FLASH PYROLYSIS OF COAL IN THE ATMOSPHERE CONTAINING SOLVENT VAPORS

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INTRODUCTION

We have recently presented a new coal pyrolysis method[1], in which coal particles swollen by hydrogen donor solvents at around 250 °C were pyrolyzed in a Curie-point pyrolyzer. Both the conversion and the tar yield drastically increased by this pyrolysis method. The increases were brought about by the pore enlargement caused by swelling and the effective hydrogen transfer from/via the solvent to the fragments of the primary coal decomposition. This method is, however, a little complicated to be scaled up to a commercial process.

In this paper, we propose a much simpler flash pyrolysis method, in which coal particles are pyrolyzed continuously in the gas stream containing hydrogen donor solvents. It is shown that this pyrolysis method successfully increases the tar yield, and presents a possibility of an in situ control of the product distribution.

EXPERIMENTAL

The coal used was Morwell brown coal. It was ground and screened to -125 +74 μm. The properties of the coal are given in Table 1. Figure 1 shows the diagram of the entrained bed type of pyrolyzer used in this study. Reactor is a coil of stainless steel tube of 1/4 inch in outer diameter. Three different length of reactors, 0.89, 2.65 and 4.64 m, were used to change the residence time of the coal. The dried coal was fed to the reactor by a teblefeeder with nitrogen gas at the feed rate of 4 to 20 g/h. The flow rate of nitrogen was 4.0 l/min (STP). Vapor of tetralin and decalin was added to the flow of coal-nitrogen mixture at the top of reactor as shown in Figure 1. The feeding ratio of the solvent to coal was 0.12 to 0.15 by weight. Experiments without the solvent were also performed for comparison. The coal was pyrolyzed while passing the reactor, and gas, tar and char produced were led to cyclone connected to the exit of the reactor to separate the gas and tar from char. The tar and the gas were led to the condensers, where the tar was trapped. A part of the gas was collected in a gas bag.

The char and the tar yields were calculated from the changes in weight of the char collector and the tar trap, respectively. The composition of the gas was analyzed by a gaschromatograph (Shimazu GC 9A) equipped with both TCD and FID. The water in the tar was analyzed using the Karl Fischer titration (Kyoto Electronics Co., Ltd.). The tar component was also analyzed by a gaschromatograph with OV-101 column and FID. The material balance of this experiment was obtained within 95 to 105 %. To estimate the effect of solvents on the pyrolysis of coal properly, the pyrolysis yields in the solvent vapors must be represented excluding the yields coming from solvents. So, the pyrolysis of each solvent was performed under same experimental conditions without feeding coal, and each yield in the solvent vapors, Y_i, was calculated by following equation:

$$Y_i = (\text{Yield in the solvent vapor}) - w(\text{Yield from solvent}) \qquad (1)$$

where w is the feeding ratio of solvent vapor to coal.

RESULTS AND DISCUSSION

Pyrolysis in an Inert Atmosphere

To examine how we can control the product distribution of the pyrolysis of in inert atmosphere, the effects of residence time of coal and the pyrolysis temperature were examined.

Effect of Residence Time

Figure 2 shows the change of conversion, tar and gas yields with the increase of residence time (t_R) at the pyrolysis temperature of 650 °C. The conversion increased with the increase of residence time, and reached a constant value over t_R=2 s. The gas yield increased monotonously with the residence time. The tar yield reached a maximum at t_R=2 s, then decreased with increasing t_R. It indicates that the decomposition reaction of tar vapor to gas becomes significant with the increase of residence time. Figure 3 shows the similar results at the pyrolysis temperature of 800 °C. The trends of the conversion and the char yield were similar as those at 650 °C, although the final conversion level was larger than that at 650 °C. The residence time which maximizes the tar yield shifted to smaller residence time. This means that the cracking reaction rate of tar vapor at 800 °C is much faster than that at 650 °C. Figures 2 and 3 show that the primary decomposition of coal is almost completed in t_R=2 s.

Effect of temperature

Figure 4 shows the change of the product distribution with the pyrolysis temperature (T_p). The char yield decreased with temperature. On the contrary, the gas yield increased with temperature. The tar yield reached a maximum, 13.1 wt% at 650 °C. These trends coincided with those of several researches[2-5] using the continuous equipments. The broken lines show the yields of the flash pyrolysis performed using a Curie point pyrolyzer[6] (CPP), in which the gas phase reaction is suppressed because only the coal is heated and the products are cooled immediately by the He flow of room temperature in CPP. The char yields of both experiments were nearly equal, indicating that the coal conversion is determined solely by the pyrolysis temperature. The gas yield of the pyrolysis in the entrained bed was larger than that of the pyrolysis in the CPP. On the other hand, the tar yield in the entrained bed was smaller than in the CPP. This indicates that the decomposition of tar is occurring in the entrained bed pyrolyzer, in which the gas stream is also heated. Figure 5 shows the product distribution of gas component with the temperature. The yield of C_4-C_6 gas reached a maximum at 700 °C, which was 50 °C higher than the temperature for the maximum tar yield. On the other hand, the yields of H_2 and C_1-C_3 gases increased drastically with the temperature. These results also show that the gas phase reaction which decomposes tar becomes significant with the increase of temperature, and the tar yield decreased. Thus, the maximum tar yield obtained in the entrained bed pyrolyzer was 13.1 wt.% daf at T_p=650 °C and t_R=2 s. This value is 17 wt.% daf lower than that obtained in the CPP. The maximum tar yield attained in the entrained bed pyrolyzer will not exceed that obtained in the CPP.

Flash pyrolysis in the Vapor of solvents

Above discussion indicates that there is a limitation to increase the tar yield by controlling the temperature and the residence time as far as the pyrolysis is performed in an inert atmosphere. Then, we intended to increase the tar yield by pyrolyzing the coal in the atmosphere containing the solvent vapor. The residence time of coal was fixed as 2 s, because the primary decomposition of coal was completed in t_R=2 s as stated earlier.

Effect of the Kind of Solvents

Figure 6 shows the changes of tar yields of the pyrolysis in N_2, in tetralin vapor and in decalin vapor with increasing T_p. The yields were calculated excluding the yield from solvent vapor by Eq. 1. The tar yield in tetralin vapor reached up to 25.2 wt.% at T_p=750 °C. This is twice larger than that in an inert atmosphere. Thus, the proposed pyrolysis method is found to be successful at least to increase the tar yield drastically. The effect of decalin vapor was only 2 to 3 wt.% larger than that in N_2 atmosphere at T_p=700 to 800 °C.

The Mechanism of Pyrolysis in Tetralin Vapor

Since the pyrolysis of coal in tetralin vapor was found to be effective to increase the tar yield, the mechanism of the pyrolysis was examined by comparing the yields obtained from the pyrolysis of tetralin, the pyrolysis of coal in N_2 atmosphere and the pyrolysis in tetralin vapor. The yields were all represented based on the unit weight of daf coal.

Figures 7 to 10 show the yields of char, tar, total gas, and hydrocarbon gasses, respectively. The broken line in each figure is the sum of the yield from the pyrolysis of coal in N_2 and that from the pyrolysis of tetralin. The yield in tetralin vapor coincides with the broken line if tetralin has no effect on the pyrolysis of coal.

The char yield in tetralin vapor almost coincided with the broken line as shown in Fig. 7, although it seemed to deviate at T_p= 800 °C. This suggests that tetralin is not effective to increase the conversion. In other word, tetralin does not affect the primary decomposition of coal. The tar yield in tetralin vapor exceeded broken line at T_p=700 to 800 °C, and it reached more than twice at T_p=750 °C as shown in Fig. 8. On the contrary, the yields of total gas and hydrocarbon gases in Figs. 9 and 10 lay far below the broken lines to compensate the increase of tar yield.

Above discussion shows that tetralin vapor contributed to the rearrangement of the product distribution of the primary decomposition of coal. The reactive radicals produced by the pyrolysis of tetralin reached mainly with light hydrocarbon gases to convert them into liquid products. The analysis of tar components, now being performed, will help us to clarify the mechanism.

CONCLUSION

A new and simple method was developed for increasing the tar yield of coal, in which coal particles were pyrolyzed in the gas stream containing the solvent vapor. The feeding rate of solvent is only around 10 wt.% of that of coal by weight. The tar yield was successfully increased up to 25 wt.% daf in the atmosphere containing the tetralin vapor from 13 wt.% daf in an inert atmosphere. This method is expected to be easily realized in a commercial scale because of its effectiveness and simplicity.

ACKNOWLEDGMENT

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Table 1 Properties of Coal

Proximate Analysis (wt%)			Ultimate Analysis (wt% daf)				
FC	VM	ASH	C	H	N	S	O
48.2	50.3	1.5	67.1	4.9	0.6	0.3	27.1

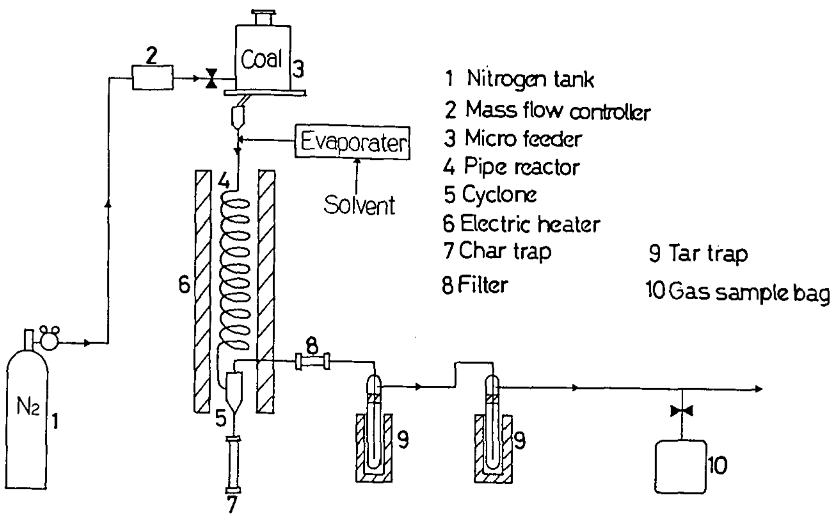


Fig.1 Schematic flow of continuous entrained bed type equiepment for the pyrolysis of the coal

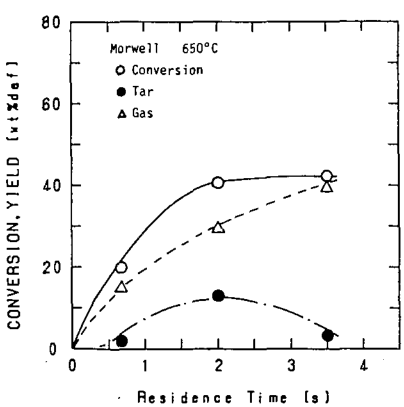


Fig.2 Effect of the residence time of coal on the product distribution (T_p=650°C)

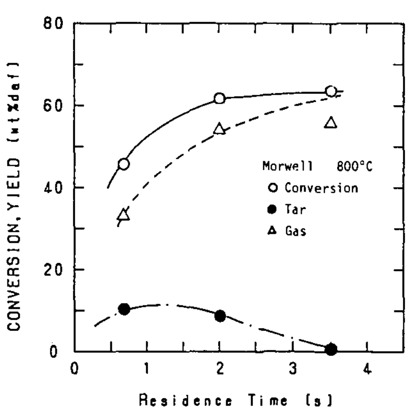


Fig.3 Effect of the residence time of coal on the product distribution (T_p=800°C)

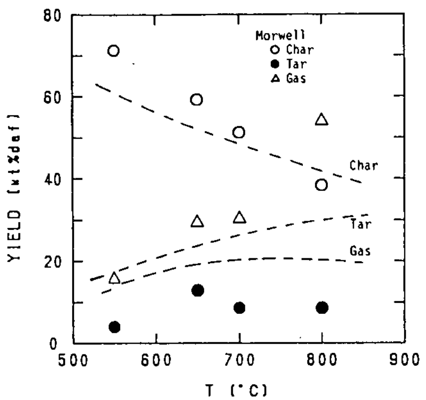


Fig.4 Effect of the pyrolysis temperature on the product distribution (t_R=2 s) (broken lines: results obtained from the pyrolysis using a Curie-point pyrolyzer)

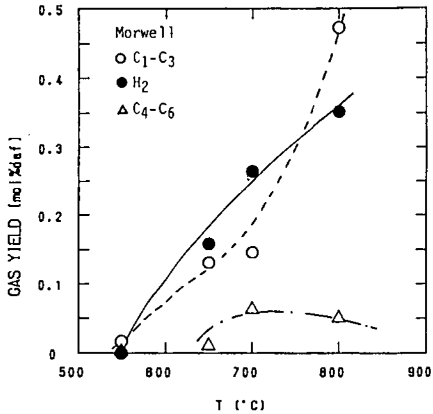


Fig.5 Effect of the pyrolysis temperature on the gas yield

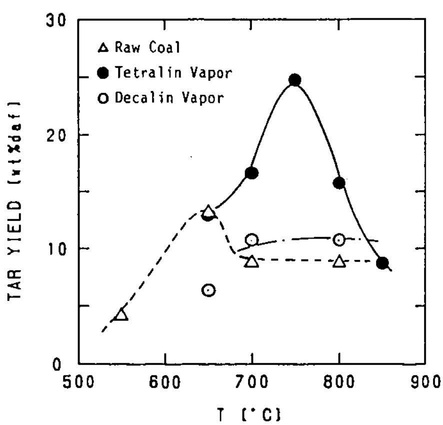
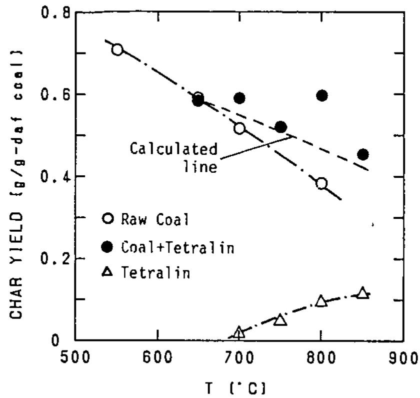


Fig.6 Effect of the atmosphere containing solvent vapor on tar yield during the pyrolysis



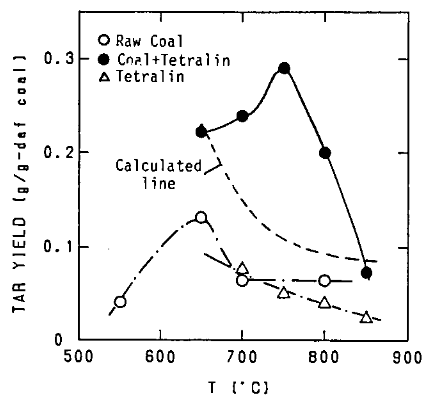
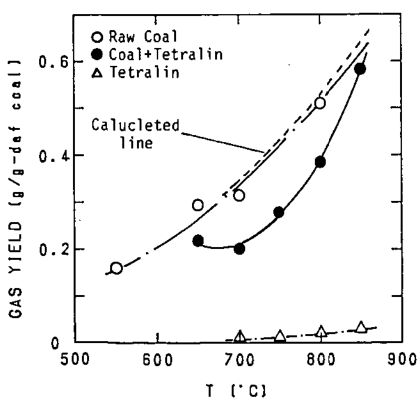


Fig.7 Effect of the atmosphere containing tetralin vapor on char yield during the pyrolysis

Fig.8 Effect of the atmosphere containing tetralin vapor on tar yield during the pyrolysis



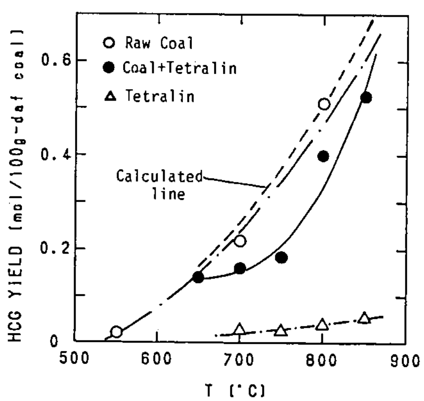


Fig.9 Effect of the atmosphere containing tetralin vapor on gas yield during the pyrolysis

Fig.10 Effect of the atmosphere containing tetralin vapor on HCG yield during the pyrolysis