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Characterization of coal char gasification with steam in a micro-fluidized bed reaction analyzer

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ABSTRACT

In this study, the so-called micro-fluidized bed reaction analyzer (MFBRA) was used to characterize the isothermal reaction of char gasification with steam at 0.1 MPa. With minimal inhibition of heat and mass transfer, the article examined the effect of reaction temperature and partial pressure of steam on char gasification behavior and reaction kinetics. It was found that at the experimental temperatures varying in 750–1100 °C, the char–steam gasification reaction can be divided into two regions according to temperatures of 750–950 °C and 950–1100 °C. The reaction was well described by the shrinking core model, and the activation energies of char–steam gasification in such two regions are 166.94 kJ/mol and 79.4 kJ/mol, respectively. The activation energy in the kinetically controlled low-temperature region is very similar to that reported in the literatures, validating the reliability of MFBRA for characterizing char gasification and estimating its kinetics. Furthermore, the reaction order for steam partial pressure was found to be about 0.5 under the tested conditions.

1. Introduction

Gasification enables an attractive route for converting carbonaceous fuels cleanly and high-efficiently into fuel gas, synthesis gas, and other valuable energy products [1,2]. The most extensively used gasification agents include oxygen, air, steam, carbon dioxide, and any mixture of these agents. Among them, steam and its mixture with other agents are widely adopted. The use of steam in gasification can promote H_2 production by enhancing the H_2-formation reactions including water–gas shift, methane reforming, tar cracking and so on. It also contributes to high carbon conversion and high gas heating value and facilitates the temperature control and gas production in gasifiers [3–5]. Compared to fuel pyrolysis involved in steam gasification, the reaction between char and steam has a much lower reaction rate. It is always the rate-limiting step that dominates the whole process of gasification. Therefore, a clear and precise understanding of the effect of steam on char gasification reaction is essentially necessary to design a gasifier [6–8].

Up to now, a huge number of studies on char gasification behavior and kinetics have been reported using a fixed bed, a fluidized bed, a drop tube, a wire mesh reactor, and especially a thermo-gravimetric analyzer (TGA) [9–11]. Among them, TGA is the most common and representative analyzer, which can continuously record the change of weight loss with time for the char sample. However, due to the limitations in measurement principle, reactor structure and heating rate (usually <100 K/min), TGA cannot upload a sample instantaneously at a required temperature, resulting in a thermal pretreatment before the occurrence of the expected reactions. The carrying gas in TGA is hard to flow through the sample surface in the crucible, causing serious gas diffusion from the main gas flow to the surface of the sample [12]. Moreover, it is difficult to analyze steam gasification using TGA, especially at temperatures above 900 °C. When testing isothermal char gasification in TGA, a switching operation from an inert gas flow to the gasification agent has to be required. The unsteady atmosphere in TGA during the process of gas replacement probably seriously affects the measured reaction, especially at high temperature, which causes thus inaccurate kinetic data [13]. Although the drop tube, wire mesh reactor and self-made fluidized bed reactor have been employed to measure char gasification reactions, there is not a standardized commercial analyzer based on these reactors. These analyzers also greatly suffer from the serious gas mixing and diffusion prevailing in their reactors. Moreover, the wire mesh reactor is hard to be used for steam atmosphere. The literature-reported kinetic data have actually big differences, which should be related to the use of many non-standardized reactors.

Recently, a new micro-fluidized bed (MFB) reactor, with both its inner diameter and particle bed height about 20 mm, has been used to test gas–solid reaction characteristics and reaction kinetics [14]. The developed micro-fluidized bed reaction analyzer (MFBRA) integrates the advantages of quick heat and mass transfers in the MFB reactor, pulse feeding of micrograms of reactant sample by electromagnetic pulse method, and fast detection of reacted gas using a process mass spectrometer. It enables the on-line feed of milligrams of solid sample at arbitrary preset temperatures, and further allows the utilization of special gas atmospheres like steam without the involvement of gas

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switching. These make the MFBRA particularly suitable for the measurement of isothermal reactions in steam-containing atmosphere. In comparison with TGA, the measurement principle of MFBRA is much different. For the former, the mass change of a sample is continuously monitored with high precision, while for the latter it measures the variation of product gas composition as well as volume through online gas analyzers, say, both mass spectrometer and gas chromatography. By far, MFBRA has been successfully used to analyze many reactions [13–16], such as pyrolysis of coal and biomass, combustion of biomass and petroleum coke, gasification of solid fuels, tar cracking, chemical reduction, mineral ore calcination, material preparation and so on.

In this study, the isothermal char–steam gasification is tested using MFBRA under atmospheric pressure. With minimized inhibition from transfer and diffusion, the article systematically investigated the effect of reaction temperature and partial pressure of steam on gasification behavior and reaction rate. The reaction kinetics of coal char gasification with steam are estimated and compared with the results reported in the literature. As a result, the work is expected to justify the capability of MFBRA for measuring the steam-involved isothermal reactions, and also to provide a kinetic understanding for the atmospheric fluidized bed coal gasification widely applied to fuel gas production.

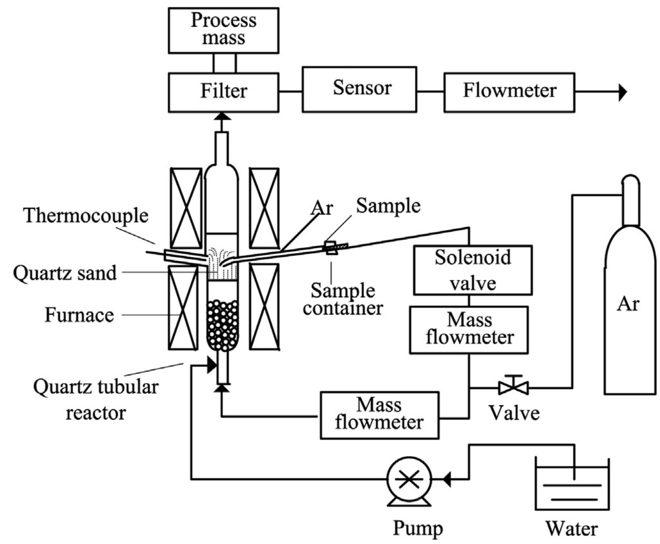

Fig. 1. Principle and schematic diagram of MFBRA adaptive to steam agent.

2. Experimental section

2.1. Experimental approaches

To prepare char sample, a kind of Xinjiang Jimusaer (JMSE) subbituminous coal was pyrolyzed in a laboratory fluidized bed reactor in atmosphere of high-purity nitrogen (99.999%) at 1000 °C. The detailed method can refer to our previous study [17]. Table 1 shows the major properties of coal char, clarifying that in the char the residual volatile was about 3 wt.% and the fixed carbon content was close to 84 wt.% (air dry base). Prior to experiment, the char sample was dried, ground and sieved to the required particle sizes.

Fig. 1 shows the principle and process of the adopted MFBRA, which consists of a micro-fluidized bed (MFB) reactor, a sample injection system, an electric furnace, a gas supply system (argon, steam), a produced gas cleaning system and an online process mass spectrometer (AMETEK) connected to the gas outlet of the MFB reactor. The quartz glass MFB reactor had an inner diameter of 20 mm and was made of three stages separated by two porous plates. The reaction zone with its length of 50 mm was between a lower stage of 150 mm long for water evaporation and gas preheating and a top stage of 40 mm in length for catching any fine particles coming from the reaction zone. The lower stage was packed with Al_2O_3 balls to ensure the full vaporization of water sent by a peristaltic pump. Quartz sand in an average particle size of about 50 μm was adopted as the fluidization medium particles in the reaction zone. The entire MFB reactor was heated with a micro-electric furnace allowing precise temperature control in ± 1 K.

After reaching the preset reaction temperature and keeping the stable fluidization of quartz sand particles by a gas mixture of argon and steam, about 30 mg char sample was instantaneously injected into the hot fluidized quartz sand through a gas jet, which in turn initiated the gasification reaction with steam. The tests were performed at 750–1100 °C, and the generated gas, after cleaning in a micro-gas cleaning system, was online analyzed in a process mass spectrometer (AMETEK). The gas was also sampled into gas bags in specified time internals to analyze the gas composition using a micro-gas chromatography (Agilent 3000A). The reaction characteristics including product composition, mass balance and kinetic parameters were studied by analyzing the data given by MS and micro-GC.

Table 1
Proximate and ultimate analyses of coal char tested.

Proximate analysis, wt.% (air dry)			Ultimate analysis, wt.% (dry ash free)				
Volatile	Ash	Fixed carbon	C	H	S	O	N
3.8	12.4	83.8	91.1	2.3	0.6	4.8	1.2

2.2. Datum analysis approaches

The carbon conversion X and reaction rate R for the isothermal char gasification in MFBRA are estimated by considering the main reactions of $C + H_2O \rightarrow CO + H_2$ and $CO + H_2O \rightarrow CO_2 + H_2$ according to Eqs. (1) to (6). In order to understand the data analysis method better, Fig. 2 shows the main parameters in the equations defined according to the MS data measured for CO_2 product from the char–steam gasification at 1000 °C.

$$w_f = w_{f(\mathrm{C-CO_2})} + w_{f(\mathrm{C-CO})} = \frac{12 \times L \times \overline{C_{CO_2}} \times (t_f - t_0)}{22.4} + \frac{12 \times L \times \overline{C_{CO}} \times (t_f - t_0)}{22.4} \quad (1)$$

$$w_{i(\boldsymbol{C-CO_2})} = \frac{S_{0\to t_{i(\boldsymbol{c-co_2})}}}{S_{0\to t_{f(\boldsymbol{c-co_2})}}} \times w_{f(\boldsymbol{C-CO_2})} = \frac{\int_0^{t_i}\left(I^{t_i}_{\boldsymbol{MS\text{-}CO_2}} - I^{t_0}_{\boldsymbol{MS\text{-}CO_2}}\right)\mathrm{d}t}{\int_0^{t_f}\left(I^{t_i}_{\boldsymbol{MS\text{-}CO_2}} - I^{t_0}_{\boldsymbol{MS\text{-}CO_2}}\right)\mathrm{d}t} \times w_{f(\boldsymbol{C-CO_2})} \quad (2)$$

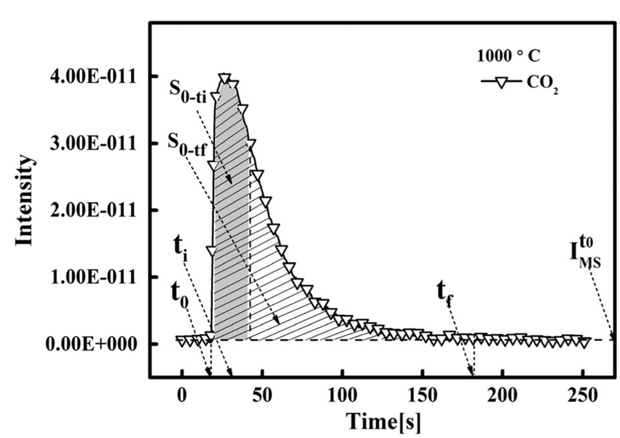

Fig. 2. Analysis approach adopted for char–steam reaction in MFBRA.

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