

THE INVESTIGATION OF THE STRUCTURAL FACTORS FOR THE APPEARANCE OF COAL PLASTICITY

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INTRODUCTION

Even now, about a half of coal consumption in Japan corresponds to coke production for steel making. Therefore, carbonization process is very important among coal utilization techniques. Much effort has been paid to the development of effective carbonization process and/or replacement of the present coking processes by new concept such as the direct iron ore smelting process because our country has been imported almost all the coking coals and worried about a precious resource exhausting problem. Therefore, a deep understanding of plastic phenomena of coal was desired earnestly. We have been studying the phenomena of fusibility of coals by the estimation of amounts of transferable hydrogen, the measurement of their solid-state ¹³C NMR spectra and their thermogravimetric analyses (TGA)[1,2]. In those investigations, we found the relationship between R_{max}/WL (obtained from TGA) and Gieseler fluidity and also that solid state ¹³C NMR can evaluate the amount of transferable hydrogen. We referred to the schematic illustration of the structural change during heating which was proposed by Spiro[3] in considering the mechanism of coal plasticity. Although Spiro's illustration was based on the chemical structure of coal of 1980's, the structural analyses of coal and the detailed analyses of structural change during heating should be examined again in order to understand fusibility chemistry of coal at the level of molecule. Snape et al.[4] reported the characterization of partially carbonized coals based on solid-state ¹³C NMR and optical microscopy: the change of aromatic cluster size with the heat-treatment was discussed. In the present study, we employed a typical coking and a non-coking coals, Goonyella and Witbank. Ruthenium ion catalyzed oxidation (RICO) reaction of two coals was performed to get information concerning aliphatic portion of these coals. At the same time, the sample coals were heat-treated in the electric furnace in order to observe the structural changes during heat-treatment at the level of molecule, and the resulting char fraction and the devolatilized tar fraction were analyzed by solid-state ¹³C NMR and FT-IR spectroscopy, respectively.

EXPERIMENTAL SECTION

Samples.

The coal samples used in this study were Goonyella coal (GNY; C 88.1%, H 5.1%, N 1.9%, daf.) from Australia and Witbank coal (WIT; C 82.7%, H 4.5%, N 2.2%, daf.) from South Africa. WIT is called as non-coking coal in the field of coke industry, however, this coal shows a little degree of plasticity. The sample coals were provided by the Iron and Steel Institute of Japan, these being pulverized (-100 mesh) and dried at 60°C under vacuum for a night prior to use.

Ruthenium ion catalyzed oxidation (RICO) reaction of coal.

Coal sample (1 g), Na₂O₄ (20 g) and RuCl₃·*n*H₂O (40 mg) were put into a glass flask and stirred in the presence of mixed-solvent, H₂O (30 ml), CH₃CN (20 ml) and CCl₄ (20 ml), under the nitrogen flow at 40°C for 48 h. The resulting carbon dioxide was purged with N₂ flow through CaCl₂ and ascarite, and the yield of CO₂ was determined by the weight increase of ascarite. The details of the products workup and analysis were indicated elsewhere[5]. We could analyze the fractions containing lower carboxylic acids, higher carboxylic acids, aliphatic polyacids, and aromatic polyacids.

Heat-treatment of coal and analysis of the products.

Heat-treatment of coal was conducted by using a tubular electric furnace (Isuzu DKRO-14K with a temperature controller EPP-14) under 50 ml/min of nitrogen stream. One gram of coal sample was placed at the center of the quartz tube, and heated up to a determined temperature at a heating rate of 3 K/min. Final temperatures of heat-treatment were softening, maximum fluidity and resolidification temperatures of each coal (these were determined by Gieseler plastometry; 397, 456 and 498°C for GNY and 412, 432 and 446°C for WIT, respectively). The resulting char and tar fractions were recovered and weighed to obtain their yields. Tar fractions were analyzed by FT-IR spectroscopy (Shimadzu FTIR-8100M), and char fraction by ¹³C NMR spectroscopy (Chemagnetics CMX-300).

RESULTS AND DISCUSSION

RICO reaction of two sample coals

In order to observe the structural differences between GNY and WIT at the level of molecule, we performed RICO reaction of these two coals. After the reaction, we recovered carbon dioxide, lower carboxylic acids, acids in organic layer and water layer, and residue with less solubility and high molecular weight materials. The yields of carbon dioxide reached around 50% of the whole product because of the high aromaticity of these coals, however, the carbon recovery of this reaction was excellent; 96% for GNY and ~100% for WIT. We determined the amount of a series of mono- and dicarboxylic acids from the analyses of lower acids fraction and organic layer. Figure 1 shows the distribution of mono- and dicarboxylic acids. Monoacids correspond to the side chains in coal, while diacids indicate the presence of bridge bonds between two aromatic moieties. From Figure 1a, we can recognize ~3 mol/100molC of acetic acid derived from methyl group in coal, and the amount of other acids derived from longer side chains decreased monotonously with the number of carbon. Diacids also showed similar tendency. As to the comparison of GNY and WIT, several differences were found: longer side chains and bridges were detected in larger amount for WIT than for GNY, and the longest side chains and bridges were found for WIT. As the other products derived from RICO reaction of coal, we obtained aliphatic polycarboxylic acids and aromatic polycarboxylic acids. The precursors of these acids were considered to be alicyclic structure attached to aromatic cluster and highly condensed aromatic cluster, respectively. However, the apparent differences of the amounts of these acids between two coals could not be observed. The results obtained by ^{13}C and ^1H NMR of two coals indicated that GNY had slightly larger aromatic cluster than WIT.

Structural changes during heat-treatment

We performed the heat-treatment of GNY and WIT in the electric furnace in order to investigate the structural changes during heating. The devolatilization started at about 300°C, and the deposition of tar fraction appeared around 400°C in the heat-treatment of coals. We recovered char and tar fractions after the end of heat-treatment. Other products were gases such as CH_4 and CO_2 , and lighter hydrocarbons such as benzene. The yields of char and tar fractions obtained by the heat-treatment of coals at above three different temperatures were shown in Table 1. The weight loss (100% - char yield) at each heat-treatment temperature was similar to the data obtained from TGA, however, they were not exactly same because of the limitation for temperature control in the furnace during heat-treatment using an electric furnace. Atomic hydrogen/carbon ratio of char fraction decreased as the heat-treatment temperature increased. The decrease of H/C for a series of char samples may be due to the structural change during heating or the devolatilization of light fraction. In order to obtain more detailed information about the structural changes during the heat-treatment, we measured solid-state ^{13}C NMR spectra of the char samples. The spectra were shown in Figure 1 together with carbon aromaticity, f_a , evaluated from the ^{13}C NMR spectra for each sample. Although f_a of raw coal was different (0.83 and 0.79 for GNY and WIT, respectively), f_a values of the heat-treated samples became similar. Then, the ^{13}C NMR spectra were divided into 16 Gaussian peaks by referring to the assignment of carbon types in several model compounds, and we estimated the carbon distribution for each sample. We evaluated the change of amounts of each type of carbon based on the carbon distribution of char samples, their elemental analysis data and char yields. The data indicated the remarkable disappearances of the region of CH_2 , CH_3 and oxygen or carbon substituted aromatic carbon. On the other hand, amounts of other type of aromatic carbon did not change. These results supported that elimination of alkyl side chains underwent during the heat-treatment at the temperature of coal plastic range but other structural changes such as the increase of aromatic cluster size did not occur. Furthermore, release of CH_4 was observed at temperature range of 400 - 600°C by TG-GC[2], and the decrease of H/C during heating could be explained by the release of aliphatic rich volatile fraction.

In the previous paper[2], we reported that the amount of volatile materials from coal at the temperature between maximum fluidity temperature and resolidification temperature was important for the appearance of coal plasticity. Furthermore, we analyzed the tar fractions from TG furnace by field desorption-mass spectroscopy to observe molecular weight distribution and aromaticity of the fractions, and indicated that the different rank coals provided volatile components with different composition. In this viewpoint, we analyzed tar fraction obtained from the heat-treatment of two kinds of coals by FT-IR and gas chromatography. For the materials which can be detected by gas chromatograph, a series of aliphatic hydrocarbons and complicated mixture of hydrocarbons were observed for WIT and GNY. The aliphaticity (evaluated from the ratio of peak intensity of 3040 cm^{-1} to that of 2956 cm^{-1}) of tar fractions for these coals seemed to be high in the FT-IR spectra (Figure 2). However, as the heat-treatment temperature increased, the aliphaticity of tar fraction evaluated from FT-IR spectra dropped. Therefore, the volatile materials in the plastic stage had higher aromaticity than those before softening. We can calculate apparent H/C ratio of the volatilized fraction (including lighter fraction than tar) based on the yield of char and elemental analysis data of raw coal and the char. It was higher for GNY than for WIT. FTIR results did not agree with them,

but we can explain this by the fact that GNY coal released more amount of CH_4 during the heat-treatment as reported previously[2].

SUMMARY

We obtained the information concerning about aliphatic portion of two sample coals by using RICO reaction, which oxidize aromatic carbon in coal, and we observed the structural changes during heat-treatment of two coals. As to the structural features of original coal, RICO reaction implied that longer aliphatic chains or bridges were existed in WIT than in GNY, and the size of aromatic cluster for GNY was evaluated to be somewhat larger than that for WIT according to the ^{13}C NMR data. The structural changes during heat-treatment were also observed. The increase of f_a and the decrease of H/C were observed in the char fraction, while the tar fraction has aliphatic carbons richly. The differences of structural feature and pyrolytic behavior between coking and non-coking coals were not so large, therefore, it is interesting to pay attention to the detailed analyses of both volatile fractions before softening and in the plastic range.

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REFERENCES

1. Kidena, K.; Murata, S.; Nomura, M., *Energy Fuels* **1996**, *10*, 672.
2. Kidena, K.; Murata, S.; Nomura, M., *Energy Fuels* **1998**, *12*, 782.
3. Spiro, C. L., *Fuel*, **1981**, *61*, 1121.
4. Maroto-Valer, M. M.; Atkinson, C. J.; Willmers, R. R.; Snape, C. E., *Energy Fuels* **1998**, *12*, 833.
5. Artok, L.; Murata, S.; Nomura, M.; Satoh, T. *Energy Fuels*, **1998**, *12*, 391.

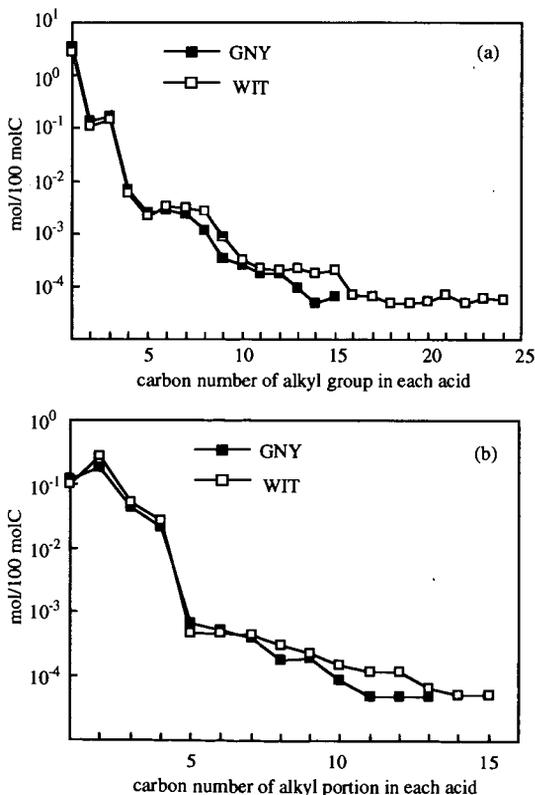


Figure 1. The yields of (a) monocarboxylic acids and (b) dicarboxylic acids from RICO reaction of GNY and WIT.

Table 1. The yields of char and tar after heat-treatment of coals and atomic H/C of char

Coal	Heat-treatment temperature (°C)	Yields (wt%, db.)		Atomic H/C ratio of char
		Char	Tar	
GNY	raw coal	-	-	0.69
GNY	397	97.5	1.4	0.68
GNY	456	89.2	7.5	0.59
GNY	498	86.9	11.0	0.56
WIT	raw coal	-	-	0.65
WIT	412	90.0	4.8	0.63
WIT	432	87.0	6.9	0.60
WIT	446	85.6	6.4	0.59

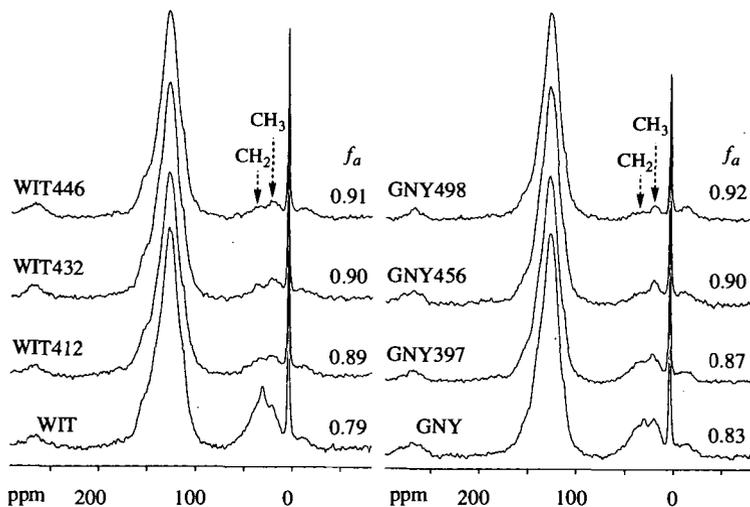


Figure 2. ^{13}C NMR spectra and their carbon aromaticity (f_a) of original coals and char samples after heat-treatment.

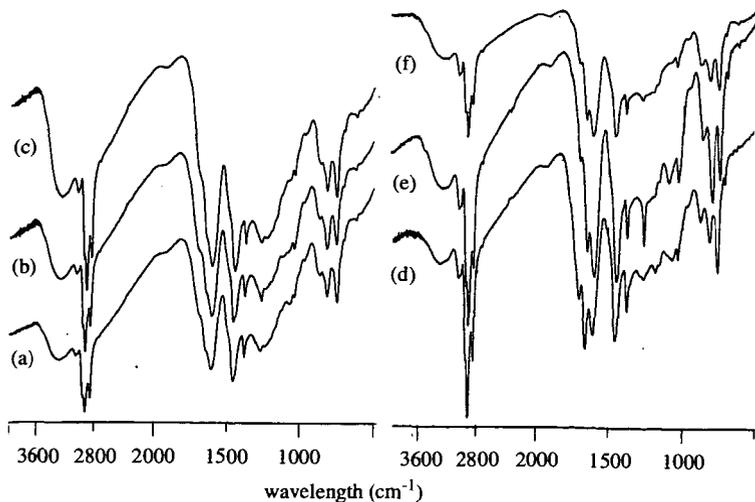


Figure 3. FT-IR spectra of the tar fraction obtained from the heat-treatment of WIT coal at (a)412, (b)432 and (c) 446 °C and GNY coal at (d)397, (e)456 and (f)498 °C.