INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 16070–16076

Available online at www.sciencedirect.com

ScienceDirect

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

Investigation on linear description of the char conversion for the process of supercritical water gasification of Yimin lignite

*Hui Jin**, *Xiao Zhao*, *Simao Guo*, *Changqing Cao*, *Liejin Guo*

State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xianning West Road, Xi'an 710049, PR China

ARTICLE INFO

Article history:
Received 24 January 2016
Received in revised form
12 May 2016
Accepted 15 May 2016
Available online 1 June 2016

Keywords:
Random pore model
Non-reacted core model
Coal gasification
Hydrogen production
Supercritical water

ABSTRACT

Lignite gasification in supercritical water has been proved an efficient and clean utilization because of high gas yields. Char conversion process is the rate-determining step for lignite gasification in supercritical water, therefore, the accurate description of the conversion process is of great importance for the reaction optimization. Special attention was paid on the progress of char conversion in the process of lignite gasification. Quartz tube reactor was employed to avoid undesired catalytic effect of the reactor wall and Yimin lignite was choose as feedstock. The experiments were conducted with the operating range of temperature 650–850 °C with 5%–25% concentration. To improve accuracy of kinetic models, volatile and fixed carbon conversion was treated individually. Lignite conversion was simulated by random pore model, non-reacted core model and homogeneous model respectively and volatile process was expressed as a modification based on the data obtained by thermogravimetric analysis. The calculation results showed that the model with non-reacted core model fit coal gasification in supercritical water best and the average error was 3.18%.

Introduction

Coal is the most widely and severe used energy resource especially in an energy-depended country such as China [1–3]. With the exhaustion of oil and natural gas and the heavy environmental pollution, clean coal utilization plays a vital role in sustainable and renewable development [4–6]. Although coal may be viewed as a dirty fuel because of its high greenhouse emissions and N, S containing pollutants when combusted, it definitely has great potential for a source of clean H_2 [7,8]which can be used in fuel cells [9–11].

Supercritical water gasification (SCWG) has been vastly investigated because of high hydrogen yield and high thermal efficiency [12–15] among the hydrogen production from coal. Supercritical water (SCW) is defined as the water with the parameters beyond the critical point (374 °C, 22.1 MPa) and has unique physical and chemical properties, such as low viscosity, high diffusivity and low dielectric [16–18]. These properties not only provide a homogeneous and rapid condition for coal gasification within a short time but also

* *Corresponding author*. Tel.: +86 2982660876.
E-mail address: jinhui@mail.xjtu.edu.cn (H. Jin).
http://dx.doi.org/10.1016/j.ijhydene.2016.05.129

higher efficiency and less residue [19,20]. Kinetic model does provide crucial information for the reactor optimization and scaling-up. In a nutshell, pyrolysis step for volatile and char gasification step made up the two main steps, within which the rate determining step is the char gasification process [21–24]. Therefore, the two steps' kinetics require specific description [25,26].

Volatile is a substance with the tendency of vaporize in the pyrolysis process. Cheng [27] once revealed that the conversion of Xiaolongtan lignite at 550 °C is almost the same with volatile mater content, indicating that SCW had a strong ability to extract the volatile mater. And dolomite catalyst was used to facilitate the extraction and decomposition of volatile matter from coal [28]. Su [29] investigated the Zhundong coal gasification kinetics in SCW. It' obviously that at the beginning of the reaction, the slope of carbon conversion versus time was high, then the slope starts decreasing and tended to be smooth ultimately. It was also proved that two different steps consisted of the whole gasification process which needed a combination of two different kinetic models.

People's attention are paid to coal gasification progress characteristics related with the physical structural change. The homogeneous pore system was proposed by Petersen [30]. Bhatia [31,32] developed random pore model (RPM) for fluid–solid reactions. It was assumed that the reaction was processing in a random pore structure system in which total pore length, total surface area and pore volume played significant role. Pore structure parameters, intrinsic kinetics and activation energy were analyzed by Su [33] with different chars.

Supercritical water has unique chemical and physical properties, especially the near-zero surface tension [34] so as to get easier access inside the porous structure [35]. Based on lumped parameter method and homogenous model, while a novel gasification kinetics model was established [36]. Vostrikov [37] conducted investigations on homogenous, nonrelated core model and RPM, however the fixed carbon conversion was not especially taken into account. Lately, it is found that RPM was applied to char gasification successfully and the unavailable pore structure parameters were perfectly solved with several integration equations so that we could get the model parameters conveniently [38].

Most coal gasification in supercritical water was investigated in the aspects of temperature, residence time and catalysts. Besides, the kinetic model which get evolved was often homogeneous model.

Using one equation to describe the whole gasification process might be easy from the point of view of mathematic, and the physical meaning might be farfetched [29]. The pyrolysis process and char gasification process might be described individually due to the huge difference between the two processes. In order to obtain precise information about the kinetic mechanism under supercritical water condition, Yimin lignite was selected to be gasified in a quartz tube reactor in supercritical water condition. Different parameters from different models which described the fixed carbon gasification were separately calculated by carbon gasification efficiency data versus residence time. Simultaneously, volatile proportion was used to improve the accuracy at the initial stage of the reaction as a modification. The best kinetic model of coal gasification process was discussed.

Experimental section

Apparatus and procedure

A 200 mm long and 1.5 mm inside diameter cylindrical micro quartz tube was used as reactor. The designed maximum temperature and pressure were 1000 °C and 45 MPa, respectively [39]. Yimin coal and deionized water were measured separately, mixed uniformly and then loaded into the bottom of the reactor with one-end sealed. The other end of the quartz tube was melted and sealed by a high temperature provided by a hydrogen flame. After the temperature was steady, the tube reactor was placed into the furnace quickly and started timing immediately.

Materials and analytical methods

The results of the elemental and proximate analyses were shown in Table 1. Yimin lignite was ground into powder ground were selected within 200 mesh.

The composition of the gaseous products were analyzed with gas chromatography (Agilent 7890A) with thermal conductivity detectors (TCDs). High-purity argon was used as the carrier gas. In order to obtain RPM parameter ψ, A thermogravimetric analyzer (Netzsch STA 449F3) with crucibles made of Al_2O_3 was used. High-purity N_2 with a 250 mL/min flow rate was used as the carrier gas [40].

Carbon gasification efficiency (CE) was used to describe the progress of carbon gasification in supercritical water and defined as the total carbon in the gaseous products divided by total carbon in the feedstock [14]. Since the concentration of the liquid residual during the gasification process was much lower than that of solid residual [36], CE basically stands for the conversion progress in the process of lignite gasification in supercritical water.

CE was used as X for all model in this work.

Results and discussion

Gasification results

The gasification results with different temperature, concentration and residence time can be seen in Table 2. Basically, for any specific condition, gasification results were better when temperature was higher which verified that temperature was one of the most important parameter that influenced the SCWG process [41]. Compared with different temperature, it was obvious that when temperature was 650 °C and 750 °C, CO_2 had the highest yield while temperature increased to 850 °C, H_2 had the highest yield. For each condition, CO always had the lowest yield which coincided with the thermodynamic equilibrium results [42]. At a certain temperature, when water content was decreasing, gas yield would increase which can be explained by carbonization reaction [43].

As the residence time increased, the yield of CO almost remained unchanged. For three other gases, gas yields tended to increase. But it's obviously that there was an inflection