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Surface CO/CO_2 ratio of char combustion measured by thermogravimetry and differential scanning calorimetry

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ABSTRACT

Char combustion is the main stage in the coal-burning process. The CO/CO_2 ratio near the surface of a char particle is an important physical quantity that determines the temperature of the particle and that can also help explore the mechanism of char combustion. In this paper, we propose an innovative method, i.e., thermogravimetry and differential scanning calorimetry, to explore the char combustion products from the perspective of heat release, and then we investigated the effect of combustion conditions on the CO/CO_2 ratio. It was found that the CO/CO_2 ratio first increased and then decreased with temperature from 600 °C to 900 °C, which confirmed the combined effect of both heterogeneous and homogeneous reactions on surface products. Further, by studying the transient products of char combustion, we observed that the CO/CO_2 ratio showed a decreasing trend with the reaction processing at higher temperature, which might be due to the change of the carbon-oxygen reaction pathway. In addition, it was suggested that the main effect of oxygen concentration was on the homogeneous reaction, which will affect the relative value of the CO/CO_2 ratio but hardly change the variation trend.

1. Introduction

Coal plays an important role in the global energy supply, and the primary utilization of coal is for combustion in electricity production. To meet the requirement of efficient and clean combustion of coal, it is necessary to fully understand the combustion characteristics of coal and then accurately predict the combustion process, which is the basis for design and optimization of coal-fired power plants. Char combustion, as the main stage of coal combustion, has the longest duration and releases most of the heat during the coal combustion process [1]. Therefore, the study of char combustion is crucially important.

Char combustion is a seemingly simple, but actually very complicated process. From the perspective of chemical elements, char combustion involves only C and O (and sometimes H is also considered) [2]. However, there are many factors that influence the char combustion process, mainly including chemical reactions, oxygen diffusion processes [3], changes in pore structure [4,5], the deactivation phenomenon under high temperature [6], and the catalytic or inhibitory effect of ash [7,8], which have all been intensively investigated. Among these factors, there is no doubt that the chemical reaction is the basis of char combustion, and the global reactions involved are as follows [9]:

$$C + O_2 \rightarrow CO_2 \quad \Delta H_1 = -396.4\ \text{kJ/mol} \tag{1}$$

$$C + 1/2O_2 \rightarrow CO \quad \Delta H_2 = -110.9\ \text{kJ/mol} \tag{2}$$

$$C + CO_2 \rightarrow 2CO \quad \Delta H_3 = 174.6\ \text{kJ/mol} \tag{3}$$

$$2CO + O_2 \rightarrow 2CO_2 \quad \Delta H_4 = -571.0\ \text{kJ/mol} \tag{4}$$

Among these reactions, reaction (3) is usually called the gasification of char, which can generally be ignored below 1000 °C [10]. Many excellent studies have been devoted to the chemical reaction mechanism of carbon and oxygen [11–15]. The general view of this reaction process is that O_2 is first adsorbed on the surface of carbon particles, combines with free-site carbon to form complexes such as C(O) or $C(O_2)$, and then escapes in the form of CO or CO_2 from the particle surfaces [11,16,17]. The common method to investigate the reaction mechanism of char combustion is to obtain the key kinetic parameters (such as activation energy and pre-exponential factor) of each step of the reaction by measuring several apparent physical quantities, such as CO/CO_2 ratio, combustion rate, and particle temperature [17–19]. Whether the mechanism is reasonable can be evaluated by predicting the char combustion process via this mechanistic model and then comparing it with a real experimental process to explain some of the observed phenomena. We find that the CO/CO_2 ratio plays an important role in the above process. Additionally, the heat release of reaction (1) is −396.4 kJ/mol, which is almost three times

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Table 1
Proximate and ultimate analysis results.

Samples	Proximate analysis (wt%, ad)				Ultimate analysis (wt%, daf)				
	Moisture	Volatile	Ash	Fixed carbon	C	H	O[a]	N	S
Coal char	3.53	3.22	13	80.3	80.5	0.8	17.13	1.30	0.27

[a] By difference.

that of reaction (2); thus, the surface CO/CO_2 ratio will further determine the particle temperature of char combustion and the reaction rate, which is a critical parameter in many char combustion prediction models, such as the carbon burnout kinetic (CBK) model proposed by Hurt [20]. Therefore, the CO/CO_2 ratio of char combustion is one of the key factors in studying the chemical reaction mechanism and predicting the combustion rate. However, due to the effect of reaction (4), the quick conversion of CO to CO_2 near the surface of char particles (or in the boundary layer) makes it difficult to accurately measure the amount of CO/CO_2 produced directly by the heterogeneous reaction (i.e., primary product). As a result, it is still debatable whether the product of char combustion is CO only or both CO and CO_2 and in addition, what the specific CO/CO_2 ratio is [21,22].

Some researchers have attempted to solve the problem of how to get CO/CO_2 onto the surface of particles [17,23,24]. In the pioneering work, Arthur [25] used $POCl_3$ vapor to inhibit the reaction between CO and O_2, and he first proposed the relationship between primary CO/CO_2 ratio and temperature, i.e., $CO/CO_2 = A * \exp(E_c/RT)$, which has been confirmed by many follow-up researches [19,20,24]. Linjewile [26] used a self-designed water-cooled *in situ* sampling probe to measure the combustion products and temperatures of large petroleum coke particle (with the diameter of 9 mm), and found a CO/CO_2 ratio of 0.1–0.55 in the temperature range from 850 K to 1650 K. Recently, a new CO/CO_2 measurement technique was proposed by Scala [27,28], who measured the burning rate of a single char particle (with the diameter of about 7 mm) at low oxygen concentration and accurately predicted the Sherwood number of particles. The results revealed that most of the CO was oxidized within the particles' boundary layer and at most, 10%–20% of the carbon can escape as CO at 850 °C.

In addition to measuring the gas product directly, it is also feasible to infer the gas product from other physical quantities, one of which is the particle temperature. Smith [9] measured the temperature of suspended burning pulverized coal particles (sized 78, 49 and 22 μm) by using a two-wavelength radiation pyrometer in the temperature range 1400–2200 K. On the basis of energy balance and assuming the reaction heat, the particle temperature was calculated by the combustion rate measured, and it was found that the calculated temperature curve coincided with the experimental results well when the primary product was assumed to be only CO. Similarly, Mitchell [29] reported that the heat released by the conversion to CO_2 must be taken into account in the energy balance to accurately predict the mass change of spherical carbon particles (sized 100–160 μm) during combustion in the temperature range 1400–2200 K. When the CO_2 percentage was assumed to be approximately 0.35, the predicted mass change is closest to the experimental value.

Subject to the analysis technique, it remains challenging to directly measure the primary CO/CO_2 ratio of char combustion because the secondary reaction cannot be avoided. However, as mentioned above, one of the main effects of the CO/CO_2 ratio is on the calorific value and then the temperatures of the char particles. It is also of practical significance to investigate the CO/CO_2 ratio of char combustion from the perspective of heat release. As pointed out by Smith [9], the key approach to ascertain the influence of CO_2 formation in the vicinity of burning char particles is by measuring both the mass loss and the particle's temperature. Thermogravimetry and differential scanning calorimetry (TG–DSC), which can measure the mass change and heat flux of a substance simultaneously, has been generally accepted as a mature and precise technique to investigate the reaction process with varying temperature [30,31]. Currently, it is widely used in researches, such as the blending of combustion and coal spontaneous combustion kinetics [32–35]. In this paper, the TG–DSC method was used to explore the CO/CO_2 ratio near the particle surface and the effects of temperature and oxygen concentration by measuring both the mass loss and heat release of char directly. In addition, there are few studies devoted to the variation of CO/CO_2 ratio with combustion process, which is usually treated as a function of only temperature. Thus, we also investigated the transient CO/CO_2 ratio during the reaction to deeply explore the char combustion mechanism.

2. Experimental

2.1. Materials

The sample used in this research was coal char. The raw coal was ground and sieved to a diameter between 45 μm and 105 μm, and then the pulverized coal was heated at 950 °C for 2 h in an Ar atmosphere to remove most of the volatiles and moisture. The proximate and ultimate analysis results are given in Table 1.

2.2. Sensitivity calibration

The principle of DSC is to measure the difference of the voltage signal between the sample thermocouple and the reference thermocouple, and the signal units are μV. For practical purposes, mW is used as the unit of heat effect to explain the actual physical meaning. The purpose of sensitivity calibration is to determine the relationship between the thermocouple signal and the heat effect, which is regarded as the sensitivity coefficient. In our experiment, the accuracy of the DSC measurement was crucial to the results. Therefore, it was necessary to conduct the sensitivity calibration before the char combustion experiments, to improve and confirm the accuracy of the DSC signal.

Six sets of standard metal samples (In, Sn, Bi, Zn, Al, and Au) were selected for sensitivity calibration experiments, whose fusion points ranged from 150 to 1100 °C. Every sample was heated to 40 °C above the fusion point so they were completely melted, and they were then cooled and solidified. This procedure was repeated three times to obtain the average real voltage signal.

2.3. Char combustion experiment

Char combustion experiments were conducted using a simultaneous thermal analyzer (Netzsch STA449 F3, Netzsch Instruments, Germany). To reduce the effects of heat and material diffusion, the char sample mass of each experiment was 10 mg. It is worth noting that, we focused on the chemical reactions between carbon and oxygen in this research, and the effects of physical diffusion should also be considered when applying it to the real conditions. In our research, to explore the influence of temperature on the combustion process, char combustion was carried out under isothermal conditions. The furnace was first heated to the target temperature at a rate of 20 K/min under an inert atmosphere (Ar), and then switched to oxidizing atmosphere (O_2/Ar). To avoid overheating effects caused by heating inertia, the furnace was