Chinese Journal of Chemical Engineering 23 (2015) 321–325

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

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

Research Notes

Changes in char reactivity due to char–oxygen and char–steam reactions using victorian brown coal in a fixed-bed reactor☆

Shu Zhang [1,2,*], Yonggang Luo [1], Chunzhu Li [1,3], Yonggang Wang [2]

[1] Department of Chemical Engineering, Monash University, Clayton, VIC 3800, Australia
[2] School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing 100083, China
[3] Fuels and Energy Technology Institute, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia

ARTICLE INFO

Article history:
Received 11 March 2013
Received in revised form 19 May 2013
Accepted 16 June 2013
Available online 2 October 2014

Keywords:
Brown coal
Gasifying agent
Char reactivity
Fixed-bed reactor

ABSTRACT

This study was to examine the influence of reactions of char–O_2 and char–steam on the char reactivity evolution. A newly-designed fixed-bed reactor was used to conduct gasification experiments using Victorian brown coal at 800 °C. The chars prepared from the gasification experiments were then collected and subjected to reactivity characterisation (*ex-situ* reactivity) using TGA (thermogravimetric analyser) in air. The results indicate that the char reactivity from TGA was generally high when the char experienced intensive gasification reactions in 0.3% O_2 in the fixed-bed reactor. The addition of steam into the gasification not only enhanced the char conversion significantly but also reduced the char reactivity dramatically. The curve shapes of the char reactivity with involvement of steam were very different from that with O_2 gasification, implying the importance of gasifying agents to char properties.

1. Introduction

Coal gasification application could be tracked back to early 19th century [1], and has been again becoming an important focus since 1970s as its product gases can be used for electricity generation, valuable chemical production and especially for liquid fuel synthesis [2–8]. Gasification science and technology has been well developed in last decades, but mainly for high rank coal. Compared to high rank coal, low rank coal (*i.e.* brown coal) generally features high contents of ash, oxygen and water with porous structure and high reactivity.

cience about Victorian brown coal gasification has been intensively studied, particularly by Monash University in Australia [9–21]. For example, it was found that volatile–char interaction was one of the most important factors affecting almost every aspect of gasification using Victorian brown coal [3,14–21]. The results also implied that gasifying agents (steam, oxygen and CO_2) might react with Victorian brown coal on different reactive sites in a fluidised-bed reactor [15,22,23]. In a fluidised-bed, the heating rate of coal particles could reach about 10^3–10^4 $K \cdot s^{-1}$ [24,25]. Heating rate is surely a critical factor for any thermal conversion technology. High heating rate applied to coal particles will result in quick cracking of coal structure, forming more volatile materials. Also, the left solid (char) from high heating rate would feature different porosity, different aromatization and so on from low heating rate. The differences in physico-chemical property of char can fundamentally affect the subsequent gasification reactions between char and gasifying agents, even the reaction pathway. In industrial gasifiers, the coal particles are mostly fed into the hot gas reaction zone in the absence of fluidised agents. Indeed, the reaction conditions (such as the heating rates) of coal in a hot gas atmosphere could be well simulated in a fixed-bed reactor. Furthermore, an industrial gasifier could conceptually be divided into a few reaction zones (gasification zone, combustion zone, *etc.*). The slow reaction zone in a gasifier normally refers to the gasification reaction region where oxygen concentrations may vary from a few to less than 1%. Understanding of char reactivity evolution in an environment of low oxygen content is very crucial for improving gasification technology. As oxygen and steam often co-exist in a practical gasifier, the influence of steam on char–oxygen reaction may also be fundamentally important regarding gasification efficiency.

The gasification efficiency at different reaction conditions could be directly measured by coal converting rates. To better understand the difference in gasification rate of coal, the chars generated at certain reaction conditions need to be further analysed. One of the most useful techniques was the isothermal reactivity measurement of chars in oxidising environments using TGA at low temperatures (such as 400 °C) [10,15,17,20,22]. At the low temperatures, the carbonaceous material in chars would be consumed gradually. Different reaction rates at different stages of char conversion in TGA can suggest some detailed information of char properties (*i.e.* carbon structure, AAEM status,

☆ Support by the Victorian State Government under its Energy Technology Innovation Strategy programme and the 12th Five-Year Plan of National Science and Technology of China (2012BAA04B02).
* Corresponding author.
E-mail address: zhangshuwo@hotmail.com (S. Zhang).

http://dx.doi.org/10.1016/j.cjche.2014.09.044
1004-9541/

etc.). Indeed, some researchers have even selected lower temperature than 400 °C for the reactivity measurement because the chars prepared under some conditions were very reactive [26]. The very reactive chars would be immediately combusted instead of slowly oxidised when oxygen was introduced into the reaction zone [22,26]. If combustion take place, it would be difficult to compare the difference in char reactivity as the exothermal reaction could cause the sudden increase in temperature. For the chars prepared from this study, 400 °C was working well for conducting the reactivity measurements.

Therefore, the purpose of this work is to study coal conversions during the gasification in oxygen and steam, as well as the resultant char's reactivity. The result shows that the char–oxygen and char–steam reactions in the fixed bed reactor have induced significant changes in *ex-situ* char reactivity characterised by TGA. The property of chars prepared in this study was very different from that of chars prepared from a fluidised-bed reactor previously used, and the comparisons was made in this paper.

2. Experimental

2.1. Coal sample

Victorian brown coal which contains ~60 % (by mass) moisture was firstly dried at very low temperatures (<35 °C). The dried coal containing about 10% moisture was then milled and sieved to obtain particle sizes between 106 and 150 μm [9]. This pre-treated coal sample is hereafter termed as raw coal with properties: C, 70.40; H, 5.40; N, 0.62; S, 0.28; Cl, 0.10; O, 23.20 (by difference) and volatile matter, 52.20 % (by mass) (daf) together with an ash yield of 1.10 % (by mass) (db).

2.2. Gasification experiments

The fixed-bed quartz reactor as shown in Fig. 1 consists mainly of four parts: inject tube, fixed-bed 1, fixed-bed 2 and steam tube. To start experiments, they were firstly assembled and also connected with accessories used for gas supply (pure argon, 0.3% O_2 in argon and/or 15% steam in argon) for feeding coal particles. The total gas flow into the reactor was always 2 $L \cdot min^{-1}$. The reactor was then put into an electrically-heated furnace heating up to the described temperature (800 °C). The coal powder (106–150 μm) in a feeder was then fed into the reactor from the top (inject tube) at a planned feeding rate (25, 50, 75 or 100 $mg \cdot min^{-1}$), feeding time (10, 20, 30, 40, 50 or 60 min) and holding time (0, 10, 20, 30 or 40 min) for each experiment. Different reaction extents (coal conversion) were realised by varying feeding rate, feeding time and holding time. The char particles formed from gasification/pyrolysis would stay on the first frit (fixe-bed 1) inside the reactor and form a char bed. The gasifying agent would pass through the char bed and react with char. The product gas went out of the reactor from the bottom of reactor. At the end of each experiment, the reactor was taken out of reactor and cooled in air. The chars were then collected for further analysis after cooling down.

2.3. Ex-situ char reactivity measurement

The reactivity of chars prepared from the gasification experiments in the fixed-bed reactor was measured at 400 °C in air (21% O_2 in nitrogen) using a PerkinElmer Pyris 1 thermogravimetric analyser (TGA) following the procedure outlined previously [27]. Briefly, an empty platinum crucible was firstly loaded up and the balance was tarred with the empty platinum crucible. About 4 mg of char sample was placed in the platinum crucible and heated in pure nitrogen (99.999%) atmosphere in the TGA to 105 °C to remove the moisture from the char. The temperature was then increased at 50 $K \cdot min^{-1}$ to 400 °C. After 2 min at 400 °C, the atmosphere was switched from nitrogen to air to commence data collection. 400 °C was chosen as the isothermal oxidation temperature in this study in order to minimise the changes in char structure due to thermal annealing and avoid the possible ignition. The specific reactivity (R) of the char was calculated using the equation:

$$R = -\frac{dW}{W dt} \quad (1)$$

where, W is the mass (dry-ash-free basis) of the char at any given time t. After the mass of the char sample became constant, the temperature was further increased at 50 $K \cdot min^{-1}$ to 600 °C for an additional 30 min to ensure the complete combustion of any carbonaceous material possibly remaining in the char [15,17,27]. The reason for choosing 600 °C rather than higher temperatures was due to that higher temperatures could possibly lead to the volatilisation of some inorganic matters

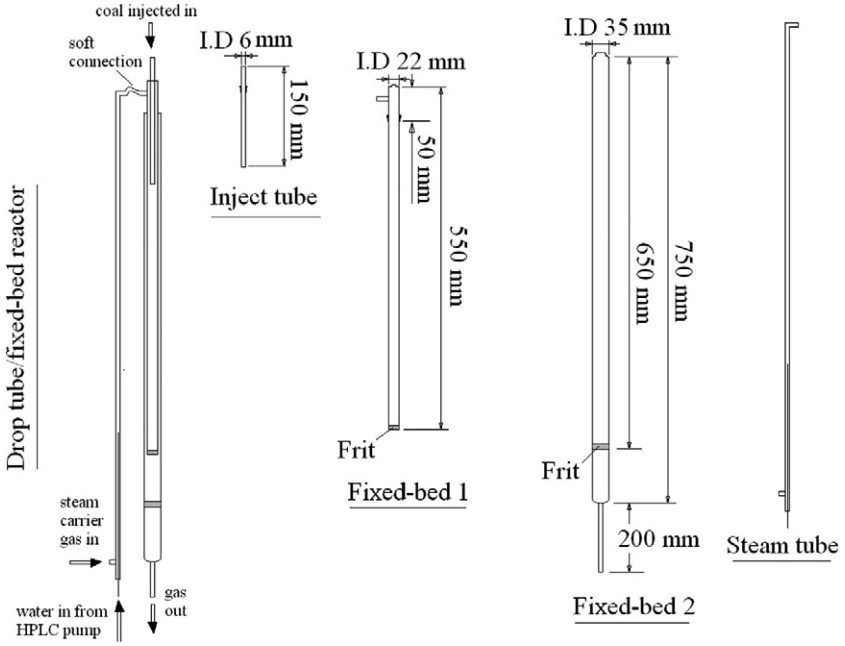

Fig. 1. Schematic diagram of fixed-bed reactor used in this study.