Effect of Preoxidation on Reactivity of Chars in Steam

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The investigation of the rate of reaction of char-steam is very important in the development of a coal gasification process and also in the production of activated cokes from coal. The objective of this work is to measure the rate of reaction of preoxidized coal char in steam and to investigate the effect of changes in the preoxidation conditions, especially in the preoxidation temperature and the degree of burn-off, on the reactivity of the char in steam.

Apparatus and Procedure

The coal used here was Taiheiyo coal, a non-caking bituminous coal from Hokkaido, Japan. The raw coal was ground and 0.35-0.42mm fractions were used. They were carbonized in N_2 at 1000°C for 2h.

The Cahn R.G. balance was used for reactivity measurements. About 100 mg of char was placed on a quartz pan (20mm i.d.), which was suspended from the balance at the center ot the furnace. The sample was then heated to the desired preoxidation temperature (400-550°C) in N_2 and the N_2 was replaced by a N_2-O_2 mixture with an O_2 concentration of 20%. The progress of the preoxidation process was followed until the desired weight decrease occurred. After that, the N_2-O_2 mixture was replaced by N_2 and the sample was heated to the desired reaction temperatures (800-900°C). Then a N_2-H_2O mixture containing water vapor at a partial pressure of 13.2 KPa was admitted to the apparatus. This water-vapor pressure was generated by bubbling N_2 through deairated distilled water of a temperature of 60°C. The weight of the sample was recorded continuously as a function of time.

The amount of CO and CO_2 given off by the preoxidized chars was measured with the induction heating pyrolyzer. The product gases were analyzed with a gas chromatograph which was coupled to the pyrolyzer.

Results and Discussion

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The gasification rates were determined for each of the preoxidized chars using the following rate expression:

$$\frac{dXc}{dt} = k\ (1 - Xc) \qquad 1)$$

where Xc represents the fractional conversion of carbon (daf) and k is the rate constant.

In Figure 1, the (dXc/dt) for typical samples are plotted against (1-Xc). As can be seen in Figure 1, the curve for the

char that was not preoxidized rises slowly to a plateau and then falls away gradually. On the other hand, the curves for the preoxidized char show a continuous gradual falling away, with no initial slow rise and no plateau.

Effect of carbon burn-off during preoxidation on char reactivity in steam

$(dXc/dt)i$ at 850°C for chars preoxidized to different burn-off levels at various temperatures are also calculated with the above procedure and plotted against the burn-off during preoxidation as a function of the preoxidation temperature, as shown in Figure 2. $(dXc/dt)i$ is the rate of reaction observed at zero conversion.

As seen in Figure 2, the $(dXc/dt)i$ for the preoxidized chars increase with burn-off during preoxidation. The extent of this is rather large for the chars preoxidized at relatively lower temperatures (400-430°C). On the other hand, as the oxidation temperature rises, the degree of increase in the rates is smaller.

Effect of carbon burn-off during preoxidation on amount of CO and CO_2 given off

In Figure 3, the total amounts of CO and CO_2 given off, when heated at 920°C, by samples that were preoxidized to varying degrees of burn-off at temperatures between 400 and 550°C are plotted against the burn-off that occurred during the preoxidation. As shown in the Figure 3, the total amounts of CO and CO_2 given off by the chars preoxidized at lower temperatures increased markedly with increases in burn-off, but the total amounts given off by the chars preoxidized at higher temperatures increased very little with increases in burn-off.

It is interesting to note that the relationship between the initial rate of reaction of char-steam and the burn-off that occurs during preoxidation, shown in Figure 2, is similar to the relationship between the total amounts of CO and CO_2 given off by samples at 920°C and the burn-off that occurs during preoxidation shown in Figure 3. In both cases, an increase along one axis yields an increase along the other.

From earlier works (1) (2), it is well known that during the reaction of pure carbon with oxygen a surface oxide is formed and that the thermal decomposition of the oxide yields a mixture of CO and CO_2. Phillips et al. (3) found that the amount of a surface oxide formed on a sample of particular burn-off decreased with increasing reaction temperature. From the experimental results shown in Figure 3, we conclude that the amount of a surface oxide increases with burn-off during preoxidation and the amount on a sample of particular burn-off decreases with increasing preoxidation temperature. Phillips et al. (3) suggested that decomposition of the surface oxide leaves highly reactive sites. Considering these works, our results suggest that the increase in the initial rate of reaction of the preoxidized char in steam is due to an increase in the number of highly reactive sites left by the decomposition of the surface oxide.

Conclusions

The reactivity of preoxidized char in steam has been investigated. It has been found that preoxidation of char markedly enhances the initial rate of reaction of steam-char and that the degree of the increase parallels the increase in burn-off during

preoxidation. However, the preoxidation temperature strongly affects the degree to which the reaction rate can be increased. It has also been found that there is a very intimate relationship between the degree to which the reaction rate can be increased and the amount of CO and CO_2 given off by preoxidized char.

References

1. Phillips, R., Vastola, F.J. and Walker, P.L., Jr., Carbon, 8, 197 (1970)

2. Laine, N.R., Vastola, F.J. and Walker, P.L., Jr., Carbon, 67, 2030 (1963)

3. Phillips, R., Vastola, F.J. and Walker, P.L., Jr., Carbon, 7, 479 (1969)

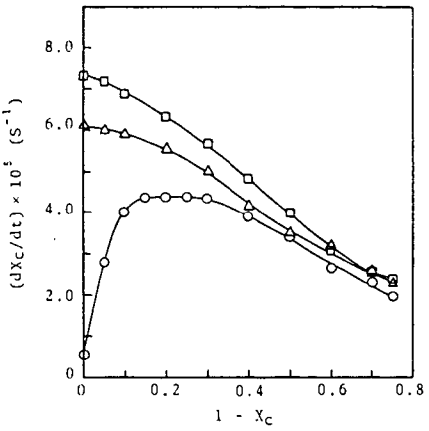

Fig.1 Variation of reaction rates in steam at 13.2 kPa and 850°C with conversion of chars. Burn-off during preoxidation at 430°C (%, daf): ○ none; △ 7.5; □ 11.1.

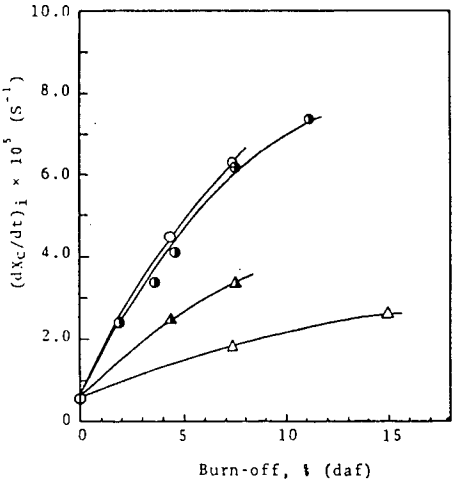

Fig.2 Effect of carbon burn off during preoxidation on char reactivity in steam at 850°C. Preoxidation temperature: ○ , 400°C; ◑ , 430°C; ▲ , 480°C; △ , 550°C.

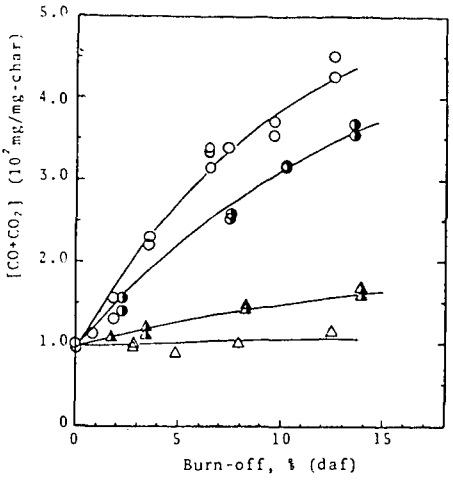

Fig.3 Effect of carbon burn-off during preoxidation on amount of CO and CO_2 given off at 920°C. Preoxidation temperature: ○, 400°C; ◑, 430°C; ▲, 480°C; △, 550°C.