Kinetics of steam gasification of in-situ chars in a micro fluidized bed

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ABSTRACT

In-situ char steam gasification was conducted using a multistage in-situ reaction analyzer based on a micro fluidized bed. Rapid pyrolysis was activated when pulverized coal was injected into the micro fluidized bed reactor. The temperature was adjusted to the gasification temperature, which was not higher than the pyrolysis temperature. In-situ char gasification was initiated by switching the atmosphere from Ar to H_2O/Ar. The procedure avoided mutation effects and monitored in-situ reactions reliably and efficiently. Char was not completely gasified below 1000 °C. The kinetic parameters calculated from relative or absolute conversions differed from each other. Absolute conversion avoided mutation effects. Gasification accelerated with increasing steam concentration from 15% to 25% but was constant from 25% to 45%. The rate constants for in-situ char were preferable for determining in-situ reactivity. Ex-situ chars were less reactive than in-situ chars. Deactivation of highly reactive char was sensitive to cooling and reheating.

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Introduction

The clean use of coal is important for reducing environmental pollution, especially in countries where coal is the main energy source [1–4]. Gasification is a feasible method for clean coal use [5–9]. Steam gasification of coal is an important method of H_2 production [8–11], which contributes to reducing carbon emission intensity [12–15]. Coal gasification is controlled by conversion of the residual char produced by coal devolatilization [16–18]. The gasification reaction between char and steam is also significant in oxy-fuel combustion and other new combustion technologies [19–22]. The kinetics of char gasification in steam is therefore fundamental to simulation of gasification processes and optimization of engineering applications.

The nature of a fuel largely determines its reaction behaviour during gasification. The source and quality of coal change frequently in industrial applications. Researchers have also been working on promoting the advanced utilization of various biomass fuels [23–29]. Reactivity parameters are required to design appropriate industrial processes. Reactors with different mass transport limitations and different accuracies are frequently used to measure gasification reactivity. The test results are often highly divergent and cannot

be directly compared. This hinders precise control of gasification reactors with variable fuel properties in industrial applications.

Evaluation of the intrinsic reactivity of a gas–solid reaction using common analytical instruments is strongly influenced by gas diffusion [30–33]. Laboratory-scale fluidized beds provide reaction conditions for achieving rapid heating of particles and maximum inhibition of external diffusion. A gas–solid reaction in a fluidized bed approximately represents the intrinsic reactivity of fuel particles [33–35]. The recently developed micro fluidized bed reaction analyzer (MFBRA) is a distinctive instrument that is based on reaction conditions of fluidization and on-line monitoring of gas release [36–39]. Significant advantages of the MFBRA are as follows.

1. Diffusion effects are effectively eliminated and reliable isothermal conditions are accurately maintained; this ensures a kinetically controlled particle reaction at the desired temperature.
2. Miniaturized bed parameters (bed diameter 18–22 mm and static bed height 4–20 mm) guarantee approximate plug flow in the pipe system. A time-series of product gas compositions can therefore be directly monitored and the process data for various forms corresponding to the real reaction process can be obtained.

Chars for char reactivity measurements were conventionally prepared in various laboratory-built reactors. Reactivity experiments were performed to determine the reactivities of the prepared chars. The analysis involved cooling and reheating. Previous work by others [40–45] has shown that cooling and reheating changed the in-situ physical/chemical properties of fresh char at the temperature at which it was formed (called in-situ char). Such measurements differ from those in industrial applications. The preparation of rapid pyrolysis chars is a lengthy procedure and is strongly affected by the reactor and operating conditions.

The main purpose of this study was to establish an efficient and reliable method for determining the steam gasification kinetics of in-situ chars. The experiments were performed using a newly developed multistage in-situ reaction analyzer based on a micro fluidized bed (MFB-MIRA). The kinetic parameters were calculated and analysed. The effects of the calculation methods for conversion on gasification kinetics and the effects of ex-situ treatment (cooling and reheating) on the reactivity of the in-situ char were investigated.

Experimental

Materials and apparatus

Two typical Chinese coals, i.e., Shenhua bituminous coal (SH) and Zhundong sub-bituminous coal (ZD) were used for the experiments. The raw coals were separately crushed to pulverized coals of mean particle diameter 60 μm. The proximate and ultimate analyses of the pulverized coal samples are listed in Table 1.

Fig. 1 shows a schematic diagram of the MFB-MIRA; it consisted of a gas supply system, a steam generator, a gas flow-switching system, a reaction system, a sample-feeding system, and an on-line gas analysis system. Hyperpure water in the steam generator was fed into a stainless-steel capillary (inner diameter 0.5 mm) quantitatively and continuously, using a precision injection pump. Ar flowed into the capillary through a micro-T-joint and carried the water to a micro heater. The mixed gas–liquid flow was eventually vaporized as a continuous H_2O/Ar gas flow. The uncertainty of steam concentration was about 2% of the set value. Ar, H_2O/Ar, and air were switched and fed into the reaction system using two four-way ball valves, according to the desired reaction atmosphere. The reaction system consisted mainly of a modified micro fluidized bed reactor (MFBR-M) and an infrared furnace.

The MFBR-M was made of quartz. The reaction zone in the MFBR-M consisted of a quartz tube (internal diameter 20 mm and height 60 mm) and two porous sintered plates. The fluidized medium was quartz sand (4.2 g, particle diameter 90–150 μm) with a static bed height of 6 mm. The most significant difference between the MFBR-M [46] and the micro fluidized bed reactors described in the literature [47–49] is the addition of a narrow annular preheating section before the entrance to the reaction zone in the MFBR-M. The thickness of the gas in the narrow annulus was 1 mm; this gave instantaneous preheating of the gas and improved the temperature uniformity of the reaction zone. The inner volume of the flow channel between the fluidized bed and the switching valves was less than 3.5 mL; this significantly improved the response of reaction atmosphere switching. The external surfaces of the narrow annular preheating section and the reaction zone were coated with silicon carbide nanoparticles to enhance heat transfer between the reactor and the heating elements. A bare wire thermocouple was immersed in the fluidized bed to measure and control the reaction temperature directly. The minimum control period of heating was less than 0.25 s, and the control accuracy of the reaction temperature was better than ±1 °C. The inner volume of the MFBR-M was 36 mL.

A solenoid valve in the sample-feeding system was opened for 12 ms to introduce 3.6 NmL of Ar (initial gauge pressure 0.1 MPa) into the feed tube and then the preplaced pulverized coal (10 ± 0.1 mg) was immediately injected into the fluidized bed. The gas released from the MFBR-M flowed into the on-line gas analysis system. The gas was first flowed through a narrow annular tube condenser (ice-water bath) for complete removal of water and then passed to a mass spectrometer (Ametek Dycor-LC-D100M). The narrow annular tube condenser consisted of a water storage ball and a narrow annular tube. The volume of H_2O in the gas flow at the condenser outlet was lower than 1%. The inner volume of the flow channel between the MFBR-M outlet and the sampling point at the mass spectrometer was about 17 mL. The mass spectrometer was calibrated on-line using a standard gas at least three times every day to convert the response signals to volume concentrations of H_2, CH_4, CO, and CO_2.

Concentration curve response tests

Diffusion and back mixing always occur in the flow pipe of an MFB-MIRA. The output from the on-line gas analysis system is probably not a faithful representation of the real process of