Fuel 212 (2018) 187–192

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Changes in char structure during the low-temperature pyrolysis in N_2 and subsequent gasification in air of Loy Yang brown coal char

Tingting Li[a], Lei Zhang[a], Li Dong[a], Penghua Qiu[a,b], Shuai Wang[a], Shengjuan Jiang[a,c], Chun-Zhu Li[a,*]

[a] Fuels and Energy Technology Institute, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia
[b] School of Energy Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China
[c] State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao 266580, PR China

ARTICLE INFO

Keywords:
Pyrolysis
Gasification
Char structure
FT-Raman spectroscopy
Reactivity
Loy Yang brown coal

ABSTRACT

This study aims to investigate the changes in char structure during the pyrolysis in N_2 and subsequent gasification in air at low temperature in a thermogravimetric analyser. The chars produced from the gasification of Loy Yang brown coal in 15% H_2O balanced with CO_2 at 850 °C in a fluidised-bed/fixed-bed reactor were used in this work. The evolution of char structure during pyrolysis and in-situ gasification was characterised by FT-Raman spectroscopy. The char-O_2 specific reactivity was measured as well. Our results show that, during further pyrolysis, the loss of O-containing structures led to the reduced observed Raman intensity from large aromatic rings and the formation of new cross-linking structures. During the subsequent gasification in air, the newly formed O-containing structures were more readily incorporated into less gasified char (0 min holding at 850 °C), but never reaching the same oxygenation level as those in the chars that had undergone extensive gasification (longer holding at 850 °C). The structural feature of the starting char (obtained at 850 °C) is the main factor determining the reaction pathway for the small/large aromatic ring systems during the low-temperature pyrolysis and in-situ gasification in air.

1. Introduction

Owing to the rapid gasification kinetics of low-rank coals, gasification-based technologies can greatly improve the effectiveness of their utilisation [1,2]. In a typical gasifier, a series of chemical reactions take place simultaneously. Among the key chemical reactions that proceed in a gasifier, char-CO_2, char-H_2O and char-O_2 are the primary reactions to produce the syngas (CO and H_2) [3]. In the absence of the external thermal energy supply, the exothermic reaction of coal with oxygen is an essential source of thermal energy to satisfy the energy demand required for drying coal, heating up the reactants to the targeted reaction temperature and various endothermic gasification reactions [3].

Based on previous work [4], it is known that a significant factor influencing the achievement of high gasification rate is the char structure. The char reactivity for low-rank coals is primarily affected by the concentration of catalysts, the chemical form of catalysts, the distribution of catalysts and the char structure [5]. Among these factors, char structure is paramount as it could not only directly determine the preferential consumption of carbon atoms but also affect the char's holding capacity of the catalyst and the catalyst distribution in the char [4–7]. Due to the important role of char structure, investigation on the char structural evolution during gasification is indispensable for the study on char reactivity.

The mechanism of char-O_2 reaction has been extensively studied. In many past studies [8–10], pitch coke, graphite or other highly ordered carbons were employed. However, for the chars produced from the pyrolysis/gasification of low-rank fuels, such as Loy Yang brown coal, the true graphitic structure does not exist [6,7,11–13]. Thus the findings based on the research on the highly ordered carbon materials are not suitable for the study on the chars produced from low-rank fuels, which is mainly composed of highly disordered carbon materials. Moreover, the main focus on the char structure should be the reactive part of the char. FT-Raman spectroscopy has been approved to be suitable for this task [6,7,11–25]. Previously, we [11] investigated the char structural changes during the catalytic gasification of brown coal char in air with FT-Raman spectroscopy. The results show that, in the absence or presence of the catalysts, the gasification occurs on different preferred reaction sites of the char. Recently, we [13] investigated the evolution of nascent char structure during the gasification of brown coal char and sub-bituminous coal char in air. We found that the

* Corresponding author.
E-mail address: chun-zhu.li@curtin.edu.au (C.-Z. Li).

http://dx.doi.org/10.1016/j.fuel.2017.10.026
Received 11 April 2017; Received in revised form 21 June 2017; Accepted 5 October 2017
Available online 16 October 2017

breakage of aromatic rings leads to the formation of dangling structures and smaller ring systems.

The structure of a char after partial gasification (gasification char) would differ from that of a pyrolysis char (such as the chars used in Refs. [11,13]) in terms of their aromatic ring systems. There would be less small rings left in the gasification char than the pyrolysis char, as the smaller rings would be easily consumed during gasification. It is still unclear if the reaction pathway in air for a gasification char that consists of relatively high amounts of large rings would be the same as those of a pyrolysis char that is rich in small rings. This very topic arouses the incentive of this study as a continuation of our previous studies [11–13] in this area. This study mainly focuses on the structural changes in the gasification char during the further pyrolysis in N_2 and in-situ gasification in air at 420 °C. The starting char samples were obtained from the gasification of Loy Yang brown coal in 15% H_2O—CO_2 at 850 °C [25]. A low gasification temperature in air was selected so as to avoid the ignition of char sample and to ensure that the overall reaction rate is limited by chemical reactions. FT-Raman spectroscopy has been employed to characterise the char structural evolution. Our results show that the original char structure determines the exact reaction pathway for the small/large rings during the further pyrolysis in N_2 and gasification in air.

2. Experimental

2.1. Char sample preparation and gasification experiments in a fluidised-bed/fixed-bed reactor

The gasification chars used in this study were produced from the gasification of Victorian Loy Yang brown coal in 15% H_2O-CO_2 with 0, 10 or 15 min holding at 850 °C in a fluidised-bed/fixed-bed reactor [25]. Briefly, around 1.5 g coal (accurately weighed) with particle sizes between 106 and 150 m were fed into the reactor by a stream of feeding gas. At the end of feeding (which was also the starting point of holding time), the chars were gasified for different periods to achieve varying conversion levels. The deionised water was delivered by a HPLC pump at the desired rate. Once delivered into the reactor, which is heated up by an external furnace, the water would instantly turn into steam (accounting for 15% of the total gas flow) and be mixed with CO_2 (99.999% purity, accounting for 85% of the total gas flow). After achieving the pre-set holding time, the reactor was lifted out of the furnace instantly and the char was collected for analysis at a later date. In order to minimise the oxidation of the samples, the char was well sealed and stored in a fridge.

2.2. Pyrolysis and gasification of the chars in air in TGA

The char sample obtained from the gasification at 850 °C was placed in a platinum crucible and heated up to 105 °C in N_2 to remove the moisture from the char in a Perkin-Elmer Pyris 1 thermogravimetric analyser (TGA).

Pyrolysis of the char. After holding for 20 min at 105 °C, the temperature was further increased to 420 °C at 20 °C/min. Once the peak temperature was reached, the char sample was cooled down in a stream of N_2 at 0.1 L/min. The TGA furnace would stay at the original position to ensure that the char would not contact with air until the temperature dropped to room temperature. The furnace was lowered down and the char sample was taken out and ground with KBr (serving as a heat-dissipating medium) for the analysis of char structural properties with FT-Raman spectroscopy.

Further gasification of the char in air. Alternative, following the pyrolysis of the char sample in N_2, the char was not cooled down and the gas atmosphere was changed to air promptly to initiate gasification at 420 °C without exposing the char to air. The char samples were held for different periods of time to obtain the chars with varying conversion levels after char-O_2 reactions. After the gasification in air reached the pre-set holding time, the char sample was again collected for characterisation.

After holding for a certain time, the weight loss of the char in air would level off and the temperature was further raised up to 600 °C to burn out any carbonaceous material, if any, left in the char. The material left in the crucible was ash and considered in the char specific reactivity calculation:

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

w is the weight of char at any given time t on the dry and ash free basis.

2.3. Characterisation of char structure

The Raman spectra of the chars were obtained with a Perkin-Elmer Spectrum GX FT-IR/Raman spectrometer [6]. The method was described in detail in Ref. [6]. Briefly, 0.25 wt% of char in the finely ground char-KBr mixture was used to facilitate the comparison of total Raman area between 800 and 1800 cm^{-1}. 150 mW laser power was used to scan the mixture of char and KBr for 200 times to obtain a Raman spectrum. 10 Gaussian bands were used to curve-fit the spectrum between 800 and 1800 cm^{-1}, following the methodology developed in our group [6]. The key focus is Gr, Vl, Vr, D and S bands, which could represent the key carbon skeletal structures of the chars investigated in this study.

3. Results and discussion

3.1. Weight loss of the char during pysolysis

Before the temperature reached 420 °C to initiate the gasification in air, the char was firstly heated up in N_2, which is termed as pyrolysis. Around 3% weight loss occurred during the pyrolysis of the char from room temperature to 420 °C in N_2 for all the selected char samples.

3.2. Changes in char structures during pyrolysis and gasification

3.2.1. Changes in the total Raman area

In Fig.1, the data plotted at “Gasification Char” represent the values of the chars obtained directly from the gasification at 850 °C [25]. Each point corresponds to one gasification experiment conducted in the fluidised-bed/fixed-bed reactor at 850 °C [25]. The data shown at 0 char conversion level stand for the values of the chars obtained after pyrolysis at 420 °C. Afterwards, the data represent the chars obtained at varying conversion levels during the gasification in air in TGA. Each point starting from 0 conversion level represents one experiment carried out in TGA. The total Raman peak intensity between 800 and 1800 cm^{-1} was integrated and expressed hereafter as the total Raman area of the char. It is known that the Raman intensity is mainly influenced by two factors, including Raman scattering ability and light absorptivity of char [6]. Some O-containing structures connected to aromatic rings tend to give a resonance effect between O and the aromatic ring that can enhance the total Raman intensity. On the other hand, the condensed aromatic ring systems in char have high light absorptivity, leading to decreased total Raman intensity.

Fig. 1 illustrates the changes in the total Raman area for the chars after pyrolysis to 420 °C and/or further gasification in air at 420 °C in TGA. After being gasified in 15% H_2O—CO_2 at 850 °C, the total Raman area of the chars increased drastically from around 2000 to 3600 as the holding time increased from 0 min to 10 and 15 min at 850 °C [25]. It is known [7,15] that the formation of O-containing structures in the presence of H_2O is the main reason enhancing the Raman peak intensity.

During the pyrolysis in N_2 from room temperature to 420 °C, the total Raman areas of all three chars decreased significantly. The decomposition of O-containing structures or the condensation of aromatic