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Effects of gasification atmosphere and temperature on char structural evolution during the gasification of Collie sub-bituminous coal

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HIGHLIGHTS

- This study aims to gain insights into the mechanisms of char gasification with CO_2 and H_2O.
- The char-CO_2 and char-H_2O reactions do not follow the same pathways.
- The char-CO_2 and char-H_2O gasification pathways do not change with temperature from 800 to 900 °C.

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ABSTRACT

Char structure is one of the important factors influencing the char reactivity during gasification. The purpose of this study is to investigate the effects of gasification atmosphere and temperature on the changes of char structure during gasification. In this study, a Collie sub-bituminous coal from Western Australia was gasified in a fluidised-bed/fixed-bed reactor at 800–900 °C in three gasification atmospheres: pure CO_2, 15% H_2O balanced with Ar and 15% H_2O balanced with CO_2. The structural features of the chars produced from the gasification of Collie sub-bituminous coal at varying levels of gasification conversion were characterised with FT-Raman spectroscopy. The recorded Raman spectra between 800 and 1800 cm^{-1} were deconvoluted into 10 Gaussian bands in order to obtain quantitative information about the key structural features of these chars. The total Raman area and the band area ratio of small and large aromatic ring systems are two important indices to study evolution of char structure during gasification. It is shown that the char structure changes drastically during gasification. The reaction pathways for char-CO_2 reaction and char-H_2O reaction are different. CO_2 and H_2O compete for active sites most likely on the char surface. For the same gasification atmospheres, the reaction pathway does not change with the gasification temperature between 800 and 900 °C.

1. Introduction

Gasification is a clean and efficient way to convert solid coal to gaseous products [1,2]. As char gasification is the rate-limiting step, high char reactivity is important for achieving high conversion levels [3]. Many factors can influence char reactivity [3–7], among which the importance of char structure is not particularly well understood [8]. The char structure could not only directly determine which carbon atoms are gasified first during gasification but also affect the interaction between char and catalysts, hence influencing the activity of catalysts [9,10]. So tracing the changes in char structure during gasification is really essential for a better understanding of gasification mechanism.

Char-CO_2 reaction and char-H_2O reaction are both fundamentally important reactions. The mechanisms of the carbon-CO_2 reaction and the carbon-H_2O reaction have been studied extensively [11–14]. Many researchers have worked on the char gasification mechanism in CO_2 or H_2O separately. A few papers focus on the char gasification in the mixture of CO_2 and H_2O. In these papers, there is a debate arguing whether there is an interaction between CO_2 and H_2O during the gasification in the mixture. Some show that char-CO_2 and char-H_2O reactions take place separately on different active sites on the char and the gasification rate in the mixture is equal to the sum of the gasification rates in each gasification atmosphere respectively [15,16]. On the other hand, some indicate that during the gasification in the mixture, the char-CO_2 and char-H_2O reactions are not independent. There are interactions such as competition or inhibition between CO_2 and H_2O. CO_2 and H_2O compete or share some active sites on the char [17,18].

According to the previous work in our group [4,6–8,19–23], FT-Raman spectroscopy is shown to be a powerful tool to investigate the structural features of highly disordered char. It is indicated that the changes of char structure take place not only on the char

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surface but also inside the char matrix. It introduces an effective method to study the bulk properties of the char.

This study aims to investigate the effects of gasification atmosphere and temperature on char structural evolution during the gasification of Collie sub-bituminous coal. Three gasification atmospheres were used: pure CO_2, 15% H_2O balanced with Ar (15% H_2O–Ar) and 15% H_2O balanced with CO_2 (15% H_2O–CO_2). Chars produced from the gasification at 800–900 °C in three gasification atmospheres were characterised by FT-Raman spectroscopy. The changes in char structure were traced by the evolution of the oxygenation of the char and the aromatic ring systems in the char. The results show that the reaction pathways for char-CO_2 reaction and char-H_2O reaction are different while the reaction pathway in each gasification atmosphere does not change with temperature between 800 and 900 °C.

2. Experimental

2.1. Coal sample preparation

Collie sub-bituminous coal was used in this study, which was obtained from Muja Power Station, Western Australia. The sample was partially dried at low temperature (<35 °C) and then ground and sieved to obtain a sample of particle sizes between 106 and 150 μm. The properties of the coal sample are presented in Table 1.

2.2. Gasification

The gasification experiments were carried out in a fluidised-bed/fixed-bed reactor. The details of the reactor can be found in Ref. [9]. Silica sand (300–355 μm) placed on the lower frit acted as the fluidised bed and was fluidised by the fluidising gas. An external furnace was used to heat up the reactor. Two thermocouples were used for monitoring the temperature distribution inside the reactor before and during the experiments. After the temperature inside the reactor was stabilised at the required temperature (e.g. 800, 850 or 900 °C) for at least 15 min, the feeding of coal started. About 1.5 g coal was fed into the reactor (at a rate of 75 mg/min) through a water-cooled probe, keeping the particles at room temperature before entering the reaction area. After rapid pyrolysis, the chars flowing out from the sand bed would form a char bed underneath the upper frit, which featured as a fixed bed. The top frit in the free board would stop the chars coming out from the reactor. The volatiles generated at a later stage would go through the char bed and experience volatile-char interaction. When the coal feeding or a pre-set holding time was achieved, the reactor would be lifted out of the furnace immediately to quench the gasification reaction. The char yields were determined by the weight difference of the reactor before and after each experiment. The moisture content of coal/char was determined by a Perkin–Elmer Pyris 1 Thermogravimetric Analyser (TGA) and considered in the calculation of char yields.

2.3. Char characterisation

The key purpose of char characterisation was to obtain information about the chemical structural feature of chars, especially their carbon skeleton. The true graphitic structure does not exist in chars from brown coal prepared at low temperature such as the chars in this study [4,6–8,19]. Furthermore, the key focus should be the reactive structure. For this reason, techniques such as X-ray diffraction would not be suitable for this purpose as it would focus more on ordered and thus less reactive structures in the chars. FT-Raman spectroscopy [4,6–8,19] appears to be most suitable for this task.

The FT-Raman spectra of chars were acquired using a Perkin-Elmer Spectrum GX FT-IR/Raman spectrometer according to the procedures outlined in Ref. [19]. The char sample was mixed and ground with KBr which served as heat-dissipating medium. In order to eliminate the influence of concentration of char-KBr mixture on the comparison of total Raman area, a concentration of 0.25 wt.% char in the mixture of char and KBr was selected after careful examination. Each sample was scanned 200 times with a laser power of 150 mW. The Raman spectrum in the range between 800 and 1800 cm^{-1} was firstly baseline-corrected and then curve-fitted using 10 Gaussian bands which was developed in our group [19]. One example of spectral deconvolution is shown in Fig. 1. As the band assignment has been well discussed in the previous work [19], only Gr, Vl, Vr and D bands will be briefly described in the later sections.

3. Results and discussion

3.1. Char yields

The gasification of Collie sub-bituminous coal was carried out in the fluidised-bed/fixed-bed reactor in three atmospheres (pure CO_2, 15% H_2O–Ar, 15%H_2O–CO_2) in the temperature range of 800–900 °C. The main purpose of this study is to investigate if the pathways for char-CO_2 and char-H_2O gasification would be the same. A steam concentration of 15% was chosen, which is within the range of steam concentrations in a typical gasifier. The CO_2 concentration was chosen so that the char-H_2O and char-CO_2 reaction rates were of similar magnitudes and comparable. Fig. 2 shows the char yields as a function of holding time during the gasification. Each point corresponded to one gasification experiment. The "0" min holding time means the time when coal feeding was completed.

It can be seen that, at each temperature, the gasification in pure CO_2 proceeded slowest among the three atmospheres used in this study. The conversion of char proceeded fastest during the gasification in the mixture of H_2O and CO_2 (15% H_2O–CO_2). However, the char conversion during the gasification in the mixture was lower than the sum of the char conversion during the gasification in pure CO_2 and 15% H_2O–Ar separately (The addition of the char conver-

Table 1
Properties of Collie coal in weight percentage (dry and ash free basis).

Ash (ar)	Volatile matter	C	H	N	S	O (by diff.)
5.7	38.8	75.7	4.5	1.4	0.5	17.9

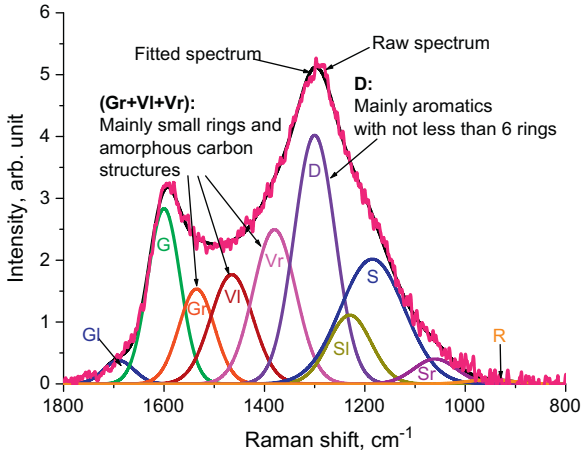

Fig. 1. A curve-fitted Raman spectrum of the char prepared from the gasification of Collie sub-bituminous coal in pure CO_2 at 800 °C.