Bull. Chem. Soc. Jpn., ***64****, 1669—1675 (1991)*

Increase of Solvent-Soluble Products of Coal by Repeated Butylation with Zinc and Butyl Iodide under Mild Conditions

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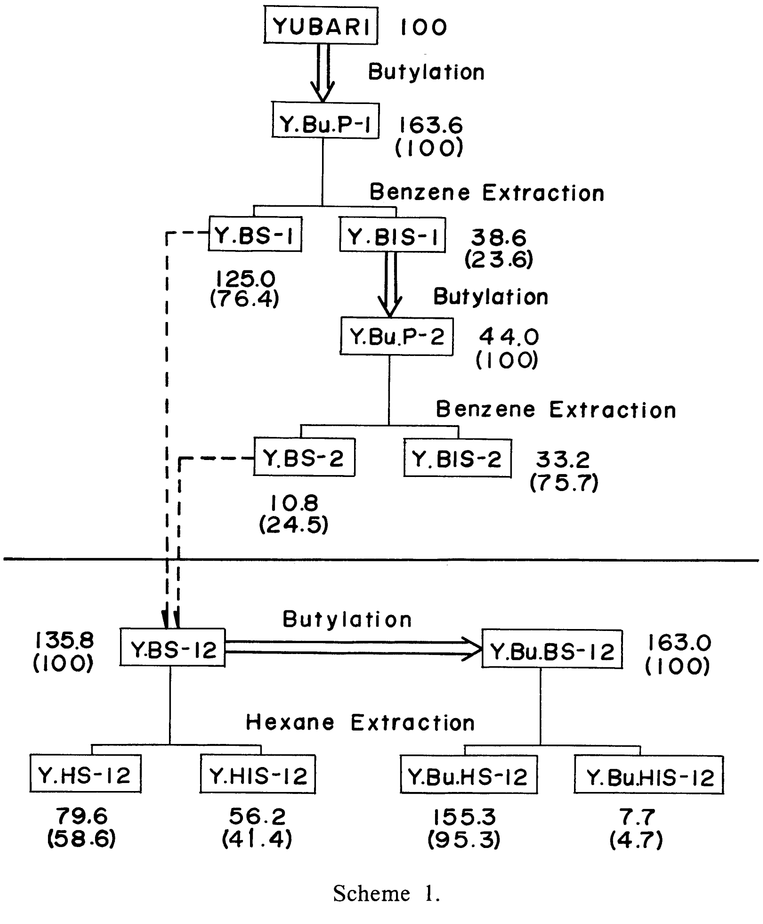
(Received November 29, 1990)

Yubari and Taiheiyo coals were repeatedly butylated with zinc metal powder and butyl iodide under mild conditions. After the benzene-soluble products (BS) from each reaction were combined the mixture was further butylated. The BS and its butylation products (Bu.BS) were fractionated by gel permeation chromatography. At each reaction step, BS with a similar structural character but different degrees of polymerization were solubilized for Taiheiyo coal; for Yubari coal BS with similar characteristics were solubilized. A large portion of these Bu.BS from both coals were solubilized in hexane. The molecular weight of BS decreased after butylation. These results suggest that this procedure brings about depolymerization as well as the introduction of butyl groups, while enhancing solubilization.

We previously developed a new alkylation procedure for coal solubilization,[1] which can effectively convert coal to benzene-soluble products under mild conditions (at 130 °C for 3—5 h under atmospheric pressure). The solvent-solubility of products is very high. Also, because of the ease of treating by the use of zinc metal powder and butyl iodide, this is a simple and safe method for coal solubilization; it is also suitable for examining coal structures.

In a previous paper we showed that the solubilization of low-rank coal in benzene is not increased by this method to a large extent,[1] and that the cleavage of the aliphatic linkage in coal structures increased with increasing number of alkyl groups attached to the aromatic rings.[2] In studies of coal solubilization under mild conditions, repeated reactions usually promoted bond cleavages.[3,4] It is thus expected that repeated butylation causes a high degree of coal solubilization; it is therefore of interest to examine changes in the degree of polymerization and that in the structural characteristics of coal products upon butylation.

The purpose of this study was to determine the solubility of reaction products obtained by repeated butylation, and to examine changes in their structural

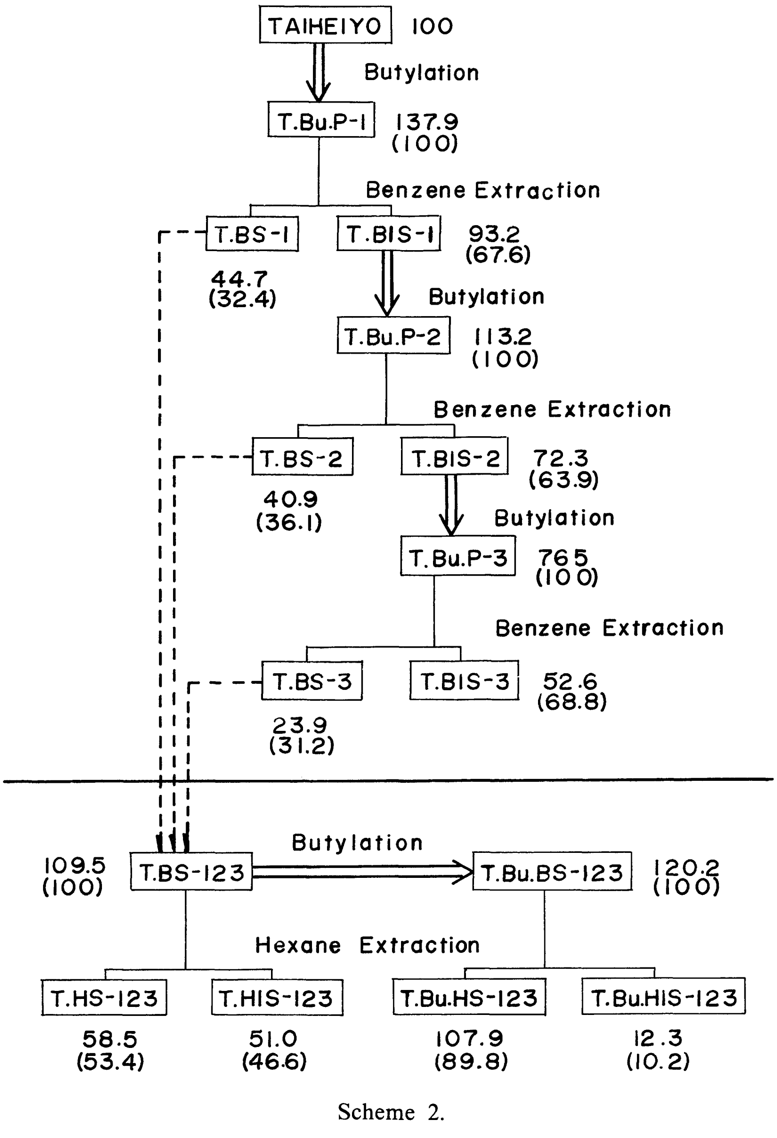


Scheme 1.

features.

Experimental

Yubari (C, 83.4%; H, 6.1%; N, 2.0%; Odiff, 8.5%; Ash, 5.1%) and Taiheiyo coals (C, 75.4%; H, 6.1%; N, 1.4%; Odiff, 17.1%; Ash, 8.3%) were used. The reaction was carried out in a similar way to that of a previous study:[1] 10 g of a coal sample, 40 g of zinc metal powder, and 100 ml of butyl iodide were placed in a 300 ml three-neck flask, while being agitated, the mixture was heated at 130 °C for 3.5—5 h under nitrogen in an oil bath. Then, unreacted butyl iodide was removed by evaporation and the mixture was washed with dilute hydrochloric acid to remove any unreacted zinc metal. The products were exhaustively extracted with hot benzene. The benzene-insoluble products (BIS) were successively butylated, twice for Yubari coal, and three times for Taiheiyo coal. The butylated products (Bu.P) were extracted with benzene, as described above. The benzene-soluble products (BS) from each reaction were combined, and the combined products further butylated. The BS and butylated BS (Bu.BS) were fractionated into hexane-soluble (HS) and hexane-insoluble products (HIS) by extraction with hexane. Details are given in Schemes 1 and 2. The BS and Bu.BS were separated into 8 and 7 fractions, respectively, by gel permeation chromatography (GPC), using packed columns of Bio-Beads S-X4 and S-X8 (25.4 mm i.d.×100 cm long); benzene was used as the eluent (cut volume, 6 ml). The number-average molecular weight (M_w) of each fraction was determined by VPO at 4—10 g kg^{-1} with a CORONA 114, using benzene as the solvent, and extrapolated to infinite dilution. Since most of the samples contained a small amount of iodine, the content was determined by the Schoeniger's method[5] to correct for analytical data. The FT-IR spectra were measured by a diffuse reflectance procedure using a JASCO FT/IR-3 spectrometer. The samples were ground with KBr prior to measurement. The structural parameters were estimated according to equations proposed by Brown and Ladner[6] and modified by Yokoyama et al.[7] The concerned structural parameters are as follows: The ratio of the number of aromatic carbons to the total number of carbons, f_a; the ratio of the number of peripheral aromatic carbons to total number of aromatic carbons (degree of aromatic ring condensation), H_{au}/C_a; the degree of aromatic ring substitution of the aliphatic chain, σ_{al}; the degree of aromatic



Scheme 2.

ring substitution of groups other than the aliphatic chain, σ_o; and the length of the aliphatic chain, n (H_o/H_α+1). ^{1}H and ^{13}NMR spectra were taken on a JEOL JNM-FX 90Q spectrometer. Samples for measurements of the ^{13}C NMR spectra were prepared by dissolving approximately 100 mg of the coal products in 0.2—0.3 ml of $CDCl_3$; the spectra were measured with proton decoupling at a frequency of 22.49 MHz. The required pulse numbers were approximately 10000.

Results and Discussion

The yields of each fraction are shown in Schemes 1 and 2. The yields (daf) are based on the weights of the original coals and reactants, and are shown out of and within parentheses, respectively. Although the first Bu.P of Yubari coal could be dissolved in benzene to a high extent, the second one was less successful. In contrast, the benzene-solubility of Taiheiyo-Bu.P was almost constant at 30%, irrespective of the number of butylations. Table 1 shows the number of butyl groups introduced per 100 carbon atoms and the values of BS/Butyl calculated by the following equation:

$$\text{BS/Butyl (wt/wt)} = \frac{\text{Bu.P Yield (wt\%)} \times \text{BS Yield (wt\%)}/100}{\text{Bu.P Yield (wt\%)} - 100}.$$

These values, which are hereafter termed "solubilization efficiency (Es)", provide diagnostic criteria for judging coal solubilization. The butyl groups were much more easily introduced into coal during the first reaction than during later reactions; further, the introduction of butyl groups did not increase additional butylations. As can be seen from Figs. 1 and 2, the IR

Table 1. Number of Butyl Groups Introduced per 100 Original Carbon Atoms of the Reactant

Product	No. of butyl groups/100C				BS/Butyl (wt/wt)
	A.R.[a]	C.B.[b]	M.B.[c]	Mean	
Yubari					
Y.Bu.P-1	13.8	17.9	16.1	15.9	1.97
Y.Bu.P-2	4.1	3.5	3.5	3.7	2.00
Taiheiyo					
T.Bu.P-1	9.3	11.6	10.6	10.5	1.18
T.Bu.P-2	4.1	6.7	5.8	5.5	2.04
T.Bu.P-3	(4.2)	1.5	1.5	1.5	5.69

a) From change of H/C atomic ratio. b) From carbon balance. c) From material balance.

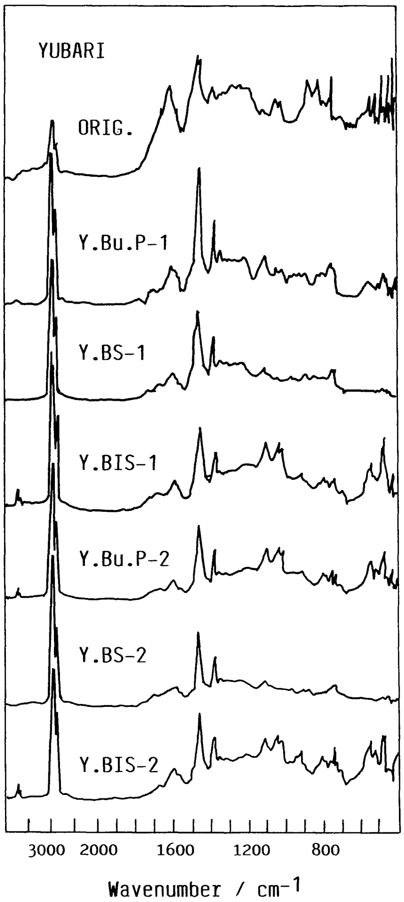


Fig. 1. FT-IR spectra of the products of Yubari coal.

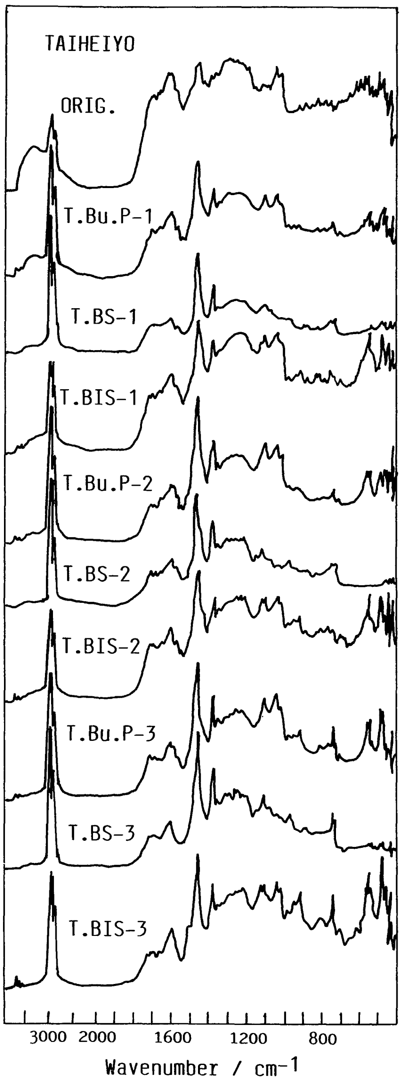


Fig. 2. FT-IR spectra of the products of Taiheiyo coal.

spectra of the BIS from both coals showed a moderately intense band of apliphatic CH stretching at 2958—2871 cm^{-1}, and an aliphatic CH deformation at 1465 and 1379 cm^{-1}, upon gradually increasing Es; this was opposite to the decrease of the number of butyl groups introduced. From these facts, it is concluded that many butyl groups remained in BIS support of further dissolution of Bu.P during additional reactions. As described above, since the cleavage of aliphatic linkages of coal structures increases with increasing number of alkyl groups attached to aromatic rings, it seems that the linkage-cleavage reactions significantly occur during later butylation.

In the solubilization of coal by alkylation methods it is difficult to determine whether the solvent-soluble products are derived from the coal or the by-products.[8] In this study the values of Es were larger than 1, and no significant absorption peaks due to by-products, which may arise from the reaction with only butyl iodide and zinc, were present in the ^{13}C NMR spectra of all the solvent-soluble products. This allows us to confirm that the solvent-soluble products are derived from coal and that butylation really occurs.

Tables 2 and 3 summarize the ultimate analyses, M_w and the results of structural analyses. For Taiheiyo coal, the M_w of the BS gradually increased upon the repetition of the reaction, while for Yubari coal their M_w were almost the same at each step. For both coals, the results of the structural analyses of BS at each step were similar each other. These results indicate that for Taiheiyo coal products with similar structures and different degrees of polymerization solubilized.

It has been reported that repeated reactions usually promote the reaction on coal solubilization under mild conditions.[3,4] A similar result was obtained in this study; even Taiheiyo coal, a low-lank coal, solubilized in benzene to a high extent.

It has also been reported that the ease of cleavage of the aliphatic linkage in the coal structure increases with increasing the number of alkyl groups on the aromatic rings.[2] In this study, all of the BS obtained during each step was combined, and then further butylated,

Table 2. Elemental Analyses, Structural Parameters, and M_w of the Products of Butylated Yubari Coal

Product	Elemental analysis/wt%$^{a)}$					Structural parameters					M_w
	C$^{b)}$	H$^{b)}$	N$^{b)}$	O$^{c)}$	I	f_a	σ_{al}	σ_o	H_{au}/C_a	$n^{d)}$	
Y.Bu.P-1	87.4	10.0	1.0	1.6	4.5	—	—	—	—	—	—
Y.BS-1	86.6	9.9	0	3.5	3.1	0.43	0.62	0.11	0.65	3.4	2540
Y.BIS-1	84.9	9.5	1.2	4.4	2.8	—	—	—	—	—	—
Y.Bu.P-2	84.8	10.4	1.0	3.8	4.1	—	—	—	—	—	—
Y.BS-2	85.0	10.1	0	4.9	3.6	0.39	0.66	0.17	0.64	3.7	2420
Y.BIS-2	83.6	10.0	1.0	5.4	3.2	—	—	—	—	—	—
Y.BS-12	85.9	9.7	0	4.5	3.0	0.44	0.61	0.15	0.60	3.5	2500
Y.Bu.BS-12	87.4	11.0	0	1.6	4.0	0.36	0.73	0.06	0.65	3.7	2670
Y.HS-12	85.9	10.5	0	3.6	2.5	0.38	0.62	0.11	0.71	3.6	1820
Y.HIS-12	80.5	8.8	0	10.7	3.2	0.45	0.52	0.29	0.77	3.1	22600
Y.Bu.HS-12	87.8	11.2	0	1.0	4.4	0.35	0.76	0.03	0.66	3.8	2360
Y.Bu.HIS-12	85.0	9.9	0	5.1	4.3	0.40	0.60	0.20	0.84	3.0	10000

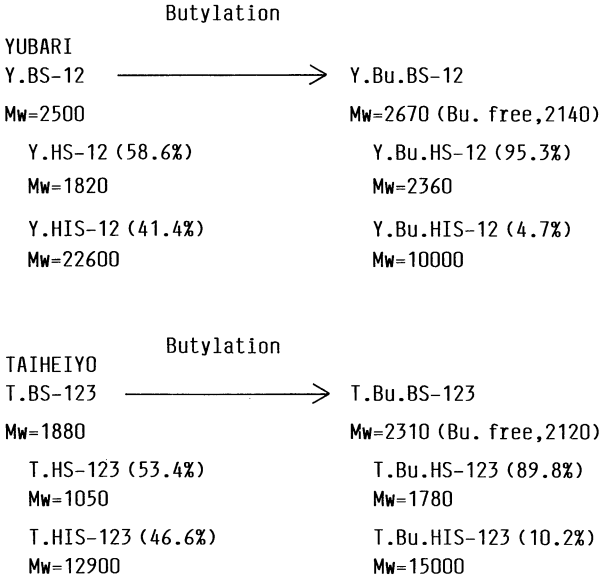
a) Dry ash free basis. b) Iodine corrected values. c) By difference. d) $n=H_o/H_\alpha+1$.

Table 3. Elemental Analyses, Structural Parameters, and M_w of the Products of Butylated Taiheiyo Coal

Product	Elemental analysis/wt%$^{a)}$					Structural parameters					M_w
	C$^{b)}$	H$^{b)}$	N$^{b)}$	O$^{c)}$	I	f_a	σ_{al}	σ_o	H_{au}/C_a	$n^{d)}$	
T.Bu.P-1	80.0	8.8	1.0	10.2	3.4	—	—	—	—	—	—
T.BS-1	84.6	10.4	0	5.0	2.7	0.38	0.62	0.18	0.65	4.1	1590
T.BIS-1	78.1	8.2	1.2	12.5	2.4	—	—	—	—	—	—
T.Bu.P-2	81.5	9.5	0.9	8.1	5.1	—	—	—	—	—	—
T.BS-2	83.3	9.8	0	6.9	4.3	0.40	0.60	0.21	0.71	3.5	2530
T.BIS-2	81.7	9.2	1.0	8.1	4.7	—	—	—	—	—	—
T.Bu.P-3	81.9	10.1	0.9	7.1	6.1	—	—	—	—	—	—
T.BS-3	84.4	10.4	0	5.2	3.5	0.36	0.65	0.17	0.74	3.6	3140
T.BIS-3	80.9	9.6	0.8	8.7	3.2	—	—	—	—	—	—
T.BS-123	83.2	10.5	0	6.3	3.6	0.35	0.59	0.25	0.65	4.8	1880
T.Bu.BS-123	84.7	10.9	0	4.4	4.1	0.34	0.66	0.17	0.66	4.5	2310
T.HS-123	84.2	10.9	0	4.9	2.9	0.34	0.61	0.18	0.69	4.6	1050
T.HIS-123	82.5	9.6	0	7.9	5.2	0.40	0.61	0.26	0.70	3.5	12900
T.Bu.HS-123	83.7	10.9	0	5.4	2.8	0.33	0.63	0.19	0.76	4.2	1780
T.Bu.HIS-123	80.7	9.7	0	9.6	5.6	0.39	0.55	0.23	0.99	2.9	15000

a) Dry ash free basis. b) Iodine corrected values. c) By difference. d) $n=H_o/H_\alpha+1$.

structural parameters of these mixture and their butylation products, which were separated by GPC, are given in Tables 2 and 3. The changes of M_w and hexane-solubility are in Scheme 3. Repeated butylation increases the weight of the reactants. Butyl-free M_w of the butylated BS of Yubari (Y.Bu.BS-12) and Taiheiyo coals (T.Bu.BS-123) were 2140 and 2120, respectively. For Yubari coal, M_w of BS decreases after butylation. For Taiheiyo coal, M_w of the butylated BS (T.Bu.BS-123) was slightly higher than that of BS (T.Bu.BS-123). However, because the yields of the hexane-soluble products (HS) increased from 46.6% to 89.8%, it seems that M_w of the BS decreases due to this reaction. These results suggest that some linkages present in coal structures may cleave, as is expected from the results obtained from a study using model compounds.[2)]


Butylation
YUBARI
Y.BS-12 → Y.Bu.BS-12
Mw=2500　Mw=2670 (Bu. free,2140)
Y.HS-12 (58.6%)　Y.Bu.HS-12 (95.3%)
Mw=1820　Mw=2360
Y.HIS-12 (41.4%)　Y.Bu.HIS-12 (4.7%)
Mw=22600　Mw=10000

Butylation
TAIHEIYO
T.BS-123 → T.Bu.BS-123
Mw=1880　Mw=2310 (Bu. free,2120)
T.HS-123 (53.4%)　T.Bu.HS-123 (89.8%)
Mw=1050　Mw=1780
T.HIS-123 (46.6%)　T.Bu.HIS-123 (10.2%)
Mw=12900　Mw=15000

Scheme 3.

The GPC elution curves are shown in Figs. 3 and 4, and the M_w and structural parameters of these GPC fractions are listed in Tables 4 and 5. In each GPC separation, the samples which do not contain benzene-insoluble products were well fractionated in order of decreasing M_w; all of them were almost recovered after elution. Larsen et al.[9)] have been reported that a larger-

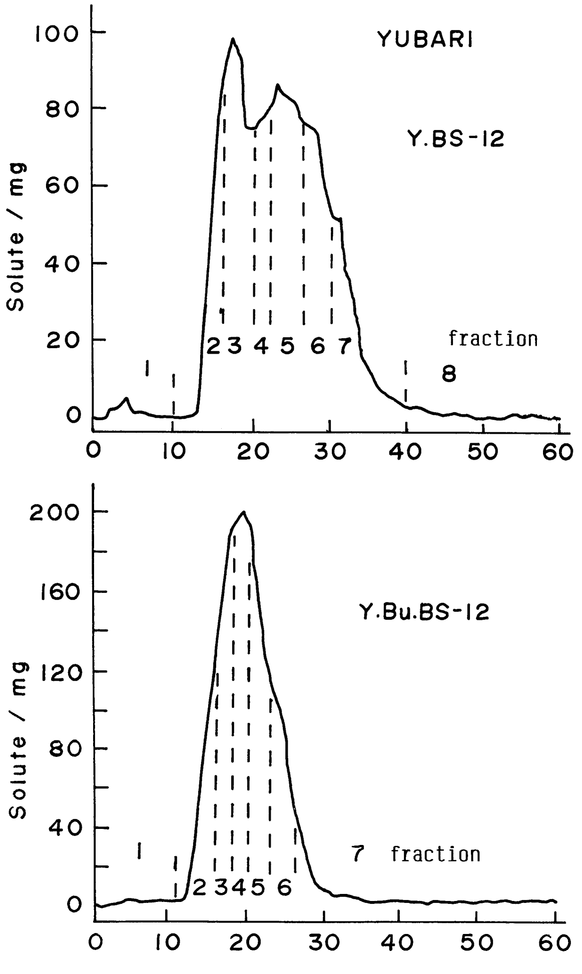


Fig. 3. GPC elution curves of benzene soluble products of Yubari coal.

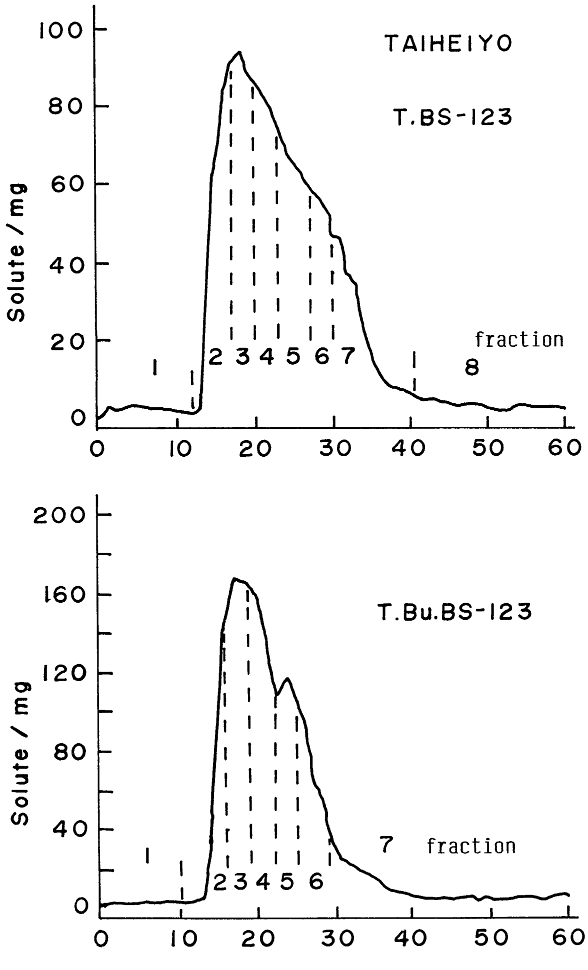


Fig. 4. GPC elution curves of benzene soluble products of Taiheiyo coal.

Table 4. Yields, M_w, and Structural Parameters of Yubari GPC Fractions

Sample	GPC Fr. No.	Yield	M_w	Atomic ratio[a]		Structural parameters				
		%		H/C	O/C	f_a	σ_{al}	σ_o	n[b]	H_{au}/C_a
Y.BS-12	1	0.4	—	—	—	—	—	—	—	—
	2	11.6	4100	1.31	0.06	0.44	0.59	0.19	3.3	0.65
	3	22.6	4090	1.36	0.04	0.42	0.64	0.15	3.7	0.58
	4	12.3	3300	1.34	0.04	0.43	0.64	0.15	3.4	0.61
	5	21.6	3010	1.34	0.05	0.42	0.64	0.17	3.4	0.62
	6	16.4	2380	1.39	0.03	0.41	0.66	0.13	3.5	0.62
	7	10.5	1170	1.46	0.03	0.38	0.63	0.13	3.9	0.66
	8	1.0	—	1.50	0.08	0.35	0.42	0.28	5.3	0.82
Bu.Y.BS-12	1	0.6	—	—	—	—	—	—	—	—
	2	17.7	5390	1.44	0.03	0.38	0.71	0.11	3.7	0.60
	3	20.2	4600	1.48	0.02	0.37	0.75	0.09	3.6	0.64
	4	21.4	4060	1.48	0.02	0.37	0.74	0.06	3.8	0.62
	5	22.7	1830	1.48	0.02	0.37	0.73	0.10	3.9	0.61
	6	12.3	1320	1.49	0.02	0.36	0.76	0.08	3.9	0.60
	7	6.3	—	1.62	0.05	0.29	0.65	0.23	5.4	0.68

a) These values are corrected by the iodine weight (except Y.BS-12 Fr. 8 and Bu.Y.BS-12 Fr. 7). b) $n=H_o/H_\alpha+1$.

Table 5. Yields, M_w, and Structural Parameters of Taiheiyo GPC Fractions

Sample	GPC Fr. No.	Yield	M_w	Atomic ratio[a]		Structural parameters				
		%		H/C	O/C	f_a	σ_{al}	σ_o	n[b]	H_{au}/C_a
T.BS-123	1	1.2	—	—	—	—	—	—	—	—
	2	19.1	4710	1.42	0.06	0.38	0.64	0.21	3.6	0.69
	3	17.6	4000	1.43	0.06	0.38	0.62	0.23	3.7	0.71
	4	19.5	2740	1.45	0.05	0.38	0.63	0.21	3.9	0.68
	5	18.0	2280	1.48	0.05	0.36	0.64	0.20	3.9	0.71
	6	12.2	1750	1.50	0.06	0.35	0.63	0.23	4.2	0.70
	7	12.0	910	1.54	0.04	0.33	0.66	0.19	4.8	0.65
	8	1.6	—	1.55	0.11	0.32	0.47	0.37	4.9	0.91
Bu.T.BS-123	1	0.5	—	—	—	—	—	—	—	—
	2	14.9	7480	1.45	0.06	0.37	0.63	0.21	3.7	0.71
	3	26.1	4620	1.41	0.03	0.39	0.70	0.15	3.8	0.60
	4	21.1	3180	1.47	0.03	0.36	0.73	0.12	4.1	0.60
	5	17.3	2560	1.53	0.05	0.34	0.65	0.20	4.3	0.69
	6	12.7	1350	1.57	0.07	0.32	0.60	0.28	4.7	0.76
	7	8.4	—	1.74	0.04	0.24	0.62	0.26	7.8	0.66

a) These values are corrected by the iodine weight (except T.BS-123 Fr. 8 and Bu.T.BS-123 Fr. 7). b) $n=H_o/H_\alpha+1$.

molecular-weight material is strongly associated with one another and significant amounts of low-molecular-weight materials were incorporated into them, consisting of a cross-linked structure found by the GPC separation. It seems that such incorporation can also occur during this reaction.

As can be seen from Tables 4 and 5, there was a downward tendency for f_a, and an upward one for σ_{al} with increasing number of butyl groups introduced. The decrease in the values of σ_o is attributed to a cleavage of the functional oxygen-containing groups, as reported in the results regarding model compound studies.[2)]

To obtain a large amount of solvent-soluble products under this mild condition, the resulting sample is suitable for estimating the coal structure. However, the solvent-soluble products are so heavy that high-molecular-weight materials incorporated a significant amount of low-molecular-weight ones. Therefore, to obtain detailed information concerning the coal structure, the pretreatment of coal products (such as hydrogenation under mild conditions and/or chemical-type separation) would be required.

Some portions of the cross-linkage of the coal structure were cleaved into solvent-soluble products, as described above. However, M_w of the HS obtained by this method corresponds to that of a preasphaltene by other methods.[10)] Sternberg and Delle Donne[11)] have reported that because petroleum asphaltene, in contrast to coal, contained a considerable number of alkyl groups attached to the aromatic clusters, they are largely soluble in benzene, in spite of the fact that they comprise a large number of aromatic rings per cluster, in comparison with coal. These facts indicate that the high extractability of butylated BS with hexane can be attained by introducing many butyl groups; the occurrence of some cleavage of the aliphatic linkages was suggested by the model compound study.

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