Research Article

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Effect of KMnO_4 on catalytic combustion performance of semi-coke

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Abstract: The effect of KMnO_4 on the combustion characteristics and kinetic behavior of semi-coke was studied by thermogravimetric analysis. When 6 wt% KMnO_4 was added, the ignition temperature of semi-coke was the lowest. The apparent activation energy of semi-coke with different addition amount of KMnO_4 was calculated by Coats–Redfern integration method, the apparent activation energy of semi-coke during combustion reaction first decreased and then increased with increase in KMnO_4 . When 6 wt% KMnO_4 is added, the apparent activation energy is minimal. The apparent activation energy of semi-coke with 2 wt% KMnO_4 added at different conversion rates was calculated using Flynn–Wall–Ozawa integration method. The results show that the apparent activation energy of semi-coke combustion decreases with the increase of conversion.

Keywords: semi-coke, KMnO_4 , combustion, kinetic

1 Introduction

As the most important energy source, coal is widely used in various industries, some of which are used as fuel for blast furnace iron making after being converted into coke. With the increasingly tight supply of coal, the price of coke is rising, and the cost of iron making is gradually rising. Blast furnace coal injection technology has been widely used as a method that can reduce the use of coke and the cost of iron making [1,2]. At present, most of the iron and steel enterprises generally use the combination of bituminous coal and anthracite for blast furnace pulverized coal injection in China, the reason is that the combustion of bituminous coal is better than anthracite, but the content of S and P in bituminous coal are higher than anthracite, and these two elements are harmful to blast furnace [3,4], it is not conducive to blast furnace production to use specific coal alone.

As a new type of fuel, semi-coke has high fixed carbon content, low S and P impurity content, and it has huge reserves in China [5]. Compared with anthracite, semi-coke has the characteristics of high calorific value, large reserves, and low price, if semi-coke is used instead of anthracite, semi-coke plus bituminous coal is used for blast furnace injection, which is expected to reduce the cost of blast furnace pig iron. However, at present, the amount of semi-coke in mixed injection coal powder is limited, too much blending will reduce the combustion performance of the mixed coal powder and increase the amount of unburned coal powder, which will affect the blast furnace forward. Therefore, studying the catalytic combustion of semi-coke to improve its combustion efficiency and the burnout rate is of great significance for increasing the amount of semi-coke.

Yao et al. [6] used thermogravimetric (TG) analysis to study the combustion characteristics and kinetic behavior of the blend of semi-coke and bituminous coal in an oxygen-rich atmosphere. They found that replacing O_2 with CO_2 can significantly change the burnout behavior of the semi-coke. When the temperature exceeds 750°C , semi-coke is easier to gasify than bituminous coal under a CO_2 atmosphere. Cui et al. [7] prepared the mesoporous perovskite-type coal combustion catalyst by sol–gel method.

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By TG analysis, it was found that the presence of the catalyst reduced the ignition temperature, maximum weightlessness rate temperature, and burnout temperature of the pulverized coal. Wang *et al.* [8] conducted an experimental evaluation of the co-combustion characteristics of semi-coke and bituminous coal and found that bituminous coal and semi-coke interacted during the combustion process and improved the combustion characteristics of semi-coke. Wang *et al.* [9] found through TG experiments that semi-coke mixed with corn stalk can reduce its ignition temperature and burnout temperature. The interaction of the mixture during the combustion process mainly occurred at 400–600°C, indicating that the combustion of fixed carbon in corn stalk temperature is delayed.

As one of the strongest oxidants, KMnO_4 will decompose O_2 and MnO_2 at about 300°C. MnO_2 is quickly reduced to metal Mn by coke at high temperature, promoting the breakage of C–C bonds in coke and forming volatiles; at the same time, MnO_2 provides oxygen ions to the coke in the process of being reduced to metal Mn, changes the surface activity of the coke, and promotes the combustion of the coke, then, the metal Mn is oxidized to MnO_2 at high temperature, and is reduced again to release oxygen ions, thereby achieving a cyclical catalytic effect [10–14]. Moinuddin *et al.* [15] found that KMnO_4 can remove sulfur in coal mines, and as the pressure increases, the sulfur removal rate increases. Irum *et al.* [16] studied the desulfurization effects of $\text{Fe}_2(\text{SO}_4)_3$, KMnO_4 , and NaOCl on coal desulfurization. The results show that KMnO_4 has a significant promotion effect on sulfur removal rate. The addition of KMnO_4 to pulverized coal is mainly for the study of sulfur adsorption in the present, but the research on the catalytic combustion of pulverized coal by permanganate is rarely involved.

At present, there is little research on the effect of additives on the catalytic combustion of semi-coke. In this paper, the effect of KMnO_4 combustion aid on the catalytic combustion performance of semi-coke was studied to achieve the purpose of increasing the amount of semi-coke in the mixed injection of pulverized coal, which is of great significance for the efficient production of blast furnace and the reduction of pig iron cost.

2 Experimental

2.1 Sample preparation

The semi-coke used in the experiment was from a smelting enterprise in Yunnan, China. The semi-coke was ground to

Table 1: Proximate and ultimate analyses results of semi-coke (wt%)

Proximate analysis				Ultimate analysis				
$M_{ad}\%$	$V_{ad}\%$	$A_{ad}\%$	FC_{ad}	C_{ad}	H_{ad}	O_{ad}	N_{ad}	S_{ad}
5.28	17.57	8.69	70.28	83.74	3.43	0.76	0.72	0.4

Note: ad = air dry basis; M = moisture; V = volatile matter; FC = fixed carbon.

200 mesh and dried to constant weight at 80°C in a constant temperature oven and then placed in a sealed bag for storage. The industrial analysis of semi-coke is shown in Table 1. The preparation of the experimental sample was as follows: 10 g of semi-coke was weighed, 2 wt% KMnO_4 and 200 mL of deionized water were added, and then the sample was magnetic stirred for 2 h at room temperature dried at 105°C for 24 h, and then taken out and ground for 10 min. The above operation was repeated to prepare mixed semi-coke samples in which 0 wt%, 2 wt%, 4 wt%, 6 wt%, and 8 wt% KMnO_4 was added and named as D1, D2, D3, D4, and D5, respectively.

2.2 Sample characterization

Experiment on a STA6000/8000 thermal analyzer manufactured by PerkinElmer. Thermal analyzer temperature deviation is $\pm 0.1^\circ\text{C}$; balance sensitivity deviation is less than 0.1 μg . In this experiment, the sample mass is about 6 mg, and the samples are raised to 1,000°C at room temperature at a heating rate of 10°C/min, 20°C/min, 30°C/min, and 40°C/min under an air flow rate of 50 mL/min.

3 Results and discussion

3.1 Combustion performance

Five samples D1, D2, D3, D4, and D5 were tested using thermal analyzer at a heating rate of 20°C/min. Figure 1 shows the TG and DTG curves of different samples. It can be seen from the DTG that the reaction process is mainly through two stages of volatilization analysis and ignition and combustion of the remaining coke. Since there is sufficient O_2 in the whole process, there is no coking gasification reaction in the later stage of combustion. As shown in Figure 1b, DTG has only one peak, which indicates that the volatile matter coincides with the

Figure 1: TG–DTG curves of the samples at the temperature rise rate of 20°C/min: (a) TG and (b) DTG curves.

ignition phase of coke, indicating that a heterogeneous ignition occurred in this process. The ignition temperature (T_i) reflects the ignition performance of the sample, the smaller the T_i , the easier the sample is to catch fire [17]. The burnout temperature (T_b) indicates the temperature at which the combustibles in the sample are completely burned out within a certain temperature range. Usually, the TG curve tends to a horizontal straight line, and the temperature corresponding to the DTG curve close to zero is T_b . T_i and T_b reflect changes in combustion performance throughout the combustion process [18]. T_i and T_b of the samples are shown in Table 2. T_i sequence of four different semi-coke samples is $D4 < D5$

$< D3 < D2 < D1$. T_b sequence is $D5 < D1 < D4 < D2 < D3$. When 6 wt% KMnO_4 was added, T_i of semi-coke was the lowest, being 448.48°C, which was 118.36°C lower than that of the semi-coke without KMnO_4 . When 8 wt% KMnO_4 was added, T_b of semi-coke was the lowest, being 754.29°C.

In the combustion process, the comprehensive combustion characteristic index S is generally used to reflect the whole process of ignition and burnout of the sample. The larger the S , the better the combustion characteristics of the sample. The calculation formula is as follows:

$$S = \frac{\left[\left(\frac{dw}{dt} \right)_{\max} \times \left(\frac{dw}{dt} \right)_{\text{mean}} \right]}{T_i^2 \times T_b} \quad (1)$$

where $\left(\frac{dw}{dt} \right)_{\max}$ is the maximum combustion rate of pulverized coal, %/min; $\left(\frac{dw}{dt} \right)_{\text{mean}}$ is the average combustion rate, %/min.

By analyzing the TG curve, the combustion rate of the sample at different temperatures can be obtained. For the convenience of analysis, the combustion rate of the sample at the combustion temperatures of 500°C, 600°C, 700°C, and 800°C is generally selected. The combustion rate is calculated using the below formula:

$$R = \frac{W_i - W_t}{W_i \times \eta} \times 100\% \quad (2)$$

where W_i is the initial mass of the sample, g; W_t is the mass after the sample is burned t minutes, g; η is the weight loss rate when the sample is completely burned without additives; R is the combustion rate of the sample.

The combustion rate and comprehensive combustion characteristic index of different samples at different temperatures are presented in Table 2. It is observed from Table 2 that when the combustion temperature is between 500°C and 700°C, the addition of KMnO_4 can increase the combustion rate of semi-coke, as the amount of addition increases, the combustion rate of the mixed samples at 500°C and 600°C also increases. At 800°C, the

Table 2: Combustion parameters of mixed semi-coke samples

Sample	T_i (°C)	T_b (°C)	Combustion ratio (%)				$S \times 10^9$ (% ² min ⁻² °C ⁻³)
			500°C	600°C	700°C	800°C	
D1	566.84	757.52	6.18	26.06	80.53	99.94	0.32
D2	490.23	777.58	18.29	45.21	84.05	99.52	0.58
D3	477.29	782.58	18.53	46.16	80.83	96.92	0.62
D4	448.48	767.58	21.37	50.07	82.74	96.27	0.69
D5	475.73	754.29	22.81	66.92	95.45	95.96	0.61

combustion rate of the mixed sample is reduced. This whole process may be because KMnO_4 can distort the macromolecular network structure in the semi-coke [19,20], weaken the bridging bond between the structural units, and the precipitation temperature of the more difficult pyrolysis component in the volatile matter after the additive is added, and the fixed carbon combines to form a complex that acts as a carrier for oxygen, promoting the transfer of oxygen between the two materials, thereby promoting the combustion of the semi-coke.

3.2 Effects of heating rates

In order to study the effect of heating rate on the mixed samples, the D2 mixed semi-coke samples were tested in air atmospheres at heating rates of 10°C/min, 20°C/min, 30°C/min, and 40°C/min. It can be seen from Figure 2 that the combustion process of the mixed sample has similar trends at different heating rates, which indicates that the heating rate has a certain influence on the burning rate during the combustion of the sample, but

it doesn't have much effect on the mechanism. As the heating rate increases, the TG curve shifts to the right, causing T_i and T_b to increase accordingly. For D2, when the heating rate is increased from 10°C/min to 40°C/min, the T_i of the sample rises from 485.27°C to 512.36°C, and the T_b rises from 641.85°C to 826.67°C. This is because the propagation and heat transfer of the medium takes a certain amount of time. If the heating rate of the program is too fast, the time for the combustion reaction of the sample will be insufficient, and then the entire TG curve will shift to the high-temperature region. It can be seen from the DTG curve that as the heating rate increases, the mass loss rate of the sample also decreases. When the heating rate was increased from 10°C/min to 40°C/min, the maximum weight loss rate of the sample decreased from 0.69%/°C to 0.25%/°C.

3.3 Dynamic analysis results

The Coats–Redfern integration method belongs to a single scan rate method and is a method for kinetic analysis of data results of a TG curve measured by an experiment at a fixed heating rate [21]. Table 3 is the integral function of the combustion reaction model, however, in the equation, it is impossible to integrate the independent variable containing temperature in the right-hand formula to obtain an accurate solution only through approximate solution or numerical integration.

According to Arrhenius's law, if the initial mass of the coal powder involved in the reaction is m_0 , the mass after the reaction t time is m , and the final mass is m_∞ after the reaction is completed, the expression of the reaction rate can be obtained as:

$$\frac{d\alpha}{dt} = A(1 - \alpha)^n \exp\left(-\frac{E_\alpha}{RT}\right) f(\alpha) \quad (3)$$

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (4)$$

where A refers to the pre-factor, min^{-1} ; α is the conversion of coal powder; n is the reaction order; E_α is the activation energy, kJ/mol; and R is the gas constant.

If the rate of temperature raises $\beta = \frac{dT}{dt}$ is brought to Eq. 3 and a temperature approximation is made, then there is:

$$\int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{ART^2 \left(1 - \frac{2RT}{E_\alpha}\right) \exp\left(-\frac{E_\alpha}{RT}\right)}{\beta E_\alpha} \quad (5)$$

Figure 2: TG–DTG curves of D2 sample at different heating rates: (a) TG and (b) DTG curves.

Table 3: Reaction model integral function.

Reaction model	Symbol	$f(\alpha)$	$G(\alpha)$
Zero-order reaction	O0	1	α
First-order reaction	O1	$1 - \alpha$	$-\ln(1 - \alpha)$
Second-order reaction	O2	$(1 - \alpha)^2$	$(1 - \alpha)^{-1}$
Third-order reaction	O3	$\frac{(1 - \alpha)^3}{2}$	$(1 - \alpha)^{-2}$
Shrink cylinder	R2	$2(1 - \alpha)^{\frac{1}{2}}$	$1 - (1 - \alpha)^{\frac{1}{2}}$
Shrink sphere	R3	$3(1 - \alpha)^{\frac{2}{3}}$	$1 - (1 - \alpha)^{\frac{1}{3}}$
One-dimensional diffusion	D1	$\frac{\alpha}{2}$	α^2
Two-dimensional diffusion	D2	$-\ln(1 - \alpha)^{-1}$	$(1 - \alpha) \ln(1 - \alpha) + \alpha$
Three-dimensional diffusion	D3	$\frac{2}{3}(1 - \alpha)^{\frac{2}{3}}[1 - (1 - \alpha)^{\frac{1}{3}}]^{-1}$	$[1 - (1 - \alpha)^{\frac{1}{3}}]^2$

when $n \neq 1$,

After Eq. 5, the Coats–Redfern equation can be obtained as:

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right] = \ln \left[\frac{AR \left(1 - \frac{2RT}{E_a} \right)}{\beta E_a} \right] - \frac{E_a}{RT} \quad (6)$$

when $n = 1$,

$$\ln \left[-\frac{\ln(1 - \alpha)}{T^2} \right] = \ln \left[\frac{AR \left(1 - \frac{2RT}{E_a} \right)}{\beta E_a} \right] - \frac{E_a}{RT} \quad (7)$$

In the combustion process of pulverized coal samples, the result of $\frac{E_a}{RT}$ is much larger than 1, so the result of $1 - \frac{2RT}{E_a}$ is about equal to 1. That is, the expression of the first term on the right side of the Coats–Redfern equation is independent of temperature. When $n = 1$, in Eq. 7, $\ln \left[-\frac{\ln(1 - \alpha)}{T^2} \right]$ is plotted against $\frac{1}{T}$, and the graph is approximated as a straight line, $-\frac{E_a}{R}$ is the slope, $\ln \left[\frac{AR}{\beta E_a} \right]$ is the intercept. So in the end, the value of the exponential pre-factor and the activation energy of the combustion reaction of the semi-coke mixed sample can be obtained.

The Flynn–Wall–Ozawa integration method belongs to the multiple scan rate method, which analyzes the experimental data obtained by samples at different heating rates [22,23]. The basic equation of the model is as follows:

$$\ln \beta = \ln \left(\frac{AE_a}{G(\alpha)} \right) - 5.331 - 1.052 \frac{E_a}{RT} \quad (8)$$

At different heating rates, if the same conversion rate is chosen, integral form of reaction mechanism mode

function $G(\alpha)$ is a fixed value, plotted as $\ln \beta$ versus $\frac{1}{T}$, the data are fitted by least-squares method, and the activation energy of the reaction can be determined from the slope.

According to the kinetic fitting results of different reaction model functions, the O1 model has the highest correlation coefficient. Therefore, the O1 reaction model is used for kinetic analysis of the five groups of samples, and the kinetic parameters of each group of samples are calculated. Figure 3 is a Coats–Redfern kinetic analysis curve of different samples at a programmed temperature rate of 20°C/min. The activation energy and pre-exponential factor calculation results are shown in Table 3.

It is shown in Figure 3 that the linearity of $\ln \left[-\frac{\ln(1 - \alpha)}{T^2} \right]$ with the $\frac{1000}{T}$ curve is very good, indicating that it is reasonable to assume that the combustion reaction of the sample under the experimental conditions is a first-order reaction. It can be seen from Table 3 that the correlation coefficients are all above 0.996, indicating that the fitting results are very good. The activation energy represents the difficulty of the combustion reaction, the smaller the value, the easier the combustion reaction is. Table 3 indicates that the addition of KMnO_4 can reduce the activation energy of semi-coke combustion and increase the reaction activity of semi-coke. When the addition amount of KMnO_4 is 6 wt%, the activation energy required for the reaction is the smallest. This is because after mixing KMnO_4 and semi-coke, KMnO_4 provides oxygen ions for semi-coke at high temperature, thereby changing the surface activity of semi-coke and promoting its combustion [24,25].

To accurately fit the experimental data of TG-DTG, the kinetic analysis of D2 samples was performed by multiscan FWO integration method. This method is to fit the experimental data by the conversion degree α within a certain

Figure 3: Coats–Redfern method plots of different samples at 20°C/min.

range. In this experiment, α is between 0.1 and 0.9. Figure 4 is an FWO kinetic analysis curve of the D2 sample reacted at different temperature-programmed rates, and Table 4 shows the activation energy and pre-exponential factor calculation results of the D2. The analysis method results of other samples are similar.

As shown in Figure 4, the straight line fitted by the FWO integral method agrees well with the original data, which indicates that the kinetic curve obtained by this method has high linearity and the result is reliable. Moreover, the slope of the fitted straight line changes as the conversion α changes, that is, the reaction activation energy also changes. As can be seen from Table 5, as the conversion degree α increases, the activation energy thereof decreases. This is because the whole experimental process is

Figure 4: FWO method plots of sample D2 in different conversion degrees.

Table 4: Combustion kinetic parameters of different samples

Sample	E_a (kJ/mol)	A (min^{-1})	R^2
D1	85.40	8.33×10^7	0.997
D2	59.61	5.35×10^6	0.998
D3	63.77	1.36×10^4	0.997
D4	59.24	3.56×10^8	0.998
D5	65.29	1.78×10^6	0.996

Table 5: Combustion kinetic parameters of sample D2

Conversion rate	E_a (kJ/mol)	A (min^{-1})	R^2
0.1	78.56	1.28×10^6	0.994
0.2	77.69	2.78×10^5	0.998
0.3	77.58	4.79×10^7	0.997
0.4	76.49	3.54×10^7	0.996
0.5	75.49	4.68×10^6	0.996
0.6	74.38	4.35×10^6	0.995
0.7	73.28	6.28×10^5	0.996
0.8	72.86	5.43×10^7	0.997
0.9	72.15	3.77×10^6	0.996
Average	75.38	—	—

carried out under programmed temperature. For the gas–solid phase reaction such as pulverized coal combustion, when the temperature is low, the surface reaction speed is slower, which is the power control zone, as the temperature rises, the surface reaction speed increases, and gradually goes to the diffusion control zone and the activation energy gradually decreases [26–28].

4 Conclusions

The effect of KMnO_4 on the combustion characteristics and kinetic behavior of semi-coke was studied by thermal analysis. The combustion characteristics of the semi-coke and KMnO_4 blends on the thermal analyzer varied with the amount of KMnO_4 added. The main conclusions are as follows:

- (1) Adding a certain amount of KMnO_4 can lower the ignition temperature and the burn-out temperature of the semi-coke. Compared with the semi-coke without KMnO_4 , when the addition amount of KMnO_4 is 6 wt%, the ignition temperature of semi-coke decreases most, which is 118.36°C; when the addition amount is 8 wt%, the burnout temperature of semi-coke decreases the most, which is 2.23°C. The combustion rate and comprehensive combustion characteristic index of different samples at

different temperatures indicate that the addition of a certain amount of KMnO_4 can promote the combustion of semi-coke.

- (2) The apparent activation energy of semi-coke with different addition amounts of KMnO_4 was calculated by Coats–Redfern integration method. The result shows that the apparent activation energy decreases first and then increases with the addition of KMnO_4 . When the addition amount is 6 wt%, apparent activation energy is reduced to a minimum of 59.24 kJ/mol. It shows that KMnO_4 can promote the combustion of semi-coke to a certain extent, that is, the mixed combustion of KMnO_4 and semi-coke can improve the overall combustion performance.
- (3) The apparent activation energy of mixed semi-coke at four heating rates was calculated by FWO integration method. The result shows that the apparent activation energy of the combustion reaction of semi-coke decreases with the increase of conversion. Under low conversion, the reaction gas temperature is lower and the calculated apparent activation energy is closer to real activation energy.

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