samples were investigated through RPM, URCM and VM models, and according to eqs. (10), (11) and (12) kinetic parameters E , k_0 and ψ were calculated and shown in Table 3. From Table 3 it could be found that the fitting performance of these models are all in good level with R^2 over 0.9600, and among them RPM has the best performance with R^2 all over 0.9900 which is higher than that of URCM and UM. When using RPM to simulate reaction process the coefficient ψ has significant influence. When sample porosity is high gas diffusion would become easy in combustion process, and if reaction happens simultaneously across the particle to certain level the reaction process would become close to VM. With increase of ψ , particle porosity becomes low and resistance for gas to get into inner particle becomes strong, and at this situation combustion reaction happens in surface of particle and the process would become close to URCM. Volatile content in BC and SC is high and in combustion process large amount of volatilization happens both inside and outside leading to production of high porosity in particle, and it could be found in Table 3 that ψ of them is small. When ψ is 0 RPM and VM are the same and this is the reason for activation energy calculated from them is close to each other. For different models the changing rule of activation energy for different samples is the same, and from high to low the order is BC, semi-coke, AC and SC, and activation energy calculated by RMP are 99.43, 57.13, 54.06 and 43.08 kJ/mol, respectively. Normally for reaction with high activation energy high temperature is needed to activate molecules into active state, so at the same temperature sample with high activation energy should have low reactivity.

Table 3: Kinetic parameters under different heating rates for RPM, URCM and VM.

Sample	RPM				URCM			VM		
	E , kJ/mol	k_0 , min ⁻¹	ψ	R^2	E , kJ/mol	k_0 , min ⁻¹	R^2	E , kJ/mol	k_0 , min ⁻¹	R^2
BC	99.4	832.05	3.05	0.9978	75.8	95.79	0.9922	105.9	2732.23	0.9977
SC	43.1	19.77	0.01	0.9985	40.1	17.98	0.9893	43.1	47.70	0.9985
AC	54.1	23.43	26.72	0.9937	54.5	39.36	0.9851	64.7	453.49	0.9861
LC	57.1	40.06	14.69	0.9925	57.6	56.36	0.9622	66.3	460.85	0.9853

However through comparison of relation between reaction rate and activation energy for different samples it could be found in this study the rule is abnormal because BC has the highest reactivity but its activation energy is also the highest. So there must be compensation effect during combustion process.

For reaction with compensation effect, the activation energy E is contained in pre-exponential factor A_0 and exponential term of Arrhenius formula. Compensation effect is often observed in gasification and combustion process of carbonaceous materials. Some researchers thought the compensation effect was purely attributed to mathematical reasons, while others gave several theoretical interpretations for it. Xie et al. [23] thought compensation effect could be attributed to similar mechanism with gasification reaction, especially for the oxygen-containing surface complexes C(O). For reactions with lower E values, it is easier for the free active sites to bond with CO₂ to produce C(O). If the C(O) bond is strong, the movement of C(O) would be limited and the char structure would be stable, leading to low value of A_0 . Activation energy is the minimum energy needed for molecule to get active in reaction and pre-exponential factor is the number of molecules with effective collision. Increase of activation energy make reaction become hard to happen but increase of pre-exponential factor would quicken reaction rate, so there is compensation effect between pre-exponential factor and activation energy. In recent years many theoretical explanations have been done to compensation effect. Through study of Sosnovski [24], in reaction process compensation effect is caused by existing of two kinds of matter with different activation energy. Through work of Galway et al. [25] compensation effect is due to non-uniformity of surface. Through work of Ding et al. [26, 27], unstable transition phase is formed during gasification and combustion of coal. In initial stage of reaction carbon oxide is first formed, because in surface of coal active site is easy to react with gasification agent so activation energy to form carbon oxide is small. At the same time connection between gasification agent and

coal is strong and the formed carbon oxide is hard to move presenting low activation entropy so pre-exponential factor is lowered with decrease of activation energy. Through different models, relationship between activation energy and pre-exponential factor for different samples is shown in Figure 3 and obvious compensation effect could be observed.

Figure 3: Relation between $\ln(k_0)$ and E .

Figure 4 shows the relationship between the calculated values and experimental data of different samples at the different heating rates. In order to quantify the errors produced by the kinetic models in predicting the values of conversion, the experimental and calculated α values are compared by calculating the deviation (DEV) between the experimental data and calculated curves using eq. (13). The results obtained from the best fitting models for all samples are summarized in Table 4. The lowest deviation from the calculated values of the conversion rates are obtained by using the RPM model for all samples and VM model for SC sample can obtain the same value as RPM model. Meanwhile, what needs to be pointed out is that experiments in this study are carried

Figure 4: Relationship between calculated value and experimental data under different heating rates.

Table 4: Deviation between the experimental and calculated conversion.

Char	DEV (α)%		
	RPM	URCM	VM
BC	1.32	1.87	1.36
SC	1.18	2.15	1.18
AC	1.65	2.43	2.27
LC	1.97	3.67	2.49

out under laboratory low heating rate condition which is significantly different from working state in blast furnace raceway, but theoretical reference could also be offered for optimization of coal selection and simulation study.

Conclusions

Non isothermal thermogravimetric analysis method was used to investigate combustion behaviors and kinetics of pulverized coal with different metamorphic grades and following conclusions are obtained:

1. Combustion property of coal is lowered with increase of metamorphic grade and combustion characteristics of semi-coke and BC are close to each other. Heating rate has obvious influence on combustion process and with increase of heating rate combustion process moves into high temperature region with higher combustion rate and shorter combustion time.
2. Combustion process of different samples could all be presented by RPM, URCM and VM with good accuracy. For BC, AC and semi-coke model calculation and experiment data has the best fitting performance by RPM. For SC the fitting performance of RPM and VM are close to each other.
3. Through RPM the calculated activation energy for BC, SC, AC and semi-coke are 99.43, 43.08, 54.06 and 57.13 kJ/mol, respectively, and there is no relevance between activation energy and combustion property which could be explained by existing of kinetics compensation effect between activation energy and pre-exponential factor.

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