ESR and FT-IR Studies for Coal Structures. Characteristics of Japanese Coals

Osamu Ito,* Hiroyuki Seki, and Masashi Iino
Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Katahira, Sendai, 980
(Received March 10, 1987)

The ESR parameters (spin concentration, line width, g-value, and spin-lattice relaxation time) of various coals mined in Japan and in many foreign countries have been measured. Low spin concentrations, broad line widths, and long spin-lattice relaxation times have been recognized as characteristics of Japanese bituminous coals (e.g., Akabira, Miike, and Shin-yubari coals) compared with the foreign coals having similar carbon contents. The origins of these differences were interpreted by the aid of the FT-IR spectra. Low fractions of aromatic carbon and rich aliphatic groups of Japanese bituminous coals are closely related to the characteristics in the ESR parameters.

Many spectroscopic methods have been used to obtain chemical information about the structures of organic solids such as coals.[1,2] In addition, the magnetic relaxation measurements give an information about the molecular motions; the nuclear spin-spin relaxation times (T_2) measured with NMR have been successfully applied to polymers and coals.[3,4] The measurements of the electron spin-lattice relaxation times (T_1) of carbonaceous materials including various coals were reported in 1950's.[5-9] Smidt and van Krevelen, however, indicated that the T_1-values were strongly affected by the adsorbed oxygen on coals.[8] Therefore, it has been believed for a long time that information about the dynamic behavior of the molecules in coals is hidden behind the interactions with oxygen. Recently, it was reported that the T_1-values for the polymers including polyacetylenes afford useful information.[10,11] Thus, it may be worth reinvestigating the electron-spin relaxation phenomena for coals. For Japanese coals, Toyoda, Sugawara, and Honda reported the various ESR parameters including T_1-values;[12] they found that the line widths of Japanese coals were broader than foreign ones, which is an only characteristic of Japanese coals; the spin concentrations and T_1-values are similar to those of the foreign coals observed by Smidt and van Krevelen.[8] On the basis of well-known properties of Japanese coals such as rich in hydrogen atom and rich in volatile matters,[13,14] it would be anticipated that Japanese coals have low spin concentrations and that the molecular motions of Japanese bituminous coals are flexible because of their high efficiency in liquefaction[15] and high solubility.[16]

In this study, we chose a wide variety of coals including Japanese and foreign coals having carbon contents from 65 to 93%. In order to help the interpretation of the ESR parameters which give a rather physical information about coals, the FT-IR spectra were measured with the diffuse reflectance method to obtain certain chemical information.

Experimental

Samples: Six kinds of Japanese coals having carbon content from 65 to 86.7% were selected. Foreign coals were selected in a wide range of the carbon contents. The ultimate analytical data were summarized in Table 1 with the abbreviation of coals.

These coal samples (under 60 mesh (<250 μm)) were dried at 80 °C in a vacuum oven. For brown coals (lignites), it is reported that the contact with air affected the ESR signals;[17] especially, coexistence of moisture and oxygen molecule strongly affected the intensities of ESR signals.[18,19] Thus, we dried coals samples in vacuum at lower temperature.

Deashing: In a solution containing 15 ml hydrochloric acid, 5 ml hydrofluoric acid, and 15 ml water, 1 g of original coal was suspended and warmed at 95 °C under nitrogen gas for 3 h; then the residues after filtration were washed with distilled water and dried in a vacuum oven at 80 °C.[20]

Maceral Separation: Some deashed coals were separated into maceral-rich groups with float sink method using a mixed solvent consisting of carbon tetrachloride and cyclohexane.[21]

Alkylation and Acetylation: Alkylation was performed by the reflux of coal (2 mg) in butyl alcohol (150 ml) with coexist of *p*-toluenesulfonic acid as a catalyst.[22] Deashed coal was acetylated with acetic anhydride in dry pyridine with refluxing under nitrogen gas during 12 h.[23]

ESR Measurements: Pulverized coals (under 100 mesh (<150 μm)) in ESR sample tube of 3 mm outer diameter were measured with a JEOL-FE3X and a Varian E-4 spectrometer (X-band/100 kHz field modulation) at room temperature. The effects of the degassing upon the line shape and saturation phenomena were examined from 4 to 10^{-4} Pa. Spin concentrations were calculated by the integration of the ESR differential signals comparing with standard DPPH. When the ESR signal contained two or more components, each curve was separated with the aid of the computer simulation method using the Lorentzian curve shape which is used for the homogeneous spin system.[24] Spin-lattice relaxation times were evaluated by the continuous wave saturation method with varying the microwave powers.[25,26] When the ESR signals were attributed to the mixture of homogeneous and inhomogeneous, some corrections were necessary according to Castner's method.[27]

FT-IR Measurements: The FT-IR spectra were measured by a JEOL JIR-100 spectrometer equipped with a diffuse reflectance apparatus; 3 mg of pulverized coals (under 200 mesh (<75 μm)) were diluted with 200 mg of KBr powder and the intensities of the IR bands were calculated by Kubelka-Munk function ($f(R_\infty)$) after averaging 200 times scan.[28,29]

Evaluation of f_a: The fraction of aromatic carbon (f_a) were calculated by Brown's method using a constant (0.42)

Table 1. Analytical Data of Coal Samples (daf)

Coal	(Abb.)	Nation	C/%	H/%	N/%	S/%	O/%	f_a
Nakayama	NK	Jpn[a)]	69.0	5.3	1.2	0.3	24.1	—[h)]
Soyakoishi	SY	Jpn	70.2	5.2	1.8	0.2	22.4	—[h)]
Taiheiyo	TY	Jpn	77.0	6.3	1.5	0.3	14.9	0.59
Akabira	AK	Jpn	80.8	6.2	1.9	0.7	10.4	0.65
Miike	MK	Jpn	82.3	6.3	0.8	2.3	8.4	0.71
Shin-yubari	YS	Jpn	86.7	6.2	1.9	0.3	5.2	0.71
Velva	VL	Am[b)]	69.1	4.8	1.4	0.6	23.9	—[h)]
Peerless	PL	Am	69.9	4.9	0.8	1.6	22.8	—[h)]
Noonan	NN	Am	70.8	4.6	1.0	0.6	23.0	—[h)]
South Beulah	SB	Am	71.6	4.7	1.4	2.9	19.2	—[h)]
Indian Head	IH	Am	72.0	5.0	1.1	1.2	9.5	—[h)]
Sufco	SF	Am	73.9	4.9	1.5	0.3	19.3	0.68
Colowyo	CW	Am	74.0	5.7	1.9	0.4	18.6	0.65
King	KN	Am	76.8	5.7	1.8	0.6	15.0	0.67
Illinois No. 6	IL	Am	78.9	5.5	1.8	5.7	8.0	0.66
Indian Ridge	IR	Am	86.5	5.1	1.9	0.9	5.5	0.84
Pittston	PT	Am	86.6	5.3	2.7	0.8	6.2	0.86
Key Stone	KS	Am	89.4	4.4	2.2	0.8	3.1	0.89
Yallourn	YL	Aus[c)]	66.1	5.3	0.6	0.3	28.0	—[h)]
Morwell	MW	Aus	67.4	5.0	0.5	0.3	26.8	—[h)]
Millmerran	MM	Aus	76.9	6.6	0.5	0.6	15.4	0.60
Wandoan	WD	Aus	78.5	5.9	1.0	0.3	14.2	0.60
Hunter Valley	HV	Aus	80.3	5.0	2.0	0.4	12.2	—[h)]
Goonyella	GN	Aus	81.7	5.4	2.1	0.7	9.9	0.81
Grose Valley	GV	Aus	81.7	5.1	1.4	0.6	11.4	0.82
Liddell	LD	Aus	83.5	5.4	2.1	0.6	8.3	0.76
Newvale	NV	Aus	84.2	5.0	1.4	0.5	8.9	0.82
Charlestone	CH	Aus	84.7	5.1		0.8	8.1	0.82
Moura	MR	Aus	85.6	5.3		0.5	7.1	0.80
Daido-unnan	DU	Chn[d)]	82.7	5.1	1.0	0.7	10.5	0.66
Hai-nan	HN	Chn	84.5	5.2			6.0	0.81
Zao-zhuang	ZZ	Chn	86.9	5.5			5.6	0.80
Sei-kan	ZK	Chn	89.7	4.0	2.5	2.0	1.7	0.81
Rhein Braun	RB	Gem[e)]	65.8	5.5	0.8	0.3	27.6	—[h)]
Leopold	LP	Gem	79.9	5.8	1.4	1.2	11.7	0.75
Zollverein	ZV	Gem	89.6	4.8	1.7	1.3	2.6	0.73
E.B.V.	EA	Gem	89.6	4.1	1.5	1.1	3.7	0.82
Coal Valley	CV	Can[f)]	77.2	4.7		0.2	17.7	0.76
Vicary Creek	VC	Can	87.8	4.7	2.1	0.4	4.9	0.86
Hongay	HG	Viet[g)]	93.7	3.3	1.2	0.4	1.3	0.95

a) Japan. b) America (U.S.A.). c) Australia. d) China (P.R.C.). e) Germany (F.R.D.). f) Canada. g) Vietnam.
h) The f_a-values could not be estimated, since the aromatic C–H band at 3030 cm^{-1} was weak.

which is the ratio of the extinction coefficient of the aromatic C–H stretching band at 3030 cm^{-1} to that of the aliphatic C–H stretching band at 2940 cm^{-1}. This ratio was estimated by the comparison of ^{1}H NMR (Hitachi R-600 ^{1}H FT-NMR) with FT-IR data of the pyridine-soluble parts of some coals.[30] This value is similar to that reported by Painter et al.[28] The f_a-values are summarized in Table 1. The f_a-values thus calculated are compatible with those evaluated by the solid state CP/MAS ^{13}C NMR.[31–33]

Results and Discussion

Hydrogen Contents. Figure 1 shows the ratios of hydrogen atom contents to carbon atom contents (in atomic unit) for all coals listed in Table 1. Dots between 70 and 85 C% show some scatter, but they seem to stud between two lines—upper line and lower line. A tendency that Japanese coals have higher hydrogen contents is confirmed for coal samples adopted in this study. From proximate analysis data, one can also find that Japanese coals contain much volatile matters.[29] These facts have been already pointed out by many investigators as characteristics to Japanese coals;[13,14] The coal samples adopted here also satisfy our purpose in disclosing how such a characteristic appears in the ESR parameters.

Apparent Characteristics of ESR Signals. Figure 2a shows ESR spectra of two kinds of bituminous coals; one is Japanese bituminous coal (Shin-yubari coal 86.7%C) and another is Canadian bituminous coal (Vicary Creek 87.8%C). Shin-yubari coal shows a single symmetric signal (line width (ΔH_{pp})=0.74 mT) which is weak and easily saturated with an increase in a microwave power for evacuated sample. On the other hand, the ESR signal of Vicary Creek coal is composed of two components; one is broad line (ΔH_{pp}=0.53 mT) and another is narrow line

(ΔH_{pp}=0.13 mT). The both lines showed the saturation phenomena at high microwave power. Similar phenomena were reported for American coals.[34] The narrow lines are observed in almost all foreign subbituminous and bituminous coals.[1]

As for the origin of the narrow lines, there have been presented some interpretations. Some investigators attributed to one of the macerals such as inertinite (fusinite) group;[34] other researchers to macromolecular component in coals.[24] In general, the spin concentrations originated from the narrow lines are less than 10—20% of the broad ones, when they were compared before saturations.

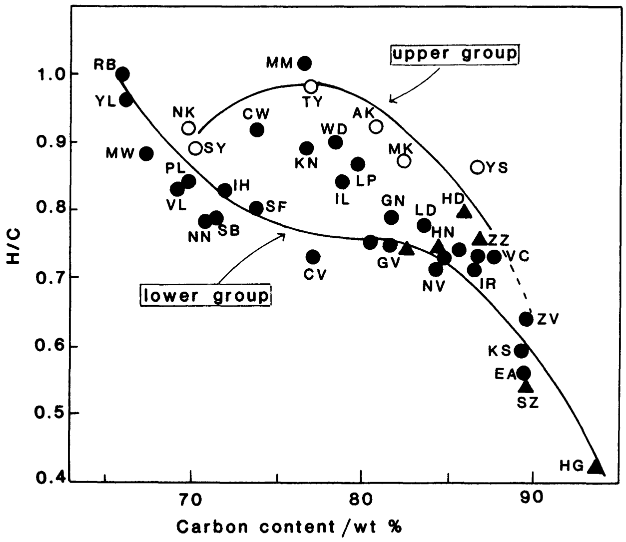

Fig. 1. Hydrogen atom contents (H/C in atomic unit) vs. carbon contents. Abbreviations of coal samples are quoted from Table 1.

Corresponding FT-IR. Figure 2b shows FT-IR spectra of Shin-yubari coal and Vicary Creek coal measured by the diffuse reflectance method. The vibrational band of the aliphatic C-H groups at 2940 cm^{-1} of Shin-yubari coal is stronger than that of Vicary Creek coal. The aromatic C-H groups (at 3030 cm^{-1}) of both coals are approximately equal, but the broad band which increases with wavenumber up to the near-IR region is observed for Vicary Creek. This broad band was not attributed to the scattering of the monitoring light which was frequently observed in the transmittance method using KBr pellet, but to the edge of the real electronic absorption band which is characteristic of the polycondensed aromatic hydrocarbons (the π-π^* transitions) and/or of their layered structures (the intermolecular charge-transfer transitions).[29] Thus, Vicary Creek coal may contain such highly polycondensed aromatic hydrocarbons; the broad band in the near-IR region seems to correspond to the narrow line in the ESR signal. This relation is generalized for other coals.

Spin Concentration. For coal samples showing different saturation phenomena, it is essential to compare the signal intensities before the saturation (at low microwave power). Among the coals investigated in this study, Akabira and Miike coals show the satura-

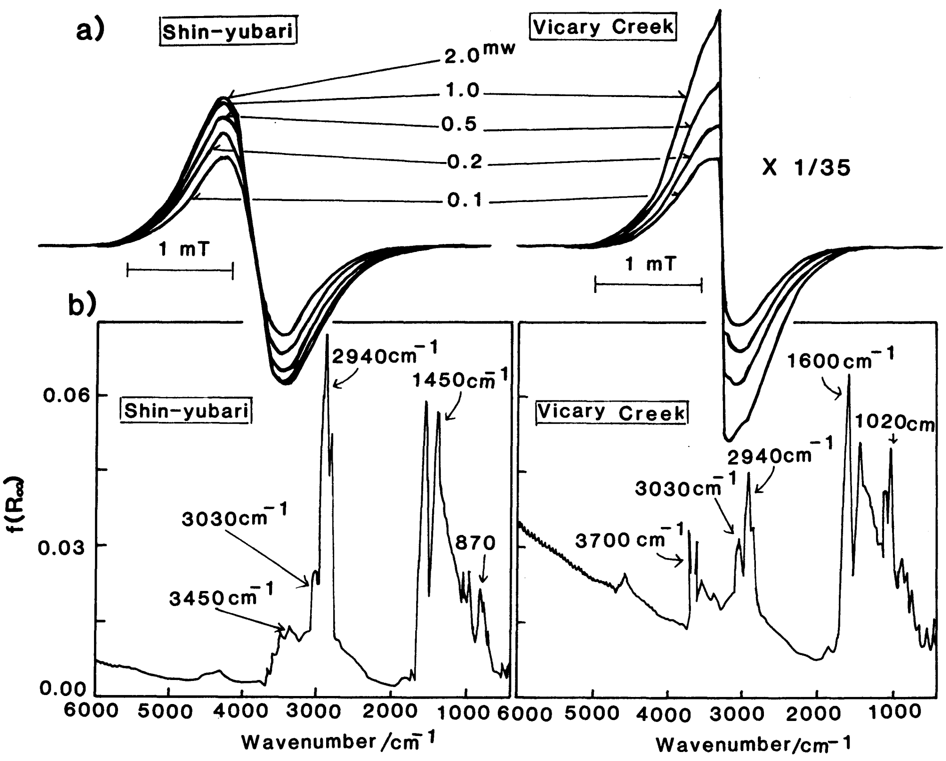

Fig. 2. (a) ESR spectra of Shin-yubari raw coal and Vicary Creek raw coal under vacuum; numbers in figure are microwave powers (JEOL-FE3X). (b) Diffuse reflectance FT-IR spectra of the coals (1 mg sample/150 mg KBr).

Table 2. ESR Parameters for Raw Coals (daf) in Degassed System

Coal	Spin$\times 10^{-19}$/g	ΔH_{pp}/mT	g-Value	T_1/μs
Nakayama	0.13	0.62	2.0035	3
Soyakoishi	0.34	0.70	2.0035	6
Taiheiyo	0.59	0.77	2.0036	9
Akabira	0.69	0.75	2.0030	55
Miike	0.49	0.75	2.0031	59
Shin-yubari	0.71	0.74	2.0028	44
Velva	0.02	0.63	2.0041	8
Peerless	0.11	0.62	2.0039	11
Noonan	1.01	0.65	2.0036	7
South Beulah	0.54	0.70	2.0033	4
Indian Head	0.47	0.63	2.0033	4
Sufco	0.78	0.61	2.0028	—[a]
Colowyo	0.55	0.67	2.0031	4
King	0.50	0.67	2.0030	15
Illinois No. 6	0.94	0.66	2.0026	24
Indian Ridge	2.48	0.54	2.0026	7
Pittston	1.02	0.51	2.0026	—[a]
Key Stone	2.01	0.54	2.0025	7
Yallourn	0.12	0.45	2.0036	8
Morwell	0.09	0.67	2.0036	17
Millmerran	0.50	0.72	2.0031	30
Wandoan	0.87	0.73	2.0033	8
Hunter Valley	0.43	0.55	2.0027	—[a]
Goonyella	1.66	0.60	2.0026	11
Grose Valley	2.29	0.55	2.0027	7
Liddell	0.86	0.68	2.0028	5
Newvale	1.23	0.55	2.0027	—[a]
Charlestone	1.20	0.65	2.0027	5
Moura	1.15	0.65	2.0027	—[a]
Daido-unnan	1.52	0.55	2.0028	—[a]
Hai-nan	0.88	0.50	2.0026	—[a]
Zao-zhuang	0.63	0.60	2.0026	<2
Sei-kan	0.92	0.55	2.0026	—[a]
Rhein Braun	0.24	0.53	2.0038	14
Leopold	0.24	0.50	2.0029	—[a]
Zollverein	1.86	0.56	2.0026	3
E.B.V.	1.70	0.63	2.0026	3
Coal Valley	1.31	0.63	2.0028	3
Vicary Creek	1.62	0.53	2.0027	5
Hongay	2.44	0.38	2.0027	4

a) The T_1-values could not be obtained, since the broad lines could not be completely resolved.

tion at the most low microwave power (1 mW in the cavity of JEOL-FE3X and 5 mW in the cavity of Varian E-4). A strict linear relation holds at lower microwave power than about a half of each maximum value; in the linear range, the spin concentrations were evaluated. They are summarized in Table 2.

In Fig. 3, the spin concentrations thus measured for original coals in evacuated system were plotted against the carbon contents of coal samples. One can see that the spin concentrations increase with an increase in carbon contents; some bituminous coals and anthracite have higher spin concentrations than brown coals and subbituminous coals by a factor of 10—50.[1,2,8,12] This tendency, however, shows a band-type correlation; the spin concentrations of the upper-lying coals are greater than the lower-lying ones by a factor of about 5 times. Around the lower group, we can find Japanese subbituminous and bituminous coals; this is one of characteristics of Japanese coals found in the ESR parameters in this study. The proportionality of the spin concentrations with the f_a-values and the inverse proportionality with the H/C-values (from Table 1) suggest the reasons for the low spin concentrations of Japanese bituminous coals.

For deashed coals, a similar correlation to Fig. 3 was found, although some decreases (1/1.5—1/2) in the spin concentrations by the deashing were observed for some coals. Thus, the band-type correlation shifts toward lower in a small extent. For the reason for the decrease in the spin concentration by deashing, one can consider the instabilization of the spin centers by the protonation of aromatic rings or semiquinone type radicals with the action of mineral acids; another interpretation is the spin-pairing by the removal of inorganic matters.[35]

Similar correlations were found for the aerated sample system; although the narrow ESR lines in foreign coals were broadened by the adsorption of oxygen

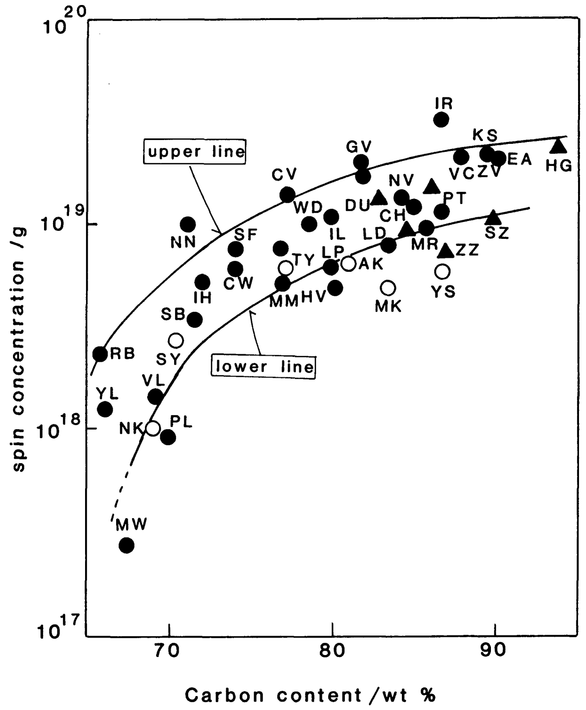

Fig. 3. Dependence of the spin-concentrations for raw coals (measured under vacuum) upon the carbon contents.

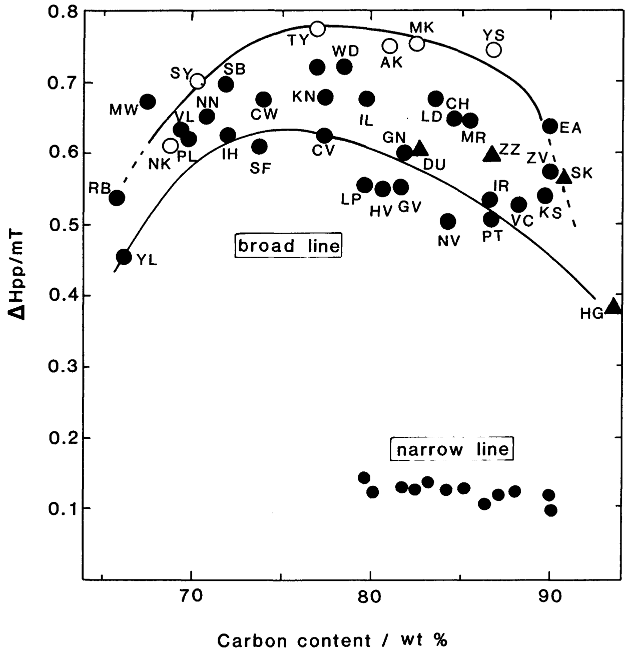

Fig. 4. Line widths (ΔH_{pp}) vs. carbon contents; for coals showing broad and narrow lines, both line widths are shown.

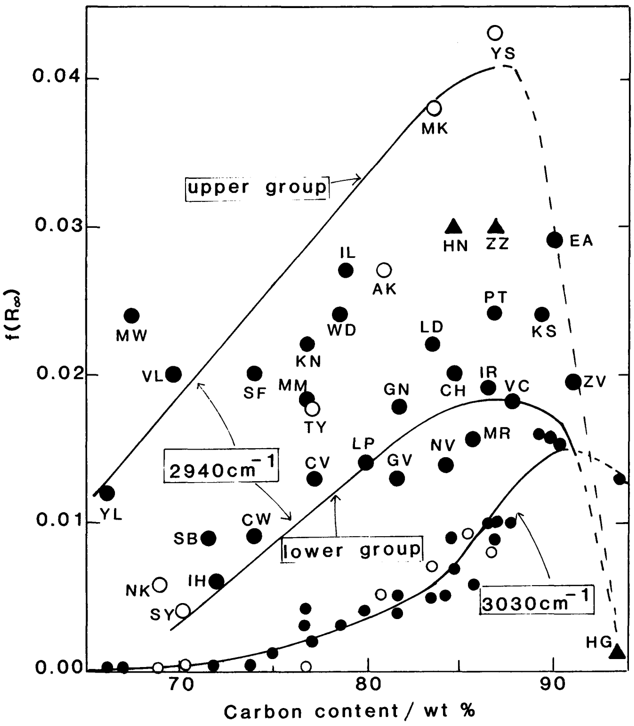

Fig. 5. Intensities ($f(R_\infty)$/1 mg coal) of IR bands at 3030 cm^{-1} (aromatic C-H) and at 2940 cm^{-1} (aliphatic C-H) vs. carbon contents.

molecules, the integrated intensities were not varied in large extent.[36]

Line Widths. In Fig. 4, the line widths of raw coals observed in evacuated system are plotted against the carbon contents; for foreign coals composed of two lines, the both line widths are shown. It can be seen in this figure that the narrow lines appear for the foreign coals having carbon contents greater than about 78% C. Among the broad lines, the lines for Japanese subbituminous and bituminous coals are wider than the foreign ones by about 0.2 mT. This finding was already indicated by Toyoda, Sugawara, and Honda, who suggested on the basis of the H/C-values that the hydrogen atoms around the spin centers broaden the line width by the hyperfine interactions.[12]

The hydrogen atoms can be divided into two groups by the aid of the IR spectra; one is the hydrogen atoms attached directly to the aromatic rings (the bands at 3030 cm^{-1}) and another is aliphatic C-H groups (the band at 2940 cm^{-1}).[28] In the IR spectra of coals having the same carbon content, the intensities of the aromatic C-H bands of the Japanese bituminous coals are similar to those of foreign coals as shown in Fig. 5. On the other hand, a pronounced increase in the intensities of the aliphatic C-H bands is found for Japanese bituminous coals. It is well-known that the hyperfine coupling constants of the hydrogen atoms at the aliphatic groups in the vicinity of the radical center (α- and β-positions) are generally similar to those by the hydrogen atoms attached directly to aromatic rings.[37] Thus, the finding that the line widths of the Japanese bituminous coals are broad is closely related to their rich aliphatic groups. For the narrow ESR lines observed mainly for the foreign coals, one can interpret similarly by the poor aliphatic C-H groups for these components in coals.

g-Values. It is well-known that the g-values of

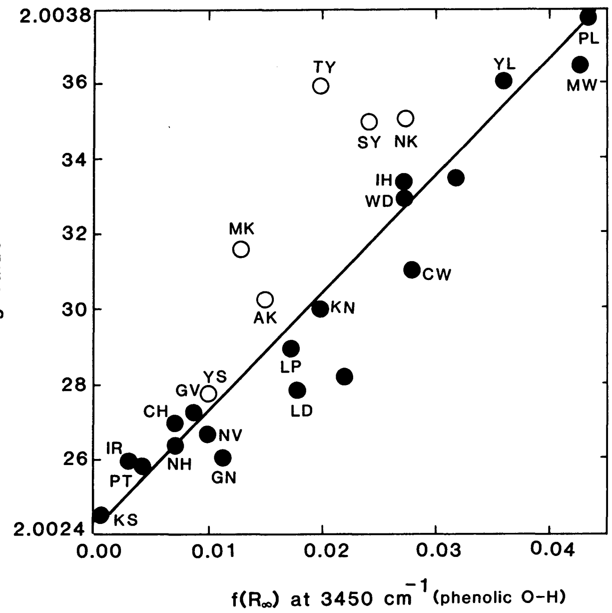

Fig. 6. Plots of g-values vs. $f(R_\infty)$/1 mg coal at 3450 cm^{-1} which is assigned to the phenolic O-H.

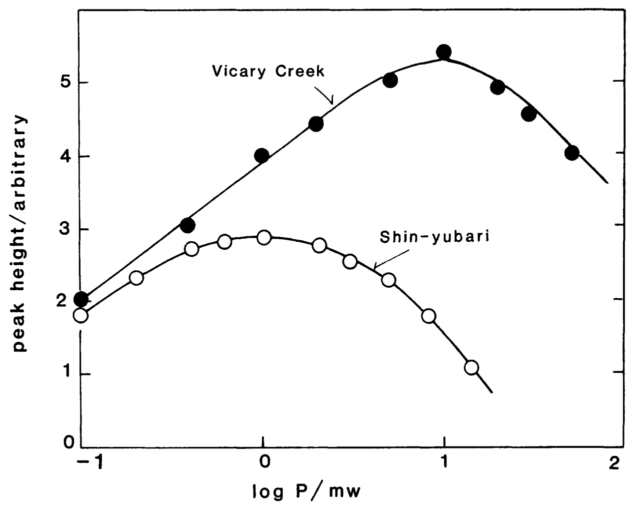

Fig. 7. Dependence of intensities of the ESR signals (peak-peak heights) upon the microwave powers (JEOL-FE3X).

coals decrease with the degree of coalification; the g-values generally increase with the amount of the hetero atoms such as oxygen, sulfur, and nitrogen atoms,[2,34] in which the oxygen content mainly determines the g-values. It would be anticipated that the oxygen atoms near the spin center are mainly the phenolic oxygen. In order to examine this assumption, we show the correlation between the g-values and the amount of the phenolic O-H which can be easily evaluated from the IR band at ca. 3450 cm^{-1}.[28] In Fig. 6, a good linear proportionality can be seen, suggesting that there are the phenolic O-H groups in the vicinity of the spin center. Although the importance of the nitrogen atom in the exinite groups was recently suggested,[34] their roles are not clear in our study because the nitrogen and sulfur atoms are contained only a small amount in coals (Table 1).

Spin-Lattice Relaxation Times. Spin-lattice relaxation times for various coals could be estimated as relative values by the continuous-wave saturation method.[24] The plots of peak-peak heights of the signals against the microwave powers observed for the samples in vacuum system are shown in Fig. 7. The Japanese bituminous coals such as Shin-yubari coal show the saturation at lower microwave power, whereas the foreign bituminous coals show the saturation at high microwave power.[38] The narrow lines show the saturation at the higher microwave power. When one ESR line is composed of both homogeneous and inhomogeneous components, the upward curvature in Fig. 7 deviated from the symmetric curve with respect to the maximum; in such cases, some corrections are necessary to estimate the maximum microwave power (P_{mx}) according to Castner's method.[27]

The T_1 values can be estimated from the following equation as relative values;

$$T_{1x} = T_{1s}(\Delta H_x/\Delta H_s)(P_{ms}/P_{mx}) \quad (1)$$

where, T_{1x} and T_{1s} refer to the spin-lattice relaxation times for unknown and standard samples, respectively; ΔH refers to the line width.[34] By adopting the T_1 values for Miike coals reported by Toyoda, Sugawara, and Honda (59 μs),[12] the relative values can be converted into the absolute values.

Table 3. Observed T_1-Values for Some Coals and Pitches. Changes with Degree of Vacuum and Densities, and Effects by Alkylation and Acetylation

Sample	Treatment	T_1/μs
Shin-yubari	4.0 Pa	70
	0.67 Pa	69
	0.0001 Pa	67
	In air	4
Zao-zhuang	Raw coal	<2
	Soluble part (33 wt%)	140
Gilsonit pitch	85.4% C (f_a=0.33)	80
Ashiland pitch	92.8% C (f_a=0.43)	490
Taiheiyo	Raw coal	9
	Acetylation	29
	Alkylation	55
Moura	Raw coal	<2
	d=1.28	12
	d=1.30	12
	d=1.33	3
	d=1.38	<2

By the comparison of the T_1-values observed in low vacuum (10^{-1} Pa during a few hours) with those in high vacuum (10^{-4} Pa during a week), any appreciable difference in the T_1-values was not observable (Table 3). By the introduction of air into the sample, the T_1-value decreases considerably.[6] These findings indicate that the oxygen effect can be easily eliminated even by low evacuation. The T_1-values summarized in Table 2 were observed for the considerably high vacuum system (about 10^{-2} Pa).

The T_1-values thus estimated are plotted against the carbon contents as shown in Fig. 8. For the low rank coals from 65% C to about 77% C, a monotonous decrease in the T_1-values with an increase in the carbon contents was observed. In the range of carbon contents greater than 77% C, coals can be divided into two groups; upper group contains Japanese bituminous coals and some foreign coals such as Millmerran coal. In the lower group, some foreign bituminous and subbituminous coals belong.

Duber and Wieckowski estimated the T_1- and T_2-values of the broad lines and narrow lines of Polish coals and observed that the T_1-values of the components showing the broad lines were longer than those of the narrow lines. This was interpreted by them on the basis of the two-phonon Raman process which suggests that the T_1-values become short in a phase with larger regions of crystalline lattice ordering strongly bounded to one another by covalent bonds.[24] Thus, it would be expected that the macromolecules with many cross linkages show shorter T_1-values than the macromolecules with less cross linkages. As shown in Table 3, we observed for Zao-zhuang (Chinese bituminous coal) that the soluble part has longer T_1-values than the corresponding original coal. This finding is compatible with the observation by Kevan et al. that the T_1-value of a SRC (solvent refined coal) is longer than the original coal.[39,40] We observed that the petroleum pitches show the long T_1-values (Table 3); this observation is in agreement with Yen's observation even though they measured in aerated system.[41] From these observations, it can be confirmed that the components strongly connected with cross linkages have short T_1-values than the components with less cross linkages or small molecules. Dependence of the T_1-value upon the degree of polymerization was indicated for polyacetylenes.[11]

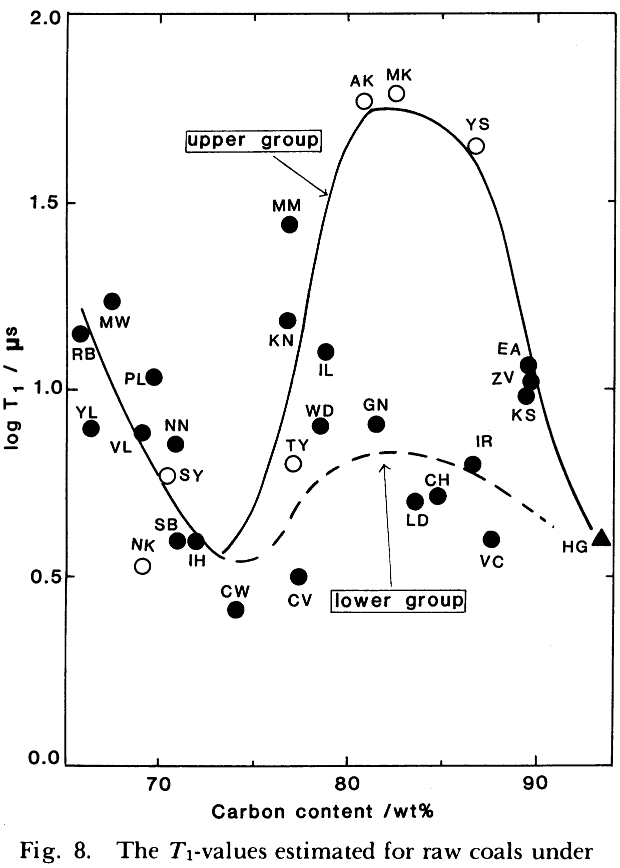

Fig. 8. The T_1-values estimated for raw coals under vacuum vs. carbon contents.

By acetylation of Taiheiyo coal which has rich phenolic O–H groups (Fig. 6), the T_1-values become longer than the original coal (Table 3). This suggests an importance of the interaction via the hydrogen bonds which connect the molecular chains. Alkylation which may occur at the aromatic rings exhibited a strong effect on the T_1-value (Table 3).

It was recently pointed out that the inertinite-rich groups exhibit uneasy saturation.[35] In this connection, we observed the decrease in T_1-values with the increase in the density of Moura coal as shown in Table 3. The inertinite components, in general, have greater f_a-values than the exnite and vitrinite components; thus, an increase in the degree of aromatization tends to decrease the T_1-values.

From these observations, we can interpret Fig. 8; a decrease in the T_1 values from 65 to 77% C may be related to the increase in the cross linkages between the polymer chains with condensation accompanying elimination of small molecules such as water and carbon dioxide as was suggested by van Kreveren's coal band.[42] In the region greater than 77% C, a large splitting was seen; the upper group contains the Japanese coals and some foreign coals which are belonging to the upper group in the H/C-plot (Fig. 1), in the line-width plot (Fig. 3), and in the aliphatic group-plot (Fig. 5), whereas they are to the lower group in the spin-concentration plot (Fig. 4). In the upper group of Fig. 8, the increase in the T_1-values from 77 to 85% C may be related to the increase in the aliphatic groups, since a similar change was observed in Fig. 5. Decrease in the cross linkages or decrease in the hydrogen bonds would be also expected to occur in this region. Decrease in the T_1-values from 83 to 93% C may be related to the increase in polycondensation of aromatic rings.

As origins of the big difference in the T_1-values between the upper and lower groups, many factors should be taken into the consideration. One is originated from the difference in the f_a-values; the coals belonging to the lower group in Fig. 8 have larger f_a-values than the lower one by a factor of ca. 0.1 (Table 1) which is considerably large difference. A large difference in the amounts of the aliphatic groups may also strongly influence the T_1-values as the result of alkylation suggested.

For deashed coals, a similar figure to raw coals (Fig. 8) was obtained excepting slightly longer T_1-values;

this may suggest that flexibility increase with a loss of the inorganic matters which might connect the coal segments by the coordinations. For the higher degree coals, inorganic matters may hinder the approach of the aromatic rings; i.e., they may destroy the crystalline phase.

It can be pointed out that a similar correlation to the upper group was reported by Yokono and Sanada in the ^1H nuclear spin-lattice relaxation times.[4] The molecular weights between bridges in the crosslinking macromolecules in coals, which were estimated from the swelling measurements in solvents by Sanada and Honda, may also support the longer T_1-values of the coals in the range of 80—86 C%.[43] One of our purposes is to find some relations between the ESR parameters (especially the T_1-value) and the solubility of coals, since it would be anticipated that the coals showing high solubility have less cross linkages or low molecular weights. In pyridine (Soxhlet extraction)[44—46] or in a mixed solvent (pyridine-CS_2 extraction),[47] a tendency that the Japanese bituminous coals are considerably soluble was found. Although such tendency seems to reflect on the T_1-values (Fig. 8), the maximum solubility in the plot against the carbon contents exists at about 86% C; a slight shift from the peak in Fig. 8 was seen. This may be partly attributed to our finding that the T_1-values are influenced not only by the real molecular weights but also by the molecular weights between the cross linkages. Furthermore, physical properties such as maximum fluidity which suggest the high flexibility of Japanese bituminous coals may be related with their observed long T_1-values.[13,14]

Summary

The ESR parameters of various coals were investigated and we found some characteristics of Japanese bituminous coals especially in the electron spin-lattice relaxation times (T_1). These ESR parameters which give a rather physical information were discussed with an aid of the IR data which afford a useful chemical information. In this study, it can be emphasized that the electron spin-lattice relaxation phenomena can be potentially used to estimate the molecular interaction including dynamic behavior of the molecules contained in the carbonized materials. We need further study for the electron spin-relaxation phenomena of the compounds which are appropriate as models for coals.

We thank Professor Masamoto Iwaizumi of Tohoku University for his useful suggestions for the analysis and interpretation of the T_1-values. We are also grateful to Professor Minoru Matsuda of Tohoku University and Dr. Takashi Iwasaki of Tohoku Technical Research Institute for their kindness for the use of ESR spectrometers. Informative discussions with Professors Yoshiyuki Nishiyama, Akira Tomita, and Yasuo Ohtsuka of Tohoku University are gratefully appreciated. Coal samples and their analytical data were kindly presented by Coal Chemistry Laboratory in our Institute.

References

1) H. L. Retcofsky, "Coal Science," ed by M. L. Gorbaty, J. W. Larsen, and I. Wender, Academic Press, New York (1982), Vol. 1, Chap. 3.

2) L. Petrakis and D. W. Grandy, "Free Radicals in Coals and Synthetic Fuels," in "Coal Science and Technology," Elsevier, Amsterdam (1983), Vol. 5.

3) K. Fujimoto, T. Nishi, and R. Kado, *Polym. J.*, **3**, 448 (1972).

4) T. Yokono and Y. Sanada, *Fuel*, **57**, 334 (1978).

5) J. Uebersfeld and E. Erb., *C. R. Acad. Sci., Paris*, **243**, 2043 (1956).

6) N. S. Garf'yanov and B. M. Kozyrev, *Zh. Eksper. Teor. Fis.*, **30**, 1160 (1956).

7) J. Smidt, *Nature*, **181**, 176 (1958).

8) J. Smidt and D. W. van Krevelen, *Fuel*, **38**, 355 (1959).

9) R. C. Pastor and R. H. Hoskins, *J. Chem. Phys.*, **32**, 264 (1959).

10) A. T. Bullock and L. H. Sutcliffe, *Trans. Faraday Soc.*, **60**, 2112 (1964).

11) J. C. W. Chien and M. A. Schen, *Macromolecules*, **19**, 1042 (1986).

12) S. Toyoda, S. Sugawara, and H. Honda, *Nenryo Kyokai Shi*, **45**, 876 (1966).

13) H. Honda, *Nenryo Kyokai Shi*, **37**, 635 (1958).

14) H. Sugimura, Y. Oosawa, M. Hatami, H. Sato, H. Sugawara, and H. Honda, *Nenryo Kyokai Shi*, **45**, 199 (1966).

15) K. Ouchi, S. Ohno, M. Makabe, and H. Itoh, *Fuel*, **64**, 1391 (1985).

16) M. Iino and M. Matsuda, *Fuel*, **62**, 744 (1983).

17) H. Oouchi, S. Shioya, and J. Souma, *Kogyo Kagaku Zasshi*, **71**, 1192 (1968).

18) S. W. Dack, M. D. Hobday, T. D. Smith, and J. R. Pilbrow, *Fuel*, **62**, 1510 (1983).

19) I. B. Goldberg, T. M. Mckinney, K. E. Chung, and R. Galli, *Fuel*, **65**, 241 (1986).

20) A. Oya, T. Fukatsu, S. Otani, and H. Marsh, *Fuel*, **62**, 502 (1983).

21) S. Parkash, D. Carson, and B. Ignasiak, *Fuel*, **62**, 629 (1983).

22) D. K. Sharman, M. K. Srkar, and Z. B. Mirza, *Fuel*, **64**, 449 (1985).

23) K. M. Patel, V. I. Stenberg, R. J. Baltisberger, N. F. Woolsey, and K. J. Klabunde, *Fuel*, **59**, 449 (1980).

24) S. Duber and A. B. Wieckowski, *Fuel*, **61**, 433 (1982).

25) R. S. Aliger, "Electron Paramagnetic Resonance: Techniques and Applications," Interscience, New York (1968), Chap. 2.

26) C. P. Poole, "Relaxation in Magnetic Resonance," Academic Press, New York (1971).

27) T. G. Castner, Jr., *Phys. Rev.* **115**, 1506 (1959).

28) P. Painter, M. Starsinic, and M. Coleman, "Determination of Functional Groups in Coal by Fourier Transform Interferometry," In "Fourier Transform Infrared Spectra; Chemical Application," Academic Press., New York (1985), Vol. 4.

29) O. Ito, H. Seki, and M. Iino, *Fuel,* in press.

30) J. K. Brown, *J. Chem. Soc.,* **1955**, 744.

31) M. J. Sullivan and G. E. Maciel, *Anal. Chem.* **54**, 1606 (1982).

32) M. A. Wilson, R. J. Karas, L. B. Alemany, W. R. Woolfenden, and D. M. Grant, *Anal. Chem.* **56**, 993 (1984).

33) T. Yoshida, K. Tokuhashi, and M. Maekawa, *Fuel,* **64**, 891 (1985).

34) B. G. Silbernagel, L. A. Gebhard, G. R. Dyrkacz, and C. A. A. Bloomquist, *Fuel,* **65**, 558 (1986).

35) G. Srinivasa and M. S. Seehra, *Fuel,* **62**, 792 (1983).

36) L. Petrakis and D. W. Grandy, *Anal. Chem.,* **50**, 303 (1978).

37) J. R. Bolton, "Radical Ions," ed by E. T. Kaiser and L. Kevan, Interscience Publishers, New York (1968), Chap. 1.

38) D. C. Doetschman and D. M. Mustafi, *Fuel,* **65**, 684 (1986).

39) S. Schlick, P. A. Narayana, and L. Kevan, *J. Am. Chem. Soc.,* **100**, 3322 (1978).

40) S. Schlick, M. Narayana, and L. Kevan, *Fuel,* **62**, 1250 (1983).

41) T. F. Yen and J. G. Erdman, *Anal. Chem.,* **34**, 694 (1962).

42) D. W. van Krevelen, "Coal," Elsevier, Amsterdam (1961).

43) Y. Sanada and H. Honda, *Fuel,* **45**, 295 (1966).

44) W. F. K. Wynne-Jones, H. E. B. Blayden, and F. Shaw, *Brennstoff Chem.,* **33**, 201 (1952).

45) H. N. M. Dormans and D. W. van Krevelen, *Fuel,* **39**, 273 (1960).

46) Y. Oosawa, I. Ishiei, T. Kakuta, and M. Fujishiro, *Kogyo Kagaku Zasshi,* **73**, 2212 (1970).

47) M. Iino and M. Matsuda, unpublished data.