Effect of pyrolysis conditions on the char gasification with mixtures of CO₂ and H₂O

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Abstract

Two kinds of char were prepared from a lignite by fast pyrolysis using a drop tube furnace and by slow pyrolysis using a fixed-bed furnace at the temperature of 1273 K. Scanning electron microscopy, X-ray diffractometry and the BET method were employed to characterize char properties. The chars were gasified with CO₂, H₂O and their mixtures in a thermogravimetric analyzer (TGA) system to investigate gasification kinetics and derive the rate expression. To validate the gasification rate equation derived from TGA, a fluidized-bed gasification experiment was also carried out. The results showed that both fast-char and slow-char were mainly composed of dense char. The shrinking core model was applicable to predict both gasification of fast-char and slow-char. It was found that the char gasification rate in the mixtures of CO₂ and H₂O was obviously lower than the sum of the two rates of the char independently reacting with CO₂ and H₂O but higher than the rate of each independent reaction, for both the fast-char gasification and slow-char gasification. Both of the results from the TGA and the fluidized-bed reactor showed that char-H₂O reaction was independent on char-CO₂ reaction, while char-CO₂ reaction was inhibited by char-H₂O reaction.

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Keywords: Char; Gasification; CO₂ and H₂O mixtures; Kinetics

1. Introduction

Optimization of the design and operation of coal gasification processes requires a good understanding of the reactivity and kinetics of char gasification with carbon dioxide and steam [1]. Numerous studies have been performed to use different kinds of kinetic models for predicting the reaction rate of char gasification with CO₂ or H₂O [1–3]. Among the models, homogeneous and shrinking core models were preferred to describe the variation of char conversion with the time if chemical reaction was the controlling step [2]. To describe the reaction mechanism of char gasification, Langmuir–Hinshelwood kinetics was widely used to express the pressure influences on adsorption and desorption reactions occurring during char gasification [1,4–9]. The mechanisms of the C–CO₂ reaction and the C–H₂O reaction have been considered to be essentially the same [1,10]. The adsorption–desorption elemental reactions have been proposed as:

\[ C(\cdot) + CO_2 \leftrightarrow_{k_1}^k CO + C(O) \] (1)

\[ C(O) \leftrightarrow_{k_2}^k CO + C(\cdot) \] (2)
\[
\text{C}() + \text{H}_2\text{O} \rightarrow k_1 \text{H}_2 + \text{C}(O) \quad (3)
\]
\[
\text{C}(O) \rightarrow k_4 \text{CO} + \text{C}() \quad (4)
\]

and the rate equations for C–CO\(_2\) and C–H\(_2\)O reactions have the following forms:

\[
r_{\text{CO}_2} = \frac{k_1 P_{\text{CO}_2}}{1 + k_{-1}/k_2 P_{\text{CO}} + k_1/k_2 P_{\text{CO}_2}} \quad (5)
\]
\[
r_{\text{H}_2\text{O}} = \frac{k_3 P_{\text{H}_2\text{O}}}{1 + k_{-3}/k_4 P_{\text{H}_2} + k_3/k_4 P_{\text{H}_2\text{O}}} \quad (6)
\]

Many previous studies have been performed to investigate the reactivities of coal chars gasified with a single gas agent (CO\(_2\) or H\(_2\)O) [5, 11–15]. However, CO\(_2\) and H\(_2\)O always coexist in the actual gasification process. Char gasification in the mixture of CO\(_2\) and H\(_2\)O has also been investigated [4–9, 16]. According to published results, two possible surface reaction mechanisms were proposed: (1) the char-H\(_2\)O and char-CO\(_2\) reactions occur at the same active sites [5, 7, 8, 16], and (2) the char-H\(_2\)O and char-CO\(_2\) reactions occur at the separate active sites [4, 6, 9]. It is known that only specific active surface sites could adsorb gas molecules in which the gasification occurred [17].

Up to now a few methods have been used to determine the active sites, such as gravimetric, TPD (temperature-programmed desorption) and OCI (the latter by performing oxygen chemisorption isotherms). However, the evaluation of chemisorbed oxygen and active sites depends on the method used and operating conditions [18]. A standardized method of active sites determination has not been established. Moreover, there is no way to determine active sites of char-CO\(_2\) and char-H\(_2\)O, respectively. But the char gasification rate is dependent on the active sites.

Based on the assumption that both reactions occur at the same active sites, a kinetic equation was derived to describe the competition of the char-H\(_2\)O and char-CO\(_2\) reactions:

\[
r_{\text{mix}} = r_{\text{CO}_2} + r_{\text{H}_2\text{O}} \left(1 - \frac{(k_1/k_3) P_{\text{CO}_2}}{1 + (k_1/k_3) P_{\text{CO}_2}}\right) \quad (8)
\]

However, Blik [9] found that the char-CO\(_2\) and char-H\(_2\)O reactions were independent on each other, and the total reaction rate was a sum of two independent reaction rates. A kinetic equation with the following form were proposed based on the assumption that the reactions of two gas agents occur at the separate active sites:

\[
r_{\text{mix}} = r_{\text{CO}_2} + r_{\text{H}_2\text{O}} = \frac{k_1 P_{\text{CO}_2}}{1 + k_{-1}/k_2 P_{\text{CO}} + k_1/k_2 P_{\text{CO}_2}} + \frac{k_3 P_{\text{H}_2\text{O}}}{1 + k_{-3}/k_4 P_{\text{H}_2} + k_3/k_4 P_{\text{H}_2\text{O}}} \quad (9)
\]

Everson [6], also using a TGA, investigated the kinetics of South African inertinite-rich coal chars prepared under N\(_2\) atmosphere at 973 K with heating rate of 20 K/min. They found that the overall gasification rate was best described with the assumption that the char-CO\(_2\) and char-H\(_2\)O reactions proceed on separate sites, by using the Eq. (9). Huang [4] investigated the kinetics of a lignite char prepared in a fluidized bed reactor at 1113 K for 20 min. Their results also confirmed that the char-H\(_2\)O and char-CO\(_2\) reactions take place on separate active sites rather than the same active sites.

The survey above indicates that, although there are many previous studies on the kinetics of char gasification in the mixture of CO\(_2\) and H\(_2\)O, there is no consensus on reaction mechanisms, i.e., whether the reactions of char-CO\(_2\) and char-H\(_2\)O occur on separate active sites or compete for the same active sites. This may be due to the properties of minerals in coal and pyrolysis conditions. Therefore, further investigation is needed to clarify the mechanism and kinetics. The purpose of this paper is to present new data on the effect of pyrolysis conditions on char gasification with the mixture of CO\(_2\) and H\(_2\)O. Two kinds of char were prepared by fast pyrolysis and slow pyrolysis and char gasification rates with CO\(_2\) and H\(_2\)O were investigated in an atmospheric TGA system and a fluidized-bed reactor, respectively.
2. Experimental

2.1. Char preparation

A Chinese lignite was used in this work with size of 74–106 μm. The chars from the lignite were prepared under laboratory conditions of fast and slow pyrolysis, denoted as fast-char and slow-char, respectively. The fast pyrolysis was carried out at atmosphere pressure under N₂ atmosphere in a drop tube furnace (DTF) at 1273 K, with a heating rate of coal particles at about 10,000 K/s. The detailed description of the DTF was presented in our previous paper [19]. The slow pyrolysis was carried out at atmosphere pressure under N₂ atmosphere in a horizontal tube furnace (HTF), in which coal particles were heated at 10 K/min to 1273 K under N₂ atmosphere, and held at that temperature for 3 h. The analyses of the lignite and the resulting chars can be found in Table 1.

2.2. Char characterization

Morphology of the chars was observed with scanning electron microscopy (SEM). The crystalline nature of the chars was analyzed by X-ray diffractometry (XRD). The spectra were acquired over the range of 2θ = 5–90⁰, with a step size of 0.0167⁰, using a Cu-Kα X-ray source. Surface areas of the chars were determined using the BET method based on nitrogen adsorption measurements at 87 K. The diameter of pores analyzed ranged from 2 to 300 nm.

2.3. Reaction rate measurements

The rates of the chars gasified in CO₂, in H₂O, and in the mixtures of CO₂ and H₂O at atmospheric pressure were measured by using a customer-designed atmospheric thermogravimetric analyzer (TGA). 3 NL/min of gas mixture (gasification agent balanced with N₂ at atmosphere pressure) and 300 mg of char sample were used for each experimental case. The flow rates of CO₂ and N₂ were controlled by mass flow meters. The flow rate of vapor was controlled by a peristaltic pump (injection of 0.8 mL/min of liquid water provides 1 NL/min of vapor). Table 2 summarizes the experimental cases for each char sample. Char gasification with a single gasification agent (CO₂ or H₂O) was investigated to obtain the kinetic parameters of each independent reaction, while char gasification with the mixtures of CO₂ and H₂O were investigated to explain the changes in law of gasification rates with the partial pressure of CO₂ at a fixed partial pressure of H₂O. The gasification rates were derived by describing the measured char conversion varying with time using the shrinking core model [2]. The kinetic parameters and elemental reaction rate expression of char gasification were derived by fitting the gasification rate with Langmuir–Hinshelwood kinetics.

2.4. Fluidized-bed gasification experiment

Gasification experiments in a fluidized-bed reactor were carried out to validate the rate expression of char gasification in mixtures of CO₂ and H₂O derived from TGA measurements. The fluidized-bed reactor is similar to the one-stage fluidized-bed reactor used in Xie’s study [20]. Firstly the reactor was heated to the holding temperature at 1273 K, in N₂ gas. Then approximately 1 g of coal sample entrained by N₂ carrier gas was fed into the reactor at 0.5 g/min, and held for 15 min to undergo fast pyrolysis. Finally, gasification agent (CO₂, H₂O or the mixture of CO₂ and H₂O, N₂ used as a balance gas) flowed into the furnace till the end of the gasification reactions. The total gas flow through the reactor was always kept at 1 NL/min. Syngas at the exit passed through concentrated sulfuric acid to absorb the moisture and the dried syngas was directed to a gas analyzer for analyzing its compositions. The concentrations of polar molecule gases, including CO₂, CO, CH₄, CₙHₙ, were detected by Non-Dispersive Infra-Red (NDIR) detectors with an accuracy of ±0.4%. The concentration of H₂ was detected by a thermal conductivity detector (TCD) and that of O₂ was detected by an electrochemical detector (ECD). The accuracies of H₂ and O₂ measurement were both ±0.6%. During the gasification, char conversion was determined based on the production rate of CO and H₂, derived from the composition of exhausted syngas at the exit of the reactor. The gasification rate was given as the half of the production rate of CO and H₂, based on the three main overall reactions:

\[ aC + CO₂ \leftrightarrow 2CO \]  

Table 1: Analyses of the coal and the resulting char samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate analysis (% , ad)</th>
<th>Ultimate analysis (% , daf)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>A</td>
</tr>
<tr>
<td>Coal</td>
<td>12.29</td>
<td>10.21</td>
</tr>
<tr>
<td>Fast-char</td>
<td>0.31</td>
<td>18.60</td>
</tr>
<tr>
<td>Slow-char</td>
<td>0.25</td>
<td>19.04</td>
</tr>
</tbody>
</table>

* By difference.
\[ bC + H_2O \rightarrow CO + H_2 \] (11)

\[ cCO + H_2O \rightarrow CO_2 + H_2 \] (12)

where \( a \), \( b \) and \( c \) are the reaction rate (mol/min) of each overall reaction. The production rate of CO and H₂ can be calculated:

\[ r_{CO} = 2a + b - c \] (13)

\[ r_{H_2} = b + c \] (14)

So the char gasification rate is expressed:

\[ r_C = a + b = (r_{CO} + r_{H_2})/2 \] (15)

3. Results and discussion

3.1. Char structure characterization

Figure 1 shows a comparison between the SEM images of the two chars, prepared in the drop tube furnace and horizontal tube furnace at the temperature of 1273 K, respectively. A lot of small fragments can be observed in the SEM image of fast-char, while no major morphological change can be observed in the SEM image of slow-char. According to the simplified char classification system of char particle structure [21–23], both fast-char and slow-char are mainly composed of dense char.

Two broad bands centered at approximately 25° and 44° 2θ can be found in the XRD spectra of the two chars, corresponding to the crystallinity extent of the chars [24–26]. There is no significant difference in the intensities of \( L_A \) (stacking height) and \( L_C \) (radial spread) between the fast- and slow-char. It indicates that the effect of heating rate during devolatilization on char crystalline structure is not significant when the holding temperature is the same. Consequently, the intrinsic reactivity properties of the char are not significantly affected by the pyrolysis conditions in this study.

The measured BET surface area, external surface area, and micropore area of the two chars are shown in Table 3. The BET surface area of the fast-char is slightly larger than that of the slow-char, while the external surface area is almost twice as large as that of the slow-char. The major effect of pyrolysis conditions on the surface area of the lignite char was that small fragments after fast pyrolysis resulted in the larger external surface area.

3.2. Effect of pyrolysis conditions on char-CO₂ and char-H₂O gasification

Figures 2 and 3 show the char conversion varying between 0.1 and 0.8 with time for the gasification at different concentrations of CO₂ and H₂O.
respectively. It can be seen that, for all the cases, the experimental data obtained were fitted by the shrinking core model. It is most likely that both fast-char and slow-char are mainly composed of dense char, and chemical reaction is the controlling step at the low temperature at the micro-size samples. Both char-\( \text{CO}_2 \) and char-\( \text{H}_2\text{O} \) gasification reactions should occur on the external surface of char particle with shrinkage.

Reaction rate constants of fast-char and slow-char gasification with \( \text{CO}_2 \) and \( \text{H}_2\text{O} \), which were calculated using the shrinking core model, are shown in Table 4. As can be seen, the reaction rate of char-\( \text{H}_2\text{O} \) is higher than that of char-\( \text{CO}_2 \) under the same condition. The reaction rate increases with the increase of the partial pressure (concentration) of \( \text{CO}_2 \) or \( \text{H}_2\text{O} \). The fast-char has obviously a faster gasification rate than the slow-char when the partial pressures of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) are the same. The gasification rates were found not proportional to the BET surface areas of the chars.

Because the concentrations of CO and \( \text{H}_2 \) were much lower than those of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) in the TGA reactor, the inhibition effect of CO and \( \text{H}_2 \) on the gasification can be ignored. As a result, the rate expressions have the following forms:

\[
\frac{1}{r_{\text{CO}_2}} = \frac{1}{(k_1 \cdot P_{\text{CO}_2})} + \frac{1}{k_2} \quad (16)
\]

\[
\frac{1}{r_{\text{H}_2\text{O}}} = \frac{1}{(k_3 \cdot P_{\text{H}_2\text{O}})} + \frac{1}{k_4} \quad (17)
\]

As can be seen in Fig. 4 the data show excellent linear relationships between \( 1/r \) and \( 1/P \). By applying Langmuir–Hinshelwood rate expression to describe the char gasification rate changing with the partial pressure of gasification agent.

### 3.3. Effect of pyrolysis conditions on char gasification with mixtures of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \)

Figure 5 shows the comparison of fast- and slow-chars conversion gasified in mixtures of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) with the change of \( \text{CO}_2 \) concentration. It can be seen that the rates of the two chars gasified in the mixtures of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) can also be well described with the shrinking core model. The obtained reaction rate constants for fast-char and slow-char gasification in all the experimental cases are summarized in Table 5. It is shown that, at a fixed partial pressure of \( \text{H}_2\text{O} \), char gasification rate increases with the increase of \( \text{CO}_2 \) partial pressure. It was found that, for all cases, the rate of the char gasified with the mixtures of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) is obviously lower than the sum of the two rates of the char independently reacting with \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) but higher than the rate of each independent reaction. It indicates that the char-\( \text{H}_2\text{O} \) and char-\( \text{CO}_2 \) reactions are not likely to occur at completely separate active sites, and these two reactions should partly occur at the same sites.

Figure 6 shows the variation of the \( r_{\text{mix}} \) (char gasification rate with mixture of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \)) with the \( r_{\text{CO}_2} \) (independent char gasification rate with \( \text{CO}_2 \) obtained in Table 4), indicating an excellent linear relationship between the two rates for all the gasification cases at a fixed partial pressure of \( \text{H}_2\text{O} \). Therefore, linear regression was
employed to derive the correlations and the results are also shown in Table 5. It is interesting that the regressed coefficient of $r_{CO_2}$ is about 0.65 and the coefficient of $r_{H_2O}$ (independent char gasification rate with $H_2O$ obtained in Table 4) is about 1 for both fast-char gasification and slow-char gasification. This may be because that $H_2O$ could be preferentially adsorbed on the surface of the char due to the lower active energy of $H_2O$ adsorption than $CO_2$ adsorption. Therefore, char-$H_2O$ reaction is independent on char-$CO_2$ reaction, and char-$CO_2$ reaction is inhibited by char-$H_2O$ reaction.

3.4. Char gasification in fluidized-bed reactor

During the experiment, it was observed that the concentration of CO or $H_2$ at the exit of the fluidized-bed reactor could reach more than 20% at the beginning of the gasification reaction. It means that the rate inhibition of char gasification by CO and $H_2$ cannot be ignored. Figure 7 shows the variations of the production rates of CO and $H_2$ in different atmosphere. Obviously, water gas shift reaction has occurred in these experimental cases. The production rate of $H_2$ was faster than that of CO in the atmosphere of 33.33% $H_2O$ because the concentration of $H_2O$ was much higher than that of $CO_2$, and water gas shift reaction occurred in the positive direction. The production rate of $H_2$ was slower than that of CO in the atmosphere of 33.33% $H_2O + 33.33% CO_2$ because the in-reactor concentration of $CO_2$ was higher than $H_2O$ due to the faster reaction rate of char-$H_2O$, and water gas shift reaction occurred in the negative direction.

The calculated char conversions varying with time based on the production rate of CO and $H_2$ are shown in Fig. 8. The experimental data were also fitted well with the shrinking core model. It was found that the rate of char gasification with the mixture of $CO_2$ and $H_2O$ is higher than the rate of each independent reaction. The rate was much faster than that of fast-char gasification in the TGA at the same atmosphere because of the better contact between char and gasification agents in the fluidized-bed reactor, increasing the collision frequency between the solid and gasses. Despite the difference in reactors, Fig. 8 indicates that the rate expression for char gasification in the mixture of $CO_2$ and $H_2O$ derived from the TGA experiments well represents char gasification process in the fluidized-bed reactor even if the rate inhibition of char gasification by CO and $H_2$ cannot be ignored. Although CO and $H_2$ inhibit the adsorption of $CO_2$ and $H_2O$ at the active sites, the competition between $CO_2$ and $H_2O$ at the same active sites may be mainly affected by the activation energy of adsorption. $H_2O$ are still adsorbed preferentially compared with $CO_2$, resulted in the similar reaction mechanism derived from the TGA experiments that char-$H_2O$ reaction is independent on char-$CO_2$ reaction, and char-$CO_2$ reaction is inhibited by char-$H_2O$ reaction.

### Table 4

<table>
<thead>
<tr>
<th>Char</th>
<th>Gasification agent</th>
<th>Reaction rate constants $r$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast-char</td>
<td>33.33% $CO_2$</td>
<td>3.084E-04</td>
</tr>
<tr>
<td></td>
<td>66.67% $CO_2$</td>
<td>4.841E-04</td>
</tr>
<tr>
<td></td>
<td>100% $CO_2$</td>
<td>6.027E-04</td>
</tr>
<tr>
<td></td>
<td>20% $H_2O$</td>
<td>4.683E-04</td>
</tr>
<tr>
<td></td>
<td>33.33% $H_2O$</td>
<td>6.214E-04</td>
</tr>
<tr>
<td></td>
<td>66.67% $H_2O$</td>
<td>9.723E-04</td>
</tr>
<tr>
<td>Slow-char</td>
<td>33.33% $CO_2$</td>
<td>1.564E-04</td>
</tr>
<tr>
<td></td>
<td>66.67% $CO_2$</td>
<td>2.077E-04</td>
</tr>
<tr>
<td></td>
<td>100% $CO_2$</td>
<td>2.316E-04</td>
</tr>
<tr>
<td></td>
<td>20% $H_2O$</td>
<td>2.314E-04</td>
</tr>
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<td></td>
<td>33.33% $H_2O$</td>
<td>3.282E-04</td>
</tr>
<tr>
<td></td>
<td>66.67% $H_2O$</td>
<td>5.617E-04</td>
</tr>
</tbody>
</table>

Fig. 4. Relation between $1/r$ and $1/P$ ($r$ is reaction rate constant of char-$CO_2$ or char-$H_2O$ gasification reaction, $P$ is partial pressure of $CO_2$ or $H_2O$).

Fig. 5. Comparison of fast- and slow-chars conversion gasified in mixtures of $CO_2$ and $H_2O$ with the change of $CO_2$ concentration.
4. Conclusions

Two kinds of char were prepared by fast pyrolysis using a drop tube furnace with the heating rate of coal particles at about 10,000 K/s, and by slow pyrolysis using a horizontal tube furnace, with the heating rate of coal particles at 10 K/min, respectively. Both fast-char and slow-char were mainly composed of dense char. The BET surface area of the fast-char is similar to that of the slow-char while the external surface area is almost twice as large as that of slow-char. Char gasification rates with CO$_2$ and H$_2$O were investigated in an atmospheric TGA system and a fluidized-bed reactor, respectively. It was found that char gasification rate in the mixtures of CO$_2$ and H$_2$O is obviously lower than the sum of the two rates of the char independently reacting with CO$_2$ and H$_2$O but higher than the rate of each independent reaction, for both the fast-char gasification and slow-char gasification. Both of the results from the TGA and the fluidized-bed reactor showed that char-H$_2$O reaction was independent on char-CO$_2$ reaction, while char-CO$_2$ reaction was inhibited by char-H$_2$O reaction.

Acknowledgements

This work was supported by the National High-tech R&D Program of China (2011AA050106), the National Major Scientific
Instruments Development Project of China (2011YQ120039) and the National Natural Science Foundation of China (51021065). The authors would also like to thank Prof. Changdong Sheng for helpful discussions, and the Analytical and Testing Center of Huazhong University of Science and Technology, for providing the facilities for the experimental measurements.

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