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Effects of char chemical structure and AAEM retention in char during the gasification at 900 °C on the changes in low-temperature char-O_2 reactivity for Collie sub-bituminous coal

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HIGHLIGHTS

- This study investigates the low-temperature char-O_2 reactivity of a sub-bituminous coal.
- The Raman-sensitive O-containing structures improve the retention of AAEM species during gasification.
- The relative ratio of small to large rings in char greatly affects the char-O_2 reactivity.

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ABSTRACT

This study is focused on the effects of char structure and alkali and alkaline earth metallic (AAEM) species on the changes in char-O_2 reactivity for a Western Australian Collie sub-bituminous coal. The char samples used in this study were acquired from the partial gasification of the sub-bituminous coal in a fluidised-bed/fixed-bed reactor in pure CO_2, 15% H_2O balanced with Ar and a mixture of 15% H_2O and CO_2 (balancing gas) at 900 °C. The structural features of the chars were characterised by FT-Raman spectroscopy. The concentrations of AAEM species in the chars were determined by inductively coupled plasma – optical emission spectroscopy. The O-containing structures in char that can cause resonance effects to give enhanced Raman intensity tend to improve the retention of AAEM species in char during the gasification at 900 °C. However, these O-containing structures do not necessarily ensue a high char-O_2 reactivity at low temperature. While AAEM species in char would catalyse the char-O_2 reactions, they are not sufficient to determine the char-O_2 reactivity. The relative ratio of small to large aromatic ring systems in char, as reflected by the Raman spectroscopy, greatly influences the char-O_2 reactivity. The sub-bituminous coal in this study does not behave in the same way as the brown coal in our previous studies in terms of the factors influencing the char-O_2 reactivity.

1. Introduction

The high efficiency and environmental performance of gasification-based power generation technologies would greatly save the consumption of our limited fossil fuels, such as coal, and reduce the emissions of CO_2 [1–3]. Compared with fast devolatilisation of coal and relatively quick reforming of volatiles, the gasification of char is known to be the rate-limiting step of the whole gasification process [4], thereby attracting great attention and research efforts.

Among several important factors that influence the char reactivity, the evolution of char structure has been extensively studied in recent years [1–3,5–25]. FT-Raman spectroscopy [5–23] has been used to characterise char structure during gasification/pyrolysis. It has proved to be a useful tool to probe the structure of highly disordered chars from two aspects, the O-containing structures in the char and the carbon skeleton (aromatic rings) structures of the char. Tay and co-workers [10] found that the electron-rich O-containing species formed during gasification could largely enhance the gasification rate. The changes in ring structure would provide insights into the quest if the char conversion processes follow the same reaction pathway.

The finely dispersed alkali and alkaline earth metallic (AAEM) species in char, especially those in the form of ion-exchangeable carboxylates or salts, act as a crucial role in the utilisation of brown coal and biomass [24–31]. The AAEM species can serve as good catalysts to enhance the gasification rate by taking part in the reaction

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[10] between char and (radicals generated from) the gasifying agent(s). In previous work [18,19,30], the AAEM species in biomass/brown coal also showed a pronounced effect on the char-O_2 reactivity at low temperature. The chemical forms and distribution of AAEM species in char, which are related to those in the coal as well as the structure of char in which AAEM species disperse, are all significant elements affecting the char-O_2 reactivity [3,30]. During gasification, the AAEM species could also gradually move from the inner char structure to the surface of the char [30,32–34]. An increase in the char-O_2 reactivity at higher char conversion level is often observed, owing to the accumulation and catalytic activity of these inorganic species [26].

A sub-bituminous coal would differ from a brown coal both in its organic structure (higher rank) and in its inorganic species. The AAEM species in a sub-bituminous coal may not be as well distributed as those in a brown coal, the latter have a lot more AAEM species dispersed at atomic levels, especially for the ion-exchangeable ones, than the former. The relative importance of char chemical structure (e.g. reflected by FT-Raman spectroscopy) and the catalytic effect of AAEM species for a bituminous coal is still unclear, which forms the motivation of this study as a direct continuation of our previous studies in this area on brown coal. This study mainly focuses on the changes in the char-O_2 reactivity of Collie sub-bituminous coal chars obtained from gasification at 900 °C in different atmospheres [11]. The ex situ char-O_2 reactivity will be investigated from both the aspects of char structural features and the concentration of AAEM species. FT-Raman spectroscopy was applied to characterise the structural features of the chars collected at varying gasification conversion levels [11]. The concentration of AAEM species left after the partial gasification of Collie sub-bituminous coal in different atmospheres has been quantified with inductively coupled plasma – optical emission spectroscopy (ICP-OES). Our results show that the changes in aromatic ring structure play a more important role in the changes in char-O_2 reactivity than the concentrations of AAEM species in char.

2. Experimental

2.1. Coal sample preparation and gasification experiments

A Western Australian (Collie) sub-bituminous coal [11] was selected in this study. Before grinding and sieving to the required particle size range (106–150 μm), the coal sample was firstly air dried at <35 °C. The coal contained 75.7, 4.5, 1.4, 0.5 wt% (daf) of C, H, N and S individually, with the ash yield being of 5.7 wt% (db) [11]. The chars prepared in pure CO_2, 15% H_2O-Ar and 15% H_2O-CO_2 at 900 °C during the gasification of Collie sub-bituminous coal in a fluidised-bed/fixed-bed reactor [30] in the previous study [11] were used in this study. The details of the gasification experiment can be found in Ref. 11. Briefly, the coal particles (around 1.5 g that was accurately weighed) were fed into the reactor at a rate of 75 mg/min. After feeding, the reactor was kept in the furnace for different periods of time to obtain chars with varying conversion levels. The deionised water was delivered by A HPLC pump at the desired rate and would immediately turn into steam and be diluted by the carrier gas (Ar, 99.999% ultra high purity) once fed into the reactor. 15% steam concentration was selected as is within the steam concentration range in a typical gasifier. Research grade (99.999%) CO_2 was used in this study.

2.2. Characterisation of char structure

The structural features of the char characterised by FT-Raman spectroscopy and reported previously [11], such as the oxygenation of the char and the changes in aromatic ring systems in the char, were used herein for comparison purposes.

2.3. Quantification of alkali and alkaline earth metallic (AAEM) species

Crucially, the AAEM species should be fully extracted from the raw coal/chars and fully dissolved with acid in order to quantify the concentrations of AAEM species accurately with ICP-OES. For this purpose, the ashing method previously developed in our group [31] was followed to remove the carbonaceous matter before digesting the resultant ash with acid [31]. Approximately, 6 mg coal/char was placed evenly in a platinum crucible and ashed in a muffle furnace in air. O_2 would bond with AAEM species, thereby minimising the loss of AAEM species. The coal/char samples were heated from room temperature to 300 °C at 5 °C/min, followed by a temperature increase to 415 °C at 1 °C/min. During the heating up process, the coal/chars were held for 10 min at 375 °C and 415 °C respectively. Within the temperature range between 300 and 415 °C, the generation of volatiles were very drastic. Thus a very slow heating rate of 1 °C/min was selected to avoid any possible ignition, so as to eliminate the loss of AAEM species. Afterwards, the temperature was further increased at a heating rate of 5 °C/min to 600 °C and then held for 20 min to burn off all the carbonaceous materials.

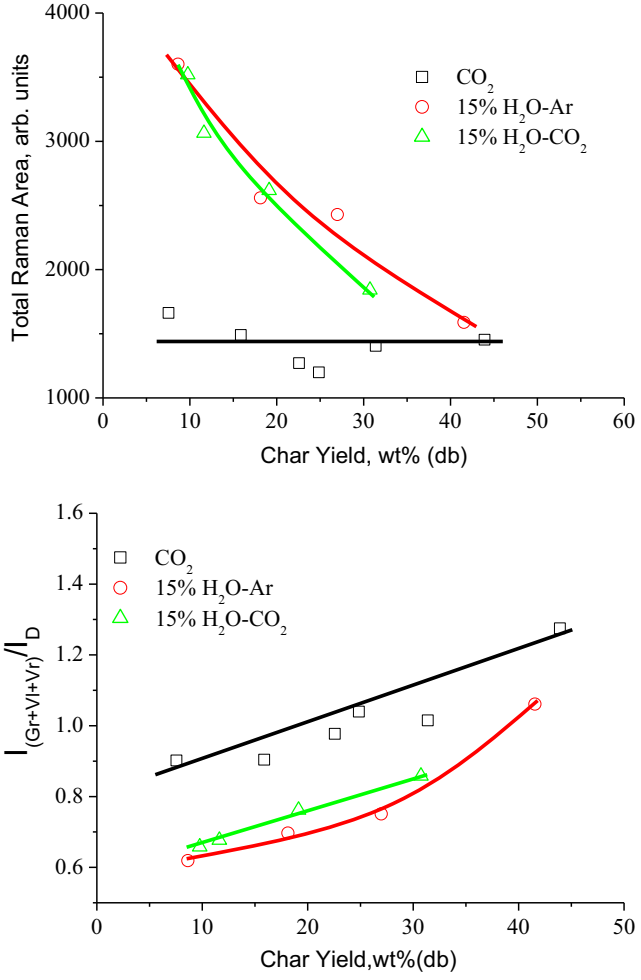

Fig. 1. Total Raman area and Raman band ratio of (Gr + Vl + Vr)/D versus char yield for the chars obtained in pure CO_2, 15% H_2O-Ar and 15% H_2O-CO_2 during the gasification of Collie sub-bituminous coal at 900 °C. (Replotted from the data in Ref. [11], with permission from Elsevier.)