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Low-Temperature Coal Liquefaction in Basic Nitrogen Compounds

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Synopsis. A high conversion (75%) of Taiheiyo coal was attained using indole at 300 °C. Morpholine and tetrahydroquinoline were also effective solvents although quinoline, aniline, and triethylamine were not effective as well as tetralin and 1-methylnaphthalene. Extraordinarily high SRC yields and their molecular weight distributions suggested the presence of a solvent dimer and hydrogen donation.

We have already reported that the conversion exceeded 80% when the Taiheiyo coal was liquefied at 300 °C for 10 h using butylamine as a solvent.[1] The presence of low molecular weight compounds in coal has been proven by the fact that coal solubilization was proceeded by mild alkylation.[2a] It was suggested that the substitution reaction of butylamine with hydroxyl groups of coal contributed to the rupture of non covalent bonds, such as hydrogen bonds between coal molecules. The undesirable condensation or polymerization reactions of coal fragments can be avoided by liquefaction at low temperatures,[3] and the chemical structures of liquefaction products which were obtained at mild conditions provide important information about coal structure.[2]

We examined the coal-liquefaction reaction with basic nitrogen compounds other than butylamine to obtain information about a liquefaction mechanism at low temperature.

Experimental

Coal Samples and Solvents. Four coals were used in this study. Analyses of these coals are given in Table 1. The coals were ground so as to pass through a 100 mesh (149 m) screen and dried at 107 °C in a nitrogen atmosphere. Reagent-grade tetralin was used after distillation under reduced pressure. Various solvents were reagent grade.

Coal Liquefaction Procedure. Coal (6 g) and solvent (18 g) were placed in a 100 ml magnetically stirred autoclave and pressurized to 3 MPa with nitrogen. Materials remaining in the autoclave after liquefaction were extracted with benzene. Any benzene-insoluble material was further extracted with tetrahydrofuran (THF). Conversion to a THF-extractable material was calculated according to the following equation:

conversion (wt%, daf basis) = 100 × (weight of coal charged—weight of THF-insoluble material)/weight of daf coal

The liquefaction solvent was recovered from the benzene extract by vacuum distillation at 240 °C and 933 Pa. The distillation residue was weighed as a solvent-refined coal (SRC):

SRC yield (wt%, daf coal basis) = 100 × weight of SRC/weight of daf coal

Analysis of SRC. For the measurement of molecular weight distributions of SRC, gel permeation chromatography (GPC) was used. In the GPC measurement, THF was used as the liquid phase and a refractometer and a UV detector (254 nm) were used for monitoring the effluents from the columns.

Results and Discussion

The conversion of Taiheiyo coal at 300 °C are shown in Fig. 1. We already reported that tetralin scarcely donated hydrogen to coal at 300 °C.[1] Tetralin seems to act only as a diluent. Furthermore, conversions using 1-methylnaphthalene, quinoline, aniline, and triethylamine as solvents were almost the same with that using tetralin. However, higher conversions than these were obtained when indole was used as the solvent. The conversion reached to 75% for a liquefaction of 10 h. Conversions using tetrahydroquinoline and morpholine were also higher than that using tetralin, although they were lower than that using indole.

The liquefaction of subbituminous coal (Wyodak coal) using indole and a high conversion of the coal (62% at 375 °C, 20 min) have already been reported by Padrick and Lockwood, although the reaction temperature was higher than 300 °C.[4] When butylamine was used as the liquefaction solvent, coal conversion depended upon the hydroxyl oxygen content of coal,[1] as shown in Table 2. The conversion tended to increase, generally, with an increase in the hydroxyl content of coal in the case of butylamine. We tried to liquefy different kinds of coal using indole. The

Table 1. Analyses of Coals (wt%)

Coal	Ultimate analysis[a]				Proximate analysis			
	C	H	N	O_{diff} (OH)[b]	ash	mois	FC	VM
Yallourn	67.5	5.7	0.6	26.2 (7.2)	2.2	13.2	41.0	43 .6
Taiheiyo	77.5	6.4	1.0	15.1 (6.8)	15.1	4.7	35.3	44.9
Wandoan	77.6	6.2	0.8	15.4 (7.3)	7.3	9.2	38.6	44.9
Miike	82.2	6.2	1.0	10.6 (3.6)	9.5	2.2	44.4	43.9

a) daf coal basis. b) Content of hydroxyl oxygen.[1]

Table 2. Conversion of Coal and SRC Yield in the Liquefaction Using Basic Nitrogen Compound at 300 °C for 1 h

Solvent	Coal			
	Yallourn	Taiheiyo	Wandoan	Miike
Tetralin	4.8	5.7	4.8	9.1
Indole	29.8	23.5	24.9	25.5
Butylamine[1]	24.0	34.7	24.6	16.3

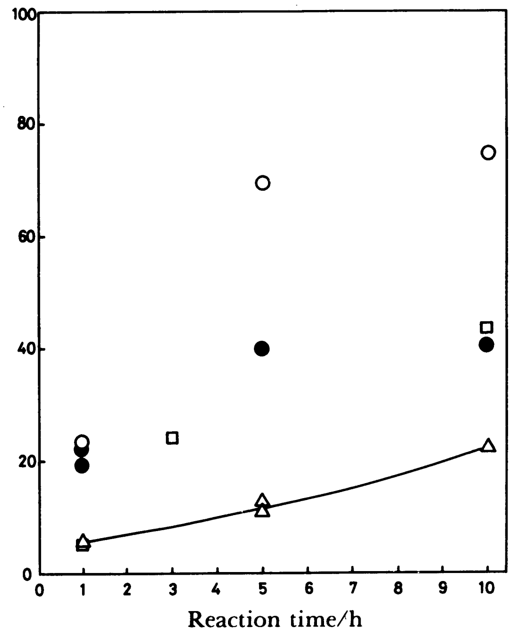

Fig. 1. Conversion of Taiheiyo coal using tetralin (△), indole (○), tetrahydroquinoline (●), and morpholine (□).

results are also given in Table 2. Coal conversions using indole at 300 °C for 1 h liquefaction were in the range from 23—30% and scarcely affected by coal rank. Indole was a more effective solvent than butylamine for Miike coal liquefaction, whose hydroxyl content was the smallest in four coals. This fact indicated that the liquefaction mechanism in indole was different from that in butylamine.

SRC yields using indole were higher than the conversions and exceeded 100% when Taiheiyo coal was liquefied for 5 and 10 h; the yields were 120 and 177%, respectively. The extraordinarily large SRC yields indicate the presence of an incorporation reaction of indole to coal or the oligomerization of indole. The molecular weight distributions of the SRCs are shown in Fig. 2. The SRCs were obtained in the liquefaction of Taiheiyo coal at 300 °C using tetralin, indole, tetrahydroquinoline, and morpholine; the yields (reaction time and conversion) were 3.0 (1 h, 5.7%), 90.3 (1 h, 23.5%), 95.5 (10 h, 40.4%), and 86.3% (10 h, 43.6%), respectively. Smooth molecular weight distributions were observed when tetralin and morpholine were used as the solvents and the same with that when butylamine was used.[1] However, clear peaks which did not arise from the solvents themselves were observed when indole and tetrahydroquinoline were used.

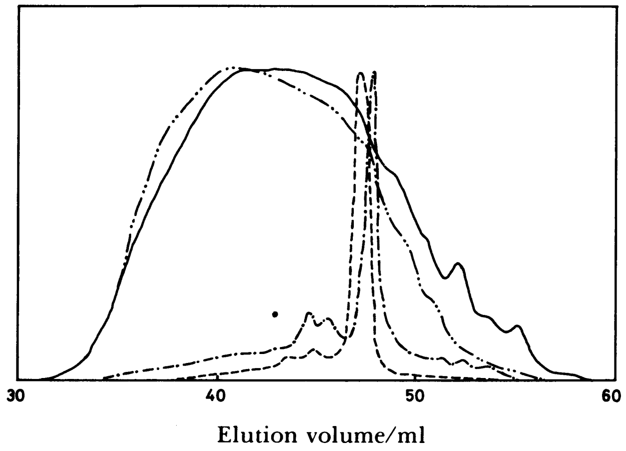

Fig. 2. Molecular distributions of Taiheiyo coal SRCs measured by a GPC UV detector. Solvents were tetralin (————), indole (— — — —), tetrahydroquinoline (—·—·—), morpholine (—··—··—).

Padrick and Lockwood reported the presence of a new peak in the product distribution of coal using indole, and concluded that the peak could be assigned as a complex between two indole molecules and one coal molecule with a molecular weight of 400.[4] However, we could not believe the above mechanism since the liquefaction products of coal had a wide range molecular weights.

It had already been reported that the heating of indole with sulfur produced an indole dimer.[5] We tried a reaction of indole and sulfur and confirmed that the elution volume of the dimer corresponded with that of the peak in Fig. 2. Furthermore, from the mass spectroscopy of the SRC the presence of the indole dimer was confirmed; its molecular weight was 232. This indicated that two indoles dimerized, evolving two hydrogen. The dimerization was also supported from the H/C values of the SRCs. The H/C of SRC in indole was 0.86; this value was fairly smaller than 1.15 in tetralin and also than 0.88 of indole itself. We could not determine the structure of indole dimer;[6] however, the presence of a dimer suggested that indole donated hydrogen to coal and dimerized. The same mechanism should be applied to liquefaction using tetrahydroquinoline. The presence of biquinoline in the reaction products under liquefaction conditions had already been reported.[7] The peak in Fig. 2 must be due to biquinoline.

To clarify the mechanism, the hydrogen donor ability of indole was measured using anthracene as a hydrogen acceptor.[8] When indole (3 g) and anthracene (3 g) was reacted at 300 °C for 1 h, 6% of the anthracene was hydrogenated to dihydroanthracene, although no anthracene was hydrogenated when tetralin was reacted with anthracene at 300 °C for 1 h.[8b] ESR studies of Petrakis and Grandy indicated that the radical concentration increased from low temperatures at 300 °C.[9] It is suggested that coal fragmentation at low-temperature occurred. It was considered that some part of the coal fragmented even at 300 °C and that the fragments were stabilized by the hydrogen donation of indole.

We already confirmed that the hydrogen donor ability of butylamine was not so large.[1] The molecular weight distribution of SRC in morpholine was smooth (Fig. 2) as with that in butylamine. An incorporation reaction in preference to dimerization was suggested because the SRC yields were larger than coal conversion and no dimer was observed by GPC and mass spectroscopy analysis. The same liquefaction mechanism as that in butylamine was considered.

In the low-temperature liquefaction of coal using butylamine, it was suggested that the substitution reaction of butylamine with hydroxyl groups in coal caused the rupture of noncovalent bonds in coal.[1] The same liquefaction mechanism was suggested in liquefaction using morpholine as a solvent. Furthermore, Mayo et al. carried out extractions and reactions of coals below 100 °C and proposed that pyridine and several amines cleaved some of the coal network to a soluble material.[10] This study suggested that the hydrogen donor abilities of basic nitrogen compounds, like indole and tetrahydroquinoline, were higher at low temperatures (like 300 °C) than expected. It was considered that at low temperature, coal solubility was attained by the complex actions of basic nitrogen compounds expressed above, such as a disruption of noncovalent bonds between coal molecules by a substitution reaction and hydrogen donation to coal fragments.

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