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The Effect of Solvent on the Liquefaction of Coal as a Function of Coal Rank

Yoshio Kamiya,* Tadashi Yao, and Shinichi Nagae
Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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In order to study the effect of solvent on the liquefaction of coal as a function of coal rank, the liquefaction of five kinds of coals from carbon content of 66% to 83% were carried out in the presence of various aromatic solvents. It was found that three ring aromatic hydrocarbons were more powerful solvent for the liquefaction. Hydrogen donor solvents such as tetralin and hydrophenanthrenes were most effective of all solvents tested independent of coal rank. A mixture of hydrogen donor and polar compounds such as phenol and quinoline was confirmed to be effective to bituminous coal but not so effective to brown coal. It should be stressed that hydrogen donating property of solvent is most important for low rank coals. The chemical analyses of products have shown that the properties of solvent refined coal are a little affected by the quality of solvent.

It has been stressed that the aromatic solvent plays an important role in coal liquefaction reaction.[1,2] At the initial stage coal is thermally decomposed to lower molecular fragments being dissolved and stabilized by the solvent. Otherwise the unstable fragments will be polymerized to form carbonaceous materials.

Partially hydrogenated aromatic compounds such as tetralin are very effective solvent because of hydrogen donating property. Polar compounds such as phenols[3-5] and quinolines[6] are also effective in the presence of hydrogen donors probably because of acceleration of cleavage of aromatic ether structures.[7]

Although the solvent effect on the coal liquefaction has been studied by many workers, the generalization of experimental results seems very difficult because of differences in preparation of coal sample, experimental conditions and apparatus. There has been hardly reported the relative effectiveness of aromatic solvents in the presence of hydrogen donor on a variety of coals.

Evaluation of solvent effect as a function of coal rank must be very important not only for designing the optimum solvent composition but also for studying the difference in the chemical structure of coals.

In this paper, is reported the effect of various aromatic solvents being contained in coal liquefaction products as a function of coal rank.

Experimental

Coal Sample and Solvent. Five kinds of Japanese and Australian coal with carbon content from 66% to 83% were selected and the analytical data of these coals are shown in Table 1. All coals were dried in a vacuum oven at 105 °C. 1,2,3,4-Tetrahydronaphthalene (tetralin) and 1-methyl-naphthalene were of reagent grade and distilled at 70 °C under reduced pressure after washing with sulfuric acid, alkali and water. Various solvents were reagent grade and used as received.

The properties of mixed solvent, creosote oil, anthracene oil, and middle distillate and heavy distillate from SRC-II process are shown in Table 2.

Middle and heavy distillates[8] were produced from Powhatan coal and supplied by Pittsburgh and Midway coal Mining Company, and these solvents seem to have some hydrogen-donating property because H_β content was 2.5% and 1.8% respectively.

Coal Liquefaction Procedure. Solvent and coal of minus 60 mesh were added to 300 ml magnetic stirring (500 min^{-1}) autoclave. After pressurizing with hydrogen, the autoclave was heated to the reaction temperature within 45 min and maintained at the temperature during reaction time.

Table 1. Elemental analyses of sample coals

Sample coals	Yallourn	Wandoan	Taiheiyo	Liddell	Akabira
C(wt%,daf)	65.8	74.5	75.3	82.0	82.7
H(wt%,daf)	5.1	6.8	6.5	5.4	5.9
N(wt%,daf)	0.5	0.8	1.6	1.5	1.9
S(wt%,daf)	0.2	0.4	0.3	0.5	0.4
O(wt%,diff.)	28.4	25.6	17.5	11.1	10.5
Ash(wt%, drycoal)	2.5	28.5	14.5	11.1	5.7

Table 2. Elemental analyses of mixed solvents

Process solvents	Anthracene oil	Creosote oil	Heavy distillate	Middle distillate
C(wt%)	90.2	90.8	86.3	88.9
H(wt%)	6.0	6.4	9.3	7.5
N(wt%)	0.9	0.7	1.1	1.4
S(wt%)	0.8	0.7	0.2	0.4
O(wt%,diff)	2.1	1.4	4.1	1.8
fa	0.92	0.91	0.69	0.57

At the completion of a run, the autoclave was cooled by electric fan to room temperature and the autoclave gases were vented through gas meter and analyzed by gas chromatography.

The liquid products were removed through glass filter, and the residual solids were extracted with tetrahydrofuran and weighed after drying.

The amount of moisture-ash-free (maf) coal liquefied during the reaction was calculated as a percentage of the maf feed coal by subtracting the percentage undissolved to give the conversion.

The recovered solution was distilled off using a Buchi GKR-50 rotary evaporator at 200 °C and 0.01 bar, and subjected to various chemical analyses.

Liquid portions of the samples were subjected to gas chromatographic analysis to determine the composition of solvent.

Analysis of THF-soluble Fraction. THF-soluble fraction, so called Solvent Refined Coal, was obtained by distilling off the tetrahydrofuran-soluble products by using rotary evaporator at 200 °C and 0.01 bar.

THF-soluble fraction was submitted to the elementary analyses, molecular weight, ^{1}H-NMR.

Results and Discussion

The conversion of Akabira coal in a mixed solvent composed of 1-methylnaphthalene and one testing solvent was measured at 425 °C for 30 min in order to compare the relative effectiveness of solvent. At initial hydrogen pressure of 20 bar, the conversion to benzene-soluble fraction was generally very low and the conversion to THF-soluble was as low as 50% except in the case of tetralin. Then, the initial hydrogen pressure was raised to 50 bar and the results are shown in Table 3. The effect of hydrogen-donating solvent was most remarkable, since the most effective solvent was tetralin and the second was acenaphthene, both of which have benzylic and donating hydrogen atoms.

Consumed tetralin could be entirely recovered as naphthalene, but reacted acenaphthene corresponding to 36% of the feed could not be recovered probably due to polymerization of dehydrogenated product, acenaphthylene.

Highly condensed aromatic hydrocarbons such as pyrene and fluoranthene have shown higher conversion of coal as reported by Davies and coworkers.[9] The order of effectiveness of solvent for Akabira coal was as follows; fluoranthene=pyrene>phenanthrene>naphthalene.

This result can be ascribed to several effects such as solubility and solvent hydrogenation as reported by Derbyshire,[10] but partly to free radical stabilization effect, because polycondensed aromatic compounds can easily react with free radicals and subsequently donate hydrogen atom to another free radical. Polar solvents such as phenol and quinoline were not so effective in the absence of hydrogen donors.

Table 3. Liquefaction of Akabira coal in synthetic solvents composed of 1-methylnaphthalene and an additive

Additive	Conversion/wt% (THF-soluble)
1-Methylnaphthalene	47
Fluorene	53
Phenanthrene	56
Fluoranthene	59
Pyrene	59
Tetralin	80
Acenaphthene	70
Quinoline	64
1-Naphthol	57
Carbazole	58
Dibenzofuran	50

a) Reaction conditions: 1-Methylnaphthalene 40 ml, additive 20 ml, coal 20 g, 425 °C, 30 min, initial H_2 pressure 50 bar.

In a practical coal liquefaction process, there exist usually some amounts of hydrogen-donating compounds, because the recycle solvent is nearly in equilibrium with high pressure of hydrogen, or solvent is used after hydrotreatment. When we compare the solvent effect of aromatic hydrocarbons, the effect will be varied depending on the pressure of hydrogen gas and reaction conditions. Therefore, it can be quite reasonable to use a solvent containing some amounts of hydrogen donors such as tetralin, in order to compare the effect of various solvents.

The yields of benzene-soluble fraction as well as THF-soluble fraction increased remarkably by replacing anthracene oil with tetralin, indicating that the formation of lower molecular products by the thermal treatment can be drastically increased in the presence of hydrogen-donating compounds. The yield of benzene-soluble fraction increased from 15% to 55%, when anthracene oil was completely replaced by tetralin.

The effect of tetralin as a function of coal rank was studied as shown in Table 4. In the case of brown coal, the conversion of coal has shown a higher value in the presence of tetralin, but the consumption of tetralin showed also a similar tendency. This result represents a higher reactivity of brown coal. Analyses of gaseous products indicated that Yallourn coal yielded very high amount of carbon dioxide and in contrast the yield of methane on the daf basis was not so varied depending on coalification grade.

The effect of various solvents of five kinds of coal from carbon content of 66% to 83% is shown in Table 5. Generally, 1-methylnaphthalene seems slightly more effective than naphthalene, and phenanthrene a little better solvent than naphthalene, and as well anthracene oil than creosote oil. These results suggest that three ring aromatic compounds are favorable solvent than two ring aromatics due to the solubility of coal fragments and also probably due to the higher hydrogen donating ability. Recently, Whitehurst and his coworkers[10] made clear that highly condensed aromatic compounds such as pyrene can easily accept hydrogen as hydrogen shuttlers and subsequently donate hydrogen atom to another free radical.

The effect of hydrogen-donating solvents having benzyl hydrog ensuch as hydroaromatics with relatively low bond dissociation energy was most remarkable. The higher conversion was clearly observed in the case of low rank coals such as Yallourn and Taiheiyo, indicating that hydrogen donating property is most important for

Table 4. Reactivities of sample coals[a)]

Sample coals C%, daf		Yallourn 65.8	Wandoan 74.5	Taiheiyo 75.3	Liddell 82.0	Akabira 82.7
Conversion/%	Coal	87	81	85	80	85
	Tetralin	47	29	28	22	27
Gaseous products (ml)	CH_4	530	350	470	440	560
	CO_2	1010	180	260	50	50

a) Reaction conditions: Coal 20 g, tetralin 30 ml, 1-methylnaphthalene 30 ml, 425 °C, 30 min, initial H_2 pressure 20 bar.

TABLE 5. EFFECT OF AROMATIC SOLVENTS ON THE LIQUEFACTION OF FIVE COALS[a)]

Additive	Conversion/wt% (THF-soluble)				
	Yallourn	Wandoan	Taiheiyo	Liddell	Akabira
Naphthalene	64	71	74	71	67
1-Methylnaphthalene	64	72	79	71	70
Phenanthrene	70	74	80	74	75
Creosote oil	66	74	81	75	85
Anthracene oil	68	75	81	75	85
Tetralin	87	80	85	80	85
Dihydroanthracene	87	83	92	83	84
Dihydrophenanthrene	91	85	91	87	85
Octahydrophenanthrene	96	84	94	85	88
Carbazole	69	75	84	79	81
Quinoline	66	74	80	79	90
Phenol	66	74	78	75	88
1-Naphthol	82	83	88	86	95
Middle distillate	69	75	82	75	—
Heavy distillate	73	76	84	78	—

a) Reaction conditions: 1-Methylnaphthalene 30 ml, tetralin 10 ml, additive 20 ml, coal 20 g, 425 °C, 30 min, initial H_2 pressure 20 bar.

coals with low coalification grade. It has been reported that the liquefaction of brown coal is sensitive to hydrogen donating property of solvent.[1,2)] The order of effectiveness of hydrogen-donor solvent has shown that tricyclic hydroaromatics give higher conversion of coal than bicyclic hydroaromatics.

Previously, we have shown that a mixture of hydrogen-donating solvent and phenolic compounds is a very effective solvent for liquefaction of bituminous coal[5)] and this result can be ascribed to the acceleration of scission of ether linkage[7)] in coal structure.

Again, in this experiment, polar compounds such as phenol, 1-naphthol and quinoline in the presence of hydrogen donor were confirmed to be effective solvent for bituminous coals.

In contrast, it was observed that the conversion of brown coal was increased in the presence of 1-naphthol but not affected in the presence of phenol at concentrations below 20 wt% in solution at 400 °C. However, it should be mentioned that at lower temperature of 350 °C, phenolic compounds became effective for dissolution reaction as shown in Fig. 1.

These different effect due to phenol on coal rank can be explained by the difference of chemical structure of coal, probably due to aromatic ether linkage.

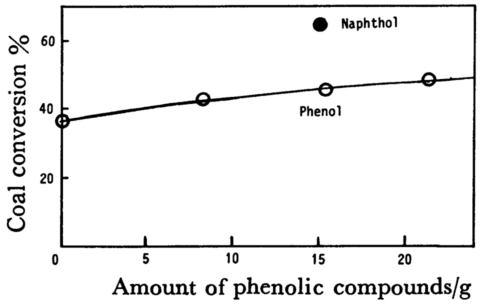

Fig. 1. Effect of phenolic compounds on the liquefaction of Yallourn coal.
Reaction conditions: Coal 20 g, tetralin 15 ml, 1-methylnaphthalene 45 ml, 350 °C, 30 min, initial H_2 pressure 20 bar.

A condensed diaryl ether can be decomposed considerably at 450 °C. On the other hand, the carbon-oxygen bond of benzyl phenyl ether or dibenzyl ether can be cleaved rapidly at temperatures below 400 °C. The rapid decomposition of brown coal can be attributed to the benzyl ether structures, which would not give the enhancing effect due to phenol at 425 °C. The slower decomposition of bituminous coal seems to be due to diaryl ether linkage.

Middle distillate as well as heavy distillate from SRC-II process contained some amounts of hydrogen donors along with about 10% of phenolic compounds.

TABLE. 6. CONVERSION OF SOLVENTS IN THE LIQUEFACTION OF YALLOURN COAL[a)]

Additive solvent	Conversion/wt%		
	Coal	Tetralin	Additive
Phenanthrene	70	86	0
Dihydroanthracene	87	75	88
Dihydrophenanthrene	91	56	98
Octahydrophenanthrene	96	35	79
1-Naphthol	82	95	70

a) Reaction conditions: See Table 5.

TABLE 7. CONVERSION OF SOLVENTS IN THE LIQUEFACTION OF AKABIRA COAL[a)]

Additive solvent	Conversion/wt%		
	Coal	Tetralin	Additive
Phenanthrene	69	59	2
Dihydrophenanthrene	85	30	97
Octahydrophenanthrene	88	22	58
1-Naphthol	93	63	39
Quinoline	89	63	26

a) Reaction conditions: See Table 5.

Table 8. Analyses of SRC from Yallourn coal

Solvent(ml)	Tetralin(30) 1-MN(30)[a]	9,10-Dihydrophenanthrene(20) Tetralin(10) 1-MN(30)[a]	Phenanthrene(20) Tetralin(10) 1-MN(30)[a]
Elemental analyses			
C (wt%)	83.7	83.6	84.1
H	6.1	5.6	5.8
N	0.9	0.7	0.6
O	9.3	10.1	9.5
Structural parameters			
fa	0.72	0.75	0.76
$H_{\mathrm{au}}/C_{\mathrm{a}}$[b]	0.75	0.72	0.72
σ[c]	0.42	0.40	0.37
n	1.8	1.9	2.0

a) 1-MN: 1-Methylnaphthalene. b) $H_{\mathrm{au}}/C_{\mathrm{a}}$: H/C ratio of hypothetical unsubst. aromatics. c) σ: Fraction of aromatic edge atoms occupied by subst.

Therefore, it is reasonable that these distillates show a little better result than aromatic hydrocarbons but not so good results as hydrogen donors such as tetralin.

Conversion of solvents in the liquefaction of Yallourn coal is shown in Table 6. In the presence of tetralin, phenanthrene was hardly consumed in the course of reaction. Dihydrianthracene and hydrophenanthrenes were remarkably decreased, but they were recovered as the dehydrogenated products, that is, anthracene and phenanthrene.

It can be concluded that, from the conversion values of tetralin and coal, the most effective hydrogen donors are octahydrophenanthrene and dihydrophenanthrene far reactive than tetralin.

In the case of Akabira coal, as shown in Table 7, 98% of phenanthrene was recovered as it is. Hydrophenanthrenes were converted to phenanthrene with higher conversions than tetralin.

Table 9. Analyses of SRC from Wandoan coal

Solvent (ml)	Tetralin(30) 1-MN(30)[a]	9,10-Dihydrophenanthrene(20) Tetralin(10) 1-MN(30)[a]	Phenanthrene(20) Tetralin(10) 1-MN(30)[a]	1-Naphthol(20) Tetralin(10) 1-MN(30)[a]
Elemental analyses				
C (wt%)	85.1	84.1	84.7	85.7
H	6.8	6.7	6.2	5.9
N	1.6	1.7	1.8	0.6
O	6.5	7.5	7.3	7.8
Structural parameters				
fa	0.65	0.65	0.70	0.82
$H_{\mathrm{au}}/C_{\mathrm{a}}$	0.67	0.70	0.66	0.74
σ	0.42	0.43	0.42	0.24
n	2.8	2.7	2.4	2.4

a) 1-MN: 1-Methylnaphthalene.

Table 10. Analyses of SRC from Liddell coal

Solvent (ml)	Tetralin(30) 1-MN(30)[a]	9,10-Dihydrophenanthrene(20) Tetralin(10) 1-MN(30)[a]	Phenanthrene(20) Tetralin(10) 1-MN(30)[a]
Elemental analyses			
C (wt%)	85.9	86.1	85.6
H	6.1	5.8	5.6
N	1.6	2.2	1.9
O (diff)	6.4	5.9	6.9
Structural parameters			
fa	0.72	0.74	0.74
$H_{\mathrm{au}}/C_{\mathrm{a}}$	0.70	0.65	0.63
σ	0.44	0.41	0.42
n	1.8	1.8	1.9

a) 1-MN: 1-Methylnaphthalene.

Solvent effect by hydrogen donor must be mainly in the stabilization of free radical fragment. In the absence of hydrogen donor, for example, 1,2-diarylethane structure[1] will be converted to a more stable form of diarylmethane after cleavage reaction and a benzyl ether structure to a diarylmethane structure.[7]

While, considerable amounts of naphthol and quinoline could not be recovered.

1-Naphthol gave a high value of coal conversion probably due to the reactive property. Recently, Derbyshire and coworkers[10] made clear that naphthol was remarkably consumed in the presence of coal. This result can be attributed to the hydrogen abstraction from 1-naphthol by alkoxyl radicals resulting from coal fragments and the subsequent reaction of naphthyloxyl radical.

The consumption of 1-naphthol is much higher in the case of Yallourn coal as compared with Akabira coal, suggesting that a lot of alkoxyl radicals are evolved when a lower rank coal is thermally decomposed.

We consider that 1-naphthol can be converted to naphthalene derivative or dimeric furan compounds *via* naphthyloxyl radical.

In the case of Yallourn brown coal, the obtained THF-soluble fraction has shown the lowest value in carbon content of 84% (Table 8). A hydrogen donating solvent as compared with phenanthrene seems to give slightly lower values in *fa* and higher values in $H_{\mathrm{au}}/C_{\mathrm{a}}$, indicating that solvent quality affects the properties of liquefaction products.

Table 9 shows analytical results of Wandoan coal, in this case, hydrogen-donating solvents give higher values in hydrogen content and lower values in *fa*. In the case of 1-naphthol, the characteristic points were in high *fa* and low σ, which can be ascribed to the addition of 1-naphthol to coal molecule or condensation reaction of 1-naphthol.

In the case of Liddell coal (Table 10), the hydrogenating effect due to hydrogen-donating solvent can be seen in hydrogen content, *fa* and H_{au}/C_a.

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