KINETICS OF STEAM GASIFICATION OF BROWN COAL AND VOLATILE-CHAR INTERACTIONS

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ABSTRACT

Victorian brown coal has high reactivity for gasification because of catalysis of inherent AAEM species. It was, however, found recently that the inhibitory effects of the volatile-char interactions on char gasification are not negligible. In this study, the effects of volatiles were examined with a novel fluidised-bed/fixed-bed reactor, and the mechanisms and kinetics model of the char gasification and volatile-char interactions were discussed to describe quantitatively the inhibition of volatiles about char gasification. Victorian brown coal sample was gasified with steam at 800 °C at various feeding rates. As a result, char yields became higher at higher feeding rate at the same feeding time because of the volatile-char interactions. The elementary reactions of the char gasification and volatile-char interactions were proposed and the L-H type reaction rate equations for brown coal gasification were newly derived, and the kinetics model was verified by the comparison with experiments. The experimental data of the char yields and the concentrations of Na in gasified char were able to be estimated by the proposed kinetics model. This model would be useful to estimate the performance of the gasifier for Victorian brown coal.

Keywords: Victorian brown coal, char, gasification, catalyst, reactivity

INTRODUCTION

Coal gasification has been considered as one of the most important clean coal technologies. Gasification technology is particularly suitable for the utilisation of low-rank coal, such as Victorian brown coal, due to its high reactivity for gasification because of catalysis of inherent alkali and alkaline earth metallic (AAEM) species. It was, however, found recently that the inhibitory effects of the volatile-char interactions on char gasification are not negligible. Volatiles from coal pyrolysis are responsible for the inhibition of steam gasification (Bayarsaikhan *et al.*, 2005), and enhance the volatilisation of the monovalent AAEM species, such as Na, to decrease the overall char gasification rate (Wu *et al.*, 2002). The volatile-char interactions are most likely the reactions between char and free radicals formed by the thermal cracking and/or reforming of volatiles.

In this study, the effects of volatiles were examined with a novel fluidised-bed/fixed-bed reactor. The mechanisms and kinetics model of the char gasification and volatile-char interactions were discussed to describe quantitatively the inhibition of volatiles about char gasification. The proposed kinetics model would be useful to estimate the performance of the gasifier for Victorian brown coal.

EXPERIMENTAL

Coal Samples

Loy Yang (Victoria, Australia) brown coal was used in this study. The sample was partially dried at the temperature lower than 35 °C, then pulverised and sieved to obtain a sample of particle size between 63–150 μm. This coal sample was termed as a 'raw' coal sample. The properties of the coal sample are: C, 70.4; H, 5.4; N, 0.62; S, 0.28; Cl, 0.10; O, 23.2 and VM, 52.2 wt% (daf) together with ash, 1.1 wt% (db) and moisture, 13 wt% (ad). Na is known as the major element of AAEM species in Victorian brown coal (Quyn *et al*., 2002), and the concentration of Na in the sample was 0.10 wt% (db).

A 'H-from' coal sample was prepared by washing raw coal sample with sulfuric acid to remove inherent AAEM species by the same procedure described elsewhere by Sathe *et al*. (1999).

Steam Gasification

Coal samples were gasified using a novel fluidised-bed/fixed-bed quartz reactor (Quyn *et al*., 2002) shown in Fig. 1. Two frits were installed in the reactor body. Silica sand was put onto the lower frit and was fluidised by the gasifying agent. The reactor was heated up with an external electrical furnace and kept at 800 ^{o}C in this study. A HPLC pump was used to deliver water directly into the reactor to generate steam as the gasifying agent. The concentration of steam in total supplied gas was 15%. The total gas flow was 2 l/min at the standard ambient temperature and pressure, and the gas velocity at reaction temperature was approximately 5.6 m/min.

Coal particles entrained in a coal feeder were fed through a water-cooled injection probe into the heated sand bed at certain feeding rates to achieve rapid particle heating rates. Char was formed in the sand bed and was elutriated out of the sand bed due to its lightness. The char formed a fixed bed underneath the top frit. The configuration of the reactor allowed the volatile-char interactions during char gasification. After coal feeding was stopped, char was gasified without the volatile-char interactions. The reactor was finally lifted out of the furnace and cooled down. The char yield was determined by the difference in the weights of reactor and coal/char before and after each experiment. The reproducibility of char yields should be within ±1%.

Char was collected after the gasification experiment and the concentrations of AAEM species in char was quantified by the same procedure described elsewhere by Li *et al.* (2000). The reproducibility of AAEM analysis should be around ±5% (Okuno *et al*., 2005).

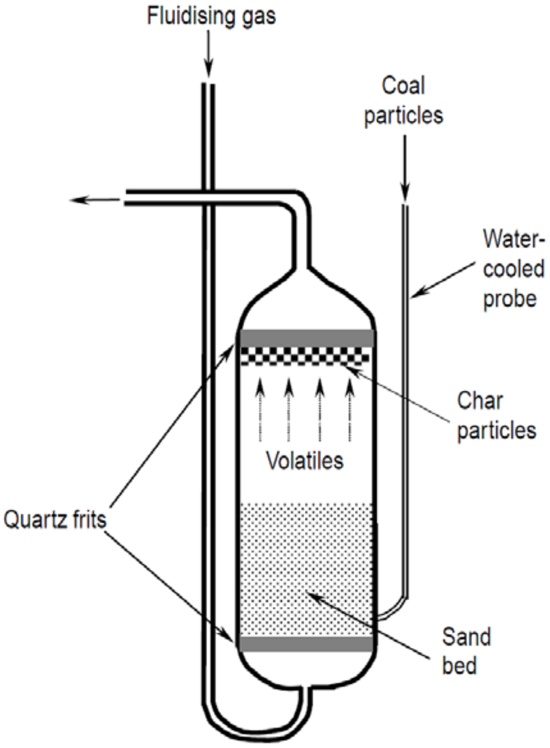

Fig. 1: Schematic diagram of a fluidised-bed/fixed-bed reactor (Quyn *et al.*, 2002)

RESULTS AND DISCUSSION

Kinetics Model

The observed gasification rate dX/dt was assumed to be described as a sum of the overall rate constant for non-catalytic gasification k_{nc} and that for catalytic gasification k_c in this study, because Bayarsaikhan *et al.* (2005) showed that non-catalytic gasification and catalytic gasification took place in parallel during steam gasification of Victorian brown coal.

$$dX/dt = k_{nc} + k_c \qquad (1)$$

where X is the conversion ratio of char and t is time. The mechanisms and reaction rate equations would be discussed as follows.

Non-Catalytic Gasification

Some evidences of dissociation of steam to H and OH during steam gasification at char surface were shown by Blackwood & McTaggart (1959) and Tay *et al.* (2009). The following dissociative adsorption model (Long & Sykes, 1948, Blackwood & McTaggart, 1959 and Laurendeau, 1978) is adopted for non-catalytic gasification of Victorian brown coal char in this work.

$$\mathrm{C_f} + \mathrm{H_2O} \xrightarrow{i_{nc1}} \mathrm{C(H)} + \mathrm{C(OH)} \tag{2}$$

$$\mathrm{C_f} + \mathrm{C(OH)} \xrightarrow{i_{nc3}} \mathrm{C(O)} + \mathrm{C(H)} \tag{3}$$

$$\mathrm{C(H)} \underset{i_{nc6}}{\overset{i_{nc5}}{\rightleftarrows}} \mathrm{C_f} + \frac{1}{2}\mathrm{H_2} \tag{4}$$

$$\mathrm{C(O)} \xrightarrow{i_{nc7}} \mathrm{CO} \tag{5}$$

Where C_f denotes the active site of carbon in char and i_{nc} is the rate constant for each elementary reaction for non-catalytic gasification. The following adsorption step of free radical from volatiles, especially H radical (Wu *et al.*, 2002), is proposed to describe the inhibition of volatiles. The partial pressure of H radical should be proportional to that of volatiles and also coal feeding rates ($P_H \propto P_{VM} \propto \text{Feeding Rate}$). Reaction 6 describes the volatile-char interactions.

$$\mathrm{C_f} + \mathrm{H} \xrightarrow{i_{nc8}} \mathrm{C(H)} \tag{6}$$

Assuming steady-state concentrations of C(H), C(OH) and C(O) , k_{nc} is given by:

$$k_{nc} = \frac{K_{nc1}P_{H_2O}}{1 + K_{nc2}P_{H_2O} + K_{nc3}\sqrt{P_{H_2}} + K_{nc4}P_H} \tag{7}$$

where $K_{nc1} = \frac{i_{nc1}n_t}{C_0}$, $K_{nc2} = i_{nc1}(\frac{1}{i_{nc3}} + \frac{2}{i_{nc5}} + \frac{1}{i_{nc7}})$, $K_{nc3} = \frac{i_{nc6}}{i_{nc5}}$, $K_{nc4} = \frac{i_{nc8}}{i_{nc5}}$, and n_t is the density of the total active sites of carbon on an initial char basis (m^{-3}-initial char). C_0 is the carbon density in initial char.

Fig. 2 shows the results of steam gasification of H-form coal char. An approximate amount of 1.5 g H-form coal was fed into the fluidised-bed/fixed-bed reactor for 17 minutes (88 mg/min). Coal feeding was finished at 0 holding time in the figure and char was gasified without the volatile-char interactions for each holding time. The char conversion ratio X can be converted to the char yield Y on a daf basis by the correlation: $Y = Y_i(1 - X)$. Y_i is initial char yield during primary pyrolysis of coal. The value of Y_i was unable to be determined directly from these experiments but the suitable value could be estimated. Eq. 7 described exactly the experimental results as the solid line in Fig. 2 when $n_t = n_{t,0}(1 - X)$ and Eq. 7 is therefore given by:

$$k_{nc} = k_{nc,0}(1 - X) \tag{8}$$

where $k_{nc,0} = \frac{K_{nc1,0}P_{H_2O}}{1 + K_{nc2}P_{H_2O} + K_{nc3}\sqrt{P_{H_2}} + K_{nc4}P_H}$, $K_{nc1,0} = \frac{i_{nc1}n_{t,0}}{C_0}$, and subscript ',0' denotes the initial value. The value of k_{nc} in 15 % steam at 800 °C was determined from the analysis of these data.

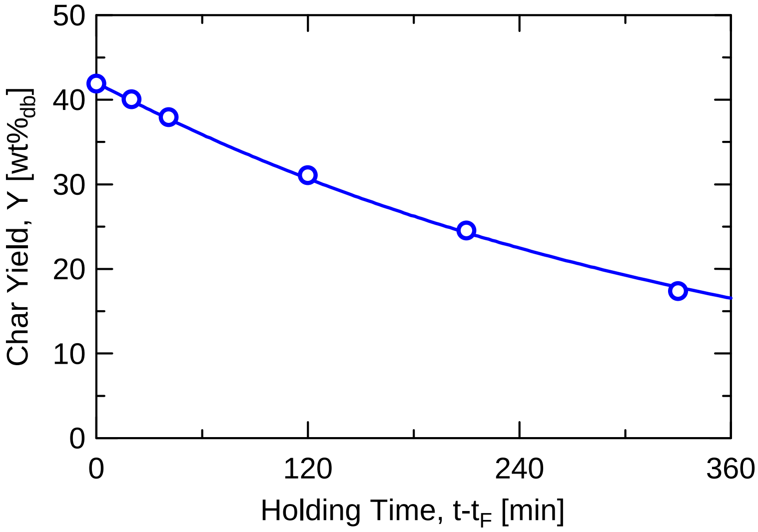

Fig. 2: Char yields form the gasification of H-form coal char in 15 % steam at 800 °C as a function of holding time. The feeding time t_F was 17 min.

(Dots: experimental results. Line: kinetics model.)

Catalytic Gasification

The dissociative adsorption model of steam to H and OH is also proposed for catalytic gasification of Victorian brown coal char, the same as for non-catalytic gasification.

$$\mathrm{M} + \mathrm{H_2O} \xrightarrow{i_{c1}} \mathrm{M(H)} + \mathrm{M(OH)} \qquad (9)$$

$$\mathrm{C} + \mathrm{M(OH)} \xrightarrow{i_{c3}} \mathrm{C(O)} + \mathrm{M(H)} \qquad (10)$$

$$\mathrm{M(H)} \underset{i_{c6}}{\overset{i_{c5}}{\rightleftarrows}} \mathrm{M} + \frac{1}{2}\mathrm{H_2} \qquad (11)$$

$$\mathrm{C(O)} \xrightarrow{i_{c7}} \mathrm{CO} \qquad (12)$$

where M denotes the catalyst which is AAEM species, especially Na. And i_c is the rate constant for each elementary reaction. The following adsorption step of H radical from volatiles is proposed to describe the inhibition of volatiles. Two mechanisms of the loss of the catalytic activity are also proposed. One is the volatilisation due to the volatile-char interactions and the other is the evaporation unrelated with the volatile-char interactions.

$$\mathrm{M} + \mathrm{H} \xrightarrow{i_{c8}} \mathrm{M(H)} \qquad (13)$$

$$\mathrm{M(H)} \xrightarrow{i_{c9}} \mathrm{C\text{-}H} + \mathrm{M_{gas}} \qquad (14)$$

$$\mathrm{M} \xrightarrow{i_{c10}} \mathrm{M}_{\mathrm{gas}} \tag{15}$$

Although the behaviours of AAEM species are complicated, Reactions 13 and 14 should describe the major reactions of volatile-char interactions, and the successive reaction of Reactions 13 and 14 is the same mechanism of the exchange of Na for H radical which is described elsewhere by Sathe *et al.* (1999) and Li *et al.* (2000):

$$\mathrm{CM\text{-}Na + H \rightarrow CM\text{-}H + Na}$$

Assuming steady-state concentrations of M(H), M(OH) and C(O), k_c and the overall rate constant for the loss of the catalytic activity k_{loss} are given by:

$$k_c = \frac{K_{c1}P_{H_2O}}{1 + K_{c2}P_{H_2O} + K_{c3}\sqrt{P_{H_2}} + K_{c4}P_H} \tag{16}$$

$$k_{loss} = -\frac{1}{n_{tM0}}\frac{dn_{tM}}{dt} = \frac{K_{loss1} + K_{loss2}(K_{c21}P_{H_2O} + K_{c3}\sqrt{P_{H_2}} + K_{c4}P_H)}{1 + K_{c2}P_{H_2O} + K_{c3}\sqrt{P_{H_2}} + K_{c4}P_H} \tag{17}$$

where $K_{c1} = \frac{i_{c1}n_{tM}}{C_0}$, $K_{c2} = i_{c1}(\frac{1}{i_{c3}n_t} + \frac{2}{i_{c5}+i_{c9}})$, $K_{c3} = \frac{i_{c6}}{i_{c5}+i_{c9}}$, $K_{c4} = \frac{i_{c8}}{i_{c5}+i_{c9}}$, $K_{loss1} = \frac{i_{c10}n_{tM}}{n_{tM0}}$, $K_{loss2} = \frac{i_{c9}n_{tM}}{n_{tM0}}$, $K_{c21} = \frac{2i_{c1}}{i_{c5}+i_{c9}}$, and n_{tM} is the density of the total active sites of catalyst on an initial char basis (m^{-3}-initial char).

Eqs. 16 and 17 suggest that k_{loss} should be proportional to k_c when gas composition is steady. This correlation described by Eq. 18 agrees qualitatively with the experimental results of Bayarsaikhan *et al.* (2005 and 2006).

$$\frac{k_{loss}}{k_c} = \frac{K_{loss1} + K_{loss2}(K_{c21}P_{H_2O} + K_{c3}\sqrt{P_{H_2}} + K_{c4}P_H)}{K_{c1}P_{H_2O}} \tag{18}$$

When it can be assumed that K_{c2} is constant value during char gasification, $k_{loss,0}$ and $k_{c,0}$ should also be constant. Therefore Eqs. 17 and 16 become:

$$n_{tM} = n_{tM,0}e^{-k_{loss,0}t} \tag{19}$$

$$k_c = k_{c,0}e^{-k_{loss,0}t} \tag{20}$$

where $k_{c,0} = \frac{K_{c1,0}P_{H_2O}}{1 + K_{c2}P_{H_2O} + K_{c3}\sqrt{P_{H_2}} + K_{c4}P_H}$, $K_{c1,0} = \frac{i_{c1}n_{tM0}}{C_0}$,

$$k_{loss,0} = \frac{K_{loss1,0} + K_{loss2,0}(K_{c21}P_{H_2O} + K_{c3}\sqrt{P_{H_2}} + K_{c4}P_H)}{1 + K_{c2}P_{H_2O} + K_{c3}\sqrt{P_{H_2}} + K_{c4}P_H}, \; K_{loss1,0} = i_{c10}, \; K_{loss2,0} = i_{c9}$$

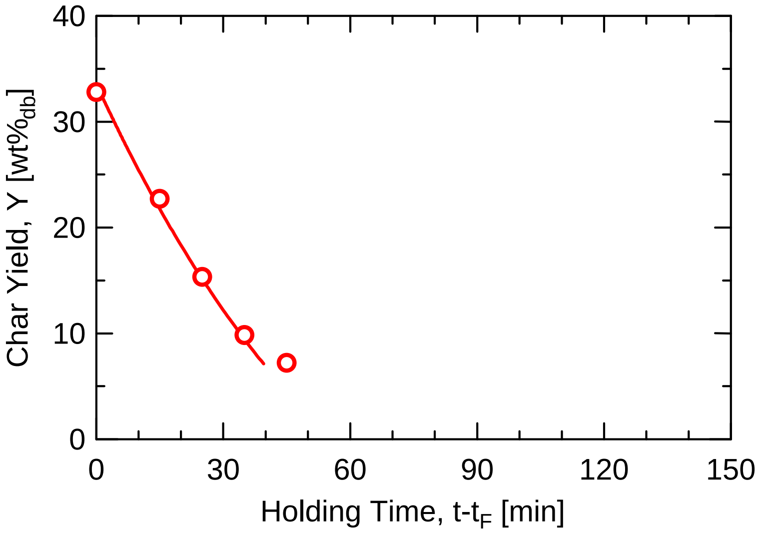

Fig. 3: Char yields form the gasification of raw coal char in 15 % steam at 800 ^{o}C as a function of holding time. The feeding time t_F was 17.5 min.

(Dots: experimental results. Line: kinetics model.)

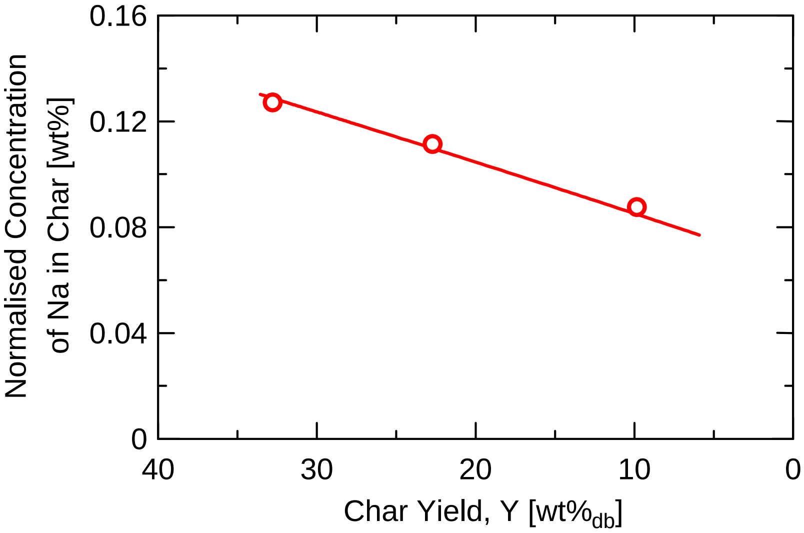

Fig. 4: Normalised Na concentrations ($Na\ Y\ /\ Y_i$) in char form the gasification of raw coal char in 15 % steam at 800 ^{o}C as a function of char yields.

(Dots: experimental results. Line: kinetics model.)

Figs. 3 and 4 show the results of steam gasification of raw coal char. An approximate amount of 1.5 g raw coal was fed into the fluidised-bed/fixed-bed reactor for 17.5 minutes (86 mg/min). Coal feeding was finished at 0 holding time in Fig. 3 and char was gasified without the volatile-char interactions for each holding time. Assuming n_{tM} is proportional to Na concentration in char, analysed concentration Na was normalised as $Na\ Y\ /\ Y_i$ on an initial char basis to compare with the char yield. Eqs. 1, 7, 16 and 17 were able to describe the experimental results of char yields and Na concentrations as the solid lines in Figs. 3 and 4. The values of k_c and k_{loss} without the volatile-char interactions in 15 % steam at 800 °C were determined from the analysis of these data.

The char gasification rate, however, seems to have dropped at the char yield of 8 $\%_{db}$ in Fig. 3.There are two possible reasons. One reason could be the change of the char structure during steam gasification (Guo *et al.*, 2008 and Tay *et al.*, 2009). The other reason could be the low reactivity of coke formed by the thermal cracking from volatiles.

Volatile-Char Interactions

The volatile-char interactions would inhibit the adsorption of steam and enhance the volatilisation of Na to decrease the overall char gasification rate. The experimental results have been reported in the previous paper (Shu et al., 2007). Raw coal was continuously fed into the fluidised-bed/fixed-bed reactor at a coal feeding rate of 100, 50 or 15 mg/min for each feeding time with no holding time in 15 % steam at 800 °C. Fig. 5 shows that the observed char yields increased with increasing the coal feeding rate at the same feeding time. Na concentrations in char were also analysed and normalised concentrations are shown in Fig. 6. Na concentrations decreased with feeding time and char yields.

The proposed kinetics model can also be used to simulate these continuous feeding experiments. Char has a distribution of residence time because of continuous feeding. The average char conversion ratio $\overline{X}$ is given by:

$$\overline{X} = \frac{1}{t}\int_0^t X dt \tag{21}$$

$$Y = Y_i(1-\overline{X}) \tag{22}$$

The normalised concentration of catalyst in char $\overline{M_c}(\propto \overline{n_{tM}})$ is also given with Eq. (19) by:

$$\overline{M_c} = \frac{1}{t}\int_0^t M_c dt = \frac{1-e^{-k_{loss,0}t}}{k_{loss,0}t} M_{c,0} \tag{23}$$

When suitable values for K_{nc4}, K_{c4} and K_{loss2} are estimated, the correlations between feeding time, char yields and Na concentrations almost agreed with the experimental results as the solid lines in Figs. 5 and 6. If there is no volatile-char interaction during continuous feeding ($P_H = 0$), char yields and Na concentrations would be on the broken lines with this model, regardless of the feeding rate. Then it is obvious that the differences between the feeding rates depend on the volatile-char interactions which are mainly caused by free radicals formed by the thermal cracking and/or reforming of volatiles. It can be said that the volatile-char interactions were described quantitatively in the proposed kinetics model.

Shu et al., (2007) suggested the char structure changed after the feeding time of 50min. The char structure should be also included in the kinetics model in the future.

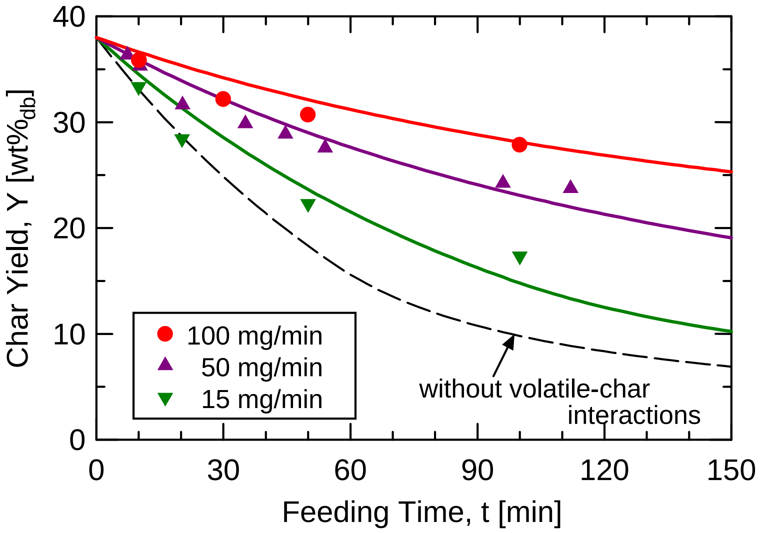

Fig. 5: Char yields form the gasification of raw coal with continuous feeding in 15 % steam at 800 ^{o}C as a function of feeding time.
(Dots: experimental results by Shu *et al.*, 2007. Lines: kinetics model.)

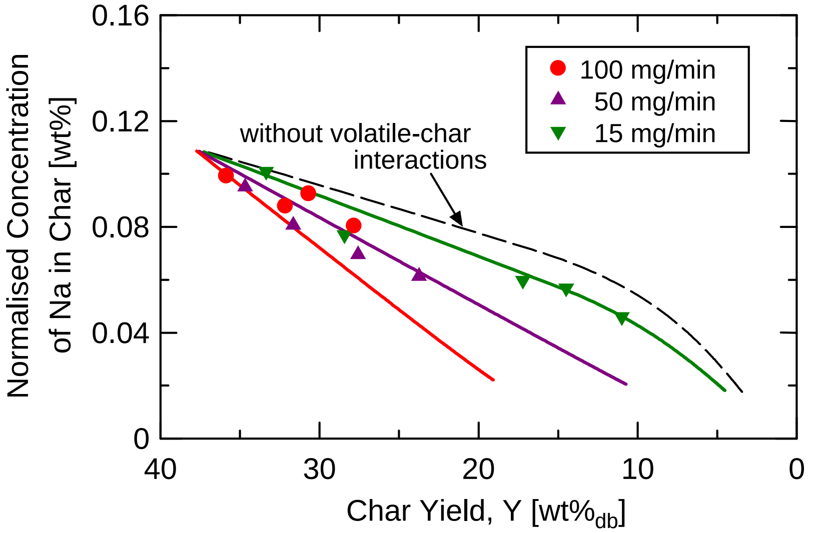

Fig. 6: Normalised Na concentrations ($Na\ Y / Y_i$) in char form the gasification of raw coal with continuous feeding in 15 % steam at 800 ^{o}C as a function of char yields.
(Dots: experimental results. Lines: kinetics model.)

CONCLUSION

The kinetics model of the catalytic gasification, the non-catalytic gasification and the volatile-char interactions were discussed to describe quantitatively the inhibition of volatiles about char gasification. The dissociative adsorption model of steam to H and OH was adopted for steam gasification. The adsorption of H radicals from volatiles and the exchange of Na for H radicals were proposed for the inhibition of volatiles. The inherent Na also evaporates unrelated with the volatile-char interactions. The L-H type reaction rate equations for steam gasification of brown coal and the volatilisation of catalyst were newly derived.

Raw coal char and H-form coal char of Victorian brown were gasified with steam at 800 °C using a novel fluidised-bed/fixed-bed reactor, and kinetic parameters for the catalytic gasification, the non-catalytic gasification and the evaporation of Na was determined. The gasification experiments of raw coal with continuous feeding, that is, with the volatile-char interactions, were simulated with the proposed kinetics model and the kinetics parameters for the volatile-char interactions were estimated. It can be said that the kinetics model is valid and the volatile-char interactions was described quantitatively in the proposed kinetics. This model would be useful to estimate the performance of the gasifier for Victorian brown coal.

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