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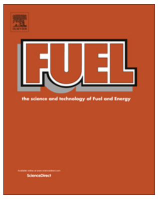

Experimental study of pore diffusion effect on char gasification with CO_2 and steam

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HIGHLIGHTS

- The char reaction kinetics with CO_2 and steam were measured in a TGA.
- The effectiveness factor with an *n*th-order model was proposed to study the diffusion.
- The experimental effectiveness factor agrees with the calculated result.
- *Tc* was proposed to compare diffusion effects on H_2O reaction and that on CO_2 reaction.

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ABSTRACT

Reactivities of three chars with CO_2 and steam were examined using a Thermogravimetric Analyzer (TGA). Similarities and differences between kinetics of char–CO_2 gasification and char–steam gasification have been discussed. As a result, for both reactions, the measured gasification rate increases with temperature and decreases as the particle size increases. And the initial rate of char–steam gasification is always several times faster than that of char–CO_2 gasification. Moreover, for the char with lower reactivity, the activity of its steam gasification reaction possesses larger difference with that of CO_2 reaction. An *n*th-order model with the effectiveness factor was used and a characteristic parameter (*Tc*, which is the temperature in the case of Thiele modulus $\phi = 3$.) was proposed to compare the difference between the pore diffusion effect on steam gasification and CO_2 gasification. The results show that the pore diffusion resistance increases with the gasification temperature and particle size. However, for each sample, *Tc* of char–steam gasification is always lower than that of char–CO_2 gasification. The pore diffusion effect on char–steam gasification is more significant than that on char–CO_2 gasification. Moreover, the difference between the pore diffusion effect on char–steam gasification and char–CO_2 gasification is larger for the char with lower reactivity.

1. Introduction

Solid fuel gasification is an efficient technology for solid fuel utilization and becomes more and more important in many industrial areas. Entrained flow gasification, one kind of most efficient and cleanest gasification technologies, is the leading technology in the field of solid fuel gasification. In general, the gasification process includes pyrolysis step and char gasification step. At the high temperature within an entrained flow gasifier, devolatilization occurs in tens of milliseconds. The reaction rate of pyrolysis is much faster than that of char gasification, so char gasification is the rate-limiting step during gasification [1]. Therefore, knowledge of char gasification kinetics is crucial for design and stable operation of entrained flow gasifiers [2,3]. Regarding kinetics, the influence of char–O_2 reaction on the gasification process is less significant as char–O_2 reaction is much faster than that of char–CO_2 and char–steam reactions [4,5]. So a clear understanding of char–CO_2 and char–steam kinetics is more important.

Char–CO_2 and char–steam kinetics have been widely investigated in the past. Bayarsaikhann et al. [6]. studied the kinetics of char–steam gasification at 800–900 °C using a novel drop tube/fixed-bed reactor. Goyal et al. [7] examined the CO_2 gasification reactivities of a typical bituminous coal char. Koba and Ida [8] found that rates of steam gasification with lignite and bituminous coal were almost 2–5 times higher than that of CO_2 gasification. Ahmed and Gupta [9] examined and compared the reactivities of woodchips char gasification using the laboratory scale experimental

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facility. The Langmuir–Hinshelwood model has been used to study kinetics of char gasification by steam and CO_2 in the presence of H_2 and CO [10]. Numerous experimental data have been obtained by these researchers, but gasification rates obtained in some literatures were affected by pore diffusion which is influenced by temperature and particle size. The effect of pore diffusion can result in an erroneous rate expression if it is not accounted for properly.

For this reason, the effect of pore diffusion has been further discussed by many researchers. Barea et al. [11] clarified the diffusional effects in CO_2 gasification with single biomass char particle and their teammates [12] studied the diffusional effect on the CO_2 gasification with wood matter from pressed oil-stone by the L–H model and the *n*th-order model. The comparison between char–CO_2 gasification kinetics under conditions of chemical reactivity regime and pore diffusion hindered regime was be analyzed by Roberts et al. [13] The random pore model was used to predict the diffusional effect on the combustion of char particles by Everson et al. [14] and the shrinking core model was also established to estimate the pore diffusion effect on the combustion of carbonaceous material [15]. Most of these literatures focused on the diffusional effect on combustion and CO_2 gasification, but there is few reported research on the diffusional effects on steam gasification and even compared the difference between the effects on CO_2 gasification and steam gasification. As discussed above, kinetics of CO_2 and steam gasification are more important steps in char gasification. So it is also important to estimate the pore diffusion effect on char–steam gasification. Moreover, the chars obtained in many investigations were biomass char. In general, reactivities of coal or coke gasification are also greatly affected by pore diffusion under most entrained flow gasification conditions [16]. Although there are many similarities in the process of biomass gasification and coal or coke gasification, there are many differences between them. For example, biomass gasification and coal or coke gasification differ from each other in the structures of chemical functional groups, as well as the contents of fixed carbon and volatile matter, which will exercise dramatic impacts on the gasification rate and its controlling steps. In general, low fixed carbon content and high volatile matter content of coals will lead to high gasification reactivities [17]. The content of fixed carbon in coal or coke is much higher than that in biomass and the content of volatile matter in coal or coke is much lower than that in biomass. Moreover, biomass possesses more micro pores than coke or coal. All these phenomena indicate that the gasification and diffusion processes of coal or coke may be much different from those of biomass. Therefore, it is also important to develop a suitable model to quantify the effect of pore diffusion on coal or coke gasification with steam and CO_2. It can provide not only theoretical basis for simulation, but also scientific basis for gasification industry.

In this study, two typical coals and a petroleum coke were gasified with different gasification agents (steam and CO_2) using TGA. Test conditions of temperature and particle size were determined to clarify the pore diffusion effect on coal or coke gasification. Moreover, an *n*th-order model with the effectiveness factor and a characteristic parameter were proposed to quantify the difference between the pore diffusion effect on steam gasification and CO_2 gasification.

2. Experiments

2.1. Char preparation

Two coals and a petroleum coke were used in this study. Two coals are Shen-fu bituminous coal (SF) and Zun-yi anthracite (ZY). The petroleum coke (PC) is from Sinopec Shanghai Gaoqiao Company. The properties of these three samples are listed in Table 1. During char preparation, All samples were heated at 25 °C/min to 850 °C and held 30 min under the high purity nitrogen atmosphere in a fixed bed reactor. After devolatilized, the prepared chars were sieved and the particle sizes of <40, ~100, ~250, and ~500 μm were used to further analysis. The average particle size of each char sample was tested by Malvern Mastersizer 2000 laser particle size analyzer. The values of the average particle size are shown in Table 2.

2.2. Char gasification

CO_2 gasification experiments and steam gasification experiments for different particle sizes of three chars were all carried out with NETZSCH STA449F3 Thermogravimetric Analyzer (TGA). The gasification procedure is described as follows: approximate 5 mg of sample particles were placed at the mouth of a crucible and heated at 25 °C/min to the desired temperature under a continuous nitrogen flow of 80 mL/min. N_2 was replaced by reactant gas after the desired temperature was reached. The final temperature was kept for gasification until no further weight loss was observed. When the reactant gas was steam, the flow rate was set as 80 mL/min and the gasification temperature was from 850 °C to 1100 °C. And when the reactant gas was CO_2, the flow rate was set as 80 mL/min and the gasification temperature was from 850 °C to 1300 °C. In order to investigate the effect of the pore diffusion on char gasification, the effect of external diffusion had been eliminated by previous tests. Fig. 1 shows the external diffusion effect of reactant gas on SF char gasification. Results showed that when the CO_2 flow $\leqslant$60 mL/min, the reactivity increased significantly with the CO_2 flow. However, when the CO_2 flow >60 mL/min, the reactivity changed little as the CO_2 flow increased. This means when the CO_2 flow >60 mL/min, the external diffusion effect of reactant gas on SF char gasification can be neglected. This trend was also observed in the other three chars. So in this study, a continuous CO_2 flow of 80 mL/min was carried out to avoid the effect of external diffusion.

Sources of uncertainties in the measurement of the TGA analysis are the atmosphere control, thermal hysteresis effects and the particle size distribution of the test sample. So in order to avoid errors, each test was carried out twice. The relative error between two measurements was less than 3%.

The carbon conversion is expressed by following:

$$x = \frac{w_0 - w_t}{w_0 - w_{ash}} \tag{1}$$

where w_0 is the initial weight of char; w_t is the weight at time t and w_{ash} is ash mass in the char. Gasification rate is defined as differential of carbon conversion to gasification time:

$$r = -\frac{1}{w_0 - w_{ash}}\frac{dw}{dt} = \frac{dx}{dt} \tag{2}$$

A representative reactivity value, the initial gasification rate (r_0), was used in this study since the bed of char particles can be considered to be constant at the initial time of gasification.

3. Results and discussion

3.1. Char reactivity with different gasification agents at various temperatures and pore sizes

The effect of gasification temperature on carbon conversions during char–steam and char–CO_2 gasification of SF char for very fine particles (<40 μm) is presented in Fig. 2. For both reactions, it is obvious that the time for complete carbon conversion decreased as the gasification temperature increased. This trend was also observed for the other chars, particle sizes and gasification