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Non-isothermal coal char gasification with CO_2 in a micro fluidized bed reaction analyzer and a thermogravimetric analyzer

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HIGHLIGHTS

- MFBRA was used to test char non-isothermal gasification with CO_2.
- Gasification behavior in MFBRA was obviously different with TGA.
- Reliability and effectiveness of MFBRA for non-isothermal reaction was validated.

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ABSTRACT

The so-called micro fluidized bed reaction analyzer (MFBRA) and a thermogravimetric analyzer (TGA) were adopted to comparatively investigate the non-isothermal gasification of coal char with CO_2. Experimental results demonstrated that heating rate obviously affected the coal char gasification reaction. Raising heating rate evidently increased the temperatures at the initiating reaction (T_i), the maximal reaction rate (T_m) and the finishing reaction (T_f). Nonetheless, it decreased the char conversion at a given reaction temperature and also the activation energy estimated by the single heating rate method. Comparing the data tested by TGA and MFBRA under the same heating rate clarified that the temperatures of T_i, T_m, and T_f were all relatively lower for MFBRA. The difference for such characteristic reaction temperatures between TGA and MFBRA increased with raising the heating rate. The measurement in MFBRA also led to the higher activation energy estimated according to both the single heating rate and the combination heating rate methods. Perhaps all these results are attributed to the lower limitation from heat and transfer including gas diffusion in MFBRA than in TGA.

1. Introduction

Gasification is an important and promising thermo-chemical process for conversing carbonaceous fuel into synthesis gas, fuel gas and other valuable energy products cleanly and high-efficiently [1–3]. In an industrial gasifier, coal gasification involves a series of reactions, including coal pyrolysis, char gasification and some complex gas phase reactions. Of them, char gasification is always the rate-determining step because of its relatively low reaction rate [4,5]. A better understanding of the char gasification behavior as well as the reaction kinetics in atmospheres of CO_2, steam, O_2 and their mixture, is thus very vital to the deep insight into the evaluation, design, scale up and operation of coal gasifiers [6,7].

Both isothermal and non-isothermal methods have been commonly used in the research of char gasification reaction. The isothermal gasification of char is performed at a given reaction temperature, reflecting the overall reaction characteristics of char in gasifier [8]. The non-isothermal gasification of char is usually conducted by exposing a sample to a programmed reaction temperature variation, which reveals the gasification behavior of char under different temperatures and clarifies the relationship between heating rate and reaction characteristics [9]. Compared with the isothermal method, the non-isothermal method is simple and easy because of avoiding the change of chemical and physical properties of the tested sample, and providing useful information via fewer experiments [10–12]. However, due to the dependence of heating rate, the experimental data tested from non-isothermal method are always difficult to analyze, resulting in obvious deviation in kinetic parameters [13]. Both of these mentioned above make the non-isothermal method lower accuracy and less adoption.

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Among the numerous gas–solid reaction analyzers, TGA is the most common and representative analyzer for examining non-isothermal gasification behavior of char and the corresponding reaction kinetics. It can simply and accurately monitor the mass change of char sample under a specified heating program [14,15]. Because of the limitations of measurement principle and instrument structure, TGA cannot load sample online at a preset temperature, has relatively low heating rate (usually below 50 K/min), serious gas diffusion and unsteady atmospheric gas concentration in gas switching from an inert gas to a reactive gas [16]. Many other facilities based on the reactors of drop tube, wire mesh, fixed bed, fluidized bed, entrained bed and so on, have also been used, but suffering from serious gas mixing and diffusion because of lacking standardized instrument or analyzer. Thus, in literatures, different methods and facilities give different gasification behaviors and kinetic data, even for the same kind of coal.

Recently, the so-called micro fluidized bed reaction analyzer (MFBRA) has been developed to test gas–solid reactions. It is based on the measurement of yield and composition for the produced gas using online analyzers, such as process mass spectrometer (MS) and gas chromatography [17,18]. Due to integrating the merits of quick heat and mass transfer by micro fluidized bed, pulse feeding reactant sample and fast detection of reacted gas by fast MS, this analyzer enables on-line adding sample at arbitrary preset temperature and utilization in special gas atmosphere like pure steam without gas switching. By far, MFBRA has been successfully used to characterize many reactions, including pyrolysis of coal and biomass, combustion of biomass and petroleum coke, gasification of solid fuels, tar cracking, mineral ore calcination and reduction, material preparation, gas absorption and so on [19,20]. Nonetheless, all the previous studies by MFBRA were conducted under the isothermal mode or conditions, and it has never been tested for non-isothermal conditions like the programmed temperatures for TGA.

This work is devoted to investigating the non-isothermal gasification reaction of char in MFBRA under different heating rates, and the results were further compared with that from an advanced commercial TGA. Kinetic data for the reaction were further calculated according to the single heating rate method and the combination heating rate method. It is expected to clarify the similarity and also the difference in char gasification behavior and kinetics for both the analyzers. The results will not only offer a further understanding of the non-isothermal gasification between char and CO_2, but also prove the effectiveness of MFBRA for the non-isothermal reaction analysis.

2. Experimental section

2.1. Experimental methods

Char sample was prepared from pyrolyzing a kind of bituminous coal from YiMa mine of China under Ar atmosphere at 1000 °C in a laboratory jetting fluidized bed reactor. The detailed preparation process can be found in our previous study [21]. The proximate and ultimate analysis of the coal char is listed in Table 1. The remaining volatile matter in coal char was below 2 wt.%. Moreover, the specific surface area of char tested by N_2 adsorption method at 77 K on an automatic volumetric sorption analyzer (Micromeritics, ASAP 2020HD88) was relatively low, about 3.0 m^2/g. Prior to experiments, coal particles were crushed and sieved to the desired sizes and dried by air at 105 °C for 2 h.

Table 1
Proximate and ultimate analysis of coal char used in experiments.

Proximate analysis, wt.% (d*)			Ultimate analysis, wt.% (daf*)				
Volatile matter	Ash	Fixed carbon	C	H	S	O	N
1.4	12.6	86.0	94.3	1.2	0.6	2.8	1.1

* d: dry basis; daf: dry and ash-free basis.

Fig. 1 shows the general principle of the adopted MFBRA, mainly consisting of a gas supply section, an electric heating system, a micro fluidized bed reactor, an-online sample feeding system, and a product purification and online measurement system. The quartz micro fluidized bed (MFB) reactor had two porous plates as gas distributors, thus forming a bottom gas preheating stage, a middle reaction stage and a top stage preventing fine sample (particles) from escaping. The particle sizes of bed material (quartz sand, density of 2800 kg/m^3) and char sample (true density of 850 kg/m^3) were in the range of 80–100 μm and 150–180 μm, respectively. According to the Ergun equation, the minimum fluidization velocities of quartz sand and char sample at 600 °C are 0.0036 m/s and 0.0035 m/s, respectively. During experiments, both of the quartz sand and char sample fluidized together. The gas flow rate of high-purity CO_2 (vol. 99.999%) adopted in the experiment was about 1.0 L/min, and the reaction was performed by heating the char sample up to 1100 °C at one of the heating rates of 1, 2.5, 5.0, 10, 20 and 40 °C/min. Previous studies have shown that, under the test conditions, there were the minimized heat and mass transfer limitations [20]. The generated gas was monitored by a fast process mass spectrometry (Ametek, Dycorsystem 2000), and all the gas produced in gasification reaction was collected by some gas bags in time series for analyzing its compositions by a micro gas chromatography (GC, Agilent 3000 A). The reaction characteristics were analyzed in terms of product composition, gas concentration, mass balance, and kinetic parameters on the basis of the testing results from mass spectrometry (MS) and micro GC.

For comparison, the non-isothermal gasification reaction of char was also tested in an advanced TGA (Nano S II 6300) by heating it to 1100 °C at one of the heating rates of 1, 2.5, 5.0, 10, 20 and 40 °C/min. The adopted sample amount, flow rate of CO_2 through the cell chamber, particle size of char sample and the crucible height were 0.8 mg, 500 mL/min, 150–180 μm and 3 mm, respectively. Under these conditions, the limitations from heat and mass transfer were minimized. A test was judged to complete when there was not more weight loss of a sample.

2.2. Datum analysis approach

For the non-isothermal gasification of char in MFBRA, the realized carbon conversion (X) is defined by considering the main reaction of $C + CO_2 \rightarrow 2CO$ according to the equations from (1) to (3). To understand the data analysis method clearly, Fig. 2 shows the main

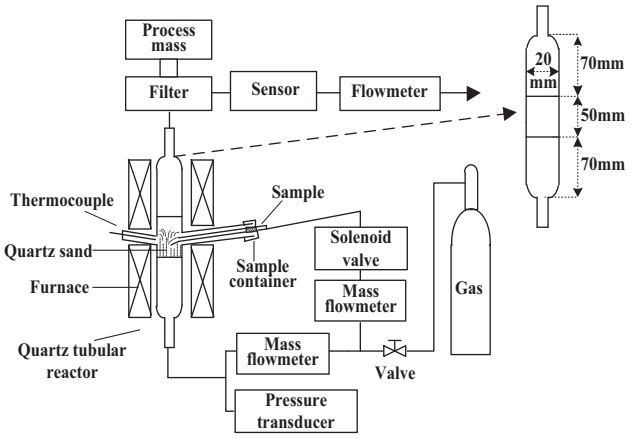

Fig. 1. A schematic diagram of the adopted MFBRA.