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Full Length Article

Experimental estimate of CO_2 concentration distribution in the stagnant gas layer inside the thermogravimetric analysis (TGA) crucible

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ABSTRACT

The measurement of char gasification reactivity and kinetic parameters by TGA is generally complicated with mass transfer limitations. There is a reactant gas concentration gradient in the stagnant gas region between the mouth of the TGA crucible and the surface of the char bed because of gas consumption by the sample. The counter-diffusions between the reactant and product gases occur in this stagnant region. The Maxwell-Stefan equation has been used to estimate the distribution of gas concentration in the stagnant gas region. However, there is some uncertainty associated with semi-empirical gas diffusion coefficients used in the equation. In this study, we propose a new method to estimate the distribution of CO_2 concentration in the stagnant gas region during CO_2 gasification of coal char in TGA. The external effectiveness factors obtained in this way were in a reasonably good agreement with the value obtained by the traditional method widely used in literature.

1. Introduction

TGA has become a common analytical choice to investigate the reactivity and kinetics of coal char gasification [1–11]. The closed-bottom crucible (CBC) filled with a certain amount of char particles is widely utilized in TGA experiments [12–14]. The measurement of char gasification reactivity and kinetic parameters by TGA is complicated due to mass transfer limitations [15–17]. The mass transfers in CBC can occur through the following steps [1,18,19]: (1) the transfer of the gasifying agent from the bulk of the gas to the external layer of the char particle packed in CBC (referred to as external mass transfer); (2) diffusion of the gasifying agent from the external layer into the bed of the char particle (referred to as internal mass transfer); and (3) diffusion of the gasifying agent from the bed of char sample into the interior of the char particle (referred to as pore diffusion). Among these steps, the external mass transfer effect plays an important role in controlling gasification kinetics. There is a reactant gas concentration gradient in the stagnant gas region between the mouth of the crucible and the surface of the char bed because of gas consumption by the sample. The counter-diffusions between the reactant and product gases occur in this stagnant region [18], which result in poor provision of the reactant gas to the char surface. From the perspective of intrinsic kinetics, this external mass transfer effect must be first eliminated.

To avoid external diffusion limitations, most authors conduct preliminary TGA tests at increasing gas flow rates until the influence on the measured rate is not found [20]. However, this method is not entirely reliable if the bed of char particles lies below the crucible mouth, because a stagnant gas region may still exist even at high gas flow rates [12,21]. Several studies have investigated the external mass transfer effect in the stagnant gas region using an external effectiveness factor. The external effectiveness factor is defined as the ratio of the rate at which the CO_2 concentration is the real concentration of the specific sectional height to the rate at which the CO_2 concentration is the concentration of the bulk flow [18,22]. The application of this factor requires priori knowledge of the concentration of the reactant gas at the char bed surface. However, none of reported studies measured the CO_2 concentration at the bed surface by experimental measurement directly. The external effectiveness factor is also defined as the ratio of reaction rate with external diffusion limitation to reaction rate without external diffusion limitation in traditional method [18,21,22]. Based on this definition, the external effectiveness factor can be obtained without the distribution of CO_2 concentration. The external effectiveness factor by the traditional method can be used to verify other new methods. Meanwhile, the Maxwell-Stefan equation has been used to estimate the distribution of CO_2 concentration in the stagnant gas region [13,18,21]. However, there is some uncertainty associated with semi-empirical gas diffusion coefficients used in the equation. To date, no attempt is made to experimentally validate the calculated concentration profiles.

In this study, we propose an experimental method to estimate the distribution of CO_2 concentration in the stagnant gas layer during CO_2

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Table 1
Properties of lignite.

Sample	Proximate analysis (wt%, db)			Ultimate analysis (wt%, db)			
	Ash	Volatiles	Fixed carbon	C	H	N	(O + S)[a]
Lignite	14.2	39.1	46.7	64.7	4.1	1.0	16.0

[a] By difference.

gasification of coal char in TGA. Beside this experimental study, this paper also includes a verification to discuss and to support the experimental results.

2. Experimental

2.1. Materials and apparatus

A lignite from the Inner Mongolia Autonomous Region in north of China was used in this study. Table 1 presents the ultimate and proximate analyses of the investigated lignite. The coal sample was pulverized to below 100 μm, a typical particle range for entrained-flow gasification, in a hammer mill and dried at 105 °C for 2 h before use.

A simultaneous thermal analyzer (Mettler-Toledo TGA/DSC-1100LF) was used for gasification of coal char. Four CBCs with an identical inner diameter of 6.8 mm and different sidewall heights of 1.5, 4.5, 6, and 8 mm were used in this study, denoted by CBC1.5, CBC4.5, CBC6, and CBC8, respectively.

2.2. Gasification reactivity studies

Char reactivity was determined via a combined pyrolysis/gasification TGA mode. For each experimental run, the sample-filled crucibles were heated under a nitrogen flow of 200 mL/min and heating rate of 50 °C/min to 900 °C, followed by an isothermal holding at this temperature for 10 min. The isothermal gasification of the sample was initiated by switching to an equivalent flow rate of CO_2 and completed until weight loss reached constant. In all cases, baseline correction was conducted by subtracting a "blank" signal that was recorded with an empty crucible from the TGA data of the sample determined under the same conditions. All experiments repeated twice or more. In this study, except for the CO_2 concentration and crucible type, all the experimental conditions are the same. Char conversion (x) and isothermal reactivity (r, s^{-1}) of the char during the isothermal gasification step were calculated by Eqs. (1) and (2), respectively:

$$x - \frac{m_0 - m_t}{m_o - m_e} \tag{1}$$

$$r = \frac{dx}{dt} \tag{2}$$

where m_0 is the initial sample mass at the start of the gasification; and m_t is the instantaneous mass at gasification time t; and m_e is the sample mass at the end of gasification, which corresponds to the mass of the ash. In this work, the reactivity at 20% char conversion was taken as the representative value (r).The nth-order reaction kinetics is often adopted in char gasification with pure CO_2 as the gasifying agent, which can be expressed by the following equations:

$$r = kC^n \tag{3}$$

$$k = A_0 \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

where k, C, n, A_0 and E_a are the rate constant, CO_2 concentration at the surface of char particles, reaction order, pre-exponential factor and activation energy respectively.

2.3. Methodology of estimating CO_2 concentrations at different sectional heights in CBC

Fig. 1 shows the diagram of the crucibles used in this study. The CBC8 was used as a target crucible to estimate CO_2 concentration distribution in the stagnant gas layer. The CBC1.5, CBC4.5, and CBC6 were used to divide CBC8 to three sectional heights according to a-a', b-b', and d-d'. The sectional height at the mouth of the CBC8 was labeled as e-e'. Among the four crucibles used, the CBC1.5 was used as a datum to unify the initial sample load. The mass of coal fully filled in the CBC1.5 was about 20 mg. Therefore, the initial sample loads 20 ± 0.2 mg was used in all TGA tests. The CO_2 concentration inside the CBC8 at the sectional heights were denoted as $C_{a-a'}^{CBC8}$, $C_{b-b'}^{CBC8}$, $C_{d-d'}^{CBC8}$ and $C_{e-e'}^{CBC8}$ respectively. Only $C_{e-e'}^{CBC8}$ was known to be the concentration of CO_2 in the bulk flow. The determination of the $C_{a-a'}^{CBC8}$, $C_{b-b'}^{CBC8}$and $C_{d-d'}^{CBC8}$ was designed in the following ways:

First, the 20 ± 0.2 mg coal sample in the CBC8 was subjected to isothermal gasification under a CO_2 flow ($C_{e-e'}^{CBC8}$ = 100%) at 900 °C. The char reactivity was calculated using Eqs. (1) and (2) and denoted by r^{CBC8}.

Next, the CBC1.5, CBC4.5 and CBC6 were all filled up with 20 ± 0.2 mg coal sample and gasified at 900 °C under six different CO_2 concentrations respectively. According to nth-order kinetic Eq. (3), the relationship between char reactivity and CO_2 concentration can be expressed by a power function. The power function equations of the CBC1.5, CBC4.5 and CBC6 can be obtained by data fitting. In the power function equation, every concentration corresponds to the only one gasification rate. Given the value of CO_2 concentration, the corresponding value of the char reactivity can be calculated by the power function equation above, vice versa.

In this study, the initial sample load was always 20 ± 0.2 mg. The geometric distinction between the CBC8 and other three types of crucibles (CBC1.5, CBC4.5 and CBC6) is that they have the different height of the stagnant gas region. The sample beds inside four types of crucibles are identical in the geometric structure and properties. The essential difference between the CBC8 and other three types of crucibles is the CO_2 concentration in the specific sectional height. Based on the comparisons above, a theoretical hypothesis was proposed that if the $C_{a-a'}^{CBC8}$ and $C_{a-a'}^{CBC1.5}$ were the same, the r^{CBC8} should be equal to $r^{CBC1.5}$,

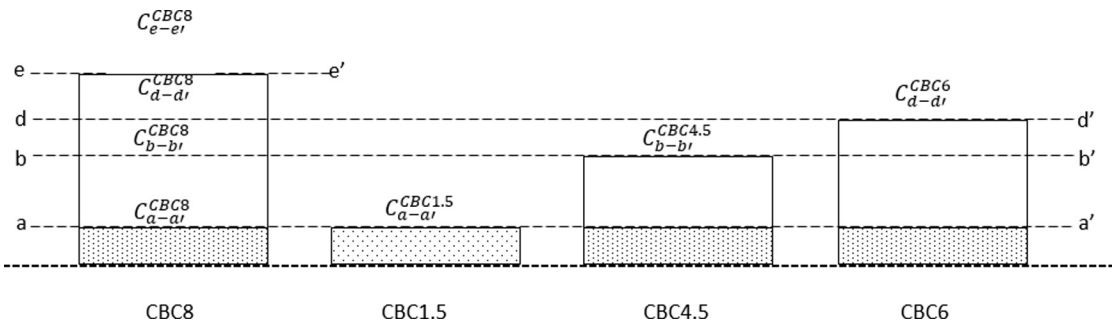

Fig. 1. The conceptual figure of the proposed methodology.