Fuel 218 (2018) 236–246

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Gasification of coal char in H_2O/CO_2 atmospheres: Evolution of surface morphology and pore structure

Yonghui Bai, Peng Lv, Xuhao Yang, Meiqi Gao, Shenghua Zhu, Lunjing Yan, Fan Li*

State Key Laboratory Breeding Base of Coal Science and Technology Co-Founded by Shanxi Province and the Ministry of Science and Technology, Taiyuan University of Technology, Taiyuan 030024, China

ARTICLE INFO

Keywords:
Coal char
Gasification
H_2O/CO_2 atmosphere
Surface morphology
Pore structure

ABSTRACT

Increasing studies focus on gasification of coal char in mixed H_2O/CO_2 atmospheres, but quite controversial results were obtained on this issue. Char porosity and pore size distribution affect the reactant gas diffusion inside the char, reaction on the char active sites and gas product diffusion out of the particle. Hence, this study aims to understand the surface morphology and pore structure characteristics of the coal chars obtained from gasification in H_2O/CO_2 atmospheres. The raw coal was heated to 800–1000 °C in a fixed bed reactor to produce coal chars. The resulting chars were gasified under 40% H_2O, 40% CO_2, and 20% CO_2 + 20% H_2O atmospheres at the same temperatures to obtain a series of residual chars with different carbon conversion levels. The morphology and pore characteristics of chars were characterized by scanning electron microscope (SEM) and N_2 adsorption method. The results show that CO_2 char has an uneven surface with irregular potholes, whereas that the surface of H_2O char is relatively smooth and distributed on the surface with honeycomb pores. CO_2 and H_2O play different role in creating the char porous structure. The CO_2 chars are mainly micropores and along with some small mesopores. Under H_2O and H_2O/CO_2 atmosphere, the char are rich in micropores, mesopores, and macropores, the pore size distribution is continuous. The total pore volume of gasified chars prepared under H_2O/CO_2 atmosphere was not significantly changed compared with H_2O atmosphere, indicating there has positive interaction between H_2O/CO_2 in developing the coal char pore structures during gasification. H_2O could create a wider porous structure that facilitates the access of CO_2 to the coal char matrix to further develop the pore structure.

1. Introduction

Coal gasification is the head of the clean coal conversion, it is the basis to support sustainable development of coal chemical industry [1]. It is generally considered that char–H_2O and char–CO_2 reactions are the rate limiting steps during coal gasification [2], and so many studies have been focused on these reactions [3–5]. Most were performed by using a single CO_2 or H_2O atmosphere. But in any commercial gasifier, both the two reactions often occur simultaneously in gasifier. Research using mixed H_2O/CO_2 and their effects on gasification behaviors have been undertaken but are relatively limited.

By summarizing the results in literatures, coal char gasification behavior in mixed H_2O/CO_2 are mainly include the following three cases. Some researchers believe that char–H_2O and char–CO_2 reaction occurs at different active sites of char, the gasification reaction rate in the mixture is equal to the sum of each reaction rate [6–8]. For instance, Guizani et al. [6] conclude that CO_2 does not affect the char structure to favor or inhibit the char–H_2O gasification reaction. Some researchers found that there is competition and inhibition between H_2O and CO_2, resulting in a lower rate of gasification in mixed atmosphere than the sum of the individual atmosphere [9–11]. Roberts et al. [9] found that the presence of CO_2 could reduce the gasification rate of C–H_2O, and believe that the slower C–CO_2 reaction inhibits the H_2O reaction by decreasing the availability of reactive surface. Chen et al. [10] found that the char gasification rate in the mixtures of CO_2 and H_2O was obviously lower than the sum of the two rates of the char independently reacting with CO_2 and H_2O, and conclude that char–CO_2 reaction was inhibited by char–H_2O reaction due to H_2O could preferentially adsorbed on the active site compared with CO_2. Other researchers found that char gasification in the mixed H_2O/CO_2 atmosphere resulting in synergies effect [12–16]. Our previous studies [12–14] indicate that the gasification rate of char in H_2O/CO_2 mixed atmosphere is higher than in single atmosphere and believe that the uniform distribution of Ca species in coal char porous structures contributes much to the synergistic effects. Tagutchou et al. [15] hypothesize that the reason why the addition of CO_2 in a H_2O atmosphere

* Corresponding author.
E-mail address: fanli@tyut.edu.cn (F. Li).

https://doi.org/10.1016/j.fuel.2017.11.105
Received 12 July 2017; Received in revised form 13 November 2017; Accepted 25 November 2017

Table 1
Proximate and ultimate analyses of the coal sample.

Proximate analysis wt/%				Ultimate analysis wt/%, daf				
M_{ad}	A_d	V_d	FC_d	C	H	O*	N	S
12.8	3.5	28.0	68.5	79.2	3.9	16.0	0.6	0.3

Note: ad, air-dried basis; d, dry basis; daf, dry and ash-free basis.
* By difference.

could led to an acceleration of gasification reaction is that CO_2 could access to the internal micropores preferentially and open certain pores to facilitate the entry of H_2O molecules. Jayaraman et al. [16] also believe that the introduction of CO_2 improved the gasification reaction rate of char but not too much to explain the reasons. At the same time, some kinetic models describing the gasification of coal char in a mixed atmosphere are presented intermittently [17–19]. Nevertheless, there is no clear understanding of the gasification behavior of coal char in H_2O/CO_2 atmosphere.

The gasification reactivity of coal char depends essentially on the properties of coal char, including (i) the physical structure of char, (ii) the chemical structure of char, (iii) the concentration and dispersion of alkali metals and alkaline earth metals with catalysis in the char [20–23]. The physical structure of coal char mainly refers to the pore structure which is an important factor affecting coal gasification. A large number of researchers have correlated the relationship between pore structure and gasification reactivity [24–27]. It is generally considered that the pore structure of coal char will affect the diffusion of gasification agent and gasification products during the gasification process, the developed pore structure is favorable to the mass transfer of reactants and products, and promotes the gasification reaction [26]. At the same time, the pore structure provides the active site for the contacting of gasification agents with coal char as well as their reaction [27].

Although many researchers studied the effect of pyrolysis conditions on the char physical structure, the effects of gasification atmosphere and temperature on the physical structure evolution of char during gasification is unclear, especially when CO_2 and H_2O are involved in the gasification reaction simultaneously. Thus, the purpose of this study is to provide further insights into the effects of gasification atmosphere and temperature on the surface morphology and pore structure of char during the gasification.

2. Experimental

2.1. Coal sample and char preparation

A bituminous coal from Xinjiang Uygur Autonomous Region of north-western China was used in this study. The coal was named as YN. The proximate and ultimate analyses of YN are shown in Table 1.

The YN coal samples were manually ground and sieved to particle sizes 1–1.4 mm. The pyrolysis of coal samples and char gasification was carried out in a fixed bed reactor. The experimental setup is shown in Fig. 1. The quartz tube used in this work has an inner diameter of 5 cm and length of 22 cm, the length of the constant temperature zone is 5 cm. First, a 10 g coal sample was placed in the sintered quartz filter, and a sweeping N_2 gas flow of 600 mL/min was used to remove the air in the reactor for 10 min. Then, the reactor was quickly put into the hot stove, the sample was heated to final gasification temperature of 800 °C, 900 °C, 1000 °C under a continuous N_2 flow of 600 mL/min and held for 30 min. Based on the pre-experiment, the heating rate under this conditions is about 150 °C/min. Fig. 2. shows an example of the heating rate of coal sample at a final temperature of 800 °C. A mixture of the reactant and carrier gases with a total flow rate of 1000 mL/min was introduced into the reactor for the gasification of residual char. The ratios of the gasification atmospheres were as follows: 40% H_2O + 60% N_2, 40% CO_2 + 60% N_2, 20% H_2O + 20% CO_2 + 60% N_2. The obtained chars with different carbon conversions were marked as gasifying agent-X%-char, for example, H_2O/CO_2 − 30%–char means char with carbon conversion of 30% obtained from gasification in 20% H_2O + 20% CO_2 + 60% N_2. The on-line gas analyzer was used to monitor the components of the outlet gas, and the carbon conversion can be estimated according to the concentration of carbonaceous gas in the inlet and outlet.

2.2. Characterization of raw/gasified char

2.2.1. N_2 adsorption analysis

Micromeritics surface area and pore size analyzer ASAP 2020 using

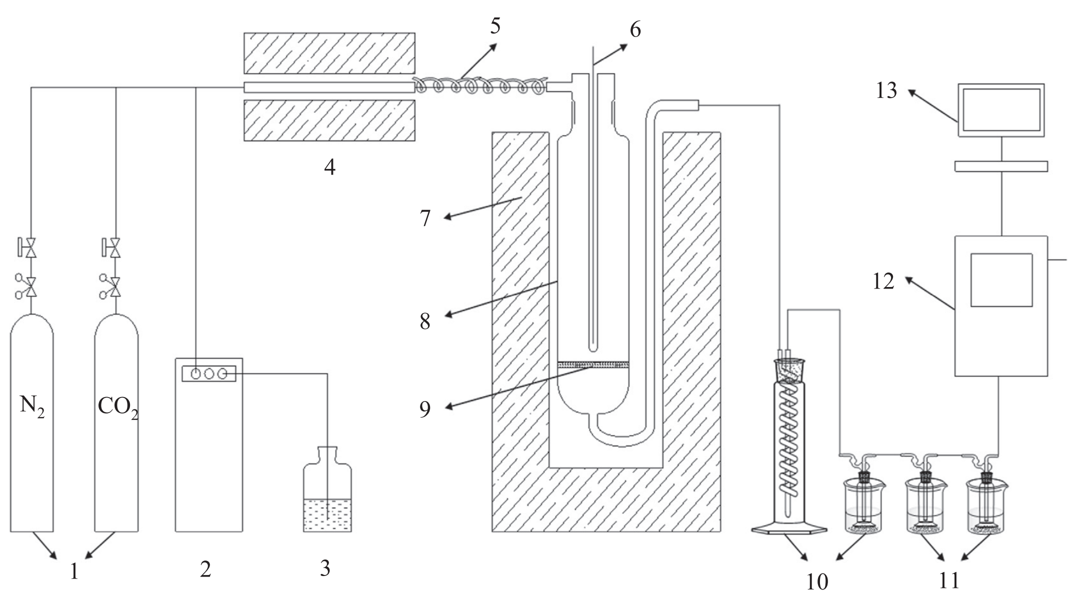

Fig. 1. Schematic diagram of the fixed bed reactor system (1 Cylinders; 2 Double plunger pump; 3 Deionized water; 4 Preheating furnace; 5 Heating coat; 6 Thermocouple; 7 Furnace; 8 Quartz tube reactor; 9 Sintered quartz filter; 10 Ice water trap; 11 Dry ice trap; 12 On-line gas analyzer; 13 Computer).