Journal of Analytical and Applied Pyrolysis 122 (2016) 76–83

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Gasification characteristics of different rank coals at H_2O and CO_2 atmospheres

Zhi-Hua Wang[a], Kang Zhang[a], Yan Li[a,b], Yong He[a,*], Min Kuang[c], Qian Li[a], Ke-Fa Cen[a]

[a] State key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, PR China
[b] Shenhua Guohua (Beijing) Electric Power Research Institute Co.Ltd., Beijing 100025, PR China
[c] Faculty of Maritime and Transportation, Ningbo University, Ningbo 315211, PR China

ARTICLE INFO

Article history:
Received 29 July 2016
Received in revised form 8 October 2016
Accepted 21 October 2016
Available online 21 October 2016

Keywords:
Gasification characteristics
Coal rank
Mixed reaction model
Synergistic effect

ABSTRACT

Gasification characteristics of Shenhua bituminous (SH) and Baorixile lignite coal (BRXL) were investigated using both a thermogravimetric analyzer and tubular furnace. Coal samples were pyrolized in a tubular furnace at five different temperatures (800–1000 °C in 50° increments), at two heating rates, 10 °C/min and 1000 °C/min. The resultant chars were gasified isothermally at (i) each of these five temperatures under a constant atmosphere (40% $H_2O(g)$ + 60% CO_2) and (ii) at 1000 °C while varying the atmosphere from pure $H_2O(g)$ to pure CO_2 by increasing the CO_2 component stepwise in 20 vol.% increments. Carbon conversion, reactivity index, and average specific gasification rate were calculated and fit to a mixed reaction model. It was found that both the gasification temperature and atmosphere composition greatly impacted gasification characteristics, and the temperature effect was more pronounced in a heterogeneous atmosphere. The char produced with a high heating rate pyrolysis process promoted gasification reactivity likely a result of the more open pore structure. The gasification reactivity was lowest under a pure CO_2 gasification atmosphere and increased continuously with the H_2O partial pressure. SH and BRXL char samples achieved peak gasification reactivity under atmospheres with 60% and 80% $H_2O(g)$, respectively. Also, a synergistic effect was observed for heterogeneous CO_2/H_2O gasification atmosphere and not all the gasification reactions obeyed a first-order reaction model. The results of this work indicate that there is an optimal gasification atmosphere and temperature combination, specific to the coal sample, for efficiently converting char to gasification products.

1. Introduction

Gasification of coal has been widely developed due to associated improvements in usage efficiency and environmental impace, such as seen in integrated gasification combined cycle implementions [1,2]. It is a thermal-chemical process, wherein oxygen, water vapor or carbon dioxide act in converting solid fuel into gas phase syngas. Gasification proceeds through several stages: dehydration, coal pyrolysis and reaction between char and ambient gases at elevated temperature.

Coal pyrolysis and indeed the entire gasification process is subject to the influence of numerous sample parameters, e.g., pore size, as well as the gasification environment [3–5]. In light of this, the systematic evaluation of factors important in coal gasification is an area of great interest to researchers. Jayaraman et al. [6] studied the effects of pyrolysis heating rate and particle size on char gasification, and found that char produced from fast pyrolysis had a larger specific surface area and had better gasification characteristics. Moreover, the activation energy of coal gasification for char increased with particle size (ranging from 138 to 193 kJ/mol in a CO_2 atmosphere when the particle size was varied from 60 to 900 μm). Marculescu [7] investigated the gas phase release from cellulose and plastic solid waste mixtures under atmospheric steam gasification conditions in a cylindrical fixed bed reactor. A pyrolysis temperature increase of 50% reduced the gasification required period by about 30% in the medium and high temperature stage. When gasifying several bituminous coals with different temperatures at 4 MPa pressure, Porada et al. [8] observed the carbon conversions varied appreciably as the temperature increased, with all samples achieving 85% yield at 900 °C. With the increase in temperature, the yields of H_2 and CO increased, the CO_2 yield decreased and the CH_4 yield changed only slightly. Wang et al. [9] added CaO as a CO_2 sorbent for $H_2O(g)$ gasification over a pressure range from 1 to 4 bar and found the H_2 production was highly promoted

---

[*] Corresponding author.
E-mail address: heyong@zju.edu.cn (Y. He).

http://dx.doi.org/10.1016/j.jaap.2016.10.019
0165-2370/

Table 1
Proximate and ultimate analyses of coal samples.

sample	proximate analysis (wt.%, ad)				ultimate analysis (wt.%, ad)				
	M	*A*	*V*	*FC*	C	H	N	S	O
SH	5.19	22.44	27.08	45.29	57.81	4.01	0.95	0.32	9.28
BRXL	8.68	9.59	34.6	47.13	58.26	4.83	1.08	0.23	10.29

Ad: dry base; *M*: moisture; *A*: ash; *V*: volatile matter; FC: fixed carbon.

in absence of CO_2. Under conditions of 750 °C, 4 bar, [Ca]/[C] = 1 and $[H_2O]/[C] = 2$, the H_2 concentration reached 78 vol.% (dry basis) while CO_2 (2.7 vol.%) was effectively captured by the CaO sorbent. By simulating Indian coal gasification with a steady-state, one-dimensional numerical model, Singh et al. [10] found that a 0.42 oxygen mole fraction in the oxidizer stream provides optimum performance in oxygen-based gasification systems. The range of optimal steam-to-coal ratios is dependent on the oxygen content in the oxidizer stream, about 0.4 and 1.5 for air-based and oxygen-based systems, respectively. As is evident, reports mainly focus on (i) effects of coal pyrolysis and gasification conditions, gasification reactor (type and configuration), catalyst and (ii) the analysis of gasification reaction kinetic models [11–14].

CO_2 and H_2O(g) are typical gasification reagents, which react with char at a high temperature. In coal pyrolysis, the various partial gasification reactions of coal and char are determined in part by the gas proportions of CO_2 and H_2O(g), which naturally vary with coal types. Therefore, investigating char gasification reaction characteristics with CO_2 and H_2O(g) at high temperatures is of great significance. However, the published investigations about gasification reagents are mainly restricted to single reagent investigations. Also, in the sparse research conducted with binary mixtures of H_2O(g) and CO_2 reagents, the results are occluded by the effects of other gasification conditions (temperature, pyrolysis rate, coal rank, etc.) in the H_2O(g) and CO_2 mixture atmosphere. Moreover, in char gasification processes complementary interaction between H_2O(g) and CO_2 hasn't been clearly disclosed. To address these deficiencies, in this work, the effects of gasification temperature, pyrolysis rate and atmosphere on gasification characteristics were evaluated using a pressurized thermogravimetric analyzer and tubular furnace, so as to discern the effects of gasification condition combined with the interaction of H_2O(g) and CO_2. From the data, carbon conversion, reactivity index, etc. were calculated and a kinetic analysis based on a mixed reaction model was discussed to better provide the basis for char utilization and the furtherance of clean coal power generation technologies.

2. Experimental methods

2.1. Coal samples and char preparation in a tubular furnace

The coal samples used in experiments are Shenhua 2# bituminous coal (SH) and Baorixile lignite coal from Inner Mongolia (BRXL). Results from the proximate and ultimate analysis of the two coals are listed in Table 1. The experimental gas reagents are Ar (99.9% purity), CO_2 (99.9% purity) and H_2O(g) from vapor generator.

The samples were first ground and sieved to less than 75 um. The coal samples were separated into two groups to be converted into char in a tubular furnace with an inert Ar atmosphere at either a low-heating-rate (LHR) or high-heating-rate (HHR). In the LHR procedure, 3 g of each ground coal sample was heated from room temperature to 800, 850, 900, 950 and 1000 °C at a heating rate of 20 °C/min. Conversely, the HHR treatment used a heating rate of 1000 °C/min at 1000 °C.

2.2. Gasification experiments in pressurized thermogravimetric analyzer

The experimental schematic for thermogravimetric system is shown in Fig. 1. Masses (10 ± 0.5 mg) of a given coal sample were placed in a crucible and loaded into the reactor of a thermogravimetric analyzer (Thermax-500, accuracy: 1ug). Using a 500 ml/min Ar flow and 20 °C/min heating rate, the reactor was heated to various terminal gasification temperatures and then held isothermal for 20 min. After that, the Ar flow was changed to a CO_2/H_2O mixture, with a flow rate of 500 ml/min, for char gasification. All gasification experiments were performed at ambient pressure, while three char gasification variable, temperature, atmosphere and pyrolysis rate, were evaluated. The experimental conditions are outlined in Table 2.

2.3. Data handling

Many parameters such as carbon conversion, average specific gasification rate, maximum gasification rate, reactivity index, and active sites can be used to evaluate char gasification characteristic [15–21]. These parameters are defined here below.

Carbon conversion is defined as follows:

$$\alpha = (m_0 - m_t)/(m_0 - m_{ash}) \quad (1)$$

where m_0 and m_t are the initial mass and the mass at time t, m_{ash} is the ash content left after char gasification.

The gasification rate is defined as the instantaneous rate of carbon conversion:

$$r = d\alpha/dt \quad (2)$$

The average specific gasification rate is the average gasification rate measured between the limits of 10% and 70% carbon conversion. It can be calculated from the following equation:

$$K = 1/(1-\alpha) * d\alpha/dt \quad (3)$$

The reactivity index R_{exp} is defined as follows:

$$R_{exp} = 0.5/\tau_{0.5} \quad (4)$$

where $\tau_{0.5}$ is the time needed to reach a carbon conversion of 50%.

To determine whether H_2O(g) and CO_2, as a mixed gasification agent, has synergistic effect on reactivity, the experimental and theoretical values of reactivity index were compared [22]. The theoretical value is calculated by the following equation:

$$R_{theo} = aR_{CO2} + bR_{H2O} \quad (5)$$

Where R_{theo} is the theoretical index of char gasification with a CO_2 and H_2O(g) mixture. R_{CO2} and R_{H2O} are, respectively, the reactivity indices of pure CO_2 and H_2O gasification, a and b are the mole fractions of CO_2 and H_2O(g) in the CO_2/H_2O gasification, respectively. If the experimental index $R_{exp} > R_{tho}$, then the combinatorial effect is indicated.

2.4. Kinetic analysis

Gasification reaction kinetics are related to various dominant parameters in the gasification process, including reaction order,