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Structural Characterization of Soluble Products from a Series of Reductively Butylated Coals Prepared in Refluxing Tetrahydrofuran

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A series of butylated Yūbari coals were prepared by an improved reductive alkylation method, and detailed structural parameters of respective solution products in pentane (PS) and benzene (BS) were estimated; this experimental procedure is likely to offer more insight into chemical structures of products and important factors effective for solubilization than any analyses on a single product. The PS and BS have average molecular weights of 700—800 and 1500—2050 and are composed of about two and more than five structural units, respectively. These values suggest that the BS molecule is quite large compared with the corresponding products obtained by other methods such as hydrocracking. On the other hand, the ring sizes of one structural unit of the respective products are roughly the same (about three rings). The BS materials are coal macromolecules with stackings loosened by introduction of alkyl groups, while the PS materials are products through cleavage of bonds connecting the structural units and through addition of so many alkyl groups as to increase the affinity for the solvent. In addition, an absence of intermolecular hydrogen bonds mainly due to OH groups contributes to quite a high solubility of the alkylated coals. Increase in BS yield accompanies an increase in aliphatic carbon ratio and polymerization degree and a decrease in size of aromatic ring systems. These results may be ascribed to the heterogeneity of coal constituents.

For the purpose of structural analysis of coals, many methods to transform coals to soluble derivatives have been reported. Among them, reductive alkylation proposed by Sternberg *et al.*[1)] is accepted to be one of the most promising methods.[2–13)] Soluble materials in reductively alkylated coals were analyzed by applying various techniques.[3,5,6,8,11–13)] Compounds contained in alkylated coals were identified by gas chromatography-mass spectrometry preceded by mild oxidation.[14)] Some information about the reaction mechanism has been obtained by conducting reactions using model compounds[5,15)] and various alkyl halides.[10,12)] However, effects of change of a series of reaction conditions, such as reaction time, on the structure of soluble products have hardly been reported, since Sternberg's procedure requires a reaction time as long as 2—14 d.[1–13)]

In our previous papers[16,17)] we have proposed an improved method which has solved the problems of Sternberg's procedure, such as long reaction time[1–13)] and contamination of an electron transfer agent, naphthalene.[18,19)] It has been demonstrated that almost all carbonaceous matters in Yūbari coal (more than 90 wt%) can be solubilized in hot benzene by only 6 h reaction.[16,17)] However, no detailed structural characterization has yet been reported.

The present study aims at a structural characterization of a series of soluble materials from butylated Yūbari coals obtained by varying the reaction conditions of the improved method. Analysis of these products is likely to offer more insight into the chemical structure of reductively alkylated coals than analysis of a single product. Furthermore, information will be obtained about key factors leading to highest solubility and the solubilization mechanism.

Experimental

Reaction Procedures. Yūbari coal (86.0% C) was used as a coal sample, whose proximate and ultimate analyses were described elsewhere.[16,17)] Dry pulverized coal (10 g) was allowed to react in a flask with stirring with molten potassium metal (4—12 g) (mp 63 °C) in refluxing tetrahydrofuran, THF, (150 cm^3) (bp 66 °C) for 2—12 h. After this anion formation reaction, the flask was cooled to −50 °C and 1 mol of butyl iodide was added dropwise. The stirring was continued at room temperature overnight to alkylate the coal anions and to destroy the excess potassium. The solid product was washed with aqueous ethanol solutions repeatedly until no iodide ion had become detected in the filtrate, and dried under vacuum at 90 °C for 12 h. The alkylated coal samples were extracted with pentane or benzene by using Soxhlet thimbles; a dried extract thus obtained will be termed PS or BS (BS contains the PS fraction), respectively. Detailed procedures were previously described.[16,17)]

To investigate the effect of OH groups on the solubilization, methylated or hydrogenated coals also was prepared by adding 1 mol of methyl iodide or ethanol, respectively, to a coal anion suspension which had been prepared by 6 h reaction with 8 g of molten potassium. They were each extracted with benzene to give BS and BI (benzene insoluble). The BS material from the methylated coal was further hydrogenated in a similar manner as described just above.

Analysis of Products. Analytical data of the alkylated coals were reported elsewhere.[16,17)] The PS and BS materials were subjected to an ultimate analysis, a ^{1}H NMR spectroscopy, and an average-molecular-weight measurement, as previously conducted.[16,17)] The hydrogens in NMR spectra are classified as follows: the hydrogen attached to an aromatic carbon, H'_{ar}; the hydrogen attached to an α carbon to an aromatic ring, H'_{α}; the hydrogen contained in a methylene group at other than α positions, H'_{β}; the hydrogen contained in a methyl group, H'_{γ}.

The amount of OH groups was determined by the acetylation method using pyridine.[20)] IR spectra of BS were obtained with hexachlorobutadiene solutions on a Hitachi 260-10 infrared spectrophotometer.

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Structural parameters were estimated according to the equations by Ouchi *et al.*[21,22] with a slight modification as follows: The contribution of sulfur atoms and inert oxygen atoms was neglected because the original Yūbari coal contained few sulfur atoms (0.3 wt%) and a relatively small amount of inert ether bonds (less than 40% of the total oxygen atoms) for the present reaction. The latter was determined from the amounts of OH groups before and after the reductive hydrogenation. Tsukashima *et al.*[3] also neglected the effect of sulfur and inert oxygen atoms with regard to structural parameters for reductively methylated Yūbari coals. Therefore, in the present study, all oxygen atoms in soluble products are assumed to be present as group $-O-(CH_2)_3CH_3$ at positions peripheral to aromatic rings. The structural parameters concerned are as follows: The carbon aromaticity, $f_a=(C'-H'_\alpha/2-H'_\beta/2-H'_\gamma/3)/C'$; the degree of aromatic ring condensation, $H'_{au}/C'_a=(H'_{ar}+H'_\alpha/2+O'+2N')/(C'-H'_\alpha/2-H'_\beta/2-H'_\gamma/3)$; the degree of substitution of aromatic nuclei, $\sigma=(H'_\alpha/2+O'+2N')/(H'_{ar}+H'_\alpha/2+O'+2N')$; the degree of aliphatic chain substitution of aromatic nuclei, $\sigma_{al}=(H'_\alpha/2)/(H'_{ar}+H'_\alpha/2+O'+2N')$; the number of aromatic carbons per molecule, $C'_{ar}=C'\cdot f_a$; the number of aliphatic carbons per molecule, $C'_{al}=C'-C'_{ar}$; the number of aromatic carbons per structural unit, $C'_{ar(u.s.)}=3/(H'_{au}/C'_a-1/2)$; the number of structural units per molecule, $n=C'_{ar}/C'_{ar(u.s.)}$; the number of aromatic rings per structural unit, $R_{a(u.s.)}=C'_{ar(u.s.)}(1-H'_{au}/C'_a)/2+1$; the number of aromatic rings per molecule, $R_a=n\cdot R_{a(u.s.)}$; the number of total rings per molecule, $R_t=C'-H'/2+1-C'_{ar}/2$; the number of naphthenic rings per molecule, $R_N=R_t-R_a$; the average number of carbon atoms in side chains, $C'_{side}=C'_{al}-3\cdot R_N$, where C′, H′, *etc.* denote the numbers of carbon atoms, hydrogen atoms, *etc.* in PS and BS molecules, respectively. Division of each of the above values per molecule by n gives the corresponding value per structural unit.

Results and Discussion

Structural Character of PS and BS. Basic data obtained for PS and BS materials are summarized in Table 1, which contains the items: yields of butylated coals and soluble materials, ultimate analyses, hydrogen distributions, and average molecular weights. The yields of the soluble materials, PS and BS, from raw Yūbari coal are trace and 2 wt%, respectively. The treatment of the coal gave PS and BS in 18—39 and 74—93 wt% yields, respectively. The average molecular weights obtained for the PS and BS are 700—800 and 1520—2050, respectively; the molecular weight of the PS is less than half that of the BS. The average molecular weights, corrected for introduced butyl groups, also are given in Table 1.

In Table 2 are given the number of butyl groups introduced per 100 carbon atoms and the values of f_a, H'_{au}/C'_a, σ σ_{al}, and n for PS and BS materials. The number of introduced butyl groups was estimated in a similar manner as reported conventionally for soluble products;[5,9] that is, it was estimated on the assumption that the change in H/C atomic ratio of products relative to raw coal is due exclusively to the introduction of alkyl groups. The numbers obtained are 9.3—17.7 and 6.1—12.1 for the PS and BS, respectively. It should be noted that the estimated values become uncertain when the soluble products themselves are different in H/C value from the original coal. The high values of σ (0.55—0.64) and σ_{al} (0.39—0.45) for both the PS and BS idicate that the aromatic nuclei have many substituents, especially alkyl side-chains. The PS material show lower f_a and slightly higher σ and σ_{al} values than the BS, suggesting themselves to be abundant in aliphatic carbons and alkyl side-chains. The number of structural units, n, in the BS molecule is more than 5.0, whereas that in the PS is less than 2.6.

The numbers of individual rings and carbons per molecule and per structural unit for the PS and BS materials are shown in Tables 3 and 4, respectively. The BS molecules have high values of R_t, R_a, C'_{ar}, and

Table 1. Basic data obtained for PS and BS materials

Fraction	Reaction time	K/coal	Yield of Bu-coal[a)]	Yield of fraction[b)]	Ultimate analysis[c)]/wt%				Hydrogen distribution				Mol wt	
	h	g/g	wt%	wt%	C	H	N	O[d)]	H'_{ar}/H'	H'_α/H'	H'_β/H'	H'_γ/H'	Obsd	Bu-free
PS	2	0.4	129	18	87.2	9.0	1.0	2.8	0.14	0.27	0.32	0.27	780	560
PS	6	0.4	139	30	84.0	9.6	0.9	5.5	0.09	0.22	0.38	0.31	700	450
PS	12	0.8	154	35	84.8	9.6	1.0	4.6	0.11	0.24	0.37	0.28	790	460
PS	6	1.2	152	39	84.1	10.1	0.9	4.9	0.09	0.21	0.41	0.29	800	470
BS	2	0.4	129	74	85.5	8.1	1.3	5.1	0.13	0.29	0.31	0.27	2050	1640
BS	6	0.4	139	81	84.9	8.7	1.3	5.1	0.14	0.26	0.31	0.29	1520	1100
BS	12	0.8	154	91	83.1	8.7	1.3	6.9	0.14	0.27	0.31	0.28	1720	1180
BS	6	1.2	152	93	83.0	9.0	1.2	6.8	0.14	0.26	0.30	0.30	1620	1100

a) Relative to feed coal (dry basis). b) Relative to butylated coal (dry ash free basis). c) Dry ash free basis. d) From difference.

Table 2. Number of butyl groups introduced per 100 carbon atoms and structural parameters of PS and BS

Fraction	Yield of fraction	No. of Bu's per 100 C's	Structural parameters				
	wt%		f_a	H'_{au}/C'_a	σ	σ_{al}	n
PS	18	9.3	0.52	0.74	0.55	0.44	2.4
PS	30	14.2	0.45	0.76	0.64	0.45	1.9
PS	35	17.7	0.46	0.81	0.61	0.44	2.6
PS	39	17.7	0.42	0.83	0.62	0.44	2.6
BS	74	6.1	0.56	0.69	0.62	0.43	5.0
BS	81	9.2	0.53	0.76	0.57	0.40	5.0
BS	91	11.8	0.52	0.84	0.61	0.40	7.0
BS	93	12.1	0.50	0.88	0.58	0.39	7.1

C'_{al}, at least higher than twice those for the PS molecules. On the other hand, the ring sizes per structural unit are roughly the same as seen from $R_{t(u.s.)}$, $R_{a(u.s.)}$, and $C'_{ar(u.s.)}$. The number of each of the rings per BS molecule decreases with an increase in the BS yield. The increase in C'_{side} and C'_{al}/C'_{ar} of both the PS and BS molecules is dependent on the increase in the number of butyl groups introduced. It should be noted that, in high yield regions of PS, the number of carbons in side chains exceeds that in aromatic rings, which has resulted from an introduction of many bulky butyl groups.

Factors Governing the Production of PS and BS. For the conventional reductive alkylation, it has been reported[1,5,15] that coals are solubilized by introduction of alkyl groups to their condensed aromatic nuclei to loosen their stacking and by cleavage of ether and some carbon–carbon linkages connecting ring systems.

Two important reaction factors to produce PS from coal or BS are considered: the first is a depolymerization, that is, cleavage of bonds connecting structural units to produce small molecules (molecular weights, 700—800 as observed; 450—560 on butyl-free basis) with about two structural units; the second is an addition of many alkyl groups, as seen from the values of C'_{al}/C'_{ar} and $C'_{side(u.s.)}$, which results in increasing the affinity for the solvent, pentane.

On the other hand, the BS materials are macromolecules (observed molecular weights, 1520—2050; n, 5.0—7.1) with a loosened stacking by introduction of alkyl groups. In addition, the absence of intermolecular hydrogen bonds due to alkylation of polar groups, such as OH group, may contribute to the attainment of quite high BS yields. Effect of this factor is to be discussed in detail in the next section.

With an increase in the BS yield, the values of H'_{au}/C'_{a}, C'_{side}, and C'_{al}/C'_{ar} increase and those of f_a and total and aromatic rings per molecule and per structural unit decrease. This result may be ascribed to the addition of many butyl groups caused under the severe reaction conditions. However, the value of n increases with an increase in the BS yield, which should have decreased by cleavage of ether and some carbon–carbon bonds when severe reaction conditions were applied. A possible interpretation for these results is that the constituents in coal are heterogeneous, that lowly polymerized materials, which are composed of more developed aromatic ring systems relatively easy to get anionized because of their high electron affinity, will preferentially be converted to BS at an early stage, and that highly polymerized materials with less condensed aromatic ring systems and higher aliphatic carbon ratios will resist the reaction so as to get converted later. This view is in accord with an observation that a BS produced at an early stage has slightly higher σ_{al} and $C'_{side(u.s.)}$ values (*i.e.*, it contains more alkyl groups) than a BS produced later, and also with a report[2,9,23] that the solubility of low rank coals, which may be considered to be composed of similar materials as contained in the BS produced later, is considerably low for the conventional reductive alkylation (or hydrogenation) method.

Effects of OH Groups on Coal Solubilization. Table 5 summarizes the yields of the BS and BI from methylated and hydrogenated coals and from further

Table 3. Number of rings in PS and BS

Fraction	Yield of fraction	Number of rings					
		per molecule			per structural unit		
	wt%	R_t	R_a	R_N	$R_{t(u.s.)}$	$R_{a(u.s.)}$	$R_{N(u.s.)}$
PS	18	7.7	6.2	1.5	3.2	2.6	0.6
PS	30	5.5	4.5	1.0	2.9	2.4	0.5
PS	35	6.1	5.0	1.1	2.3	1.9	0.4
PS	39	5.0	4.5	0.5	1.9	1.7	0.2
BS	74	23.4	17.8	5.6	4.6	3.5	1.1
BS	81	14.0	11.8	2.2	2.8	2.4	0.4
BS	91	14.5	11.9	2.6	2.1	1.7	0.4
BS	93	11.6	10.5	1.1	1.6	1.5	0.1

Table 4. Number of carbons in PS and BS

Fraction	Yield of fraction	Number of carbons						
		per molecule				per structural unit		
	wt%	C'_{ar}	C'_{al}	C'_{side}	C'_{al}/C'_{ar}	$C'_{ar(u.s.)}$	$C'_{al(u.s.)}$	$C'_{side(u.s.)}$
PS	18	29	27	23	0.93	12.4	11.5	9.6
PS	30	22	27	24	1.23	11.5	14.2	12.6
PS	35	25	30	27	1.20	9.6	11.6	10.3
PS	39	23	33	31	1.43	9.0	12.6	12.1
BS	74	81	65	48	0.80	16.1	12.8	9.5
BS	81	57	50	44	0.88	11.4	10.1	8.8
BS	91	62	58	50	0.94	8.8	8.3	7.2
BS	93	56	56	52	1.00	7.9	7.9	7.4

Table 5. Properties of methylated and hydrogenated coals

Coal	Yield of fraction/wt%		No. of OH's per 100 C's		OH per O/%	
	BS	BI	BS	BI	BS	BI
Me-coal[a)]	84	16	0.4	3.1	7	58
Hy-coal[b)]	18	82	2.6	3.7	47	67
Hy-Me-BS[c)]	50	50[d)]	2.1	3.9	38	48

a) Methylated coal. b) Hydrogenated coal. c) BS from Me-coal was further hydrogenated. d) Starting material contained no BI fraction.

hydrogenated BS of the methylated coal, the amount of OH groups per 100 carbon atoms, and the ratio of OH groups to the total oxygen atoms contained. The number of OH groups per 100 carbon atoms in the original Yūbari coal is estimated to be 3.0.

The yield of BS from the hydrogenated coal is only 18 wt%, extremely low compared with the value of 84 wt% for the methylated coal. The fractions from the hydrogenated coal contain more OH groups than those from the methylated one, since the ether bonds and OH groups in the original coal are converted to $-O-CH_3$ and $-OH$ groups by the methylation and hydrogenation, respectively.[1,3)] The decrease in OH groups caused by the methylation has also been suggested with the conventional procedures.[3)] In all the cases, the OH groups are caused to accumulate in the BI fractions. This suggests that the presence of OH groups in large quantity will hinder the solution probably through formation of hydrogen bonds. When the BS from the methylated coal which has already been released from the stacking is further hydrogenated, the amount of OH groups is increased by a demethylation on $-O-CH_3$ groups[1)] and a large amount of BI (50 wt%) is newly formed, into which the OH groups are also made to accumulate.

IR spectra of various BS's are shown in Fig. 1. The BS materials from the hydrogenated coal and from the further hydrogenaed BS of the methylated coal show absorption bands assignable to intermolecular hydrogen bonds at about 3100—3600 cm^{-1}, whereas the corresponding absorption is hardly observed for the BS from the methylated coal. Hence, it has been demonstrated that the extremely high BS yield from the reductively alkylated coals is due at least to the absence of intermolecular hydrogen bonds.

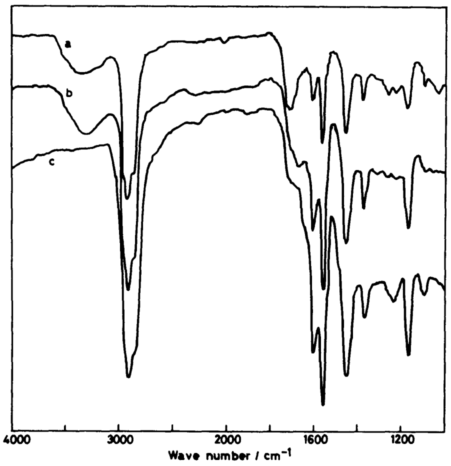

Fig. 1. IR spectra of BS fractions from (a) hydrogenated coal, (b) further hydrogenated BS of methylated coal, and (c) methylated coal.

References

1) H. W. Sternberg, C. L. Delle Donne, P. Pantages, E. C. Moroni, and R. E. Markby, *Fuel*, **50**, 432 (1971).

2) H. W. Sternberg and C. L. Delle Donne, *Fuel*, **53**, 172 (1974).

3) H. Tsukashima, T. Katoh, F. Wakita, T. Kuruma, and N. Nei, *Nenryo Kyokai Shi*, **55**, 254 (1976).

4) B. S. Ignasiak and M. Gawlak, *Fuel*, **56**, 216 (1977).

5) T. Ignasiak, A. V. Kemp-Jones, and O. P. Strausz, *J. Org. Chem.*, **42**, 312 (1977).

6) R. Doğru, G. Erbatur, A. F. Gaines, Y. Yürüm, S. Içli, and T. Wirthlin, *Fuel*, **57**, 399 (1978).

7) B. S. Ignasiak, J. F. Fryer, and P. Jadernik, *Fuel*, **57**, 578 (1978).

8) L. B. Alemany, S. R. King, and L. M. Stock, *Fuel*, **57**, 738 (1978).

9) H. Wachowska, *Fuel*, **58**, 99 (1979).

10) L. B. Alemany, C. I. Handy, and L. M. Stock, *Adv. Chem. Ser.*, **192**, 207 (1981).

11) T. Katoh, S. Hashimoto, and H. Tsukashima, *Nenryo Kyokai Shi*, **60**, 432 (1981).

12) L. B. Alemany and L. M. Stock, *Fuel*, **61**, 250 (1982).

13) L. B. Alemany and L. M. Stock, *Fuel*, **61**, 1088 (1982).

14) R. Doğru, A. Gaines, A. Olcay, T. Tuğrul, *Fuel*, **58**, 823 (1979).

15) L. Lazarov and S. Angelov, *Fuel*, **59**, 55 (1980).

16) M. Miyake, M. Sukigara, M. Nomura, and S. Kikkawa, *Fuel*, **59**, 638 (1980).

17) S. Kikkawa, M. Miyake, M. Sukigara, and M. Nomura, *Nippon Kagaku Kaishi*, **1980**, 939.

18) J. A. Frantz and W. E. Skiens, *Fuel*, **57**, 502 (1978).

19) J. W. Larsen and L. O. Urban, *J. Org. Chem.*, **44**, 3219 (1979).

20) Y. Hasegawa, K. Tokuhashi, and Y. Maekawa, 47th Annual Meeting of Coal Science Jpn., Tokyo, October 1980, Preprints No. 3.

21) N. Kanda, H. Itoh, S. Yokoyama, and K. Ouchi, *Fuel*, **57**, 676 (1978).

22) K. Ouchi, T. Katoh, and H. Itoh, *Fuel*, **60**, 689 (1981).

23) K. Ouchi, Y. Hirao, M. Makabe, and H. Itoh, *Fuel*, **59**, 751 (1980).