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Full Length Article

Changes in char structure during the thermal treatment of nascent chars in N_2 and subsequent gasification in O_2

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HIGHLIGHTS

- Changes in nascent char structure during the thermal treatment/gasification were studied.
- Significant changes can take place easily to the structure of nascent char, especially from brown coal.
- Formation of dangling structures was observed during the cleavage of aromatic rings.
- Changes in nascent char structure are closely related to its reactivity.

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ABSTRACT

This study aims to investigate the structural features of nascent char. Two nascent chars were prepared from the pyrolysis of Loy Yang brown coal and Collie sub-bituminous coal in a wire-mesh reactor by heating at 1000 K s^{-1} to 600 °C. Structural changes in nascent chars were investigated by reheating the chars in N_2 at low temperatures (≤600 °C) followed by subsequent gasification in O_2/N_2 mixtures at 370 °C. FT-Raman spectroscopy was applied to characterise the chemical structural features of the chars. Our results indicate that the nascent char from the brown coal is much less stable that from the sub-bituminous coal. The thermal treatment of Loy Yang brown coal nascent char even at ~300 °C caused obvious changes to its aromatic ring systems while the corresponding changes to the Collie nascent char were insignificant. During the gasification of Loy Yang nascent char in O_2, oxygenation might preferentially happen on the larger rings, which activates and breaks the aromatic rings (to form dangling structures). With the opening of aromatic ring systems, O_2 might be much easier to access into the char matrix and to improve the dispersion of alkali and alkaline earth metallic (AAEM) species, which in turn enhances the gasification reactivity. Collie nascent char showed much less changes in char structure during gasification. Additionally, the preferential breakage of cross-linking structures in O_2 would also loosen the char structure and enhance the gasification reactivity for both nascent chars.

1. Introduction

Gasification is a continuously evolving clean energy technology. One of the advantages is that it is particularly suitable for the utilisation of low rank fuels to produce synthesis gas due to their high gasification reactivity [1]. During gasification, there are four main factors influencing the char reactivity [2]: the chemical form of catalyst, the concentration of catalyst, the distribution of catalyst on char (pore) surface and the physico-chemical structure of char. Among these factors, the changes in char structure would affect the reactivity directly and also the distribution of catalysts such as alkali and alkaline earth metallic (AAEM) species or the holding capacity of AAEM species of char. The latter would, in turn, influence the char reactivity [3,4].

Due to the significant roles of char structure in gasification, many techniques have been developed to characterise structural features of char, such as X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), FT-IR spectroscopy and Raman spectroscopy. Particularly, Raman spectroscopy has been widely used to understand the highly disordered carbonaceous matters in low-rank fuels during pyrolysis and gasification [5–23]. The Raman spectrum in the range between 800 and 1800 cm^{-1} was deconvoluted into 10 bands that can provide detailed information about the structural features such as the O-containing functional groups (total Raman area), the aromatic ring

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systems (D band and Gr + Vl + Vr band), the cross-linking structures (S band) and aliphatic structures (R band) [5].

The reaction of coal char with O_2 is inevitable in a gasifier, hence many mechanistic studies in this field have been performed extensively. Some highly ordered carbon materials such as graphite and pitch coke were used to investigate the gasification mechanism [24–26]. These findings cannot be directly applied to the study of gasification of low-rank fuels, which consist of highly disordered carbon. The gasification of low-rank fuels in O_2 has been widely investigated by employing Raman spectroscopy. Li and co-workers [7] compared the catalytic gasification (Na/Ca-loaded Loy Yang brown coal) with the non-catalytic (acid-washed Loy Yang coal) gasification mechanism. It is believed that the catalyst causes the gasification reaction to take place at the sites associated with the catalysts unselectively. Keown and co-workers [12] studied on the biomass char structural evolution during the gasification in O_2. This study showed the preferential consumption of small aromatic rings and aliphatic structures that caused the char structure to become more condensed.

However, there was little study focusing on the structural changes during the gasification of "nascent" char in O_2. The term "nascent char" is used herein to represent char that has undergone minimal extent of secondary cracking or other reactions. Obviously, "nascent char" is a relative term. There is no fixed temperature that has to be used to prepare a "nascent char". A relatively low temperature e.g. 600 °C can be used to prepare a nascent char: 600 °C is sufficiently high to ensure all tar has practically been released and is also sufficiently to minimise the extent of secondary reactions. According to the previous studies [23,27], nascent char structure changed significantly during the initial holding at temperatures from 600 to 1200 °C, which indicated large differences between the char structure of nascent char and aged char. Additionally, nascent char structure, which keeps some reactive structures such as O-containing functional groups, may play a different role in gasification reactions in O_2 compared to aged char. Further studies using nascent char would be necessary to understand the rapid changes in char structure during the initial stages of gasification.

In this study, two nascent chars were produced from the fast pyrolysis of Loy Yang brown coal and Collie sub-bituminous coal in a wire-mesh reactor, which was capable of minimising the volatile-char interactions. The nascent chars firstly underwent further pyrolysis in N_2 by TGA from room temperature to 600 °C. The changes in the chemical structural features of nascent chars during the further pyrolysis in N_2 were characterised with FT-Raman spectroscopy. The reaction between nascent char and O_2 was carried out at 370 °C to avoid ignition and to ensure that the gasification would take place in the chemical-reaction-controlled regime. The changes in char reactivity and structure during gasification were thus discussed.

2. Experimental

2.1. Nascent char samples preparation

Two nascent chars were produced from the pyrolysis of two coals (Loy Yang brown coal and Collie sub-bituminous coal) in a wire-mesh reactor [23]. Briefly, around 10 mg raw coal was loaded into the wire-mesh reactor, heated up to 600 °C at 1000 K s^{-1} and immediately cooled down to room temperature at ~500 K s^{-1}. Since the amount of char from one experiment was limited (~5 mg for Loy Yang coal and ~7 mg for Collie coal), the experiment was repeated ten times for each coal, and then the chars were well mixed and stored in the fridge for the further experiments.

2.2. Pyrolysis of the nascent chars in TGA

The nascent char from the wire-mesh reactor was heated in a Perkin-Elmer Pyris 1 TGA to different peak temperatures up to 600 °C in N_2 at a heating rate of 20 K s^{-1} in N_2 flowing at 0.1 L min^{-1}. After it reached the target temperature, the TGA would stop heating, and the char would be cooled down in N_2 without coming into contact with air. After the sample temperature had dropped down to room temperature, the sample was taken out and finely ground with KBr for subsequent Raman spectroscopic analysis.

2.3. Further in-situ gasification of nascent char in O_2 and the specific reactivity analysis

Two O_2 concentrations were used in the study: 5 and 21%. 370 °C was chosen as the gasification temperature. After the nascent char was pyrolysed to 370 °C in N_2, the gas was directly switched to 5 or 21% O_2 balanced with N_2 and the temperature was held at 370 °C. From the weight loss curve as a function of holding time, the specific reactivity (R) was calculated according to the equation

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

where W represents the weight (daf basis) of the char at any given time t. During the gasification in O_2, the chars at different char conversion levels were collected and mixed with KBr for Raman analysis.

2.4. FT-Raman spectroscopy for char characterisation

A Perkin-Elmer GX FT-Raman spectrometer was used for the characterisation of the char structure. The char sample was firstly mixed and ground with the spectroscopic grade potassium bromide (KBr). The weight percentage of char in the mixture was chosen as 0.25%, at which the total Raman area already reached the plateau value. The Raman spectra in the wavenumber range between 800 and 1800 cm^{-1} were curve-fitted with 10 Gaussian bands by the GRAMS/32 AI software (version 6.0) [5]. The total Raman area between 800 and 1800 cm^{-1}, ($G_r + V_l + V_r$) band area, D band area, S band area and R band area were used to characterise the structural features of chars.

3. Results and discussion

3.1. Changes in the char structure during the thermal treatment of nascent chars in N_2 in TGA

3.1.1. Further weight loss during the pyrolysis of nascent chars in TGA

Fig. 1 shows the char conversion in TGA as a function of peak temperature. It is clear that reheating the nascent char has led to further weight loss with increasing temperature from room temperature to 600 °C. In particular, significant weight loss was observed at temperatures above 400 °C. The weight loss of Loy Yang coal nascent char was greater than that of Collie coal nascent char during the pyrolysis in TGA, indicating the lower stability of Loy Yang coal nascent char than the Collie char.

3.1.2. Changes in char structure during the further pyrolysis of nascent chars

The total Raman peak area between 800 and 1800 cm^{-1} and the various band area ratios obtained for the further pyrolysed nascent chars are shown in Fig. 2. Firstly, the changes in the total Raman