XRD ANALYSIS OF CARBON STACKING STRUCTURE IN COAL TREATED WITH HEAT AND SOLVENT

H. Takagi, K. Maruyama, N. Yoshizawa, Y. Yamada, Y. Sato*
National Institute of Advanced Industrial Science and Technology AIST Tsukuba West, 16-1 Onogawa Tsukuba-shi, Ibaraki-ken 305-8569, Japan

Introduction

X-ray diffraction (XRD) analysis is a fundamental method to evaluate the carbon stacking structure in coal and carbon materials. However, the vagueness of XRD pattern of coal, which has the low crystallinity, often makes it difficult to evaluate the stacking structure quantitatively. In a previous study [1,2], we reported the standard analysis of carbon stacking structure in coal by XRD technique (Standard Analysis of Coal – by XRD, STAC-XRD). STAC-XRD is based on the procedures proposed by Hirsch et al. [3] and Shiraishi et al. [4].

In the present study, the STAC-XRD has been applied to coals treated with heat and solvent, and the change of the carbon stacking structure in these treated coals was discussed.

Experimental

Table 1 summarizes the elemental analyses of raw coals used in this study. All the coals were pulverized to particles under 149μm.

Heat-treatment was carried out in Ar atmosphere at 440°C and 920°C for 1 h with a heating rate of 3°C/min. Hereafter, this treatment is referred to as HT-440 and HT-920-1h, respectively. In order to investigate the influence of the heating time, the coals were pyrolyzed at 920°C for 1 min with a heating rate of 300°C/min in Ar atmosphere (HT-920-1min). Solvent-treatment was performed in a batch-autoclave at 440°C for 1 h in N_2 pressure of 2MPa. Decalin was used as a solvent. This treatment is referred to as ST-440.

According to the previous study, the stacking structure of raw and treated coals was characterized using the STAC-XRD, and the number of aromatic layers in the stacking structure (N) and the average of N ($N_{ave.}$) were estimated.

Results and Discussion

Figure 1 shows the distribution of the number of aromatic layers (N) in raw coals. The $N_{ave.}$ value of NE and HE coal was larger than that of FO, BU and EB coal. The significant difference in the distribution of N between FO, BU and EB coal was not observed, i.e., over 70% of the stacking structure in these coals consisted of 2 layers. In the case of NE and HE coal, the ratio of 2 layers decreased, and that of 3-4 layers increased, compared with FO, BU and EB coal. This indicates that the stacking structure of aromatic layers in the higher rank coal, whose carbon content is more than 85wt%, is different from that in the subbituminous and brown coal.

Figure 2 shows the change of $N_{ave.}$ for treated coal at 920°C as a function of the carbon content, together with that of raw coal. The $N_{ave.}$ value increased as the result of heat-treatment, especially that of lower rank coals. This can be attributed to both the development of aromatic structures by heat-treatment and their packing of aromatic structures by the release of volatile components. The $N_{ave.}$ value after heat-treatment for 1 h was larger than that for 1 min. Since the yield of HT-920-1min was roughly equal to that of HT-920-1h,

Table 1. Elemental analyses of raw coals and yields after the treatment with heat and solvent

coal	abbreviation	elemental analysis [wt% - daf]				ash [wt%]	yield after treatment [wt%]			
		C	H	N	(O+S)[a]		HT-440	ST-440	HT-920 -1h	HT-920 -1min
Foutuna	FO	62.4	5.0	0.7	31.9	4.6	62.3	66.3	51.2	49.1
Buckskin	BU	71.7	5.4	1.5	21.4	7.1	72.4	74.0	61.0	58.5
Ebenezer	EB	81.2	6.1	1.6	11.2	14.9	70.2	82.1	64.4	59.7
Newlands	NE	85.9	4.9	1.7	7.5	15.4	81.6	91.0	73.4	71.8
Hebu Semi-Ant	HE	90.6	4.2	1.3	1.3	16.8	97.6	100.0	90.3	90.4

[a] Determined by difference.

as shown in Table 1, the difference of the $N_{ave.}$ value between HT-920-1min and HT-920-1h might be related to the development of aromatic structures.

Figure 3 shows the change of $N_{ave.}$ for coals heat- or solvent-treated at 440°C (HT or ST) as a function of carbon content of the raw coal. The $N_{ave.}$ value after the treatment with solvent was larger than that with heat, in spite of the same temperature. The π-π interaction between aromatic structures in the coal plays an important role in the stacking structure. This result suggests that the increase in the mobility of aromatic structures with the introduction of the solvent into the coal accelerates the formation of π-π interaction during heat treatment.

Conclusions

The carbon stacking structure in the higher rank coal, whose carbon content was more than 85wt%, was different from that in the subbituminous and brown coal. The increase in the $N_{ave.}$ value on the condition of heat-treatment and kinds of coal. The addition of the solvent was effective for the development of the stacking structure in the coal during heat-treatment.

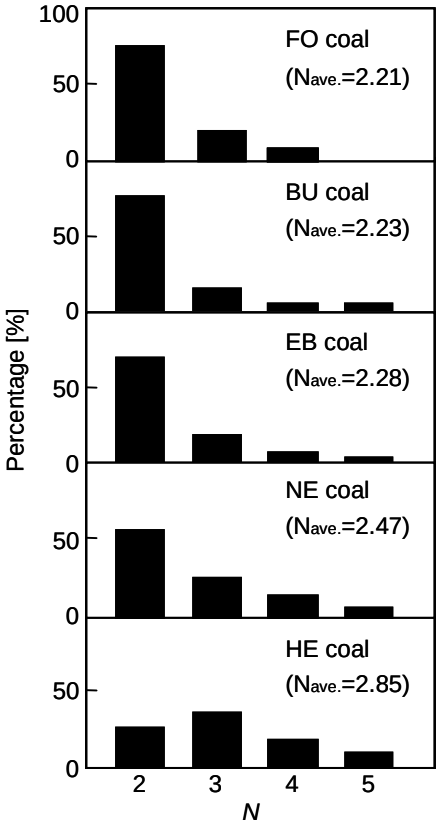

Figure 1. Distribution of the number of aromatic layers (*N*) in raw coals.

Acknowledgment

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References

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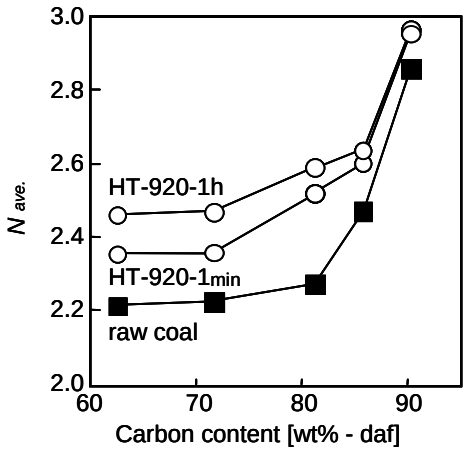

Figure 2. Change of $N_{ave.}$ for treated coals at 920°C.

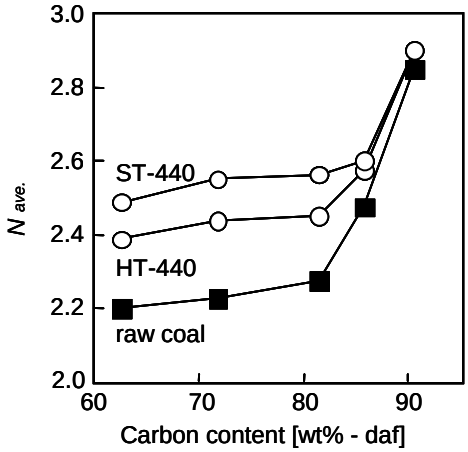

Figure 3. Change of $N_{ave.}$ for coals heat- or solvent-treated at 440°C.