

A NOVEL METHOD FOR FLASH PYROLYSIS OF COAL

Kouchi Miura, Kazuhiro Mae, Tomonori Yoshimura
and Kenji Hashimoto*

Research Laboratory of Carbonaceous Resources
Conversion Technology,

*Department of Chemical Engineering, Kyoto University
Kyoto 606, Japan

Introduction

Flash pyrolysis of coal is a promising process for producing chemicals such as benzene, toluene and xylene (BTX). But, the yield of liquid products including BTX (tar) is limited because of low hydrogen to carbon ratio in coal. It is necessary to supply hydrogen to coal efficiently for increasing the tar yield. Hydropyrolysis is one of the means to supply hydrogen to coal. This is, however, realized under only severe reaction conditions: high hydrogen pressure, high temperature and long residence time.

Recently, several attempts have been made to supply atomic hydrogen or radicals from super critical steam^{1,2)} or solvents³⁾ to coal. This paper presents a new efficient method for increasing both the conversion and the tar yield in which the coal swollen by solvents was pyrolyzed in a flash mode in an inert and a hydrogen atmospheres. We will show drastic increase of coal conversion and tar yield are brought about by a physical effect and effective hydrogen transfer from/via tetralin.

Experimental

Sample Preparation

A Japanese coal, Taiheiyo coal, was used as a raw coal. Its properties are given in Table 1. The coal was ground and the particles less than 74 μm were used. The coal was dried in vacuo at 110 °C for 1 h before use.

The coal particles were mixed with tetralin by the ratio of 10 to 6 by weight, then heated to the temperatures between 25 and 350 °C under the 1 MPa of nitrogen. By this treatment coal particles were swollen, and tetralin was retained in the coal matrix. This sample is abbreviated to tetralin treated coal (TTC).

The tetralin treated coal was degassed at 70 °C in vacuo for 1 h to completely remove the retained tetralin (vacuum dried coal; VDC). When the swelling is irreversible, swollen but tetralin free coal is obtained. This sample was pyrolyzed to examine the physical effect of swelling on the pyrolysis. Several partially degassed samples were also prepared to examine the effect of the amount of tetralin retained on the pyrolysis.

Char produced under a high temperature pyrolysis of Taiheiyo coal, this is not pyrolyzed further, was also treated by tetralin in the same manner as was employed to prepare TTC. This sample was pyrolyzed

to obtain the yield of each component from tetralin. This result was utilized to estimate the contribution of pyrolysis of tetralin on the product yields from TTC. Thus, four kind of samples were prepared from the Taiheiyo coal.

Flash pyrolysis of samples

Samples prepared above were pyrolyzed in an inert and high-pressure hydrogen atmospheres. Pyrolysis in the inert gas of atmospheric pressure was performed using a Curie-point pyrolyzer (Japan Analytical Ind., JHP-2S). About 2 mg of sample were wrapped in a ferromagnetic foil, and heated up to a temperature between 650 to 920 °C at the rate of 3000 °C/s by induction heating coil to be pyrolyzed rapidly. The products were immediately cooled down by the inert gas of high flow rate. Then, the tar was trapped completely by the silica wool placed just below the foil. The inorganic gases and hydrocarbon gases were led to gas chromatograph and analyzed. On the other hand, the pyrolysis under high pressure was performed using a specially designed Curie-point pyrolyzer. This reactor consisted of high pressure vessel and a quartz reactor as shown in Fig. 1. This was designed to keep the inner and outer pressure of the reactor same. About 5 mg of sample were pyrolyzed at 764 °C under 0.1 to 7.5 MPa of hydrogen. Produced tar was again trapped by the silica wool, but produced gases were collected in a gas holder once. Then a part of gas was introduced to a gas chromatograph to be analyzed. The column used was Porapak Q. The yields of char and tar were measured from the weight changes of the foil and the reactor. The same experiment was performed several times to check the reproducibility of experiment.

Analysis of structure change of coal by swelling

The swelling ratio, elemental composition, the pore volume and the surface area were measured to examine the change of coal structure by swelling. The swelling ratio of tetralin-treated coal was measured by volumetric method^{6,7)}. The pore volume and surface area of raw coal and TTC were calculated from the adsorption isotherm of CO₂ measured at 0 °C. Furthermore, to estimate the interaction between coal surface and tetralin, the thermal desorption curve of tetralin from the TTC was measured under the heating rate of 5 °C/min using a thermobalance (Shimazu Co. Ltd., TGA 50).

RESULTS AND DISCUSSION

Effect of pretreatment temperature on product distribution

Figure 2 shows the change of swelling ratio of TTC and VDC against swelling temperature. Taiheiyo coal began to swell by tetralin at 70 °C, and the swelling ratio reached 1.34 at above 170 °C. Taiheiyo coal swollen at below 100 °C shrank reversibly to its original state by vacuum drying, but the coal swollen at above 100 °C did not shrink completely, and the swelling at 250 °C was almost irreversible. At 250 °C, the coal structure was expected to change as mentioned in earlier works^{6,7)}. The micropore volume and the internal surface area of VDC of coal swollen at 250 °C were larger than those of raw coal

as shown in Table 2.

Figure 3 shows the curves of the thermal desorption of tetralin from TTC. Since tetralin desorbs at higher temperatures from the coal treated above 100 °C as compared with that treated at 25 °C, the interaction between coal and tetralin is stronger for the coals treated above 100 °C. Coals treated by tetralin at several temperatures were pyrolyzed at 764 °C under 0.1 MPa of He. The product yield of each component of treated coal, Y_i , was represented based on daf coal excluding the yield from the pyrolysis of tetralin. The yield, Y_i , is defined by

$$Y_i = \{(\text{Yield from TTC}) - w(\text{Yield from solvent})\} / (1-w) \quad (1)$$

where w is the weight fraction of tetralin in TTC.

Figure 4 shows the tar yield against the swelling temperature. The tar yield was same as that of raw coal at the swelling temperature of 25 °C, but it reached about 1.5 times larger than that of raw coal at 100 to 250 °C. This result and Figure 3 show only the tetralin retained strongly by coal is effective to increase the tar yield.

The tar yield decreased at the swelling temperature of 350 °C, because the coal was almost decomposed during the treatment at this temperature. From above results, the swelling temperature was decided to be 250 °C.

Effect of the amount of tetralin in the coal

The effect of the amount of tetralin retained in the coal on the tar yield was examined at the pyrolysis temperature of 764 °C. The amount of tetralin was varied by changing the vacuum drying time of TTC prepared at 250 °C. Figure 5 shows the tar yield during the flash pyrolysis against the amount of tetralin retained in the coal. The sample of zero tetralin content was completely dried one (VDC). Even a trace of tetralin was not detected in this sample, judging from the mass balance during the vacuum drying and the FTIR measurements. Since the VDC is still swollen by 30 %, this coal has much larger pore volume than the raw coal. The tar yield of the VDC was about 4 wt.% larger than that of raw coal. This means that the pore enlargement by swelling increases the tar yield. This is just a physical effect. On the other hand, the gradual increase of the tar yield with the increase of tetralin content is the chemical effect produced by tetralin. These are discussed in more detail in relation to the yields of the other products in the next section. The tar yield of the coal treated at 25 °C is almost same as that of raw coal as stated earlier.

Flash Pyrolysis in an Inert Atmosphere

Figure 6 shows the char yields of TTC, VDC and raw coal against the pyrolysis temperature. The char yield of TTC is lower than that of raw coal at all the temperature by 4 to 10 wt.%. The char yield of VDC is also 4wt.% lower than that of raw coal. These results show the swelling of coal by tetralin is effective to increase the conversion

of coal into gas and liquid. This effect was brought about from the pore enlargement and the tetralin retained strongly in the coal as stated earlier.

Figure 7 shows the tar yield. The tar yield of TTC increased drastically up to 30 wt.% daf at the pyrolysis temperature of 764 °C, which was 1.5 times larger than that of raw coal. This indicates the effectiveness of the proposed method for increasing the liquid product. The tar yield of TTC at 920 °C, however, was almost equal to that of raw coal. The trend of tar yield of TTC with the temperature is similar to that of the H₂ yield from the pyrolysis of tetralin. On the other hand, the tar yield of vacuum dried coal increased by 4 wt.% irrespective of pyrolysis temperature, as compared with that of raw coal. Figures 8 and 9 show the yields of other products. The inorganic gas (IOG) yield was nearly equal between three samples. The hydrocarbon gas (HCG) yield and the total yields of benzene, toluene and xylene (BTX) were nearly equal at the temperatures lower than 764 °C. These yields of TTC at 920 °C, however, were larger than those of the other two samples. The H₂ yield of TTC was smaller than that of raw coal at temperatures lower than 800 °C, but exceeded that of raw coal at 920 °C. The H₂ yield of VDC was almost same as that of raw coal at all temperatures.

The physical effect and the effect of hydrogen donability of tetralin are summarized from above results as follows: The increase of micropore caused by tetralin pretreatment facilitated the escape of the tar vapor, which would be stabilized as char, from coal particles. Then the tar yield of VDC was increased at all the temperatures. On the other hand, the effect of hydrogen donability from the tetralin to coal depends on the pyrolysis temperature.

The conversion of coal to volatile matter is expected to increase when hydrogen atom is supplied timely to the reactive fragments of coal which would be stabilized as char without hydrogen supply. At both 670 and 764 °C, the char yield of TTC was smaller than that of VDC. So, hydrogen atom was effectively transferred from tetralin to the coal fragments at these temperatures. This is substantiated by the small H₂ yield and large tar yield of TTC at these temperatures. This indicates that the rates of the dehydrogenation of tetralin and the formation of coal fragments matched well at these temperatures. Then the mechanism of the pyrolysis of TTC is schematically represented as given in Fig. 10.

On the other hand, the char yield of TTC was almost same as that of VDC at 920 °C. So, tetralin did not contribute to increase the conversion of coal at this temperature, but contributed to increase the yields of light hydrocarbons as shown in Fig. 8. This was supposed to be brought about by the radicals produced by the decomposition reaction of tetralin, which was prevailing over the hydrogenation reaction at this temperature. The radicals were very reactive, and decomposed primary pyrolysis products of coal, though the reaction mechanism is not clear now.

Pyrolysis in hydrogen atmospheres

It has been reported that the yield of volatile matter during flash pyrolysis decreases with increasing hydrogen pressure⁸⁻¹⁰. This is said to be because the escape of tar vapor from coal particles is suppressed under pressurized conditions. The flash hydrolypyrolysis of TTC, however, is, as it were, liquefaction within the pore space. Therefore, the increase of tar yield is expected under pressurized hydrogen.

Figure 11 shows the hydrogen pressure dependency of the char yields of TTC, VDC and raw coal at the pyrolysis temperature of 764 °C. The char yield of VDC was smaller than that of raw coal by 2 to 4 wt.%. This was considered to be brought about by the pore enlargement. The char yield of TTC was smaller than that of VDC and tended to decrease with increasing hydrogen pressure. This means that the tetralin treatment is more effective for the pyrolysis in high pressure hydrogen. This is because molecular hydrogen is expected to be transferred to the reactive coal fragments via tetralin as is transferred in coal liquefaction. The char yields of both VDC and raw coal did not decrease with increasing hydrogen pressure contrary to previous works⁸⁻¹⁰. We examined the effect of hydrogen flow rate on the char yield, and found that the char yield increases significantly with increasing pressure under low hydrogen flow rate as reported previously. The increase of char yield was suppressed with increasing hydrogen flow rate. So, our experiments were all performed under high hydrogen flow rate. This is the reason that our char yield did not decrease with increasing hydrogen pressure.

Figure 12 shows the tar yields corresponding to Fig. 11. The tar yield of TTC increased with the increase of hydrogen pressure, and reached up to 38 wt.% at 5 MPa, which was 1.8 times larger than that of raw coal. This clearly shows that proposed method is effective for increasing the tar yield as well as the coal conversion, especially in high pressure hydrogen atmospheres. Both tar yields of VDC and raw coal decreased with increasing hydrogen pressure. This was due to the decomposition of tar to lighter hydrocarbons under high hydrogen pressure.

CONCLUSION

A novel flash pyrolysis method of coal was developed for drastically increasing the tar yield, in which the coal swollen by solvents was pyrolyzed in a flash mode. The tar yield was increased by the factor of 1.5 for the flash pyrolysis, and by the factor of 1.8 for the flash hydrolypyrolysis. The increase of tar yield is brought about by the pore enlargement caused by swelling and by the effective hydrogen transfer from/via tetralin.

ACKNOWLEDGMENT

This work was performed in the framework of the "Priority-Area Research" and "Japan-Canada Joint Academic Research Program" which was sponsored by the Ministry of Education, Culture and Science of Japan.

REFERENCES

1. Graff, R.A. and Brandes, S.D., Energy & Fuels, 1, 84(1987)
2. Khan, M.R., Chen, W.Y. and Suuberg, E., Energy & Fuels, 3, 223(1989)
3. Hutterling, K.J. and Sperling, R.E., Proc. 1987 International Conference on Coal Science, Oct.(Maustrich) p.699
4. Nelson, J.R., Mahajan, O.P. and Walker, P.L., Fuel, 59, 831(1980)
5. Green, T.K., Kovac, J. and Larsen, J.W., Fuel, 63, 935(1984)
6. Medeiros, D. and Peterson, E.E., Fuel, 58, 531(1979)
7. Brenner, D., Fuel, 62, 1347(1983)
8. Anthony, D.B., Howard, J.B., Hottel, H.C. and Meissner, H.P., Fuel, 55, 121(1976)
9. Gavaras, G.R., Coal Pyrolysis, Coal Science and Technology 4 Elsevier, New York, 1982
10. Wantzl, W., Fuel Processing Technology, 20, 317(1988)

Table 1 Properties of Coal

	Proximate Analysis (wt%)			Elemental Analysis (wt% daf)			
	FC	VM	ASH	C	H	N	S+O
Raw coal	43.2	45.8	11.0	74.5	6.0	1.3	18.20
Treated coal	-	-	11.0	72.7	5.9	1.5	19.90

Table 2 Change of Pore Volume and Surface Area during Swelling

Coal	Solvent	Temp. (°C)	Pore Volume (cc/g)	Surface Area (m ² /g)
Taiheiyō	Raw	-	0.039	108.2
	Tetralin	100	0.039	102.4
		170	0.040	102.5
		250	0.061	152.9

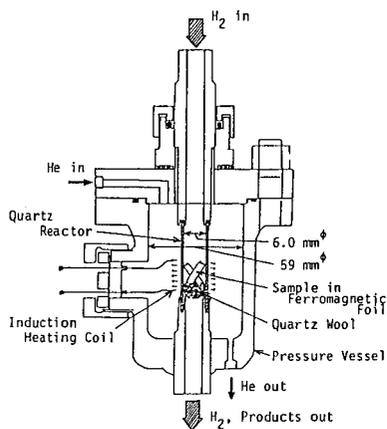


Fig.1 Schematic of a high pressure Curie-point pyrolyzer

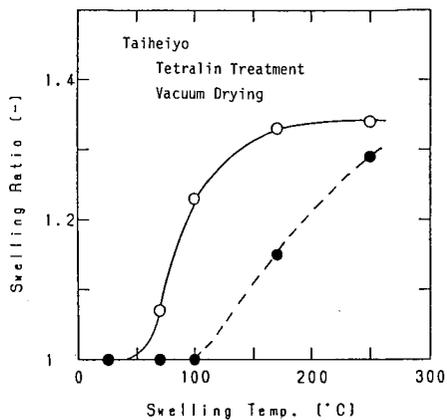


Fig.2 Change of the swelling ratio of tetralin treated coal and vacuum dried coal with the pretreatment temperature

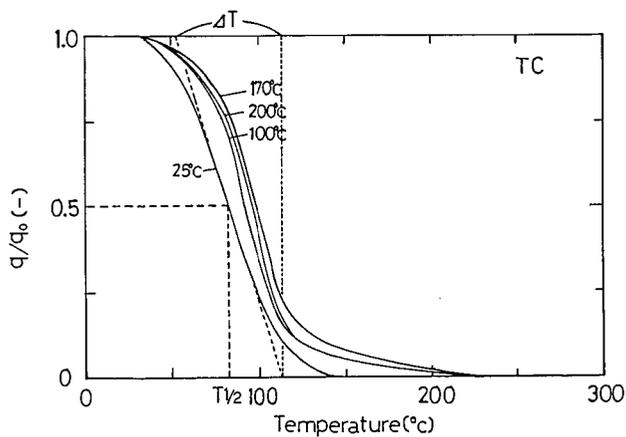


Fig.3 Thermal desorption curves of tetralin from the coal treated with tetralin at different temperatures

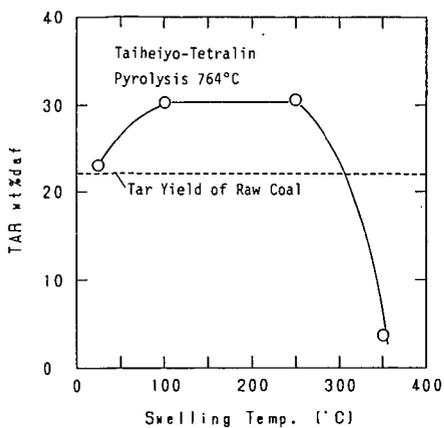


Fig.4 Effect of the pretreatment temperature on the tar yield during the pyrolysis of tetralin treted coal

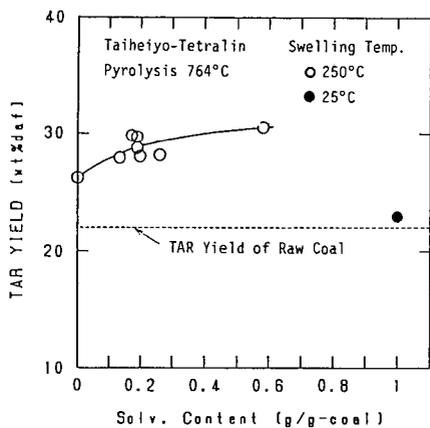


Fig.5 Effect of the amount of solvent remaining in the coal on the tar yield

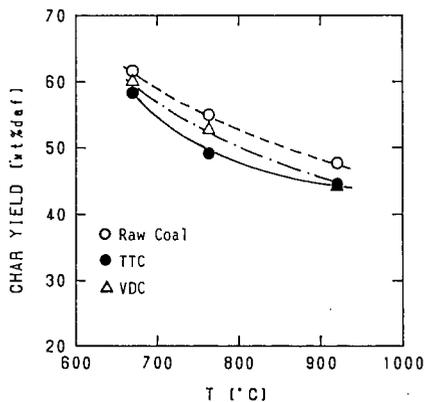


Fig.6 Effect of the pyrolysis temperature on the char yield during the pyrolysis for coal, tetralin treated coal and vacuum dried coal

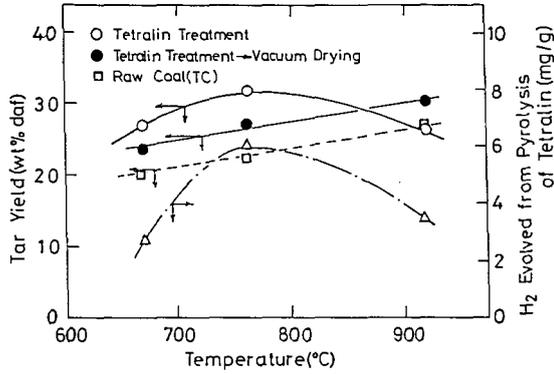


Fig.7 Effect of the pyrolysis temperature on the tar yield during the pyrolysis for coal, tetralin treated coal and vacuum dried coal

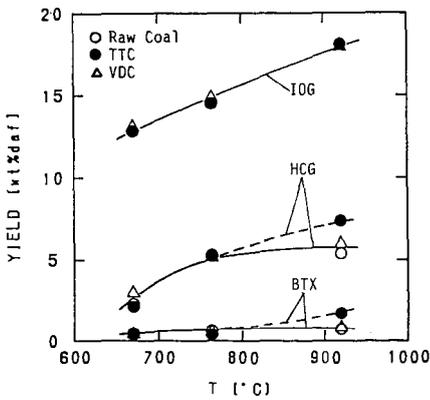


Fig.8 Effect of the pyrolysis temperature on the IOG, HCG and BTX yields during the pyrolysis for coal, tetralin treated coal and vacuum dried coal

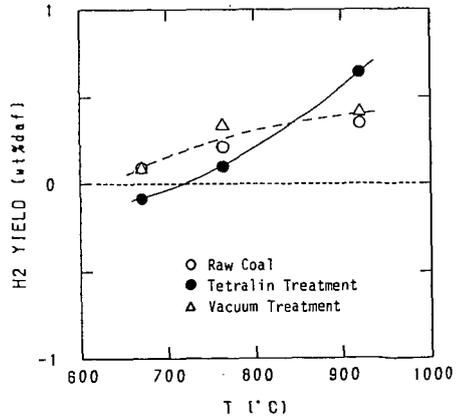


Fig.9 Effect of the pyrolysis temperature on the H₂ yield during the pyrolysis for coal, tetralin treated coal and vacuum dried coal

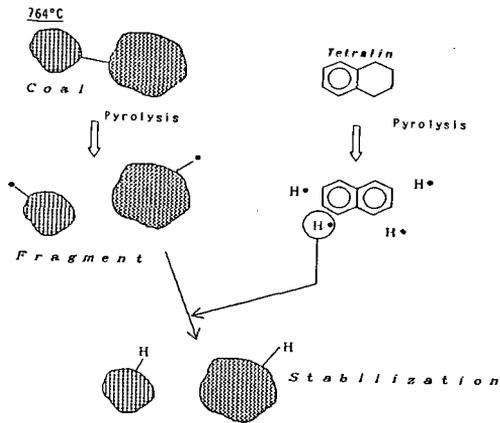


Fig.10 Presumed mechanism of pyrolysis of tetralin treated coal at temperatures lower than 764 °C

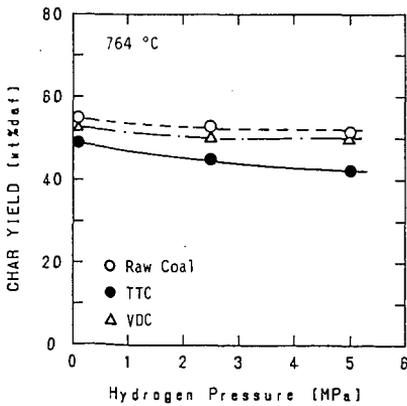


Fig.11 Change of the char yield during the pyrolysis with increasing hydrogen pressure

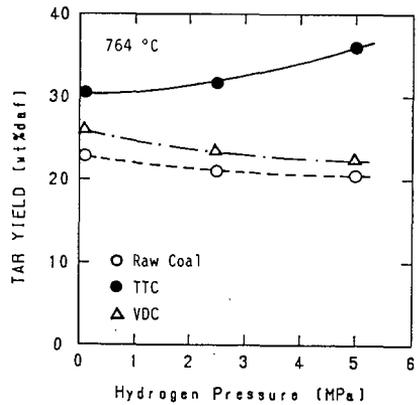


Fig.12 Change of the tar yield during the pyrolysis with increasing hydrogen pressure