

# A New Coal Flash Pyrolysis Method Utilizing Effective Radical Transfer from Solvent to Coal

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*Received August 16, 1990. Revised Manuscript Received January 4, 1991*

A new coal flash pyrolysis method was developed for drastically increasing the total volatile matter and the liquid products under mild conditions. The original idea of this method lies in the realizations of effective hydrogen transfer from the hydrogen donor solvent to the coal fragments during the flash pyrolysis. To realize it, we found the contact at the molecular level between the solvent and the coal functional groups was essential in addition to the matching of the dehydrogenation rate of the solvent and the primary decomposition rate of coal. Contact at the molecular level was achieved by swelling the coal with solvent at 100–250 °C under a pressurized atmosphere (1 MPa). When two coals were swollen by tetralin, tetralin penetrated into the micropores of its molecular size by enlarging the pores. Pyrolyzing the swollen coal in a Curie-point pyrolyzer at 670, 764, and 920 °C in a helium stream at atmospheric pressure resulted in production of 56% of volatile matter for Taiheiyo (TC, Japanese subbituminous coal) and surprisingly 67% for Morwell (MW, Australian brown coal). A maximum liquid yield from MW reached more than 42%, which was larger by 24% than that from the raw coal. It was clarified that this significant increase was brought about by a physical effect as well as the effective hydrogen transfer from tetralin.

## Introduction

Since pyrolysis of coal is the first step of all coal conversion processes, its understanding is essential for the effective use of coal. The pyrolysis of coal consists of two series of reactions: the first is primary decomposition, which consists of the formation of radical fragments and their stabilization, the other is the secondary gas-phase reaction of the gaseous components produced by the primary decomposition. The product yield during the pyrolysis depends strongly on coal type and operating

hydrogen from other sources to coal for increasing the tar yield.

Several methods have been proposed to supply hydrogen to coal during the pyrolysis. Hydrolysis is a representative one of such methods. This generally requires severe reactor conditions: high hydrogen pressure, high temperature, and long residence time. Even if the total volatile matter was increased by this method, the increase of liquid yield could not be expected as Wanzl indicated.<sup>1</sup>

Flash pyrolysis in methane,<sup>2,3</sup> toluene,<sup>4</sup> or methanol<sup>5</sup> atmosphere was proposed. These methods intended to supply hydrogen or methyl radicals produced by the de-

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composition of the gases, but these methods did not succeed in increasing the total volatile matter by an appreciable amount.

Next, an attempt was made to pretreat coal before the pyrolysis by gases such as hydrogen, carbon dioxide, Steam, and so on.<sup>6</sup> A similar attempt involved the adsorption of organic substances on coal before pyrolysis.<sup>7</sup> These attempts intended to supply some radicals from the gases or organic substances to coal during the pyrolysis. These methods, however, could attain only a slight increase of the total volatile matter.

More recently, Graff et al.<sup>8,9</sup> have proposed the pretreatment of coal by subcritical steam before pyrolysis. They reported drastic increases of both the total volatile matter and the tar yield by pyrolyzing a bituminous coal (Illinois No. 6) at 900 °C under 50 atm of steam. Graff et al. concluded that this significant effect was brought about through the modification of coal by the subcritical steam, probably by the breakage of some ether links in the coal. However, Kahn et al.<sup>10</sup> could not observe such significant increase when they traced this method. This may present some uncertainty about Graff's method.

Another approach is a catalytic steam pyrolysis of coal. The consensus obtained from many studies<sup>11-17</sup> seems to be that the catalyst is effective only for the secondary gas-phase reaction. Therefore, the increase of total volatile matter may not be expected by the catalytic steam pyrolysis.

To summarize, only Graff et al. succeeded in the drastic increase of both the total volatile matter and the liquid yield, although they employed fairly severe experimental conditions. Their idea lies in the modification of coal before the pyrolysis. On the other hand, other methods intend to supply some radicals from hydrogen or organic substances to coal during the pyrolysis. The failure of these methods seems to suggest the difficulty in controlling the primary decomposition of coal. To supply the radicals to coal effectively and to increase the total volatile matter, the formation rate of the radicals must match that of the radical fragments from coal at first. Furthermore, both radicals must be in close enough spatially to react with each other, because the reaction rates among the radicals are much faster than the transport rate of the radicals. So, it is necessary to find some means to fulfill the above requirements for increasing the total volatile matter during the pyrolysis.

In this paper we present a new efficient method for increasing both the total volatile matter and the tar yield during the pyrolysis under a mild condition. Our idea is to supply the hydrogen radical from the hydrogen donor solvent to the coal fragments within the coal particles. To accomplish intimate contact between the solvent and the coal, the coal was pretreated by the solvent at 100-250 °C under 1 MPa of nitrogen. Through this treatment, the coal particles were swollen and the solvent was retained intimately within the micropores of coal. The coal swollen by the solvent was pyrolyzed in a flash mode in an inert gas atmosphere. Drastic increase of the total volatile matter and the tar yield was attained. We will show this drastic

**Table I. Properties of Raw Coals and a Vacuum-Dried Coal**

	proximate analysis, wt %			elemental analysis, wt %			
	FC	VM	ash	C	H	N	S + O
Morwell (MW)	48.2	50.3	1.5	67.1	4.9	0.6	27.40
Taiheiyo (TC)	43.2	45.8	11.0	74.5	6.0	1.3	18.20
VDC of TC <sup>a</sup>			11.0	72.7	5.9	1.3	19.90

<sup>a</sup>This was swollen at 250 °C and then degassed for 1 h at 70 °C.

**Table II. Comparison between the Amount of Tetralin in the TTC and That Removed by Vacuum Drying**

coal	wt of tetralin in TTC, <sup>a</sup> kg/kg	wt of tetralin removed from TTC by vacuum drying, <sup>a</sup> kg/kg
TC	0.5805	0.5813
MW	0.7113	0.7104

<sup>a</sup>Dry and ash free coal basis.

increase is brought about by a physical effect and the effective hydrogen transfer from/via tetralin.

## Experimental Section

**Sample Preparation.** A Japanese coal Taiheiyo (TC), and an Australian brown coal, Morwell (MW), were used as raw coals. Their Properties are given in Table I. The coal, whose particle size was ca. 1 mm, was predried at 110 °C for 24 h. Then the coal was ground into fine particles of less than 74 μm and was dried in vacuo again at 110 °C for 1 h before use.

Coal samples retaining tetralin within the particles were prepared as follows: the coal particles were mixed with tetralin in the ratio of 10 to 6 by weight in a stainless tube reactor, then they were heated to a temperature between 25 and 350 °C under the 1 MPa of nitrogen by immersing the reactor into a temperature-regulated sand bath. By this treatment coal particles were swollen when the temperature was between 100 and 250 °C, and tetralin was retained in the coal matrix.

To estimate properly the effect of tetralin during the flash pyrolysis, two other samples were prepared by the following procedure: 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 was irreversible, swollen but tetralin free coal was obtained. This sample was pyrolyzed to examine the physical effect of swelling on the pyrolysis. To do so, however, tetralin must be removed completely from the tetralin-treated coal (TTC) and chemical characteristics of the coal should not be changed significantly by the vacuum drying. This was examined for a TC which was swollen at 250 °C. Table II gives the amount of tetralin removed in the tetralin-treated coal and the amount of tetralin removed by the vacuum drying. Both amounts coincide within experimental error, confirming that tetralin was almost completely removed from the tetralin treated coal by the vacuum drying. Significant difference was not found between the ultimate analysis of the raw coal and that of the vacuum dried coal as shown in Table I. So, we assumed that the vacuum-dried coal prepared from TC was different from the raw coal mainly in physical properties. Several partially degassed samples were also prepared to adjust the amount of tetralin retained. These samples were utilized to examine the effect of the amount of tetralin retained on the pyrolysis.

Another sample was prepared to estimate the contribution of pyrolysis of tetralin on the product yields from the tetralin treated coal. A char produced under a high-temperature pyrolysis of Taiheiyo coal, which was confirmed not to be pyrolyzed further, was also treated by tetralin in the same manner as was employed to prepare the tetralin-treated coal. The amount of tetralin in the char was adjusted to be nearly equal to that of the tetralin-treated coal. This sample was pyrolyzed to obtain the yield of each component from tetralin.

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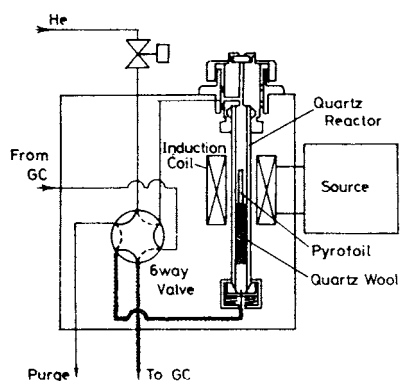


Figure 1. Schematic of Curie-point pyrolyzer.

The swelling ratios of the tetralin-treated coal and the vacuum-dried coal were measured by a volumetric method.<sup>18</sup> The volume of micropores less than 1 nm in diameter was obtained for the raw coal and the vacuum-dried coal by analyzing the adsorption isotherm of CO<sub>2</sub> measured at 0 °C. The temperature-programmed desorption (TPD) of tetralin from the tetralin-treated coal was also performed using a thermobalance (Shimadzu Co. Ltd., TGA 50).

**Flash Pyrolysis.** Samples prepared above were pyrolyzed with a Curie-point pyrolyzer (Japan Analytical Ind., JHP-2S) in the helium flow of atmospheric pressure. Figure 1 shows the schematic diagram of the experimental apparatus. About 2 mg of sample wrapped up tightly by a ferromagnetic foil was placed in a small quartz reactor (4.0 mm i.d.) and heated to a temperature between 670 and 920 °C at the rate of 3000 °C/s by an induction heating coil to be pyrolyzed rapidly. Since this heating scheme heats up only the foil with the coal particles, volatile products were immediately cooled down by the helium gas flowing at a high flow rate. The gas-phase secondary reactions were largely suppressed, which enables the examination of the primary decomposition of coal solely as mentioned in earlier works.<sup>1,19,20</sup> Tar produced was trapped completely by the quartz wool placed just below the foil. Gaseous products were all led to a gas chromatograph equipped with a Porapak Q column to analyze inorganic gases (H<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O) and hydrocarbon gases (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub>, C<sub>6</sub>, and C<sub>6</sub> gaseous compounds, benzene, toluene, and xylene). 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 the results.

**Calculation of the Product Yield of the Tetralin-Treated Coal.** Since tetralin is also pyrolyzed during the flash pyrolysis of the tetralin-treated coal, its estimation is necessary to represent properly the product yield deriving solely from the coal. However, it is impossible in a strict sense, because we are expecting interactions between tetralin and the coal. Then we used the following equation to calculate the yield of each component, Y<sub>i</sub>, deriving from the coal as a first approximation

$$Y_i = \frac{\text{(yield from the tetralin-treated coal)}}{\text{(yield from tetralin)/(1 - w)}} \quad (1)$$

where w is the weight fraction of tetralin in the tetralin-treated coal. This equation is suitable to judge if there is an interaction between the coal and the solvent. The yield calculated by this equation coincides with that of raw coal if there are no interactions between tetralin and the coal.

## Results and Discussion

**Change of Physical and Chemical Properties during the Swelling of Coal.** The swelling characteristics of several coals by various solvents were examined in detail

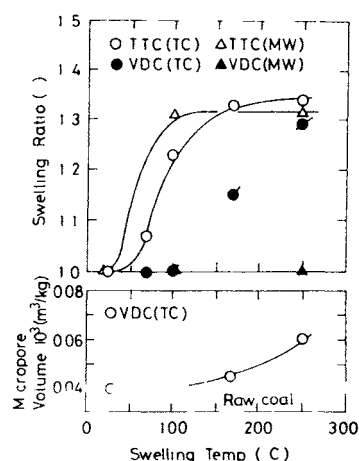


Figure 2. Change of the swelling ratio and the micropore volume against the swelling temperature

in a separate paper.<sup>21</sup> In this paper the swelling characteristics that would be intimately related to the pyrolysis are discussed. The upper graph of Figure 2 shows the change of the swelling ratio against the swelling temperature. TC (open circles) began to swell with tetralin at 70 °C, and the swelling ratio reached up to 1.34 at above 170 °C. MW (open triangles) began to swell at lower temperatures and reached a maximum swelling at around 100 °C. The swelling ratio of MW at 100 °C was nearly equal to that of TC swollen above 170 °C.

The swelling ratio of the VDC is also shown by the closed symbols in Figure 2. The TC 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 interestingly almost irreversible. On the other hand, the MW swollen returned to the original volume apparently at all the swelling temperatures. This is probably because MW consists of smaller and more flexible structures.

By utilizing the vacuum-dried coal prepared from TC, we can examine the physical change brought about by the swelling. The lower graph of Figure 2 shows the volume of micropores less than 1 nm in pore radius for the VDC. The micropore volume of the vacuum-dried coal prepared from the TC swollen at 250 °C is about 1.5 times larger than that of the raw coal. This indicates that tetralin penetrated into these micropores by enlarging the pores during the swelling. Since the dimensions of these micropores are comparable to those of tetralin molecule, tetralin is expected to interact both physically and chemically with the functional groups in the coal such as -OH, -COOH, etc.

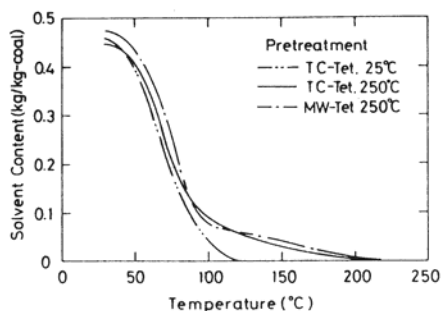
The strength of interaction between the coal and tetralin in the tetralin-treated coal can be examined by the TPD of tetralin from the tetralin-treated coal. Figure 3 shows the TPD curves for several samples. The TPD curve of the TC treated at 25 °C just corresponds to that of the evaporation of tetralin, but the other curves show that about 0.1 kg/kg of tetralin is retained strongly by the coal. This figure suggests that a part of tetralin in the tetralin-treated coal of MW is also retained in the micropores of the dimension of tetralin molecule. Thus it can be

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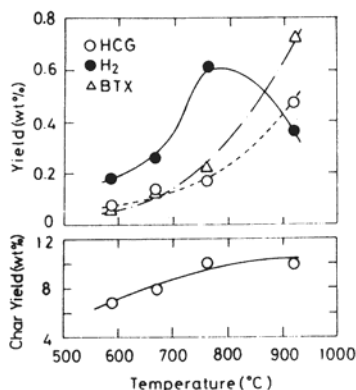
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**Figure 3.** Temperature-programmed desorption curves of tetralin from several tetralin-treated coals.



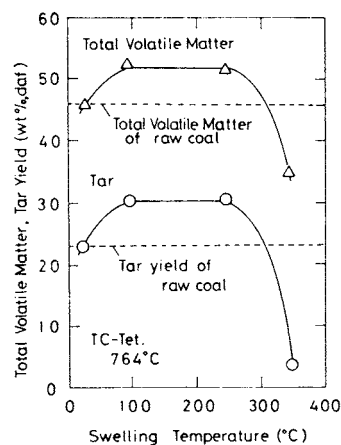
**Figure 4.** Product yields during the flash pyrolysis of tetralin.

visualized that the micropores in the tetralin-treated and swollen coal are filled by tetralin and that tetralin and the functional groups of coal are in close contact. This situation is completely different from the tetralin-treated but nonswollen coal such as the one prepared at 25 °C.

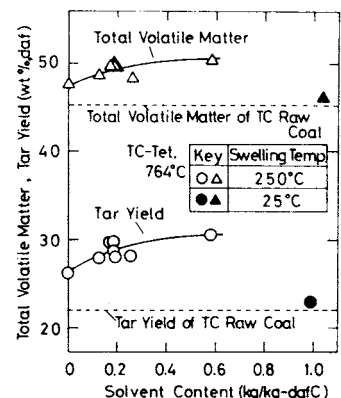
**Flash Pyrolysis of Tetralin.** Figure 4 shows the product yield obtained by pyrolyzing the char retaining tetralin. The char yield from tetralin was less than 10% at all temperatures. The yields of other components are all less than 1 wt % as shown in the above graph, but the temperature dependency is different among the components. Both the hydrocarbon gas (HCG) yield and the yield of the sum of benzene, toluene, and xylene (BTX) increased monotonously, whereas the H<sub>2</sub> yield had a maximum around 750 °C. This shows that reaction rates among the hydrogen radical and other small radicals such as methyl radical are accelerated above 750 °C. The amount of hydrogen used for these reactions is fairly large if it is represented in molar basis. To summarize the above results, there is a possibility that the reactions between the hydrogen radical deriving from tetralin and the radical fragments of coal will occur if they are close enough spatially.

**Effect of Pretreatment Temperature on Tar Yield.**

To find an optimum swelling temperature, the tetralin-treated coals prepared at several temperatures were pyrolyzed at 764 °C. Figure 5 shows the total volatile matter and the tar yields against the swelling temperature. Both the total volatile matter and the tar yield of the tetralin-treated coal were the same as those of the raw coal at the swelling temperature of 25 °C, but they reached about 1.5 times larger than those of the raw coal at 100-250 °C. This result shows that tetralin is effective in increasing the total



**Figure 5.** Effect of the pretreatment temperature on the volatile matter and the tar yield of the tetralin-treated coal for TC.

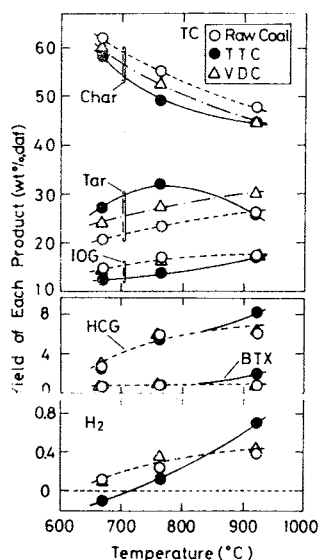


**Figure 6.** Effect of the tetralin content on the total volatile matter and the tar yield of the tetralin-treated coal for TC.

volatile matter and the tar yield only when the coal is swollen and tetralin is retained in the micropores as Figure 2 shows. The amount of total volatile matter and the tar yield were very small at the swelling temperature of 350 °C. This is because the coal partly decomposed and reacted with tetralin during the treatment at this temperature. For MW, both the total volatile matter and the tar yields of the tetralin-treated coal were much larger than those of the raw coal at the swelling temperatures of 100-250 °C, although the results are not shown. However, it was found that MW started to decompose at around 170 °C. From above results, the swelling temperature was decided to be 250 °C for TC and 100 °C for MW.

**Effect of the Amount of Tetralin in the Coal.** The effect of the amount of tetralin retained in the coal on the total volatile matter and the tar yield was examined at the pyrolysis temperature of 764 °C. Samples of different tetralin content were prepared by changing the vacuum-drying time of the tetralin-treated coal prepared from TC at 250 °C. Since these samples are different only in the tetralin content judging from the swelling ratio of the vacuum-dried coal (VDC) shown in Figure 2, they are suitable to examine the effect of the amount of tetralin.

Figure 6 shows the total volatile matter and the tar yield during the mash pyrolysis against the amount of tetralin



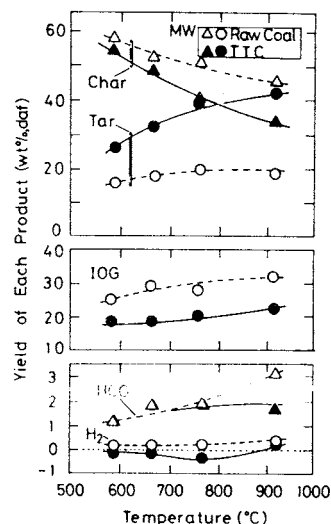
**Figure 7.** Product distribution during the flash pyrolysis of the tetralin-treated coal for TC.

retained in the coal. The Sample of zero tetralin content was completely dried (VDC). Since the vacuum-dried coal is still swollen by 30%, this sample has much larger pore volume than the raw coal as shown in Figure 2. The total volatile matter and the tar yield of the vacuum-dried coal were About 3-4 wt % larger than those of the raw coal. This means that the pore enlargement by swelling contributed to the increase of the tar yield. This is simply a physical effect. Both the total volatile matter and the tar yield increased gradually with the increase of tetralin content. These increases are judged to be brought about by a chemical effect of tetralin. The total volatile matter and the tar yield of the coal treated at 25%, which are shown for comparison, are almost same as those of the raw coal, although the tetralin content of the coal is the largest. This indicates again that the swelling is essential for increasing the coal conversion.

Since swelling is realized by enlarging micropores as fully discussed in a separate paper<sup>21</sup> and as briefly mentioned earlier in this paper, tetralin is penetrating into the micropores of the dimension of tetralin molecule in the tetralin-treated coal. This penetration will cause some interactions between tetralin and some functional groups of the coal. Therefore, tetralin is probably retained by the Stronger attractive force in the swollen coal than in the nonswollen coal. Thus, tetralin in the swollen coal is expected to have stronger interactions with the coal fragments during the pyrolysis, which will contribute to increase the total volatile matter. On the other hand, tetralin in the nonswollen coal did not penetrate into micropores. Therefore, little increase of the total volatile matter is expected.

**Effect of the Pyrolysis Temperature on the Product Yield.** Figure 7 shows each yield of the TTC, the VDC, and the raw coal against the pyrolysis temperature for TC. The char yield of the tetralin-treated coal is lower than that of the raw coal at all the temperatures by 4-10 wt %. The char yield of the vacuum-dried coal is also 4 wt % lower than that of the raw coal.

The tar yield of the tetralin-treated coal increased with the increase of temperature and reached a maximum value

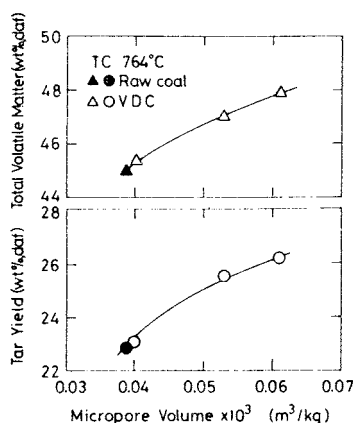


**Figure 8.** Product distribution during the flash pyrolysis of the tetralin-treated coal for MW.

of 32 wt % daf at the pyrolysis temperature of 764°C, which was 1.5 times larger than that of the raw coal. Then it decreased and was almost equal to that of the raw coal at 920°C. This temperature dependency is similar to that of the H<sub>2</sub> yield from the pyrolysis of tetralin (see Figure 4). On the other hand, the tar yield of the vacuum-dried coal was larger than that of the raw coal by 4 wt % irrespective of pyrolysis temperature.

The inorganic gas (IOG) yield of the tetralin-treated coal was slightly smaller than that of the raw coal or the vacuum-dried coal. This difference was due to the difference of H<sub>2</sub>O yield. 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 the tetralin-treated coal at 920°C, however, were larger than those of the other two samples. The H<sub>2</sub> yield of the tetralin-treated coal was smaller than that of the raw coal at temperatures lower than 800°C, but exceeded that of the raw coal at 920°C. The H<sub>2</sub> yield of the vacuum-dried coal was almost same as that of the raw coal at all the temperatures.

Figure 8 shows the yield of each product of the tetralin-treated coal and the raw coal for MW. The properties of the vacuum-dried coal prepared from MW were almost the same as those of the raw coal, and the product distribution during the pyrolysis of the vacuum-dried coal was also almost the same as that of the raw coal. Therefore, the results of the vacuum-dried coal are not involved in Figure 8. The char yield of the tetralin-treated coal was much smaller than that of the raw coal at all temperatures. The tar yield of the tetralin-treated coal increased with the increase of temperature and surprisingly reached 42 wt % daf at 920°C, which is 2.3 times larger than that of the raw coal. This yield is almost comparable to that of the liquid yield attained in the coal liquefaction.<sup>22</sup> On the other hand, the HCG yield of the tetralin treated coal was equal to that of the raw coal up to 764°C, but was lower at 920°C. The inorganic gas and the H<sub>2</sub> yields of the tetralin-treated coal were much lower than those of the raw



**Figure 9.** Effect of the pore enlargement caused by the swelling on the tar yield.

coal at all the temperatures. The large difference of the inorganic gas yield between the raw coal and the tetralin-treated coal again came from the difference of the  $H_2O$  yield.

#### Mechanism of the Increase of Total Volatile Matter

**And Liquid Yield.** Figures 7 and 8 clearly show that the proposed method is effective for increasing both the total volatile matter and the tar held with pyrolysis under such a mild condition. We will examine the mechanism of the pyrolysis of the tetralin-treated coal based on the above results.

The physical effect can be examined solely by comparing the product distribution between the vacuum-dried coal and the raw coal for TC. The total volatile matter of the vacuum-dried coal increased by 3-4% at all temperatures in comparison with that of the raw coal as shown in Figure 7. This increase was due to the increase of the tar yield. It was supposed that the increase of micropore volume caused by the tetralin pretreatment facilitated the escape of the tar vapor, which would be captured by the char radical in the nonswollen coal, from the coal particles. This is further substantiated by pyrolyzing several vacuum-dried coal samples of different micropore volumes. The vacuum-dried coal samples were prepared by changing the degree of swelling. The total volatile matter and the tar yield are plotted against the micropore volume of the vacuum-dried coal in Figure 9. Good correlations indicate the validity of the above reasoning. It is possible to increase the total volatile matter by several percents by utilizing only the physical effect: pore enlargement caused by the swelling.

Next, we will discuss the chemical effect of tetralin on the pyrolysis of coal. Since the effect of tetralin seems to be different between TC and MW, we will examine the effect for each coal.

For TC, we can discuss solely the chemical effect of tetralin by comparing the product distribution between the tetralin-treated coal and the vacuum-dried coal. Tetralin contributed to increase both the total volatile matter and the tar yield at the temperatures less than 800

. At 920 the effect was only to rearrange the product distribution of the total volatile matter. We presume that the increase of both the total volatile matter and the tar yield was brought about by not only the effective hydrogen transfer from tetralin to the coal but by the effective utilization of small radicals such as OH and H from the coal for stabilizing the coal fragments. The latter. Transfer

was expected because the yields of  $H_2O$  and  $H_2$  of the tetralin-treated coal were significantly smaller than those of the vacuum-dried coal. At 920 tetralin contributed only to decompose the primary pyrolysis products further. This is probably because the decomposition rate of tetralin did not match the primary decomposition rate of TC at this temperature.

For MW, we cannot distinguish the physical effect and the chemical effect. So, we will discuss the chemical effect by assuming that the physical effect is similar to that for the pyrolysis of the tetralin-treated coal of TC. Then we regard the significant decrease of the  $H_2O$  yield and the  $H_2$  yield of the tetralin-treated coal in comparison with those of the raw coal as the chemical effect caused by tetralin. Since the large increase of the tar yield of the tetralin-treated coal is compensated by the decrease of the char yield, the  $H_2O$  yield, and the  $H_2$  yield, and partly by the hydrocarbon gas yield as shown in Figure 8, the significant amount of small radicals (H, OH, CH<sub>3</sub>, etc.) deriving from the coal was judged to be utilized to stabilize the coal fragments as tar. This must be realized in virtue of the presence of tetralin, although we cannot clarify the mechanism now.

To summarize the discussion, we can say that two conditions are essential for the proposed method to be valid. The first one is the contact of molecular level between tetralin and the functional groups of coal, and the other one is the matching of the decomposition reactions of the coal and tetralin. The second condition is probably fulfilled by choosing a proper combination of coal and solvent, but the first condition is difficult to realize. Therefore, the success of the proposed method lies in the realization of the contact at molecular level between the solvent and the coal through the swelling by the solvent prior to the pyrolysis. Tetralin in the micropores of the swelling coal will have strong interactions with the functional groups of coal including the noncovalent linkages such as phenolic acid hydrogen bonds. When this swelling coal is pyrolyzed in a flash mode, strong interactions will arise between tetralin and the functional groups. Our image of the pyrolysis is the reaction of tetralin and the functional groups in a confined microspace. The reaction conditions are probably comparable to those under a high pressure of tetralin. So, this is, so to speak, the flash liquefaction of coal in the micropores. We must also stress the derivative effect of swelling on the pyrolysis. The swelling facilitates the escape of the coal fragments from the coal particles by enlarging the micropores of coal.

#### Validity of the Proposed Method from a Practical

**Viewpoint.** Up to now we have shown the effectiveness of the proposed method based on the yield calculated by eq 1. Equation 1 is suitable to judge if there is an interaction between the coal and the solvent, with the difference between the yield calculated by eq 1 and that of the raw coal is due to the interaction. Then the fact that the yield of total volatile matter calculated by eq 1 was much larger than that of the raw coal for both TC and MW clearly indicates the effectiveness of the proposed method for increasing the total volatile matter.

From a practical viewpoint, however, the following criticism may arise: discussion based on eq 1 is not fair, because tetralin is also pyrolyzed and a part of it is converted to char. So, even if the amount of total volatile matter calculated by eq 1 is larger than that of the raw coal, the effectiveness of the proposed method could not be proven. This could only be established when the amount of total volatile matter obtained by the method is larger than the sum of the amount of tetralin used and

**Table III. Overall Material Balance of Tetralin-Treated Coal<sup>a</sup>**

	TC (764 °C) <sup>b</sup>				MW (920 °C) <sup>c</sup>		
	raw	calcd <sup>d</sup>	TTC	VDC	raw	calcd <sup>d</sup>	TTC
char	0.5501	0.5501	0.5499	0.5268	0.4560	0.4560	0.4044
tar	0.2279	0.8079	0.8205	0.2645	0.1780	0.8880	1.0495
gas	0.2220	0.2220	0.2095	0.2087	0.3660	0.3660	0.2561

<sup>a</sup>All values in kg/kg of dry and ash-free coal. <sup>b</sup>Tetralin 0.58 kg/kg, dry and ash-free coal basis. <sup>c</sup>Tetralin 0.71 kg/kg, dry and ash-free coal basis. <sup>d</sup>The amount of tetralin in the TTC was simply added to the tar yield of the raw coal.

the amount of the total volatile matter obtained from the raw coal. To answer this criticism, the following examination was performed.

In Table the amounts of char, tar, and gaseous products obtained by pyrolyzing the raw coal and the tetralin-treated coal, and also the vacuum-dried coal for TC, under the specified conditions are shown for both TC and MW. The values are all represented on the basis of unit weight of the raw coal to facilitate the direct comparison of each other. The values in the column identified by calcd were obtained by simply adding the amount of tetralin in the tetralin-treated coal to the amount of tar obtained from the pyrolysis of the raw coal. Then the comparison of the amount of each product between the TTC and the calcd columns allows us to judge if the proposed method is practically effective.

For TC, the amount of tar deriving from the tetralin-treated coal is a little larger than the calculated one, but the char yield is almost the same. This indicates that the proposed method is not so effective for TC in a practical sense. For this coal, the increase of the total volatile matter brought about by the interaction with tetralin was canceled by the char produced through the pyrolysis of tetralin. For MW, on the other hand, the amount of tar from the tet-

ralin-treated coal is larger than the calculated one by 0.1615 kg/kg of coal, indicating that the proposed method is effective even in practical applications.

The pyrolysis of the tetralin-treated coal was not effective in increasing the total volatile matter for TC in the practical sense, but there is an option for this coal. As discussed earlier, the tar yield and the total volatile matter of the vacuum-dried coal were 3-4% larger than those of the raw coal at all temperatures. A typical result is found in Table III. Since it is possible to recover all the tetralin used for the swelling through the vacuum drying, the above-mentioned values are the net increase of the tar yield and the total volatile matter. So, the pyrolysis of the vacuum-dried coal definitely increases both the tar yield and the total volatile matter in practical processes also.

In the discussion of this section the tetralin recovered was not distinguished from the tar produced. This is partly because we could not analyze the tar composition, but mainly because tetralin is just a model solvent used for the swelling to show the validity of the proposed method. In practical applications, less expensive solvents such as the partly hydrogenated coal tar<sup>23</sup> could be used. In that case there will be no need to distinguish the solvent used for the swelling from the tar produced during the pyrolysis.

Summarizing the above discussion, it can be safely stated that the proposed method is effective for increasing the total volatile matter during the flash pyrolysis of coal.

**Acknowledgment.** This work was financially supported by the Ministry of Education, Culture and Science of Japan through the Grant-in-Aid on Priority-Area Research (Grant No. 62603014, 63603014 and 01603012).

**Registry No.** Tetralin, 119-64-2.

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