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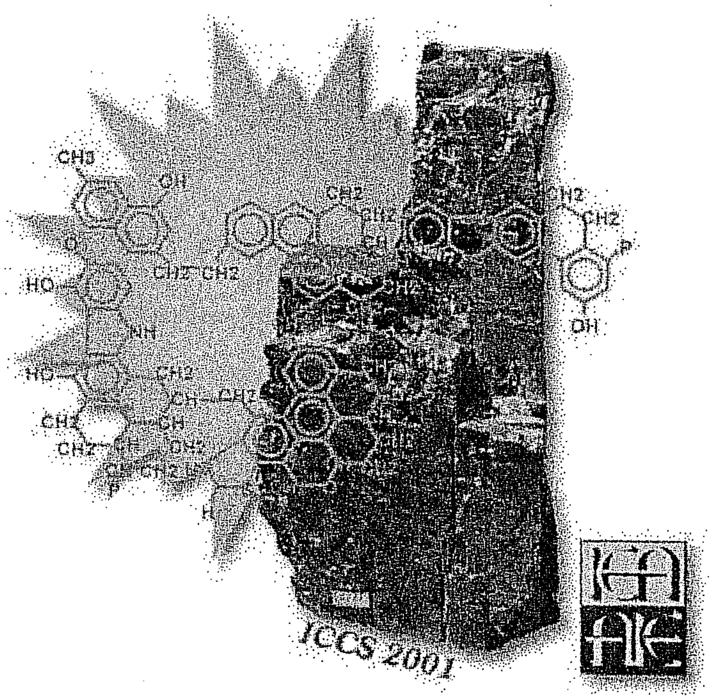

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Laser-Raman microscope studies on coal characterization and char burnout

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ABSTRACT

To investigate coal quality impacts on char burnout, carbon structure in raw coal was measured by Laser-Raman microscope (LRM) for 40 coals. LRM is a very useful technique for characterizing heterogeneous carbons, however, little is known about LRM data of coals so far.

We found useful parameters to characterize coal carbon structure. The ratio of the Raman G-band (1580cm^{-1}) intensity, G, and the background intensity at G-band, F, is effective parameter to characterize coal rank and distribution of heterogeneous carbons in coal. G/F was closely related to the fraction of total aromatic carbons, which was measured by carbon-13 NMR. Generally, low rank coals have low G/F value and narrow distribution of G/F.

And also, this paper describes relationships between G/F and char burnout, which is obtained by drop tube furnace experiments. It is found that G/F has good correlations with char combustion rate.

Keywords: Raman, Char burnout, Coal characterization

1. INTRODUCTION

In Japan, most of the steaming coal has been imported from various coal producing countries such as Australia, United States, China, Indonesia, South Africa, Russia and Canada. Since it is required to use a wide variety of coals, evaluation of acceptability of potential imported coals, more than 100 different coals, is one of the most critical issues for Japanese coal users.

Char burnout are the most important controlling factors to determine the acceptability of coals in combustion because it determines boiler efficiency. The char combustion rates are usually controlled by surface chemical reaction at low temperatures, oxygen pore diffusion at moderate temperatures and oxygen bulk diffusion at high temperatures. Chemical structure of residual carbons seems to play a pronounced role in the char conversion because the temperature of the final stage of char conversion processes is low.

The objective of this study is to examine carefully the effects of variation of carbon structures on char burnout and find out useful parameters from LRM measurements to evaluate carbon burnout of various coals in pulverized coal combustion.

2. EXPERIMENTAL

2.1 Coal samples

Basic information on 40 coals used in this study is listed in Table 1. Those coals are prepared as standard research coals for BRAIN-C project (current national coal research programs in Japan) by CCUJ. These programs provide coal characterization data and gasification reaction data.

2.2 Laser Raman Microscope

Some methods (e.g. X-ray diffraction, ^{13}C-NMR, FT-IR) have been used to characterize carbon structure. Especially, Carbon-13 NMR spectroscopy is a powerful method for identifying carbon structural parameters in coal. However, NMR requires high instruments cost and long analysis time. LRM can promptly obtain carbon structural parameter by a low cost.

The laser Raman spectra were measured by using Renishaw system 2000. The polished pulverized coal sample was placed under the microscope. The emission of an argon ion laser at 514.5nm was used as exciting radiation. Low laser power (0.65mW at sample surface) and laser diameter of 0.05mm were used so that coal particles should not burn by sample-heating effect. Raman spectra from more than 50 different coal particles among the same coal sample were measured.

2.3 Drop tube furnace

A drop tube furnace (42mm diameter and 1150mm length) was employed to collect char burnout data. The pulverized coal feed rates were controlled at 5g/hr and oxygen contents of flue gas were kept at 3.0% at 1500C. This DTF has nine sampling ports, SP1 to SP9, every 125mm along with furnace wall for gas and char sampling during combustion. Collected some char samples were analyzed carbon content, and char combustion rate (g/cm^{2}s) was calculated. Combustion tests were performed for 15 coal samples. (See Table.1)

3. RESULTS

3.1 Characterization of carbon structure by LRM

Figure 1 shows Raman spectra of coal SS001. As reported in several previous works

Table 1: Fuel analysis, the fraction of total aromatic carbons by NMR, carbon structural parameters by LRM, and char combustion rate by DTF at 1500C.

		Proxi. Analysis (%,ad)			Ultimate Analysis (%, daf)					13C-NMR	LRM Anlysis		Rc by DTF
Coal #	Mine	Mois.	Ash	VM	C	H	N	O	S	fa	G/F	CV*	g/cm2s
SS001	AUS	3.1	14.6	27.7	84.07	4.91	1.79	8.98	0.26	0.83	0.61	1.02	2.5
SS002	AUS	7.0	13.7	38.4	80.30	6.20	1.58	11.32	0.60	0.68	0.22	0.29	4.0
SS003	AUS	7.4	7.7	27.4	82.32	4.43	1.90	11.08	0.27	0.80	0.58	0.72	3.1
SS004	CHN	8.8	8.5	28.3	82.56	4.57	0.92	11.11	0.83	0.81	0.69	0.89	2.3
SS005	JPN	5.6	11.5	43.9	78.40	6.28	1.15	14.06	0.11	0.62	0.18	0.35	5.6
SS006	AUS	3.6	11.4	35.4	82.37	5.53	1.83	9.75	0.52	0.77	0.31	1.31	3.9
SS007	AUS	2.8	14.6	32.4	83.53	5.30	2.03	8.41	0.72	0.76	0.40	0.96	3.2
SS008	AUS	3.2	11.8	32.1	83.45	5.32	1.88	8.89	0.45	0.77	0.51	1.15	3.6
SS009	IDN	11.5	4.6	40.8	74.78	5.26	1.29	18.42	0.25	0.68	0.25	0.53	4.0
SS010	IDN	4.7	5.3	40.2	79.55	5.64	1.75	12.35	0.71	0.69	0.26	0.34	4.1
SS011	IDN	13.2	1.5	40.5	73.96	5.06	1.16	19.80	0.02	0.68	0.23	0.59	-
SS012	IDN	19.4	3.2	37.5	73.19	5.18	1.78	19.07	0.78	0.68	0.34	1.47	-
SS013	AUS	2.9	13.8	29.6	83.54	4.90	1.77	9.46	0.34	0.81	0.58	1.01	-
SS014	AUS	3.8	13.9	31.4	81.91	4.99	2.09	10.87	0.14	0.77	0.47	1.09	-
SS015	COL	3.9	14.1	31.4	81.66	4.78	1.89	11.56	0.10	0.76	0.51	1.24	-
SS016	USA	4.6	8.9	42.6	79.97	5.66	1.47	12.40	0.51	0.65	0.26	0.55	-
SS017	IDN	4.2	11.0	42.2	78.66	5.82	1.32	13.31	0.89	0.64	0.21	0.23	-
SS018	CHN	3.1	9.0	34.4	82.37	5.01	1.56	10.61	0.44	0.75	0.47	0.95	-
SS019	ZAF	3.9	13.8	27.1	83.43	4.36	1.98	9.77	0.46	0.84	1.00	0.94	-
SS020	ZAF	3.0	13.2	31.6	80.50	4.85	2.09	11.84	0.72	0.81	0.48	0.92	-
SS021	ZAF	2.7	14.4	25.2	83.11	4.46	2.02	10.06	0.35	-	0.95	0.82	-
SS022	ZAF	19.4	3.2	37.5	73.19	5.18	1.78	19.07	0.78	-	0.68	0.84	-
SS023	USA	2.9	13.8	29.6	83.54	4.90	1.77	9.46	0.34	0.68	0.24	0.22	-
SS024	USA	3.8	13.9	31.4	81.91	4.99	2.09	10.87	0.14	-	0.34	0.48	-
SS025	USA	6.2	7.7	37.4	78.51	5.54	1.64	13.70	0.61	-	0.31	0.24	-
SS026	USA	9.4	13.9	35.9	77.61	5.44	1.32	15.23	0.40	-	0.27	0.43	-
SS027	CHN	4.1	8.9	29.2	81.25	4.58	1.05	12.57	0.55	-	0.76	1.21	-
SS028	AUS	5.4	7.8	27.5	82.33	4.53	1.87	11.00	0.27	-	0.56	0.78	3.5
SS029	JPN	6.0	11.0	43.7	76.57	6.18	1.22	15.94	0.09	-	0.24	0.32	-
SS030	JPN	2.0	19.4	37.8	81.22	6.20	1.27	9.06	2.25	0.71	0.22	0.14	4.4
SS031	CAN	6.6	11.2	32.4	78.09	4.95	1.05	15.78	0.15	-	0.51	2.15	3.2
SS032	AUS	19.4	3.2	37.5	73.19	5.18	1.78	19.07	0.78	-	0.48	1.11	3.2
SS033	IDN	2.9	13.8	29.6	83.54	4.90	1.77	9.46	0.34	0.66	0.26	0.46	-
SS034	IDN	3.8	13.9	31.4	81.91	4.99	2.09	10.87	0.14	-	0.22	0.27	-
SS035	AUS	1.2	14.9	19.3	88.34	4.48	1.53	5.15	0.50	-	1.39	1.03	-
SS036	AUS	1.1	22.1	19.7	87.62	4.70	1.72	5.50	0.46	0.87	0.92	1.14	1.7
SS037	CHN	1.4	15.8	9.2	91.21	3.47	1.33	3.66	0.33	0.96	5.32	0.56	-
SS038	COL	5.2	0.9	37.8	82.00	5.30	1.66	10.56	0.48	-	0.35	1.86	-
SS039	AUS	8.2	12.5	35.4	76.61	5.21	1.56	16.26	0.36	-	0.38	0.57	-
SS040	IDN	5.4	7.0	44.0	78.47	5.91	1.30	13.58	0.74	-	0.22	0.23	-
Max		19.4	22.1	44.0	91.21	6.28	2.09	19.80	2.25	0.96	5.32	2.15	5.6
Min.		1.1	0.9	9.2	73.19	3.47	0.92	3.66	0.02	0.62	0.18	0.14	1.7
Ave.		5.9	10.9	33.2	80.77	5.13	1.63	12.00	0.48	0.75	0.58	0.79	3.5

*CV: coefficient of variation

[1-4], presence of graphite band (G-band) at 1580 cm^{-1} and disordered band (D-band) at 1380 cm^{-1} are recognized. Although the degree of graphitization in many carbon materials is given by D/G, D/G is not suitable index for coal characterization so that the difference of D/G for 40 coals used in this study is small. To characterize coal carbon structure, some quantitative parameters were examined. As the results, it is found that G/F is good parameter for coal characterization. F is the background intensity that indicates fluorescence level of coal particles by argon laser exciting.

Figure 2 shows relation between G/F and fa obtained by ^{13}C-NMR. It is seemed that G/F intensity that indicates fluorescence level of coal particles by argon laser exciting. Figure 2 shows relation between G/F and fa obtained by ^{13}C-NMR. It is seemed that G/F indicates accurately coal carbon structure.

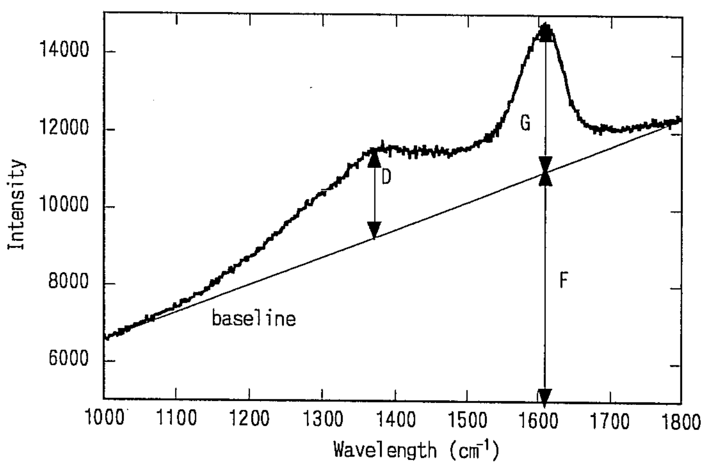

Fig.1 LRM spectrum and suggested LRM parameters

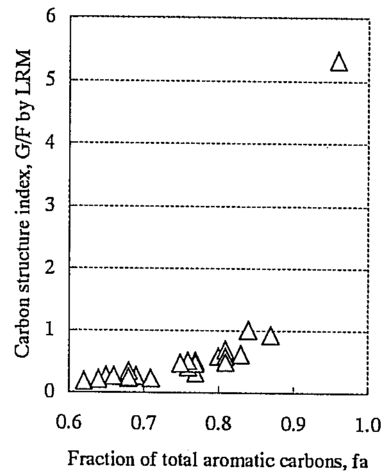

Fig.2 Relation between fa and G/F

3.2 Relation between LRM parameters and combustion rate

Carbon burn out of coal is generally estimated by fuel ratios (fixed carbon/volatile matter). However, there is no good relationship between fuel ratios and unburned carbon, because fuel ratios cannot explain char reactivities. We think that carbon burnout largely depends on original coal carbon structure. As shown in Figure 3, combustion rate obtained by DTF has good correlation with G/F.

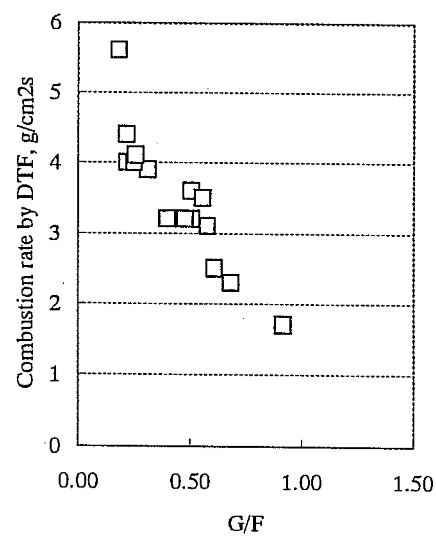

Fig.3 Correlation with G/F

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