Synergistic Effect of Alcohol–Benzene Mixtures for Coal Extraction

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Coals were extracted with alcohol–benzene mixtures at room temperature. For coals of high oxygen content, Yallourn and Taiheiyo coals, the extraction yields for the mixtures were much greater than those for alcohols and benzene alone. This synergistic effect was more marked for less bulky alcohols: The order was methanol>ethanol>isopropyl alcohol>*t*-butyl alcohol. The degree of swelling and the apparent density of the coals in alcohols were measured. The results show that smaller alcohols may permeate into pores of the coals more extensively and cause greater swelling than larger alcohols. It is reasonable to consider that this swelling of the coals then facilitates the extraction with benzene or alcohol–benzene mixtures, which are better solvents in solubility for coal molecules than alcohols. For Shin-yubari coal having low oxygen content, no such a synergistic effect was observed, probably due to the lower degree of swelling of this coal.

Solvent extraction at room temperature, which causes no chemical change of coals, provides useful knowledge about coal structure through the studies on extraction mechanism and the characterization of extracts, even though extraction yields are usually low. It is also connected with coal liquefaction, which includes a step of coal dissolution with a suitable solvent under pyrolysis conditions. Many studies on solvent extraction have been reported[1] and attempts have been made to explain the extraction mechanism.

Dryden[2] has extensively studied solvent extraction; he used about 30 British coals and many organic solvents at or above room temperature. His conclusion concerning extraction yield is that a good solvent contains a nitrogen atom or an oxygen one (less efficient than nitrogen) possessing an unshared pair of electrons. He has also found that the quantity of imbibition of solvents used, which correlates to the swelling degree of coals in the solvents, is related to extract yields.

Marzec and coworkers[3] have presented a model for extraction of coal: Coal consists of a macromolecular network and extractable substances filling the pores of a network; the donor-acceptor interactions proposed by Gutmann[4] are responsible for binding together the network and the extractable substances. According to their model, solvent extraction is a substitution reaction in which extractable substances are replaced by a solvent molecule through donor-acceptor interaction of solvent and network or solvent and extractable substances.

Another approach to the extraction mechanism is a theoretical one from thermodynamics, namely, a correlation between the solubility parameter, δ, and the coal extractability or the solubility of coal-derived matter.[5] This theory states that a solvent having a δ value like that of the coal used will give the highest extraction yield. Hombach[6] has reported a result which may demonstrate the theory by using mixtures of solvents having different δ values. δ also has been found to be related to the swelling of coals.[5b,7]

However, there are some examples[8,9] indicating insufficient extraction which means that considerable amount of substances soluble in the solvent still exists in coal after the extraction. For example, the carbon disulfide-soluble part of pyridine extract is 4% based on coal, but the yield in a direct extraction of the same coal with carbon disulfide is only 0.2%.[8] Similarly, 13% is the chloroform-soluble part of the pyridine extract, but only 2.4% is the chloroform extraction yield.[9] Insufficient permeation into coals may be responsible for this result.

A mixed solvent is considered to be a powerful means in the elucidation of such a complex extraction mechanism, especially when this shows a large synergistic effect. We have reported[10] that the carbon disulfide–pyridine mixture shows a very large synergistic effect for extractions of bituminous coals. For Shin-yubari coal, the extraction yields for 1 h at room temperature are 0.9, 3.0, and 28.7% for carbon disulfide, pyridine, and their 1 : 1 mixture, respectively. The mechanism for this extraction is not clear at present. In this study we will report the mechanism of the extractions with alcohol–benzene mixtures. Alcohol–benzene mixtures are well known to show synergistic effects for coal extractions[11] and are often used to obtain wax and other coal-derived materials from brown coals.[12]

Experimental

Materials. Yallourn, Taiheiyo, and Shin-yubari coals, stored in water, were dried in air, ground, and sieved to <60 mesh. The coals were further dried at 107 °C under nitrogen atmosphere to constant weight (usually 1—2 h). The proximate and ultimate analyses (daf) are shown in Table 1.

All the solvents for extraction studies were reagent-grade (>98%) and were used without purification.

General Solvent Extraction Procedure of Coals. 4 g of coal sample was extracted with 100 ml of a solvent or a solvent mixture with stirring using a magnetic stirrer in an Erlenmeyer flask for 1 h at room temperature. After separation by centrifugation and filtration, the solvent was removed from the solution by a rotatory evaporater. The extract and the residue were dried *in vacuo* at 80 °C to constant weight. Extraction yield (daf) were determined from Eq. 1 and ash % is the value on dry-base. The yields were reproduced within ±10% for repeated runs.

Table 1. Ultimate and proximate analyses of coals

Coal	Proximate analysis (wt%)				Ultimate analysis (wt/%, daf)				
	Moisture	VM[a]	FC[b]	Ash	C	H	N	S	O[c]
Yallourn	14.3	47.3	37.6	0.8	66.1	5.3	0.6	0.3	27.7
Taiheiyo	4.4	49.2	34.1	12.3	75.4	7.0	1.2	0.3	16.1
Shin-yubari	0.9	38.0	54.1	7.0	86.7	6.2	1.7	0.3	5.1

a) Volatile matter. b) Fixed carbon. c) Difference.

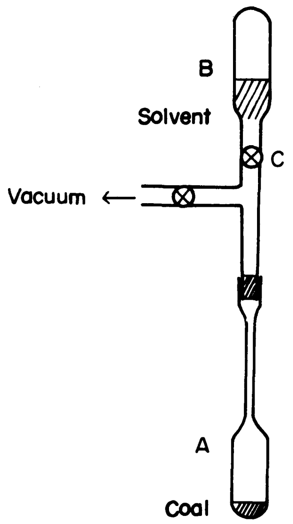

Fig. 1. The apparatus for apparent density measurement.

$$\text{Extraction yield (\%)} = \frac{\text{extract (g)} \times 100}{(1-\text{ash}(\%)/100) \times \text{coal feed (g)}} \quad (1)$$

For the extraction with alcohols, benzene, and their mixtures the recoveries of extracts+residues are always nearly or below 100%, indicating negligible inclusions of solvents in extracts and residues.

Relative Swelling Degree Measurement of Coals. The method reported by Hombach[6] was used. 600 mg of ground coal sample (<170 mesh) was placed in a cylindrical glass tube (d=10 mm, l=170 mm). 1.5 ml of solvent was added and the tube was immersed in a thermostat regulated at 30 °C, occasionally shaking the mixture to remove the gas which evolved. The height of the coal powder layer was measured after 1 and 24 h, respectively. The relative swelling degree for a solvent was estimated from the ratio of the height for a solvent to that for hexane as a standard and was reproduced within ±10% for repeated runs. The measurements at a time longer than 24 h showed no significant change. This rather simple method enables the relative swelling degree of a coal immersed in a solvent to be estimated easily.

Apparent Specific Gravity Measurement of Coals. 10 g of coal sample was charged into a glass ampoule, A, with a glass tube of 4 mm i.d. in Fig. 1. After evacuation for 3 h at room temperature the solvent in a tube, B, which was connected with a needle valve, C, was introduced into the ampoule, A, and the ampoule was immersed in a water bath regulated at 30 °C for 20 h. Then the position of the meniscus of the solvent was marked. The quantity of the solvent introduced was measured gravimetrically. The volume, V, of the coal-solvent mixture was determined by replacing it with distilled water, measuring the volume of water from its weight and specific gravity. A temperature of 30 °C was used, since t-butyl alcohol has freezing point higher than 25 °C. The apparent density was determined from Eq. 2 and was reproduced within ±5% for repeated runs.

$$\text{Apparent density (g/ml)} = \frac{\text{coal feed (g)}}{V\ \text{(ml)} - \text{volume of the solvent (ml)}} \quad (2)$$

Results

Extraction with Alcohol-Benzene Mixtures at Room Temperature. Figure 2 shows the effect of solvent composition of methanol–benzene mixture on extraction yields. For Yallourn and Taiheiyo coals, the yields for the mixture are higher than those for methanol and benzene alone. No such synergistic effect was observed for Shin-yubari coal.

Table 2 shows the effect of the structure of the alcohols on the extraction yields for Yallourn and Taiheiyo coals. The yields increase in the order of methanol>ethanol>isopropyl alcohol>t-butyl alcohol for the cases of the alcohol alone and of the mixture with benzene. The degree of the synergistic effect was estimated from the ratio of the yield for the mixtures to the sum of those for the alcohol and benzene alone; this is listed in the parentheses of the third and fifth columns in Table 2. These values also increase with decreasing the bulkiness of the alcohols used here.

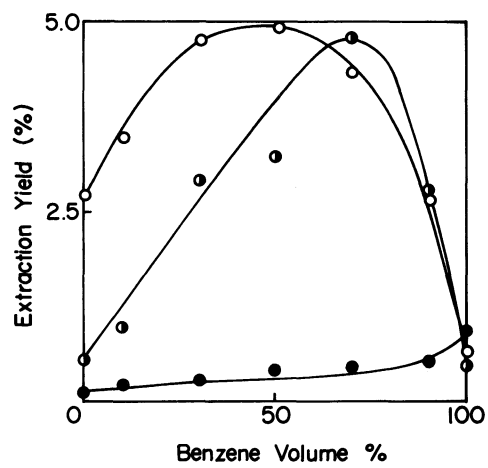

Fig. 2. Effect of solvent composition on the extraction with methanol–benzene mixture.
○: Yallourn coal, ◑: Taiheiyo coal, ●: Shinyubari coal.

Table 2. Extraction with alcohols, hexane, and their mixtures with benzene[a)]

Solvent	Extraction yield/%			
	Yallourn		Taiheiyo	
	Single[b)]	Mixture[c)]	Single[b)]	Mixture[c)]
Methanol	2.6_5	4.6_5 (1.40)[d)]	0.6_0	3.4_0 (3.10)[d)]
Ethanol[e)]	2.6_0	4.4_0 (1.35)[d)]	0.4_0	2.1_5 (2.40)[d)]
Isopropyl alcohol	1.9_5	3.5_0 (1.30)[d)]	0.3_0	1.1_5 (1.45)[d)]
t-Butyl alcohol	0.6_5	1.4_5 (1.20)[d)]	0.2_0	0.9_0 (1.30)[d)]
Hexane	0.4_5	0.4_0 (0.35)[d)]	0.1_0	0.3_5 (0.60)[d)]
Benzene	0.7_0	—	0.5_0	—

a) 4.0 g of coal (−60 mesh) in 100 ml of the solvent for 1 h at room temperature. b) The solvent in the first column was used. c) 1:1 mixture by volume with benzene was used. d) The ratio of the yield for the mixture to the sum of those for the alcohol (or hexane) and benzene alone. e) 95% ethanol.

Table 3. Relative swelling degrees of Yallourn, Taiheiyo, and Shin-yubari coals[a)] in alcohols, hexane, and benzene at 30 °C

Solvent	Yallourn		Taiheiyo		Shin-yubari	
	1 h	24 h	1 h	24 h	1 h	24 h
Methanol	1.3_5	1.4_0	1.2_5	1.2_5	1.0_5	1.0_0
Ethanol[b)]	1.3_5	1.4_5	1.3_0	1.3_0	1.0_5	1.0_0
Isopropyl alcohol	1.3_0	1.4_0	1.2_5	1.2_5	—[c)]	1.0_0
t-Butyl alcohol	1.0_0	1.0_0	1.1_5	1.2_0	—[c)]	0.9_0
Hexane[d)]	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
Benzene	1.0_0	1.1_0	1.1_5	1.1_5	1.0_5	1.1_0

a) −170 mesh. b) 95% alcohol. c) Insufficient sedimentation. d) A standard solvent.

The extract from Taiheiyo coal with 1:1 methanol-benzene mixture is soluble in benzene and almost insoluble in methanol. Its carbon and hydrogen % (daf), 81.0 and 10.4%, are higher than those for the raw coal, indicating that a hydrocarbon-like extract was obtained. The extraction yields increase with decreasing particle size, namely 0.3_0, 0.5_5, 1.4_0, and 3.3_5% for 9—16, 16—60, 60—100, and 100—170 mesh, respectively, probably due to the increase of the surface area of the coal. The extraction for 3 h gave a little higher yield (5%) than that for 1 h, in the extraction with 1:1 methanol–benzene mixture.

Shin-yubari coal showed no synergistic effect for other alcohols than methanol.

Relative Swelling Degrees and Apparent Densities in Alcohols. Table 3 shows that relative swelling degrees in alcohols were in the order of ethanol> methanol≃isopropyl alcohol>*t*-butyl alcohol≃benzene≃hexane for Yallourn and Taiheiyo coals, and benzene>methanol≃ethanol≃isopropyl alcohol≃hexane>*t*-butyl alcohol for Shin-yubari coal. Here hexane is known to be inert for swelling of coals. It is clear from Table 3 that alcohols induce a swelling of Yallourn and Taiheiyo coals, but not for Shin-yubari coal, and that this swelling is generally more marked for less bulky alcohols.

Apparent densities measured at 30 °C are summarized in Table 4. This apparent density is considered to reflect the extent of permeation of a solvent into coal; greater density may correspond to greater permeation of a solvent. Table 4 shows that the order of the densities among the alcohols is the same as that of the extraction yields for Yallourn and Taiheiyo coals (Table 2). Namely, smaller alcohols have greater permeation and extraction yield than larger alcohols. Table 4 also shows that apparent densities for Taiheiyo coal were greater than those for Shin-yubari coal in all solvents measured. Toda, Yoshida, Honda, and Hatami[13)] have obtained a similar result in their extensive studies on pore structures of various coals that Taiheiyo coal (*C*%, 77.8%) has greater apparent densities than Yubari coal (*C*%, 86.2%) both for methanol and hexane solvents. They discussed these results from the viewpoints of the true densities of the coals and the permeation of the solvents into the coals.

Table 4. Apparent densities of Taiheiyo and Shin-yubari coals in alcohols and hexane at 30 °C

Solvent	Density (g/cm^3)	
	Taiheiyo[a)]	Shin-yubari[a)]
Methanol	1.425	1.321
Ethanol[b)]	1.390	1.305
Isopropyl alcohol	1.348	1.275
t-Butyl alcohol	1.322	1.253
Hexane	1.369	1.313

a) −60 mesh. b) 95% alcohol.

Extraction with Various Methanol-organic Solvent Mixtures. Various methanol-organic solvent

TABLE 5. EXTRACTION WITH VARIOUS ORGANIC SOLVENTS AND THEIR MIXTURES WITH METHANOL[a)]

Solvent	Extraction yield/%					
	Yallourn		Taiheiyo		Shin-yubari	
	Single[b)]	Mixture[c)]	Single[b)]	Mixture[c)]	Single[b)]	Mixture[c)]
Carbon tetrachloride	0.2 (98)[d)]	4.5 (102)[d)]	0.5 (98)[d)]	2.5 (100)[d)]	0.2 (101)[d)]	0.3 (101)[d)]
Benzene	0.7 (98)[d)]	4.7 (97)[d)]	0.5 (99)[d)]	3.4 (101)[d)]	0.9 (100)[d)]	0.4 (100)[d)]
Carbon disulfide	1.9 (100)[d)]	5.3 (98)[d)]	1.0 (98)[d)]	7.0 (100)[d)]	0.7 (101)[d)]	3.5 (101)[d)]
Tetrahydrofuran	5.7 (101)[d)]	6.6 (100)[d)]	3.1 (98)[d)]	4.4 (102)[d)]	0.9 (101)[d)]	0.4 (101)[d)]
Pyridine	7.3 (105)[d)]	6.8 (102)[d)]	6.4 (110)[d)]	4.4 (104)[d)]	3.0 (101)[d)]	0.7 (101)[d)]

a) 4.0 g of coal (−60 mesh) in 100 ml of the solvent for 1 h at room temperature. b) The solvent in the first column was used. c) 1 : 1 mixture by volume with methanol was used. d) [(extract+residue) (g)/coal feed (g)]×100.

mixtures were examined. The results are summarized in Table 5, together with the result for methanol-benzene mixture. For Yallourn and Taiheiyo coals, methanol mixtures with carbon tetrachloride, benzene, carbon disulfide, and tetrahydrofuran gave higher extraction yields than these organic solvents alone. For Shin-yubari coal, carbon disulfide and pyridine gave higher and lower yields for the mixture with methanol, respectively.

Discussion

Synergistic Effect of Alcohol-Benzene Mixtures. Figure 2 and Table 2 show that the synergistic effect for alcohol-benzene mixtures was observed for Yallourn and Taiheiyo coals; this was more marked for less bulky alcohols. Tables 3 and 4 show that smaller alcohols may permeate into pores of a coal more extensively and may cause greater swelling than larger alcohols. It is not unreasonable to consider that this swelling, in turn, may facilitate an extraction with another solvents.[14)] The solubility test for the extracts of Taiheiyo coal with methanol-benzene mixture indicates that benzene has a greater solubility than alcohols. Swelling with alcohols may facilitate extraction with benzene or alcohol-benzene mixtures. In the case of Yallourn coal, an extracting solvent may be alcohol-benzene mixtures, not benzene alone, since 15% of the extract was not soluble in benzene nor methanol. Swelling has been suggested by Dryden[2)] to be an important factor for extraction. Pajak and Marzec[15)] have also reported that the extraction yields with solvents of low extraction power, for example, benzene and diethyl ether, increased when a coal (*C*% 80.7%) was pre-swollen with methanol, tetrahydrofuran, dimethyl formamide, or pyridine.

For Shin-yubari coal, on the other hand, neither swelling by alcohols nor any synergistic effect were observed. This may be attributed to low content of hydroxyl groups, which is deduced from the IR spectrum and from the oxygen content of Shin-yubari coal. Nelson, Mahajan, and Walker[16)] have found that methanol-induced swelling increases linearly with the oxygen content of coals, due to an increased affinity of coal molecules for methanol.

Patel and coworkers[17)] have reported that the solubility of solvent-refined coal and solvent-refined lignite in benzene or chloroform increased from 50—60 to 80—100% upon either acetylation or silylation and this can be explained by the disruption of the intermolecular hydrogen bond in coal. The similar increase of benzene or chloroform extract yield has been reported by Liotta and coworkers[18)] in alkylation of coal which proceeds under mild conditions; this is again ascribed to the reduction of intermolecular associations in coals. In our case, hydrogen bonding between coal molecules in Yallourn and Taiheiyo coals may be broken by hydrogen bonding with the permeating alcohols and the swelling of coal may thus be induced.

Although the extraction yields in our experiments are low, the mechanism proposed here may apply to other solvent systems and may be one example where bulkiness of solvents plays an important role in extraction.

Extraction with Various Methanol-organic Solvent Mixtures. Table 5 shows that the recovery of extract+residue considerably exceeds 100% in extractions of Yallourn and Taiheiyo coals with methanol-pyridine mixture. Collins and coworkers[19)] have reported that pyridine and ethylenediamine were retained in both the extract and residue even after washing with benzene. In our case the solvent may be retained in the extract and residue. Other solvents in Table 5 than pyridine showed nearly 100% recovery. The increased yields for the methanol mixtures with carbon tetrachloride in Yallourn and Taiheiyo coals may be caused by the same mechanism as in the case of the mixture with benzene. On the other hand, decreased yields in the case of pyridine for Shin-yubari coal may be caused by its hydrogen bonding with methanol. Dryden[2)] has reported that ethylenediamine loses its high extractability when it contains water, since it forms hydrogen bonds with the nitrogen atoms of ethylenediamine.

Carbon disulfide seems to be different from other solvents listed in Table 5, in that its mixture with methanol is effective for all the coals in Table 5. We have found and reported that carbon disulfide-pyridine mixture is a very efficient solvent for Shin-yubari coal: It gives about 40% extraction yield at room temperature.[10)]

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14) It is not clear why methanol has smaller swelling, but greater extraction yields than ethanol, as shown in Tables 2 and 3. One tentative explanation is that strong interaction between methanol and the surface of the coals, which is suggested by Franklin, makes the pore volume inside the coal increase and facilitates the extraction; R. E. Franklin, *Trans. Faraday Soc.*, **45**, 274 (1949).

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