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Effects of gasifying agent on the evolution of char structure during the gasification of Victorian brown coal

Hui-Ling Tay [a,b], Shiro Kajitani [a], Shu Zhang [a], Chun-Zhu Li [a,b,*]

[a] *Fuels and Energy Technology Institute, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia*
[b] *Department of Chemical Engineering, P.O. Box 36, Monash University, VIC 3800, Australia*

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ABSTRACT

Steam plays a vital role in the gasification process. This study aims to investigate the changes in char structure and reactivity during the gasification of Victorian brown coal. A Loy Yang brown coal sample was gasified at 800 °C in a novel fluidised-bed/fixed-bed reactor in three different gasification atmospheres: 15% H_2O balanced with argon, 4000 ppm O_2 balanced with CO_2 and 4000 ppm O_2 + 15% H_2O balanced with CO_2. The intrinsic reactivities of chars with air were measured with a thermogravimetric analyser (TGA) at low temperatures (380 or 400 °C). The char structural features were characterised using FT-Raman spectroscopy followed by spectral deconvolution. Our results indicate that steam, when it is present in the gasifying atmosphere, has a drastic effect on char structure and the subsequent reactivity of char with air at low temperatures. The presence of steam during the gasification at 800 °C also impacts on the volatilisation of Mg and Ca by altering the char structure. Our data provide evidence that the char–H_2O gasification follows a different reaction pathway from the char–CO_2 gasification, at least for the gasification of Victorian brown coal under the current experimental conditions.

1. Introduction

Gasification involves a complex set of reactions. The gasification of char with steam is of great importance because steam gasification not only produces the target gaseous products through the primary reaction (i.e. $C + H_2O \rightarrow CO + H_2$) and the secondary water–gas-shift reaction (i.e. $CO + H_2O \rightarrow CO_2 + H_2$), but also allows thermochemical energy recuperation and chemical heat pumping to greatly improve the efficiencies of combined-cycle power generation and hydrogen production [1]. Many researchers have attempted to clarify the mechanism of carbon/char gasification by steam, either by experimental techniques [2–4] or through computational chemistry [5,6]. As was pointed out in our previous work [7], steam could dissociate into O-containing and hydrogen radicals through interaction with char during the gasification in steam. The hydrogen radicals from the steam dissociation on char play a significant role in terms of char structure and reactivity. However, it remains unclear how steam (especially the H or other radicals originated from steam) would influence char structure or reactivity in an atmosphere containing both steam and oxidising agents (e.g. CO_2 and O_2).

From a thermodynamic point of view, the gasification of low-rank coal (such as Victorian brown coal) can be achieved at lower temperatures than that of high-rank coal for improved efficiency [1]. The high reactivity of low-rank coal [8] also makes the gasification at lower temperature possible. Information about char reactivity is important for the effective utilisation of coal, especially low-rank coals, in the low-temperature gasification processes.

The reactivity of Victorian brown coal char is affected by a few factors [8]. Firstly, Victorian brown coal contains inherent alkali and alkaline earth metallic (AAEM) species [9]. When the AAEM species are retained in the char during pyrolysis, they could act as catalysts for the gasification of char. Therefore, the concentration of the AAEM species in the coal/char has a direct influence on the char reactivity [10,11]. Secondly, the dispersion of the AAEM species in the char matrix also plays an important role in terms of char reactivity. This is because a catalyst could only be active for gasification if it is on the char (pore) surface and accessible to the gasifying agents [8]. Thirdly, the char structure could also affect the char reactivity. These factors also inter-influence each other. For example, when the concentrations of large aromatic ring systems in char increased, the dispersion of Na in char appeared to deteriorate to affect the char gasification reactivity [12].

The char structural features could be characterised with FT-Raman spectroscopy [13]. The chars from brown coal have distinctively different structures from that of graphite. In fact, the char structures could undergo continuous changes during gasification [8,12,14]. More recently, we have examined [15] the changes in

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* Corresponding author at: Fuels and Energy Technology Institute, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia. Tel.: +61 8 9266 1131; fax: +61 8 9266 1138.

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

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char structure during gasification in dilute O_2 and also in pure CO_2. However, the changes in char structure remain unclear when these oxidising gasifying agents (O_2 and CO_2) are present simultaneously with (reducing) steam as would be the case in a practical gasifier. Therefore, different gasifying atmospheres including 15% H_2O balanced with argon, 4000 ppm O_2 balanced with CO_2 and 4000 ppm O_2 + 15% H_2O balanced with CO_2 were used in this study in order to investigate the effects of steam on the evolution of char structure, which in turn affects the overall reactivity in these gaseous mixtures.

2. Experimental

2.1. Coal sample

Victorian (Loy Yang) brown coal [16] was used in this study. The coal was partially dried at low temperature (<35 °C), before being sieved in order to get the particle sizes between 63 and 150 μm. The coal properties are shown in Table 1, with the ash yield being 1.1 wt.%.

Table 1
Properties of Loy Yang raw coal sample in weight percentage (dry and ash free basis) [16].

Volatile matter	C	H	N	S (total)	Cl	O (by diff.)
52.2	70.4	5.4	0.62	0.28	0.10	23.2

2.2. Gasification

Gasification experiments were carried out in a novel fluidised-bed/fixed-bed quartz reactor for which more details can be found elsewhere [16]. Two frits were installed in the reactor body. The lower frit acted as a support for the bed material (sand) and as a gas distributor for the incoming fluidising gas (gasifying agents). Hence the bottom fluidised sand bed was referred to as a fluidised-bed reactor in which the coal particles were heated up rapidly, pyrolysed and partially gasified. The majority of char particles were elutriated out of the sand bed due to their lighter density. The second (upper) frit installed in the freeboard then acted as a filter to stop the char particles from being carried out of the reactor. These particles formed a fixed bed underneath the top frit in the freeboard. This means that the nascent char from the pyrolysis/gasification of brown coal in the fluidised bed was kept within the reactor until being completely gasified or until a pre-set holding/gasification time had been reached, at which time the whole reactor assembly was lifted out of the furnace to quench the gasification reactions. This reactor set up would thus be able to reach complete char gasification, or a pre-set period of gasification, without the need of a char recirculation facility.

The reactor was heated externally by an electric furnace to the reaction temperature of 800 °C. When the reaction temperature was stabilised, an approximate amount of 1.5 g coal (accurately weighed) was fed into the reactor through a water-cooled probe. After all the coal had been fed into the reactor, the reactor was lifted out of the furnace in a ‘‘no holding time’’ experiment. In a ‘‘with holding time’’ experiment, the reactor was left inside the furnace for a pre-set amount of time for gasification before being lifted out of the furnace.

Three different atmospheres were used in this study: 15% H_2O balanced with argon, 4000 ppm O_2 balanced with CO_2 and 4000 ppm O_2 + 15% H_2O balanced with CO_2. Deionised water was continuously fed into the reactor (underneath the bottom frit) with a HPLC pump in order to generate the steam required in the experiment, which was then completely mixed with other gasifying agents before coming into contact with the coal/char particles.

2.3. Char characterisation

Char was collected at the end of the gasification experiment and subjected to the following analyses.

2.3.1. Reactivity measurement

A Perkin–Elmer Pyris 1 thermogravimetric analyser (TGA) was used to measure the reactivity of the char following our procedures established earlier [17]. Briefly, about 4–5 mg of char was spread in a platinum crucible in the TGA. It was then heated up to 105 °C in nitrogen and held for 20 min in order to fully dry the sample. This weight was taken as the dry weight of char. The char was then heated to 400 °C (or 380 °C) in nitrogen, during which the observed weight loss was <3 wt.% of the sample. The atmosphere was switched to air when 400 °C (or 380 °C) was reached and the reactivity measurement commenced. The reactivity, *R*, was calculated by:

$$R = -\frac{1}{W}\frac{dW}{dt} \tag{1}$$

where *W* is the char weight (daf) at any given time *t*.

When the weight loss had levelled off, the temperature was increased to 600 °C and held for 30 min in order to burn off any remaining carbonaceous material. The resultant mass was considered as the weight of ash. This ashing conditions were based on our previous study [18] in order to ensure that all carbonaceous material was burned but the volatilisation of AAEM species was minimal.

2.3.2. Determination of inherent catalysts in the char

The concentrations of the alkali and alkaline earth metallic species in coal and char were quantified using a Dionex DX-500 ion chromatograph (IC) [18]. The coal/char sample was firstly ashed in TGA and the resultant ash was then digested in HF and HNO_3 acids (1:1 ratio) for 16 h. The acid mixture was subsequently evaporated and the digested ash was finally dissolved in 0.02 M CH_3SO_3H (MSA) for injection into the IC. All ash after digestion was dissolved in the acid (no particulates were observed).

2.3.3. Char structure characterisation

The FT-Raman spectra of chars were acquired using a Perkin–Elmer Spectrum GX FT-IR/Raman spectrometer [13]. The char sample was firstly diluted and ground with IR grade KBr to a concentration of 0.25 wt.%. This diluted sample was then used to record the Raman spectrum. An InGaAs detector cooled with liquid nitrogen was used to collect Raman scattering using a back scattering configuration. The excitation laser wavelength was 1064 nm, the laser power was 150 mW and the spectral resolution was 4 cm^{-1}. The Raman spectra recorded were deconvoluted into 10 Gaussian bands following the methodology that was given in detail elsewhere [13].

3. Results and discussions

3.1. Char yields

Fig. 1 shows the change in char yield with holding time in various gasifying atmospheres at 800 °C. In all experiments, about 18 min were used to feed the required amount of coal (∼1.5 g, accurately weighed) into the reactor. The trend for the changes in char yield during the gasification in 15% H_2O was rather similar to that in O_2 + CO_2 mixture, albeit the reaction was slightly slower at the later stage for the gasification in 15% H_2O. As expected, the chars were consumed most rapidly in the O_2 + H_2O + CO_2 mixture.