Clarification of gasification behavior of solid fuel char prepared under CO$_2$ atmosphere

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This study aimed to examine the effect of CO$_2$ atmosphere during pyrolysis of solid fuel on the gasification of its char by using thermobalance. As the sample, alkali-rich lignin was prepared. The lignin sample was pyrolyzed at heating rate of 1K/s to 700°C under CO$_2$ and Ar, and these chars (ligninchar-CO$_2$, ligninchar-Ar) are gasified in air at various temperatures, from 700°C to 1140°C. The difference of gasification behavior between ligninchar-CO$_2$ and ligninchar-Ar was varied according to rate limiting process, in fact, kinetic controlled region (Zone I) or internal and external diffusion controlled region (Zone II&III). At Zone I, carbonate formation by reacting alkali metal with CO$_2$ has a possibility to inhibit gasification. At Zone II&III, on other hand, the gasification rate of lignin char prepared in CO$_2$ was higher than that of lignin char made in Ar. This is considered to be caused by its porous morphology due to CO$_2$ in char preparation.

Keywords: O$_2$/CO$_2$; char; pyrolysis; gasification; carbonate; morphology;

1. Introduction

As one of the clean methods to utilize fossil fuels, O$_2$/CO$_2$ combustion, which is suitable for CCS, has been attracting more attention from all over the world. In O$_2$/CO$_2$ combustion, it’s been well known that the combustion undergoes in CO$_2$-rich condition, however the effect of enriched CO$_2$ on char gasification has not been well examined yet. Our previous study has revealed that carbonate was formed in alkali-rich lignin char when it was pyrolyzed in CO$_2$ atmosphere[1]. The carbonate is suggested to work as catalyst of gasification[2], but the detailed function has not been revealed yet. In addition to this, the physical property of char prepared in CO$_2$ has not been well investigated as well. In this study, by focusing on the characteristics of pyrolysis in CO$_2$ atmosphere, it was aimed to clarify the effect of those characteristics on the gasification behavior of solid fuel char with thermobalance.

2. Experiment

In order to investigate the effect of CO$_2$ on gasification of solid fuel char, the lignin powder which contains relatively high ash and alkali metals reactive with CO$_2$ was used. This lignin was also used in our previous study[1]. The proximate and ultimate analyses of this lignin are shown in Table 1 and 2 respectively. Figure 1 shows the schematic diagram of thermobalance. The pressure in the glass reactor was set as atmospheric pressure. In pyrolysis
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experiment, CO$_2$ or Ar was introduced into the reactor. In order to extract pyrolysis behavior, approximately 40mg sample was heated up at 1K/s to 700°C, at which the CO$_2$ gasification process doesn’t proceed notably. When the temperature reached 700°C, the atmospheric gas was switched to air and the temperature of the sample was kept constant at 700°C, 750°C, 800°C, 850°C, 900°C, 1100°C and 1140°C to investigate gasification behavior at each temperature. In addition to this experiment, chars of lignin were prepared by heating the raw sample at 1K/s to 800°C in CO$_2$ and Ar atmosphere, respectively. This temperature was set by referring to our previous study, at which the significant difference between the lignin chars prepared under CO$_2$ and Ar appeared. These chars were analyzed by FT-IR, N$_2$ BET method, and SEM images.

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<th>Table 1 Proximate analysis [wt.-%-dry]</th>
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<th>Table 2 Ultimate analysis [wt.-%-dry]</th>
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3. Result and discussion

Figure 2 shows the pyrolysis and gasification profile in the case when char prepared in CO$_2$ was gasified at 800°C in air, where $W_i$ corresponds to the initial weight in gasification region. In order to examine the gasification behavior, Arrhenius plot was drawn as shown in Figure 3. Zone I, Zone II and Zone III indicate kinetic controlled, internal diffusion controlled and external diffusion controlled reaction, respectively. $X$ represents char reaction ratio, defined as $X=W/W_i$, and ligninchar-CO$_2$ and ligninchar-Ar represent the lignin char prepared under CO$_2$ and Ar respectively. It was found that the lowest temperature at which gasification of ligninchar-CO$_2$ advances is 800°C, while that of ligninchar-Ar is 650°C. In order to clarify this, FT-IR analysis was conducted for ligninchar-CO$_2$ and ligninchar-Ar, and the result is shown in Figure 4. The peaks of carbonate appeared at the wavelength of 1440 cm$^{-1}$ and 880 cm$^{-1}$ can only be seen in ligninchar-CO$_2$, and this result corresponds to that of the previous study$^{[1]}$. From these results, it was suggested that the formation of carbonate by the reaction between CO$_2$ and alkali metal has possibility to inhibit gasification at lower temperature. At higher temperature above 900°C, on the other hand, it can be seen that ligninchar-CO$_2$ has much higher gasification rate than ligninchar-Ar. In order to clarify this phenomenon, SEM images of ligninchar-CO$_2$ and ligninchar-Ar were taken as shown in Figure 5(a)(b). From the
can be clearly seen that ligninchar-CO₂ has more porous surface than that of ligninchar-Ar. Also from N₂ BET analysis, it is found that the specific surface area of ligninchar-CO₂ is about 500 times larger than that of ligninchar-Ar, as shown in Table 3. These results show that ligninchar-CO₂ is abundant with both micro- and macro pores than ligninchar-Ar. This porous surface helps the gasifying agents to diffuse so that reaction rate increases especially at higher temperature (zone II & III), above 900°C.

4. Conclusion

Lignin chars were prepared in CO₂ and Ar environments (defined as ligninchar-CO₂, ligninchar-Ar) in order to examine the role of CO₂ during pyrolysis on its gasification behavior (700-1140 ℃). The lowest temperature of ligninchar-CO₂ at which gasification advances was higher than that of ligninchar-Ar. It was suggested that the formation of carbonate by reacting alkali metal with CO₂ inhibited gasification at lower temperature (Zone I). At high temperature (Zone II&III), on the other hand, ligninchar-CO₂ showed higher gasification rate than ligninchar-Ar. This was considered as the result of the high porosity and larger specific surface area of ligninchar-CO₂ than ligninchar-Ar. It can be concluded that the difference of gasification behavior between ligninchar-CO₂ and ligninchar-Ar was varied according to rate limiting process.

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Reference