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Experimental studies on gasification of the Shenmu coal char with CO_2 at elevated pressures

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Abstract−The gasification rates of Shenmu coal chars with CO_2 were experimentally studied with a pressurized thermo-gravimetric analyzer (PTGA). Shenmu coal is a typical Chinese coal, and the coal char was prepared by a fixed-bed reactor in nitrogen at 900 ℃. The experiments were carried out in the dynamic heating segments from 750 ℃ to 1,000 ℃, and the reaction pressure increased from 0.1 MPa to 3.1 MPa with pure CO_2. The external diffusion resistances were minimized by increasing the flow rates and decreasing the thickness of sample layer before the test, to ensure the reactions were under kinetic control. The results show that the gasification rates increase proportionally to the 0.1 power of the CO_2 partial pressure. The unreacted-core shrinking model was applied to predict the reaction rate by changing the molar fraction of CO_2 at 0.6 Mpa and 1.6 Mpa total pressures, which showed a good match with experimental data.

Key words: Coal Char, Gasification, Pressurized TGA

INTRODUCTION

With the rapid growth of the world economy, the energy consumed also increases dramatically. Because of high oil prices and restrictive environment protection policies, coal gasification has become an attractive technology, especially for the countries with rich coal reserves, which plays an important role on the high efficiency integrated gasification combined cycle (IGCC) process and on syngas-based chemical production.

Understanding the kinetics of coal gasification is essential to optimize the gasifier design and effective operation. Heterogeneous reaction rate of char and CO_2 or steam usually controls the overall conversion process, which has been studied extensively for decades. High-pressure wire-mesh reactor (PWMR) [1], pressurized drop tube furnace (PDTF) [2,3] and pressurized thermo-gravimetric analyzer (PTGA) [4-6] were the most popular experimental apparatus for the gasification reaction study at high pressure. Liu and Niksa [7] have reviewed data from these apparatus. PTGA is capable to successively record the sample weight change, and repeat the experiments well at given conditions. It is regarded as a conventional and standard tool for kinetic study.

But in a TGA, the diffusion resistances cannot ignored. If not properly minimized, the external diffusion resistances may severely contaminate the experimental data, inducing remarkable discrepancy in analyzing the chemical kinetics of the reactions. This effect was suggested to be minimized by increasing the reactant gas flow rates and decreasing the thickness of the sample layer [8].

There are three types of pressure effects on the reactivity that have been studied [9]: the effect of total pressure with fixed partial pressure, the effect of total pressure with fixed mole fraction and the effect of partial pressure with fixed total pressure. It was commonly accepted that apparent gasification rates increase for progressively higher reactant partial pressures, especially when at low pressure. An *n*th-order equation and a Langmuir-Hinshelwood type equation were often applied to describe the effect of pressure. Reactivity of some Chinese coal char has been studied, but not much of them were conducted at an elevated pressure [10,11]. In this study, the gasification rates of Shenmu coal chars under CO_2 environment were experimentally studied with a PTGA.

EXPERIMENTAL

1. Char Preparation

Shenmu coal is one of the typical Chinese bituminous coals, the properties of which are shown in Table 1.

The coal char was prepared prior to the gasification experiments in a fixed-bed reactor in nitrogen environment at atmospheric pressure. The sample was subjected to a heating rate of 10 $K \cdot min^{-1}$ up to 1,173 K and stayed at the temperature for 20 minutes. Then the devolatilized char was cooled with nitrogen to room temperature and was ground to a size less than 100 μm. The char particle shows a spherical shape with the layered structure.

Table 1. Properties of Shenmu coal sample

Proximate analysis %				Ultimate analysis %				
M_{ad}	A_{ad}	V_{ad}	C_{ad}	C_{ad}	H_{ad}	O_{ad}	N_{ad}	$S_{t, ad}$
8.52	9.53	31.00	50.95	63.95	4.10	12.49	0.99	0.42

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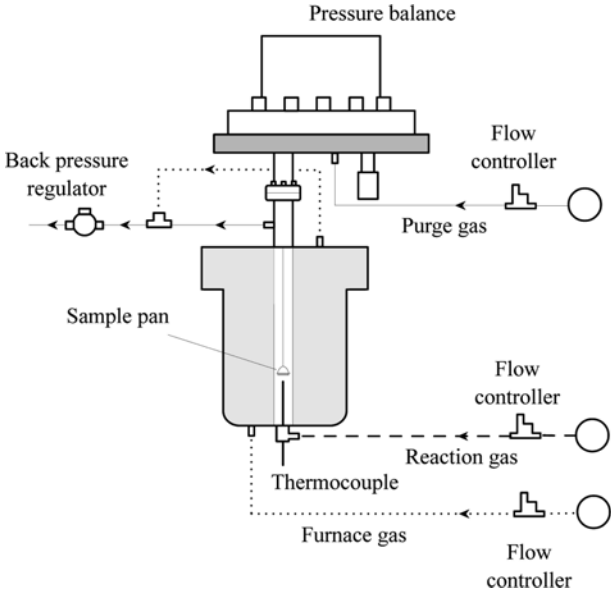


Fig. 1. Schematic diagram of Thermax500 PTGA.

2. Experimental Apparatus

Kinetic measurements were performed in a Cahn Thermax500 pressurized thermogravimetric analyzer. Fig. 1 shows the schematic diagram of Thermax500 PTGA, which consists of three parts: the pressurized balance, the pressurized furnace and the control system. A ceramic extension wire, hanging on one arm of balance, extends into the quartz reaction tube. A platinum sample pan was hung on the end of extension wire. A set of thermocouples is installed about 8 mm below the sample pan to measure the temperature of reaction zone. The reactant gas flows through the sample pan from bottom to up with the controlled flow rate. A manual back pressure regulator was applied to minimize the fluctuation of pressure.

3. Char Gasification

The char sample was loaded into the sample pan with the weight of 10.5±0.4 mg before each run, and then the system was pressurized to the set pressure. The molar fraction of reactant gas was adjusted by the flow rates of CO_2 and N_2, respectively. Then the system was heated from room temperature to 750 °C with high heating rate of 25 °Cmin^{-1}, and from 750 °C to 1,000 °C with slow heating rate of 2 °Cmin^{-1}. The reaction was completed before the temperature increased to 1,000 °C.

The pressure changed by two ways, one was increasing the total pressure with pure CO_2 and another was to increase the partial pressure at total pressure of 0.6 Mpa and 1.6 Mpa, in which N_2 acted as the inert gas. Four different pressures were selected for the pure CO_2 reaction: 0.1 MPa, 0.6 MPa, 1.6 MPa and 3.1 MPa. At each pressure, trial experiments were done to minimize the external diffusion resistances by increasing the flow rates. If the adjacent two records were overlapped, the external diffusion resistances were minimized, and this test data was chosen for further analysis. Furthermore, a set of blank runs were performed with some flow rates at the same pressure, to remove the effect of buoyancy and drag force.

The effect of partial pressure change with fixed total pressure

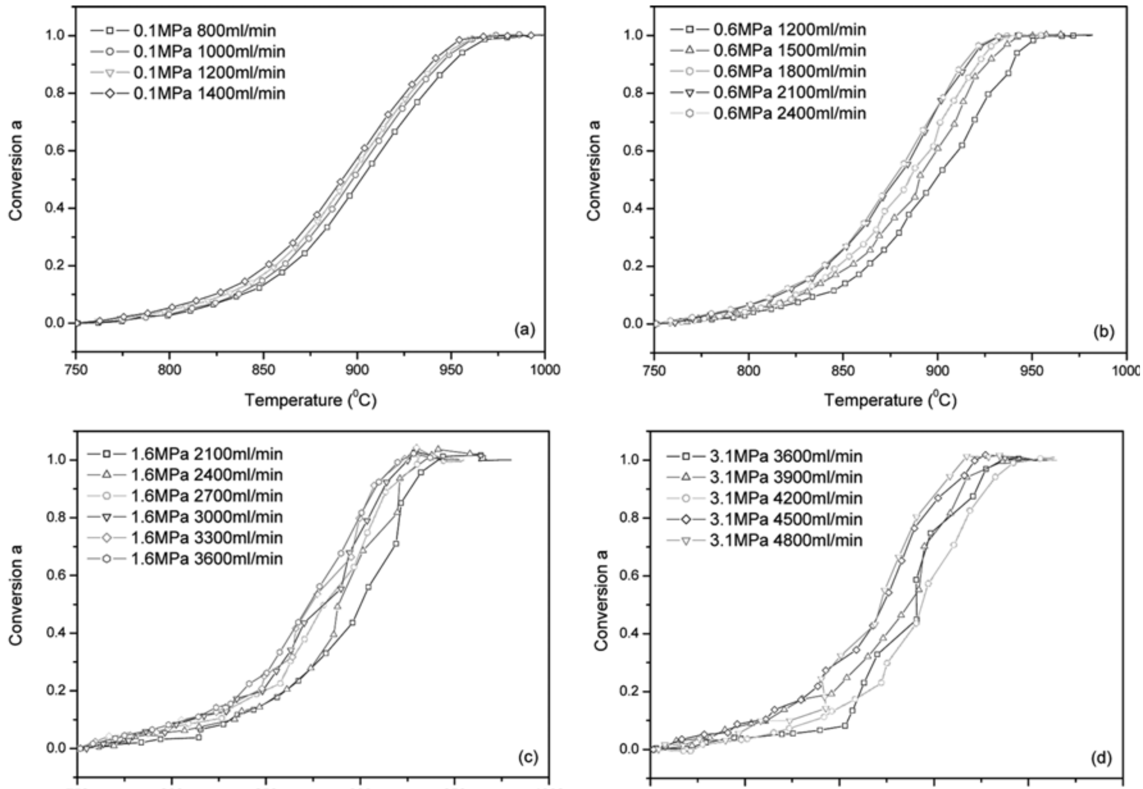


Fig. 2. External diffusion resistances minimization by increasing flow rates.

was studied at 0.6 MPa and 1.6 Mpa, the molar fraction of CO_2 was arranged from 20% to 80% with intervals of 20%.

4. Reaction Rates Definition

The conversion of coal char was calculated from the recorded weight loss curves by using the relationship

$$a=\frac{W_0-W}{W_0-W_\infty} \tag{1}$$

Where W is the instantaneous char weight, W_∞ is the weight of ash and W_0 is the weight of initial char. The apparent reaction rate was defined as change rate of conversion **a**.

$$R=\frac{da}{dt} \tag{2}$$

RESULTS AND DISCUSSIONS

1. External Diffusion Resistances Minimization

The sample pan was 8.3 mm in diameter and 3 mm high, and the thickness of sample layer was about 0.5 mm. The reactant gas flows upward through the sample pan; the external diffusion resistance is rather high, then the gas velocity is low, especially at high pressures. At a certain pressure, it was found that the reaction rates increased with flow rates. When flow rate was high enough, the two experiments' data overlapped, indicating the external diffusion resistances were minimized. Fig. 2 shows the experimental data with increasing flow rate at 0.1 MPa, 0.6 MPa, 1.6 MPa and 3.1 MPa pressures.

The flow rates at different pressure for minimization of the external diffusion resistances were obtained from the experiments, 1,200 ml/min for 0.1 MPa, 2,400 ml/min for 0.6 MPa, 3,600 ml/min for 1.6 MPa, and 4,800 ml/min for 3.1 MPa. As the pressure was elevated, the reactant gas density increased, and higher flow rates were required to minimize the external diffusion resistances.

2. Effect of Pressure on Pure CO_2 Reaction

The effect of pressure can be obtained from the experimental results on reaction rates as shown in Fig. 3. The reaction time decreased when the pressure elevated, that means the apparent reaction rate increased. And from Fig. 3, it can be found that the reaction rate increased slowly at high pressure, where the power to the CO_2 pressure is 0.1.

The *n*th-order equation was applied to obtain the kinetic parameters of char-CO_2 reaction.

$$\frac{da}{dt}=A\cdot\exp\left(\frac{-Ea}{RT}\right)\cdot(1-a)^{2/3}\cdot P_{CO_2}^{n} \tag{3}$$

Where P_{CO_2} is the partial pressure of reactant gas, n is the power to P_{CO_2}, which is 0.1 in this study, A is the frequency factor and Ea is the activation energy. All experiments were carried out in the range of 750-1,000 °C, assuming the overall reaction rates were controlled by the kinetics. An unreacted-core shrinking model was developed as Eq. (3). When the partial pressure of reactant equals to 1 atm, the parameters A and Ea can be derived from the experimental results at atmospheric pressure of pure CO_2. In this study, A was obtained as 2.89E+11 and Ea was obtained as 285.5 kJ/mol. The activation energy is close to the 249-312 kg/mol, which was obtained by Zhou with the char from Shenmu coal at atmospheric pressure [12]. Hence, Eq. (3) can be expressed as

$$\frac{d\alpha}{dt}=2.886\times10^{11}\cdot p_{CO_2}^{0.1}\cdot\exp\left(\frac{-285490}{RT}\right)(1-\alpha)^{2/3} \tag{4}$$

The calculated value is also shown in Fig. 4.

3. Effect of Partial Pressure of CO_2

With the constant heating rate, conversion **a** was solved from Eq. (4) through numerical method. Because the CO_2 molar fraction was 100%, the total pressure equaled the partial pressure of the reactant. Accounting for the effect of partial pressure, four runs experiments with various molar at 0.6 MPa and 1.6 MPa total pressure were carried out. Fig. 4 shows the model matches well with the experiment data with the high CO_2 molar fraction, above 40% for 0.6 Mpa and above 60% for 1.6 Mpa, but one cannot predict the data with lower fraction. The low fraction resists the reaction rates and counteracts the positive effect of pressure.

CONCLUSIONS

The gasification rates of the Chinese Shenmu coal chars under CO_2 environment were experimentally studied with a PTGA at elevated pressures. The external diffusion resistances were minimized by increasing the gas flow rate and decreasing the thickness of sample layer. The apparent reaction rate shows proportional to the $P_{CO_2}^n$. In pure CO_2, the power n is 0.1, and the activation energy is 285

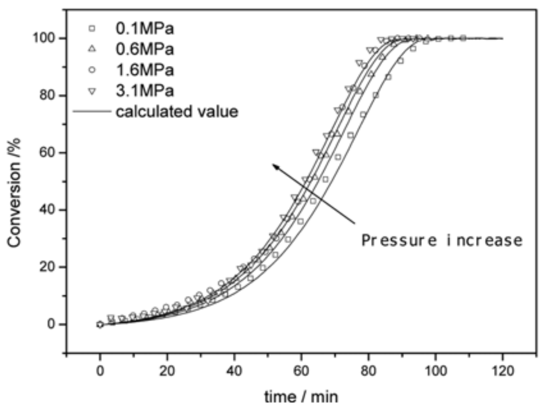
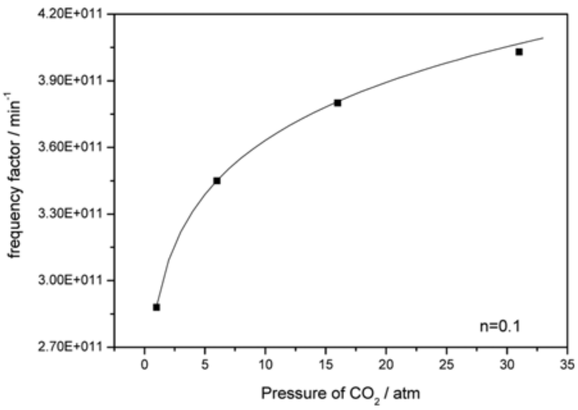


Fig. 3. The effect of pressure on the reaction rates.



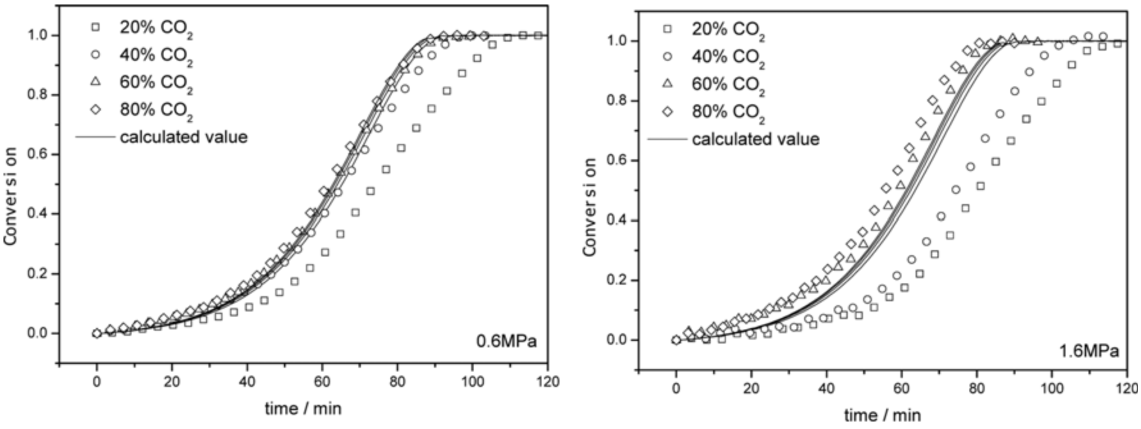


Fig. 4. Effect of CO_2 molar fraction at 0.6 and 1.6 Mpa total pressure.

kJ/mol, which is close to Zhou's results. And the reaction rate equation can also predict the reaction rate by changing the CO_2 partial pressure at 0.6 Mpa and 1.6 Mpa total pressure, but the low fraction of CO_2 resists the reaction rates and counteracts the positive effect of pressure.

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