Study on combustion characteristic of coal-char in oxygen-enriched environments

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Abstract- **Oxygen-enriched (O_2/CO_2) combustion in circulating fluidized bed(CFB) is one of the most promosing clean coal combustion technology which shows good gaeous pollutants control, especially greenhouse CO_2. In the paper, the thermogravimetric experiments of Hennan lean coal-char under O_2/CO_2 and O_2/N_2 atmosphere have been carried out, the influence of atmosphere, O_2 concentration and heating rate on the combustion characteristic of coal-char being analysed. The results of the experiment show that O_2 concentration and heating rate have a great influence on the coal-char combustion characteristics in oxygen-enriched environment. The coal-char combustion characteristic ameliorates with increasing the O_2 concentration and improving the heating rate. Under the same O_2 concentration, the coal-char combustion characteristic in O_2/CO_2 atmosphere is a little poorer than that in O_2/N_2 atmosphere. A reaction kinetic model for coal-char combustion in oxygen-enriched environment was also deduced and it agreed well with experimental data.**

Keywords- oxygen-enriched combustion; thermogravimetric analysis; coal-char; kinetic

I. INTRODUCTION

Oxygen-enriched combustion is one of the most promising technologies which can more easily and economically separate CO_2 from the flue gas generated by coal-fired power plants. Besides that, it has many Other advantages, for example, a higher combustion efficiency resulting from the higher oxygen concentration in the combustion chamber [1,2], or a higher thermal efficiency of the boiler owing to the reduction in the volume of the flue gas leaving the combustion chamber[3,4]. A positive feature of the oxygen-enriched combustion, which is especially important in the case of the circulating fluidized bed (CFB) boilers, is also a possibility of utilizing different kinds of fuels, especially low-rank fuels. Apart from the economical advantage, the use of low calorific-value fuels has an additional advantage, i.e. the capability to obtain a lower adiabatic combustion temperature. This is important because the difficulties with temperature control and heat transfer are the major problems connected with this combustion process[5–7]. In fact, there are well known solutions applied in pulverized fuel boilers, where flue gas recirculation is used for temperature control[8–10]. However, such a method requires a preliminary treatment of the recirculated gases, i.e. the elimination of gaseous pollutants and fly ash, as well as the moisture. On the one hand, the flue gas treatment is quite difficult and, on the other hand, it is also rather expensive. Because of that, it can be anticipated that CFB boilers will successfully face the problems, where the presence of the bed material makes the temperature control easier[11]. However, due to the nature of oxygen-enriched combustion, the construction of CFB boilers, as well as the organization of the fluidization process and fuel combustion, would be significantly different from those in the conventional CFB systems.

At present, the study on oxygen-enriched combustion in CFB boiler is still in its starting stage in China, with lacking of relevant theory and experiment data. In order to have a preliminary understanding about the combustion mechanism of oxygen-enriched combustion, the combustion characteristic and reaction kinetics of coal-char in oxygen-enriched atmosphere have been investigated with thermogravimetric analyzer. It will provide theoretical basis for the following development and design of oxygen-enriched combustion in CFB boiler.

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II. EXPERIMENTAL

A. *Sample preparation*

Hennan lean coal was selected, and its properties are shown in TABLE Ⅰ. The coal-char samples were prepared by heating the parent coal (already dried) in a muffle at 1173 K for 7 minutes, and then sieved to a size range of 74 -100μm.

B. *Apparatus and methods*

The combustion experiments were carried out in a TGA(NETZSCH STA 409C, Germany). The sample was placed uniformly on the bottom of an aluminium oxide cruible. To mitigate the difference of heat and mass transfer, the sample weight was kept at ~5 mg . The flow rate of carrier gas was kept at 100 ml/min. The sample was heated up to 1173 K at various heating rates in O_2/CO_2 and O_2/N_2 atmospheres. According to the TG and DTG curves that received, the parameters which represent coal-char combustion characteristics were evaluated. A reaction kinetic analysis was also carried out. The kinetic model for coal-char combustion in oxygen-enriched environment that better fitted the experimental data was deduced and the relevant kinetic parameters were calculated.

TABLE.I Proximate and ultimate analyses of coal sample

sample	proximate analysis（wt.%）					Ultimate analysis（wt.%）				
	M_{ar}	M_{ad}	V_{daf}	A_{ar}	FC_{ar}	C_{ar}	H_{ar}	N_{ar}	S_{ar}	O^{a}_{ar}
Hennan lean coal	7.62	0.52	12.08	14.46	68.51	67.52	3.62	1.41	0.25	5.40

a: O content was calculated by difference, ad: on air dried basis, ar: on air received basis, daf: on dry ash free basis

III. RESULTS AND DISCUSSION

A. *effect of O_2 concentration on coal-char combustion characteristic*

The DTG curves of coal-char in the O_2/CO_2 atmosphere at the heating rate of 20 k/min are shown in Fig. 1. As the volatile matter and water have been removed from the sample and the coal-char is mainly composed of fixed carbon, only one main peak appeared on the DTG curve. The coal-char began to combustion at about 773 K, and burnout temperature extended to about 1023 K. As shown in Fig. 2-5, with the increase of oxygen concentration, the igniting[12] and burnout temperature rose nearly linearly, the maximum weight loss rate increased, the corresponding temperature decreased and the combustion duration reduced. The result showed that: under oxygen-enriched environment, the combustion characteristics of coal-char can ameliorate with the increase of oxygen concentration. However, for oxygen-enriched combustion in CFB boiler, the tendency of improving effect on coal-char combustion characteristics will become slow when the oxygen concentration is too high[13], causing a significant increase of investment cost. How to choose a proper oxygen concentration needs a further investigation.

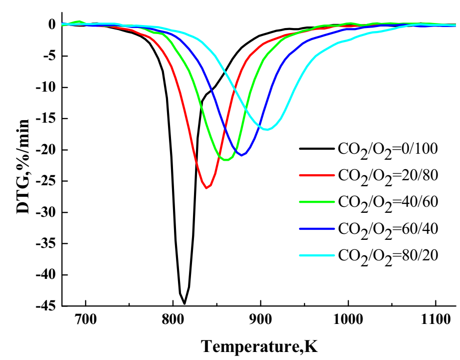

Figure1. DTG profiles of coal-char with different O_2 concentrations

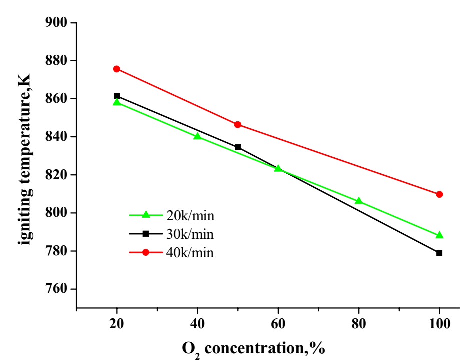

Figure2. Igniting temperature at different O_2 concentrations

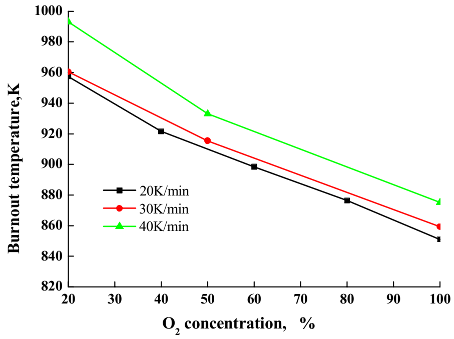

Figure3. Burnout temperature at different O_2 concentrations

B. effect of heating rate on coal-char combustion characteristic

As shown in Fig. 2 and Fig. 3, the igniting and burnout temperature rise at a small scale as the heating rate increases. It's because that the phenomenon of thermal hysteresis is intensified with the increase of the heating rate ,which results in the starting temperature and ending temperature of coal-char combustion on the TG curves moving toward the direction of higher temperature. From Fig. 4 and Fig. 5, it can be seen that the increase of heating rate results in the increase of the sample's maximum weight loss rate and its corresponding temperature and shorten the combustion duration. On the whole, the combustion characteristic of coal-char ameliorates with the increase of heating rate. It can be supposed that under the condition of oxygen-enriched combustion in CFB boiler, the flame property will be greatly enhanced due to a very high heating rate.

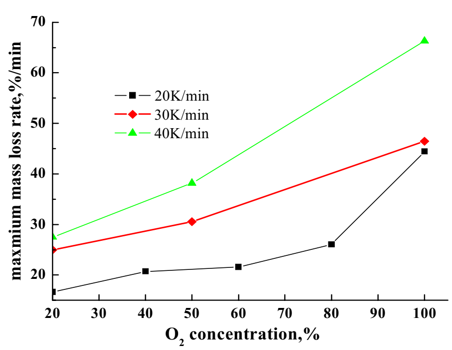

Figure4. Maximum mass loss rate at different O_2 concentrations

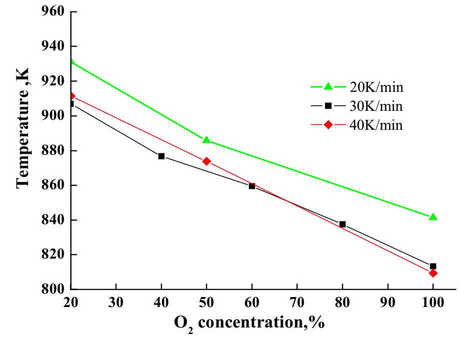

Figure5. Temperature corresponding with maximum mass loss rate

C. effect of atmosphere on coal-char combustion characteristic

The combustion profile parameters of coal-char under different atmospheres are shown in TABLEⅡ.As shown in Fig. 6 and TABLEⅡ, under the same oxygen concentration, coal-char combustion in O_2/N_2 atmosphere was more acute than that in O_2/CO_2 atmosphere, which is corresponding to the results obtained by Miyamae, etc[14]. The possible reason is that the higher specific heat of CO_2 compared with N_2 will lead lower flame temperature than for an equivalent oxygen concentration in O_2/N_2 environment. In addition, replacing O_2/N_2 with O_2/CO_2 would cause a delay ignition of coal particles, which was indicated by the shifting of the peak temperature on DTG curves in Fig. 6. Therefore, oxygen concentration in the furnace should be high to maintain the combustion stability during oxygen-enriched combustion in CFB boiler. It can be realized by improving the oxygen concentration of the secondary air or installing oxygen nozzle.

TABLE.II Combustion profile parameters of coal-char under different atmospheres

atmosphere	concentration ratio	T_i (K)	T_{max} (K)	V_{max} (%·min^{-1})	T_b (K)
CO_2/O_2	40/60	822.1	860.5	21.6	898.4
	60/40	839.4	878.2	20.9	921.5
O_2/N_2	40/60	813.4	844.8	25.2	880.3
	60/40	824.0	859.3	23.4	899.0

T_i: igniting temperature; T_{max}: temperature corresponding to maximum weight loss rate; V_{max}: maximum burning rate; T_b: burnout temperature

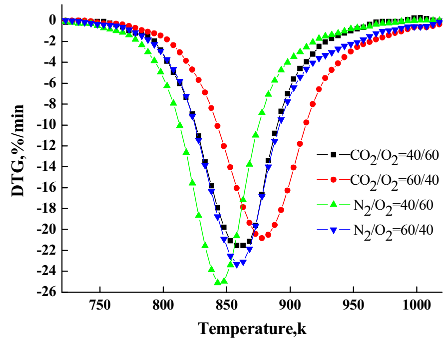

Figure6. DTG curves in O_2/CO_2 and O_2/N_2 atmospheres for coal-char samples

D. apparent kinetic model of coal-char combustion in oxygen-enriched environment

In the work, the kinetic model derivated doesn't reflect the real product formation process during coal-char combustion, it's just a kinetic model in allusion to the main reaction region of coal-char combustion. The kinetic relationship of the coal-char combustion can be described as[15]:

$$d\alpha / dt = kf(\alpha) p_{O_2}^m \tag{1}$$

with

$$k = A\exp(-E/RT) \tag{2}$$

$$f(\alpha) = (1-\alpha)^n \tag{3}$$

where k is the apparent reaction coefficient, A is the apparent pre-exponential factor, E is the apparent activation energy, α is the mass loss fraction, n is the reaction order , m is the exponential of the partial pressure of O_2, determined by the thermogravimetric experiment.

Firstly, kinetic parameters of coal-char combustion in pure oxygen atmosphere were calculated. By using Coats-Redfern method, Coats-Redfern equations could be derivated as:

$$\ln g(\alpha) = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{4}$$

where

$$g(\alpha) = \begin{cases} \dfrac{-\ln(1-\alpha)}{T^2} & n=1 \\ \dfrac{1-(1-\alpha)^{1-n}}{T^2(1-n)} & n\neq 1 \end{cases} \tag{5}$$

As the term of *2RT/E* can be neglected since it is much less than 1, (4) could be simplified as :

$$\ln g(\alpha) = \ln\frac{AR}{\beta E} - \frac{E}{RT} \tag{6}$$

The term of *lng(α)* varies linearly with *1/T* as slope of the line is *–E/R*. Meanwhile, the intercept of the line with y-axis is related to *A*. Both *E* and *A* can be determined by the slope and intercept of the line. To perform linear regression, trial values of *n* were used to determine *A* and *E*. Then the optimal value of *n*, *A* and *E* which correspond with the maximal relation coefficient *R* were obtained. The kinetic parameters of coal-char combustion at different values of *β* are shown in TABLE Ⅲ.

As can be seen in Table 3, the values of *A* and *E* at different heating rates(*β*) were a little different. It's because that the *A* determined from (5) is extremely sensitive to small variations in the slope. So the compensation effect should be introduced to mitigate the influence. By introducing the compensation effect, the final value of *E* and *A* was that: E=145.221KJ/mol, $A=3.1159\times10^7 S^{-1}$.

TABLE.III the kinetic parameters of coal-char combustion in pure oxygen environment

β(K/min)	n	A(10^7/S^{-1})	E(KJ/(K.mol))	R
20	2	3.117	145.098	0.979
30	2	3.120	145.893	0.983
40	2	3.111	144.856	0.976

All of the kinetic parameters above were obtained in pure oxygen atmosphere. However, under the condition of high CO_2 concentration, the impact of atmosphere should be considered because of the reduction reaction and thermal decomposition reaction of CO_2. In the paper, a partial pressure function of $P_{O_2}^m$ was introduced to characterize the impact of atmosphere.

If the catalysis of ash in coal-char is ignored, coal-char combustion process equates with pure carbon combustion process. To the same chemical reaction process for the same matter, the value of E and A is invariable. The main difference is m. The value of m can be determined by using the experiment data, kinetic parameters obtained in pure oxygen atmosphere and proportion relationship under different atmospheres. The detailed steps were as following: Firstly, a group of oxygen-enriched reaction condition and 100 points on the TG curves were chosen, and a initial value of m was given. Then the value of m was trial-calculated and adjusted on the basis of mean error between simulation and experiment. Finally, the nearest value of m was obtained by comparing the value of m and error calculated under different conditions. In this way, the final value of m for Henan coal-char was 1.12 , and the minimum value of R under different conditions was 0.956.

Hence, the apparent kinetic model of coal-char combustion in oxygen-enriched environment was as following:

$$\frac{d\alpha}{dt} = A\exp(-E/RT)(1-\alpha)^n P_{O_2}{}^m = 3.1159\times10^7 \exp(-17467/T)(1-\alpha)^2 P_{O_2}{}^{1.12}$$

IV. CONCLUSION

Under oxygen-enriched condition, the combustion characteristics of coal-char ameliorates with the increase of oxygen concentration and heating rate. However, for oxygen-enriched combustion in CFB boiler, there is a certain limitation to the increase of oxygen concentration. How to choose a proper oxygen concentration needs a further investigation.

Under the same O_2 concentration, the coal-char combustion characteristic in O_2/CO_2 atmosphere is a little poorer than that in O_2/N_2 atmosphere. Therefore, the oxygen concentration need to be further increased to improve the furnace flame property in oxygen-enriched combustion CFB boiler.

A reaction kinetic model for coal-char combustion in oxygen-enriched environments has been deduced, and it provides theoretical basis for the development and design of oxygen-enriched combustion in CFB boiler.

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