

NATURE OF CROSS-LINK BONDS
FOR SOME BITUMINOUS COAL

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INTRODUCTION

The two-component (phase) model of coal structure, in which coal consists of two components, i.e., a macromolecular, covalently cross-linked network and a relatively low molecular weight, molecular component trapped inside the network, seems to be widely accepted, from NMR relaxation(1) pyrolysis(2), and catalytic hydrogenation(3) studies for bituminous coals, and from liquefaction study(4) for low-rank coals. Nishioka(5), however, suggests that one-component model, in which coal consists of one component of physically associated molecules, i.e., aggregates of coal molecules of various molecular weight, is more suitable for some bituminous coals.

In this paper structure model of bituminous coals, especially nature of bonds which form a cross-linked network, is discussed from our results, including the results already published(6-13), about the extraction of coals with CS₂-N-methyl-2-pyrrolidinone (NMP) mixed solvent and characterization of the extracts and residues obtained with the mixed solvent.

EXPERIMENTAL

Extraction and fractionation procedures are shown in Figure 1. The coals were exhaustively extracted with CS₂-NMP mixed solvent(1:1 by volume) at room temperature under ultrasonic irradiation, according to the method described before(6,11). The solubility of the extract fractions was determined from the amount of the insoluble part when 400mg of the sample in 50ml of the CS₂-NMP mixed solvent was ultrasonically irradiated for 30min at room temperature, in the presence or absence of an additive(9). The swelling ratio(Q) was measured by the volumetric method(14).

RESULTS AND DISCUSSION

Extraction Yield with the CS₂-NMP Mixed Solvent

The two-component model assumes the existence of a large amount of

covalently cross-linked network which is not soluble, i.e., which is not extracted with any solvents. In fact, the extraction yields higher than 40wt%(daf) are hardly obtained so far without covalent bond breaking in coal. CS₂-NMP mixed solvent(1:1 by volume), however, was found to give very high extraction yields at room temperature. Table 1 shows the extraction yields with the mixed solvent for the coals which gave the yield higher than 40wt%(6). ZZ(China), SY(Japan), and UF(USA) coals gave the yields higher than 50wt%. Another ZZ coal, which was obtained recently, gave 77.9wt% of the extraction yield(10). No solubilization reactions in the mixed solvent extraction, such as covalent bond breaking, is suggested from several experimental results including characterization of the extracts and residues obtained. One of the important results supporting the conclusion above is that the heavier fraction than preasphaltene, i.e., the pyridine insoluble extract fraction, could be obtained by this extraction.

Table 2 shows the effect of TCNE addition on the extraction yield with the CS₂-NMP mixed solvent. UF(Argonne sample) coal increased the extraction yield from 60.4wt% to 85.0wt%, and UF-P(PSOC sample), LK, and SG coals gave the yield higher than 50wt%, by the addition of TCNE. The effect of TCNE can be explained by the breaking of associations between coal molecules by TCNE, as described in the last section, not by the breaking of covalent bonds in coal. This indicates that UF coal, for example, have 85wt% of solvent soluble component.

The extracts swell in the solvent which does not dissolve them, suggesting that they have a kind of a cross-linked structure(12). Since an extract is soluble in the extraction solvent and cross-linked network consisting of covalent bonds is insoluble in any solvent, the extracts, which was obtained here with the high yields, seem to be a giant assembly(aggregate) of a small molecules by noncovalent bonds such as hydrogen bonds and charge transfer interaction.

Similarity of the Extract and Residue. Continuity of Coal Structure

Figure 2(7) shows the fraction distribution of E-AS, E-PS, E-PI, and residue, which were obtained from the extraction with the CS₂-NMP mixed solvent and subsequent fractionation. Table 3(7) shows that the values of ultimate analysis of each fractions are similar, or gradually increase or decrease with the order of E-AS, E-PS, E-PI, and residue. No clear discontinuity was found between E-PI and residue. VM(daf) in proximate analysis of the extracts(E-PS + E-PI) and residues were found to be very similar(7). Similar swelling ratios(Q) of E-PI and the residues in methanol, benzene, and THF for ZZ, SY, and LK coals were also obtained(12).

The results above that there is no discontinuity between the extract fraction and the corresponding residue suggest that one-component model is more suitable than two-component model, in which coal consists of two quite different components, for some bituminous coals used here.

Association of Coal Molecules

Coals have several kinds of noncovalent interactions such as hydrogen bonding, charge transfer, aromatic(π)-aromatic(π), and dipole(ion)-dipole(ion) interaction, which varies depending on coal rank. E-PI from ZZ coal was found to become partly insoluble in the CS₂-NMP mixed solvent due to the association of coal molecules and the addition of the separated lighter fractions, i.e., E-AS and E-PS, or other compounds such as TCNE and p-phenylenediamine(PDA) recovered its solubility in the mixed solvent(9), probably due to the breaking of the association of coal molecules by the additive. Similar result was obtained for E-PI from UF coal, i.e., the addition of only 0.025(g/g coal) of TCNE and PDA increased the solubility of E-PI in the mixed solvent from 55.1wt% to 99.0 and 96.5wt%, respectively.

Figure 3 shows IR spectra of the mixed solvent insoluble E-PI(E-PI-I) and soluble E-PI(E-PI-S(a)) fractions after TCNE treatment and E-PI-S after washing with benzene(b), THF(c), DMSO(d), and pyridine(e), respectively. Figure 3 shows that TCNE retained in E-PI-S was removed by better solvents than acetone(E-PI-S(a)) for coal molecules. Thus, the order of the degree of the TCNE removal, i.e., acetone < benzene < THF < DMSO < pyridine, agrees with that of the extraction yields obtained in the extraction with these solvents. The result that TCNE can be removed by solvent washing suggests that TCNE is retained by adsorption to PI due to noncovalent interactions, not by some chemical reactions such as Diels-Alder reactions.

CONCLUSIONS

High extraction yields obtained by using the CS₂-NMP mixed solvent, similarity between the extracts and residues, and association and dissociation behavior coal molecules of coal molecules suggest that some bituminous coals such as UF and ZZ coals have coal structure in which coals consist of one component of a giant assembly (aggregates) of relatively small molecules. Covalently bonded cross-linked network, which is assumed in two-component model of coal structure, does not seem to be a main structure for these coals.

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Table 1. The selected^a extraction yields with the CS₂-NMP mixed solvent^b

Coal	Symbol	Specification	Country	C% (daf)	Extraction yield (wt%, daf)
Zao Zhuang	ZZ	————	China	86.9	65.6
Shan Jia Ling	SJ	————	China	86.8	45.4
Shin-yubari	SY	————	Japan	86.7	60.6
Upper Freeport	UF	Argonne	USA	86.2	54.0
Ding Tian	DT	————	China	86.0	46.6
Ping Ding Shan	PS	————	China	85.4	43.0
Thurston Property	TP	SBN	USA	84.9	45.4
Lower Kittanning	LK	PSOC815	USA	84.0	46.8
Lingan	LG	SBN	Canada	83.6	41.2
Pittsburgh No.8	PB	Argonne	USA	82.6	40.1

^aThe yields higher than 40wt%(daf) were selected. ^b1:1 By volume.

Table 2. Effect of TCNE addition on the extraction of various coals with the CS₂-NMP mixed solvent

Coal	C% (daf)	Amount of TCNE (g/g coal)	Extraction yield (wt%, daf)
SW	88.4	none	37.9
(Swell B)		0.100	47.9
UF	86.2	none	60.4
		0.025	85.0
UF-P*	85.0	none	44.2
		0.100	50.1
LK	84.0	none	46.2
		0.100	61.5
PB	82.6	none	39.0
		0.025	42.6
SG	77.8	none	37.5
(Stiglier)		0.100	52.3

*UF coal from PSOC.

Table 3. Ultimate analyses of the raw coals, extract fractions and residues

	Extract			Residue	Raw coal
	E-AS	E-PS	E-PI		
Zao Zhuang					
C	89.1	85.9	85.5	85.3	86.9
H	6.8	5.3	5.1	4.7	5.1
N	1.2	1.7	1.8	1.6	1.5
S	1.1	1.8	1.7	2.1	1.6
O*	1.8	5.3	5.9	6.3	4.9
H/C	0.91	0.74	0.71	0.66	0.70
O/C	0.015	0.046	0.052	0.055	0.042
Upper Freeport					
C	88.5	86.6	85.8	81.7	86.2
H	6.7	5.4	5.0	4.7	5.1
N	1.1	1.8	2.1	1.8	1.9
S	0.5	1.0	1.1	5.5	2.2
O*	3.2	5.2	6.0	6.3	4.6
H/C	0.91	0.75	0.70	0.69	0.71
O/C	0.027	0.045	0.052	0.058	0.040
Lower Kittanning					
C	86.4	84.7	83.4	79.9	82.3
H	6.7	5.3	5.1	4.9	5.2
N	1.1	1.9	2.1	1.6	1.7
S	1.1	1.3	1.2	5.0	3.9
O*	4.7	6.8	8.2	8.6	6.9
H/C	0.92	0.75	0.73	0.73	0.75
O/C	0.041	0.060	0.074	0.081	0.063

*By difference

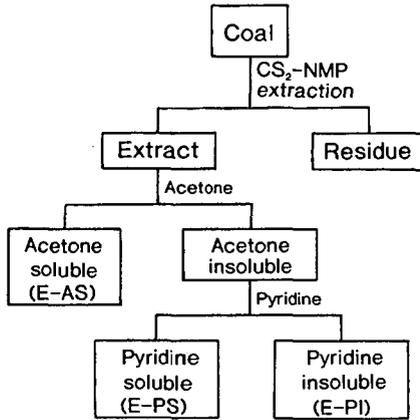


Figure 1. Solvent fractionation procedure of the extract obtained from the CS₂-NMP mixed solvent extraction.

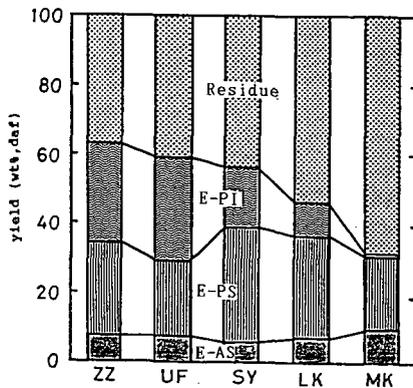


Figure 2. Fraction distribution for ZZ, UF, SY, LK and Miike(MK) coals

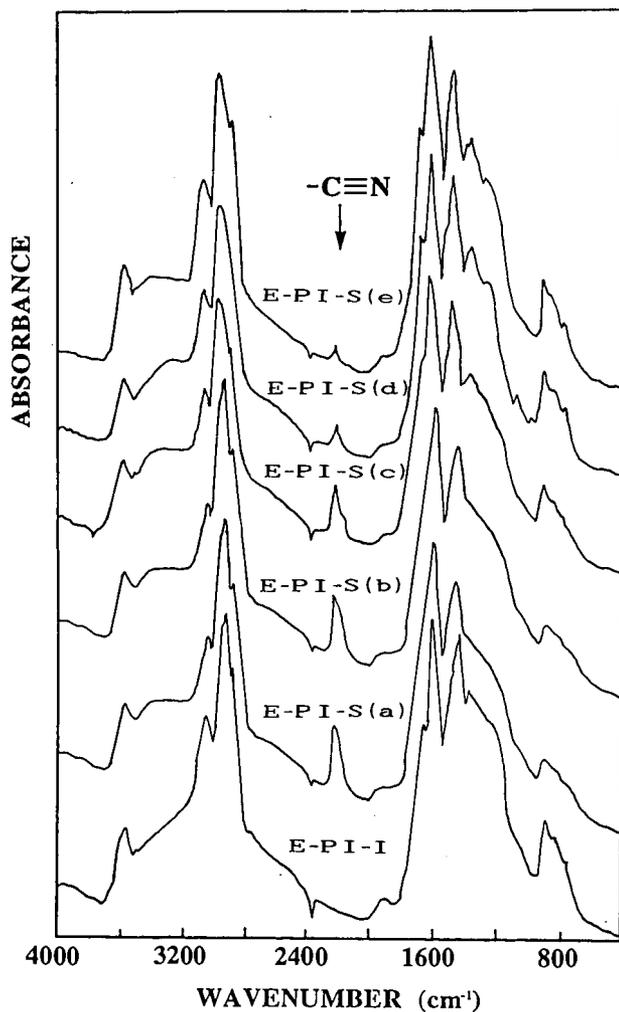


Figure 3. FT-IR spectra of the mixed solvent insoluble E-PI (E-PI-I) and soluble E-PI (E-PI-S(a)) fractions after TCNE treatment and E-PI-S after washing with benzene (b), THF(c), DMSO(d), and pyridine(e), respectively.