

LIQUEFACTION OF INDONESIAN COALS WITH BOTTOM RECYCLE USING FeNi CATALYST SUPPORTED ON CARBON NANOPARTICLES

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Abstract

A series of coal liquefaction with bottom recycle was performed using FeNi catalyst supported on carbon nanoparticles (Ketjen Black: KB) at 450°C for single- and two-stage. In the single-stage, FeNi/KB catalyst gave excellent catalytic activity providing oil yield over 74% with successful reduction of catalytic loading to 0.15 wt% Fe and 0.15 wt% Ni d.a.f coal base.

Keywords: coal liquefaction; bottom recycle; iron nickel supported on KB

Introduction

The main key of catalyst cost reduction for direct liquefaction of coal are recovery and repeated use of the catalyst. The major difficulty for the catalyst recovery comes from the mineral presence in coal. There are two approaches for catalyst recovery and regeneration. The first one is to eliminate or reduce the mineral in the coal, and another one is to design catalysts of ultrafine particle size and low specific gravity for recovery.¹

Dow Chemical Co developed very small particles of molybdenum sulfide used as catalysts and were recovered and recycled with a novel hydroclone process.² The catalyst support can also provide such functions. The authors proposed a novel type of liquefaction catalyst with high activity and functions for recovery and repeated use.³⁻⁶ NiMo and FeNi sulfides supported on particular carbon nanoparticles are catalysts, which can provide high distillate yields and can be separated from the solid residue by gravimetric separation for repeated use.

One of the major contributions for recycle of the catalyst or drastic reduction of its amount is to recycle non-distillate coal liquefaction products back to the initial stage of the process, which is termed as bottom recycle.⁷ It has been recognized that large polycondensed aromatic rings from non-distillate products are very effective to disperse solvents for the very polar initial products of coal dissolution. Moreover, they can be hydrogenated easily to hydro aromatic structures, and have ability to shuttle hydrogen between unreacted coal, reacting molecules, and solvent components.^{8,9}

In the present study, liquefaction of Tanito Harum and Adaro coals (Indonesian coals) was performed by using FeNi/KB catalyst to examine the effect of bottom recycle on the oil yield and the performance of H-donor (tetralin):

Experimental Section

Catalyst and Materials

A prescribed amount of Ketjen black was dispersed in methanol by ultrasonic irradiation for 15 min. Then, iron(II) fumarate and Ni(NO₃)₂ dissolved in methanol were mixed to the KB-methanol slurry with a small amount of nitric acid (1% vol.) as an additive to prepare FeNi/KB catalyst. The slurry was dispersed by ultrasonic, and then, heated at 40°C for 2 h before the slurry was dried at 120°C for 12 h in vacuo. The catalyst was presulfided by flowing 5% vol H₂S/H₂ at 360°C for 2 h prior to the reaction.

The elemental analysis of Tanito Harum coal is summarized in Table 1. Commercially guaranteed grade tetralin (TL) was used as liquefaction solvent.

Liquefaction Procedure

Coal liquefaction was performed in an electromagnetic-driven autoclave of 50 ml capacity at 450°C for single stage, 380°C and 450°C for two-stage liquefaction.¹⁰ Three grams of coal, 3 grams of solvent, and 0.09 grams of catalyst were charged to the autoclave.¹¹ The single- and two-stage liquefaction was performed under 15 MPa of hydrogen pressure. The heating rate to the reaction temperature was 20°C/min. The stirring speed was 1300 rpm. For two-stage liquefaction, the first stage was performed at 380°C for 15 min, and then the reactor was cooled down. Hydrogen gas was renewed after releasing out gaseous products. The second stage reaction was carried out at 450°C, 15 MPa for 105 min.

The liquefaction with repeated use of catalyst was done by recycling asphaltene, preasphaltene, residue, and used catalyst from run 1 to run 2 after they were separated from oil as illustrated in Figure 1. The liquefaction with bottom recycle was performed in 7 runs as illustrated in Figure 2. After the third run, a third of asphaltene, preasphaltene, residue, and used

catalyst was purged to prevent the accumulation of ash and unconverted materials. The remainder was recycled to the following run. To keep the the sulfidation state of the catalyst, CS_2 was added in every run.¹²

The liquid and solid products of coal liquefaction were recovered with THF. After THF was removed by evaporation, the product was extracted in sequence with n-hexane, acetone, and THF. The n-hexane-soluble (HS), hexane-insoluble but acetone-soluble (HI-ACS), acetone-insoluble but THF-soluble (ACI-THFS), and THF-insoluble (THFI) substances were defined as oil(O) and solvent, asphaltene(A), preasphaltene(PA), and residue(R), respectively. The gas yield was calculated by weight difference between initial coal and recovered product. The oil yield was calculated by subtracting the solvent weight from the total weight of HS. The reaction under the same conditions was repeated at least three times to make sure the experimental result that were within 1wt% daf coal base.

Results and Discussion

Recycle of Heavy Residual Product and Repeated used of FeNi/KB catalyst

Table 1 describes results of residual product recycle in the single-stage liquefaction of Tanito Harum coal with FeNi/KB catalyst using process as illustrated in Figure 1. The liquefaction process in run 2 gave 69% oil yield that was comparable to that of run 1. It must be noted that there was no addition of fresh catalyst in run 2. It means that the activity of repeated use of FeNi/KB catalyst in run 2 was still high enough. Moreover, the oil yield was increased by hydrogenation of asphaltene and preasphaltene. The asphaltene, preasphaltene, and residue yields in the run 2 was average value of run 1 and 2.

Effects of Reaction Procedure with Bottom Recycle Mode on the single-stage Liquefaction

Figure 3 describes effect of reaction process results in the single-stage liquefaction of Tanito Harum coal with FeNi/KB catalyst. The liquefaction yields from single run were showed in Figure 3a, and the yields from liquefaction with bottom recycle were showed in Figure 3b.

The liquefaction with heavy residual recycle was performed in 7 successive runs(see Figure 2). In the run 1 to 3, the liquefaction was done by utilizing bottoms recycle without purging to obtain the recycled catalyst/fresh catalyst ratio of 2. The liquefaction with bottom recycle provided average oil yield of 74%, which was 5% higher than that of liquefaction without bottom recycle. It is also be noted that the liquefaction only used fresh catalyst of 0.045 g each run compared to liquefaction without bottom recycle that used 0.09 g catalyst. It was suggested that high recycle ratio (recycled catalyst/fresh catalyst ratio) can improve significantly oil yields.

Table 3 shows liquefaction yields from liquefaction of Tanito Harum coal with bottom recycle each run. The lowest oil yields was obtained in the first run, which only carried the total catalyst of 0.045 g. In the second run, the oil yield highly improved in line with the addition of fresh catalyst. The highest improvement of oil yield occurred in this run followed by increasing gas yield reaching 18%. Large oil yield may be due to the conversion of asphaltene and preasphaltene sent from the first run.

The highest oil yield occurred in the third run. In this run, the total catalyst (fresh and used catalyst) reached 0.135 g. The highest oil yield in this run may be caused by a number of total catalyst that still had high activity and heavy residual products from previous runs. After the third run, the oil yield tended to decrease down to 74%, which showed the decrease of the catalyst activity. The oil yield appeared to be constant from the fifth run. In those run the activity of catalyst and a number of heavy residual products recycled become stationary.

Table 4 summarizes the conversion of tetralin into naphthalene after liquefaction of 60 min at 450°C, 15 MPa. Single-stage liquefaction with bottom recycle in the second run allowed 16% conversion that was much lower than that of liquefaction without bottom recycle (21% conversion), indicating that polynuclear aromatic ring of crude liquid bottom can aid in utilizing gaseous hydrogen. However, in the sixth run allowed 20% conversion inspite of higher total catalyst than that of the second run. This indicated the decrease of catalyst activity in the run.

Effects of Reaction Procedure with Bottom Recycle Mode on the Two-stage Liquefaction

Figure 4 illustrates results of the two-stage liquefaction of Adaro coal with FeNi/KB catalyst. The liquefaction yields from single-stage, two-stage, and two-stage with bottom recycle was showed on Figures 4a, 4b, and 4c respectively. Single- and two-stage liquefaction of Adaro coal provided 68% and 80% oil yields respectively (see Figure 4a and 4b). The two-stage liquefaction with bottom recycle provided average oil yield of 82% that was 2% higher than that of liquefaction without bottom recycle. The combination of two-stage and bottom recycle gave very high oil yield.

Table 5 summarizes gas and oil yields from two-stage liquefaction of Adaro coal with bottom recycle in several runs. The highest oil yield occurred in the third run. After the fifth run, the oil yield tended to be constant.

Conclusions

The liquefaction of coal with bottom recycle mode in the present study successfully improved oil yield, hydrogen transfer efficiently, and reduction of catalyst amount required. In this procedure, FeNi catalyst supported on carbon nanoparticles showed an excellent catalytic activity in the liquefaction with bottom recycle mode that can keep its activity in the repeated use.

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Table 1 Elemental Analyses of Coals Used in The Present Study

	C ^a	H ^a	N ^a	O ^a	S ^a	Ash ^b	H/C
Adaro Coal	66.6	5.3	0.9	26.7	0.44	3.0	0.96
Tanito Harum Coal	71.2	5.5	1.6	21.7	0.16	3.9	0.93

^a in Wt % (d.a.f.)

^b in Wt.%

Table 2 Liquefaction yields from Single-stage Liquefaction of Tanito Harum Coal with Repeated used Catalyst

Run	Total catalyst g	Gas Yield Wt %	Oil yield Wt %	Asp ^a Wt %	Preasp ^a Wt %	Residue ^a Wt %
1	0.09	15	69	-	-	-
2	0.09	15	69	10	5	1

^a average value of run 1 and 2

Table 3 Liquefaction yields from Single-stage Liquefaction of Tanito Harum Coal with Bottom Recycle

Run	Total catalyst g	Gas Yield Wt % (d.a.f)	Oil yield Wt % (d.a.f)	Asp Wt % (d.a.f)	Preasp Wt % (d.a.f)	Residue Wt % (d.a.f)
1	0.045	14 ^b	67 ^b	-	-	-
2	0.09	18 ^b	75 ^b	-	-	-
3	0.135	16 ^b	77 ^b	7 ^a	3 ^a	1 ^a
4	0.135	15 ^b	76 ^b	7 ^b	2 ^b	1 ^b
5	0.135	15 ^b	74 ^b	10 ^b	1 ^b	1 ^b
6	0.135	15 ^b	74 ^b	9 ^b	2 ^b	1 ^b
7	0.135	15 ^b	74 ^b	9 ^b	2 ^b	1 ^b

^a average value of run 1, 2, and 3

^b relative value of each run based on its coal feed

Table 4 Conversion of Tetralin during Coal Liquefaction ^a

Reaction Process	Total Catalyst g	Tetralin Conv (%)
Single-stage	0.09	21
Single-stage with bottom recycle ^b	0.09	16
Single-stage with bottom recycle ^c	0.135	20

^a Reaction Condition : 450°C, 60 min, 15 MPa; stirring speed : 1300 rpm.

^b in the second run (see table 3)

^c in the sixth run

Table 5 Gas and Oil Yields from Two-stage Liquefaction of Adaro Coal with Bottom Recycle

Run	Total Catalyst g	Gas Yield ^a Wt %	Oil Yield ^a Wt %
1	0.045	13	74
2	0.09	19	84
3	0.135	14	87
4	0.135	14	85
5	0.135	14	85
6	0.135	15	81
7	0.135	15	81

^a relative value of each run based on its coal feed

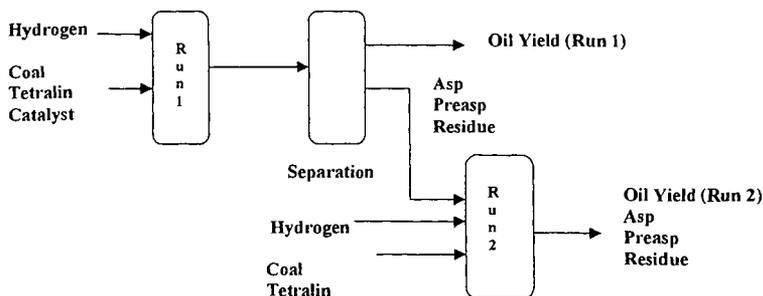
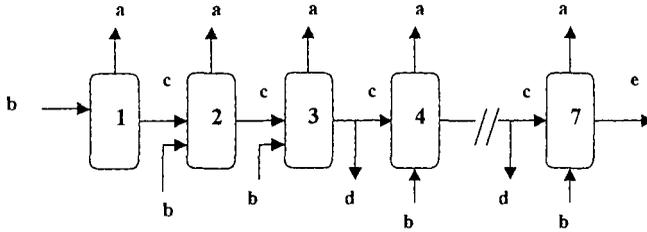


Figure 1 Coal liquefaction process in series



- a Oil Yield
- b Feed of coal(3 g), tetralin(3 g), and catalyst(0.045)
- c Yields of Asphaltene, preasphaltene, reused catalyst, and residue
- d Purge of asphaltene, preasphaltene, used catalyst, and residue
- e Last output of oil, asphaltene, preasphaltene, and residue

Figure 2. Liquefaction Process with Bottom Recycle

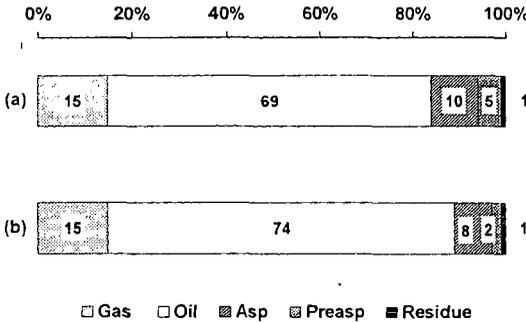


Figure 3. Effects of reaction process in the single-stage liquefaction of Tanito Harum coal with FeNi/KB catalyst, reaction conditions: 450°C, 15 MPa. Reaction processes: (a) Single stage at 60 min (b) Single-stage with bottom recycle performed for 60 min as given on Fig.2. For (a) coal/solvent/catalyst = (3 g)/(3 g)/(0.09g) and (b), coal/solvent/catalyst = (3 g)/(3 g)/(0.045 g)

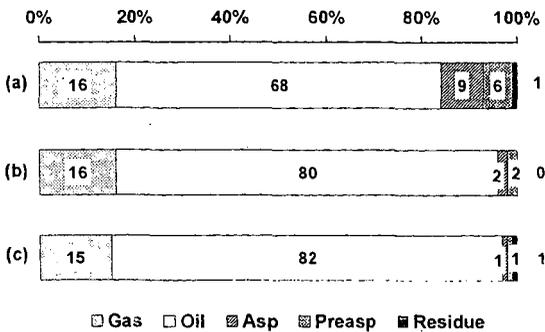


Figure 4. Effects of reaction process in the single- and two-stage liquefaction of Tanito Harum coal with FeNi/KB, Reaction Process: (a) is single-stage, and (b) is two-stage while (c) is two-stage with bottom recycle as given by Figure 2. Reaction times: (a) single-stage at 60 min; (b) 15 min at the first stage and 105 min at the second stage; (c) 15 min at the first stage and 105 min at the second stage each run. For (a) and (b), coal/solvent/catalyst = (3 g)/(3 g)/(0.09 g); For (c), coal/solvent/catalyst = (3 g)/(3 g)/(0.045 g).

LIQUEFACTION PATHWAYS OF SUBBITUMINOUS AND BITUMINOUS COALS

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KEYWORDS: coal liquefaction, reaction pathways

INTRODUCTION

Lumped parameter kinetic models have successfully been used to describe industrially significant and complex chemical processes such as catalytic cracking (e.g. 1), catalytic reforming (e.g. 2) and addition polymerization (e.g. 3). The complexity of the liquefaction process has necessitated the use of this approach in studying the thermal and catalytic pathways of this process. In this work, the lumped parameters used are the standard solubility class: a) oil plus gases (O+G), b) asphaltenes and preasphaltenes (A+P) and, c) coal insoluble organic matter (IOM). The lumped solubility classes produced from the thermal liquefaction of a large number of U.S. bituminous coals were plotted on a ternary plot. The resulting data suggested a common pathway for all of the bituminous coals. A Wyodak coal was also studied to determine the pathway of a subbituminous coal for comparison.

EXPERIMENTAL

The description and the range of values of some of the key coal properties of the 69 high volatile bituminous coals used in the initial study are given in Table 1. The properties of the three coals (W. Ky. #9, W. Ky. #6 and Wyodak) used in the more extensive studies are given in Table 2.

All of the liquefaction experiments were done in 50 mL batch microautoclaves using a hydrogen atmosphere. Details of the liquefaction procedure and solubility class determinations are given elsewhere (4). In this work, oils are defined a pentane solubles, asphaltenes are benzene soluble and pentane insoluble, preasphaltene are pyridine soluble and benzene insoluble and IOM are pyridine insoluble. In the catalytic experiments, all catalysts, with the exception of Shell 324, were sulfided *in-situ* by adding twice the stoichiometric amount of dimethyldisulfide required to sulfide the metal of the catalyst. The Shell 324 catalyst was presulfided prior to the additions of coal and liquefaction solvent to the reactor.

RESULTS AND DISCUSSION

The lumped parameters obtained from the thermal liquefaction of the initial 69 coals at a 15 min. residence time and three reactions temperatures (385°C, 427°C, 445°C) were plotted in a ternary graph (Figure 1). These data suggest a common liquefaction pathway for all of the coals. A Western Kentucky #6 and #9 were selected to verify the apparent pathway. Reaction conditions were selected to cover a maximum range of conversions.

The thermal liquefaction pathway of the W. Ky. #6 coal is shown in Figure 2. As can be seen in Figure 2, the thermal pathway over a large range of conversions is identical to the pathway suggested in Figure 1 for the diverse set of coals. There appears to be two distinct stages in the liquefaction of these coals. In the initial stage, the primary reaction is the conversion of the coal to asphaltenes plus preasphaltenes. This reaction continues until the A+P and coal conversion reaches a maximum yield. During this stage, the oil plus gas yield remains relatively constant. In the second stage of the thermal pathway, the primary reaction is the conversion of A+P to O+G. The coal conversion increases very little in this stage of the pathway. At the higher temperature and long residence times, the pathway appears to change again. Both the O+G and A+P yields decrease suggesting the possibility of retrograde reactions are taking place. These results suggest that these bituminous coals have a common thermal liquefaction pathway.

The pathway defined for the bituminous coals indicates that a maximum in the A+P yields is achieved before there is a substantial increase in the O+G yield. It is desirable to change the pathway in such a manner as to achieve increases in the O+G yield as coal conversion increases. A supported catalyst (Shell 324) and an oil-soluble catalyst precursor (molybdenum naphthenate) were utilized in an attempt to favorably alter the liquefaction pathway to increase the O+G yields as coal conversion increases. The same W. Ky. #6 sample was used in the catalytic studies. The results of these experiments are shown in Figure 3. The pathway defined using both catalysts are similar to

the defined thermal pathway for this coal. The major effect of catalyst addition on the pathway is to increase the rate of production of the intermediate, A+P, and has no major effect on the selectivity defined by the solubility classes. Therefore, the observed data for the thermal and catalytic processes of the bituminous coals are consistent for the following series of reactions:



A subbituminous Wyodak coal was studied next to determine if the lower rank coal has the same thermal and catalytic pathway as those defined for the bituminous coals. The results of similar experiments performed for the Wyodak coal are shown in Figure 4. Both the thermal and catalytic pathways defined for the Wyodak coal are significantly different from the pathways defined for the bituminous coals. For the subbituminous coals, as conversion increases, there is a parallel increase in both the O+G and A+P yields. These yields continue to increase until a maximum in coal conversion is achieved. The major reaction taking place after these maxima have been achieved is the conversion of A+P to O+G with little additional coal conversion taking place. This stage is similar to the second stage of the bituminous coal pathway. The addition of a catalyst does not alter the subbituminous coal pathway (Figure 4). As was observed with the bituminous coals, the addition of a catalyst only increases the rate of production of the intermediates and does not alter the selectivity defined by the thermal pathway.

CONCLUSIONS

The utilization of a lumped solubility class parameters plotted on a ternary plot show that the bituminous coals studied have a common liquefaction pathway. Attempts to change thermal pathway by catalyst addition were unsuccessful. The addition of a catalyst only increased the rates of production of products. The addition of a catalyst had no effect on the selectivity defined by the pathway.

The pathway defined for a subbituminous coal was significantly different than that defined for the bituminous coals. For the subbituminous coal, as conversion increases in the first stage, both the O+G and A+P yield increase. In the first stage for the bituminous coal only the A+P yield show a substantial increase in yield with conversion and the O+G yields remain fairly constant. The second stage of the pathway for the subbituminous coal, the primary reaction in the conversion of A+P to O+G which is similar to the second stage of the bituminous coal pathway. The addition of a catalyst to the subbituminous coal had no effect on the selectivity of the pathway.

ACKNOWLEDGMENT

This work was supported by the Commonwealth of Kentucky and DOE contract #DE-FC88PC8806.

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A. Distribution of Samples by State:		B. Distribution by ASTM Rank Classification:					
Kentucky	36	High volatile bituminous A, B, C					
Indiana	22						
Ohio	10						
West Virginia	1						
C. Ranges of Key Properties							
	Wt.% V.M. (daf)	Wt.% C(daf)	Wt.% Total S. (daf)	Wt.% Org.S. (daf)	Wt.% Pyr.S. (daf)	Vol% Vitrinite (dmmf)	R _o max
minimum	34.27	76.04	.70	.55	.03	80.06	.388
maximum	48.34	86.48	13.78	4.72	8.87	92.70	.984
mean	43.15	80.67	4.15	2.25	1.70	86.78	.606

Table 2			
Coal Analyses			
Ultimate (wt.%, daf)	Wyodak	W. KY. #6	W. Ky. #9
Carbon	82.87	76.80	71.02
Hydrogen	5.42	5.41	5.42
Nitrogen	1.72	1.90	1.37
Sulfur	5.15	8.41	1.00
Oxygen ¹	4.84	7.40	21.29
Reflectance (R _{o,max})	.77	.54	---

1. By difference.

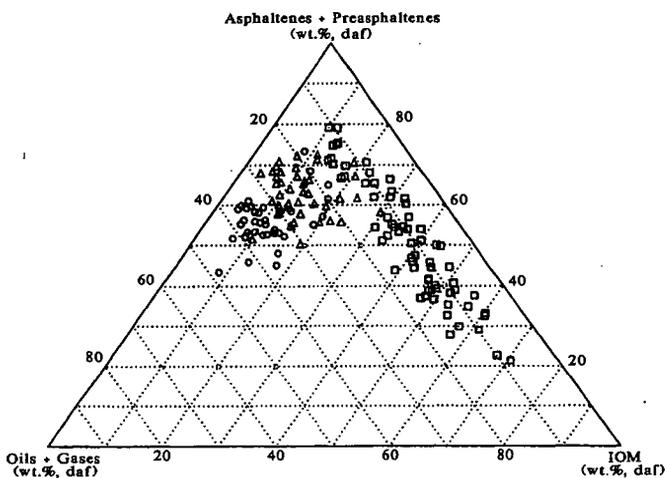


Figure 1. Solubility class distribution of the liquefaction products obtained from the thermal dissolution of bituminous coals using a 15 min. residence time, 3 reactions temperatures (385°C, □; 427°C, △, 445°C, ▲, ○) and a H₂ atmosphere (ca. 2000 psig @ 445°C).

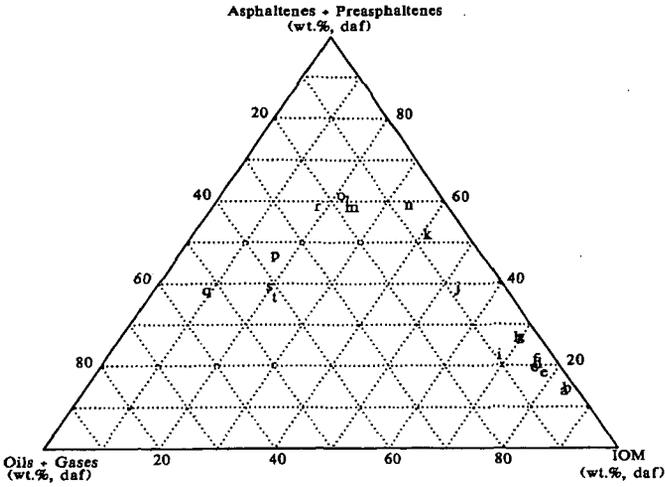


Figure 2. The thermal liquefaction pathway of a W.Ky. #6 bituminous coal using a H_2 atmosphere (ca. 2000 psig @ 445°C) using various reactor temperatures and residence times (325°C and 2.5 min., l; 5 min., b; 10 min., c; 15 min., d; 20 min., e; 30 min., f; 40 min., g; 60 min., h; 385°C and 5 min., i; 15 min., j; 30 min., k; 60 min., l; 90 min., m; 427°C and 5 min., n; 15 min., o; 30 min., p; 60 min., q; 445°C and 5 min., r; 15 min., s; 30 min., t).

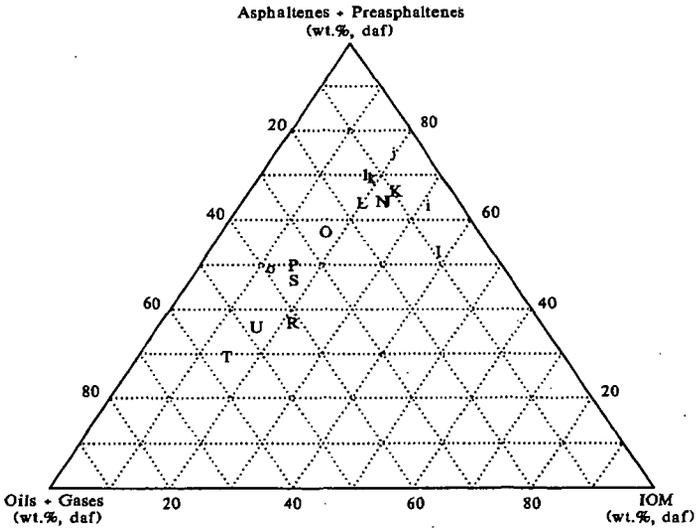


Figure 3. The catalytic liquefaction pathway of a W.Ky. #6 bituminous coal using a H_2 atmosphere (ca. 2000 psig @ 445°C) and a Shell 324 catalyst (385°C and 5 min., I; 15 min., J; 30 min., K; 60 min., L; 427°C and 5 min., N; 15 min., O; 30 min., P; 445°C and 5 min., R; 15 min., S; 30 min., T; 60 min., U) and a molybdenum naphthenate catalyst (385°C and 5 min., i; 15 min., j; 30 min., k; 40 min., l; 427°C and 15 min., o).

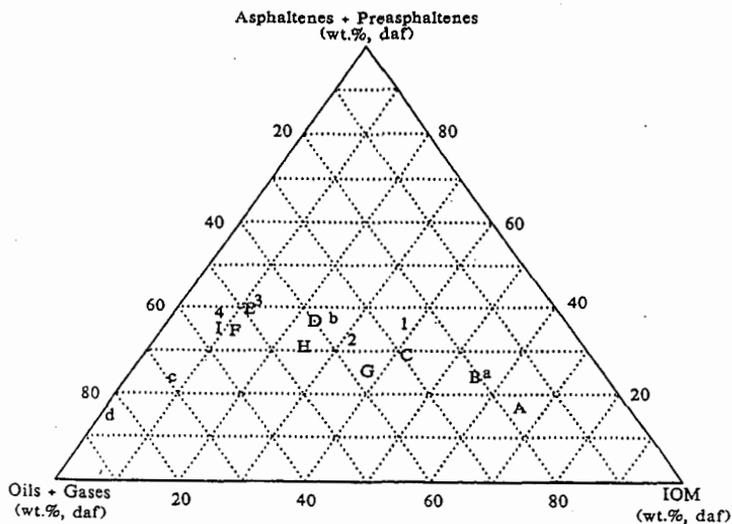


Figure 4. Thermal and catalytic liquefaction pathway for a Wyodak coal using a H_2 atmosphere (ca. 2000 psig @ 445°C) and a number of different reactor temperature and residence times (No catalyst: 385°C and 5 min., A; 15 min., B; 30 min., ; 427°C and 15 min., D; 30 min., E; 60 min., F; 445°C and 5 min., G; 15 min., H; 30 min., I; ultrafine Fe_2O_3 : 385°C and 15 min., 1; 30 min., 2; 427°C and 15 min., 3; 30 min., 4; No naphthenate: 385°C and 5 min., a; 15 min., b; 427°C and 30 min., c; 60 min., d).

MOLECULAR COMPOSITION OF COAL LIQUID OIL CHARACTERIZED BY GAS CHROMATOGRAPHY WITH ATOMIC EMISSION DETECTOR

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Heteroatom-containing species in the coal liquid oils (CLO) were identified and quantified by the aid of gas chromatography with atomic emission detector (GC-AED). Four different CLOs from different rank coals, processes and cut points were investigated in the present study. Thiophene and its derivatives were found to be the major sulfur compounds, pyridines and anilines, and phenols were the major nitrogen and oxygen compounds, respectively in the oils of boiling range < 300 °C. An oil of boiling range (300 - 420°C) carried more dimethyldibenzothiophenes and benzoquinolines. The correlation between feed coal and liquid product was discussed in terms of the compositions of heteroatomic compounds.

Key words: coal liquid oil, heteroatomic compounds, GC-AED

INTRODUCTION

Coal liquefaction has been expected to supply liquid transportation fuels to moderate the indispensable dependence on the petroleum products since the supply of crude oil may not meet the increasing demand in near future [1]. Coal liquid oil (CLO) of gas oil fraction tends to carry more heteroatoms such as sulfur, nitrogen and oxygen than the corresponding petroleum product [2]. Higher content of such heteroatoms causes serious problems to produce the pollutants, and to cause the poor stability in storage. Furthermore, they may play as inhibitor and poison in the catalytic refining processes, where molybdenum or tungsten sulfide promoted by cobalt or nickel supported on alumina or silica alumina have been usually applied as catalyst [3-6].

It is very necessary to quantify the heteroatom-containing molecular species in the coal liquids to clarify their chemical roles and behaviors in the hydrotreatment. Molecular level analyses of sulfur species in gas oil and their reactivity have been reported [7]. Although GC-MS can be applied to measure all species, identification of all molecular species is very tedious.

The present study reports the distribution of heteroatom containing compounds (sulfur, nitrogen and oxygen) in CLOs by the aid of gas chromatography equipped with atomic emission detector (GC-AED). AED is a multi-element detector that can measure more than 20 elements [8,9]. Recently it has been applied to the quantitative analyses of sulfur, nitrogen compounds in gas oil and metal containing compounds in vacuum gas oil [10]. Molecular distribution of heteroatom species may reflect compositional characteristic of starting coal, efficiency of liquefaction process for heteroatom removal, and their cutting point.

EXPERIMENTAL

Coal liquids sample

Crude liquid oils used in this study were supplied from liquefaction pilot plants in Japan, using 4 coals as listed in Table 1. Analyses of 4 raw coals are summarized in Table 2. Basic and non-basic fractions of SBCL-B were separated by acid extraction.

Gas Chromatography with Atomic Emission Detector

The identification of heteroatom containing compounds in the CLO was carried out using a HP 6890 with split/splitless injector port gas chromatograph (GC) with a HP G2350A atomic emission detector (AED) system. The chromatographic separation was done on a 30 m HP-1MS 0.32 internal diameter capillary column with film thickness of 1.0 µm (HP).

Carbon, sulfur, nitrogen and oxygen atomic emissions at 179, 181, 174 and 171 nm were used to obtain the high selectivity. Two injections of 1 µl were carried out with every

sample. The first injection was for determination of carbon, sulfur, nitrogen, while the second one was for oxygen. Hydrogen was used for the major reagent gas for both analyses. Oxygen and pure methane was added for the former analyses while 10 % methane in nitrogen was for latter analyses. The HP AED ChemStation was used to control the GC-AED and to perform the data acquisition and peak integration.

Results

Figure 1 shows the carbon, sulfur, nitrogen, and oxygen chromatograms of SBCL measured by GC-AED. Thiophenes, and dibenzothiophenes derivatives were the major compound identified in the SBCL. Pyridines, aniline and phenols and their derivatives were nitrogen and oxygen compounds respectively.

The carbon chromatograms from 4 CLOs are shown in Figure 2. The sample contained paraffinic hydrocarbon up to C17 for SBCL-A because of its end point of 300 °C, and C12 for the others of cutting point of 260°C. C9 and C10 were found to be the highest peak found in the tatter samples. Chromatograms of sulfur compounds in coal liquid distillates are illustrated in Figure 3. The sulfur species observed in CLOs were mostly thiophene and alkyl-substituted thiophenes. Thiophene content in SBCL-A was relatively small compared to those of the others three CLOs. Benzothiophene and its derivatives appeared in SBCL-A at longer retention times corresponding to their higher boiling points. Figure 4 illustrates the nitrogen chromatograms. The nitrogen components identified in CLO were mostly pyridine, aniline and their derivatives. Quinoline, indole and alkyl-substituted indoles were found only in SBCL.

The chromatograms of oxygen species in coal liquid distillates are illustrated in Figure 5. Phenols and alkyl-substituted phenols were the major oxygen compounds found in CLOs, although dibenzofuran was identified only in SBCL-A.

Chromatograms of SBCL-B are illustrated in Figure 6,7 and 8 for carbon (hydrocarbon), sulfur and nitrogen, respectively. SBHD contained paraffinic hydrocarbon of C17 to C29. Dibenzothiophene (DBT) and its derivatives were found as major sulfur species. Basic nitrogen species identified in SBHD are mostly aniline, quinoline, benzoquinoline and their derivatives.

Discussion

GC-AED was confirm to be able to identify basically all molecular species in CLO of boiling range up to 420 °C. The content and distribution of heteroatoms containing species in CLOs appear to reflect the liquefaction process, rank of feed coals as well as boiling range although very similar species were usually contained. Sulfur levels of South Banko, Adaro, and Ikeshima oils were much the same around 0.1 wt% except for Tanitoharum, although the contents of sulfur in the raw coals were significantly different. The distributions of sulfur species in the former three oils are different. SB carried dimethyl, trimethyl BT and dibenzothiophene in the boiling range < 300 °C, while Adaro and Ikeshima oils did not carried. TH oil carried similar species to those of Adaro and Ikeshima, although the sulfur level of the former oil was certainly less than the latter oils. Major difference was observed in the content of thiophene.

Nitrogen content appears more different in oils. The CLO carried nitrogen of 0.4 – 0.9 wt%, which was much larger than Sulfur. The CLOs of the same boiling range appear to carry the respective nitrogen content, which reflected the contents of the raw coals. The distribution of nitrogen species in the four oils is similar although SB carried quinoline and indoles due to the higher boiling range. TH oil carries more aniline, methyl and dimethylanilines compared to others.

Oxygen contents in CLO reflected the oxygen contents in the starting feeds. CLO carried oxygen of 1 – 3.7 wt%, which was the largest heteroatom found. SB of the highest oxygen content produced the much oxygen compound in the oil. The three feed shows the similar content. During liquefaction processing, most of oxygen were found phenols. Dibenzofuran believed to be refractory oxygen species was found only in SB.

The representative aromatic and non-aromatic fraction of SBHD as illustrated in Figure 6, were clearly separated according to the standard procedure of ASTM D-2549. The percentages of aromatic and non-aromatic fraction were 82.1 and 17.9 wt%, respectively. It is clear that the humping reflects the aromatic fraction. Overlapped peaks of aromatic, condensed

naphenic-aromatic, aromatic olefin and heteroatom species such sulfur, nitrogen and oxygen lead to the humping. Non-aromatic fraction contains a series of normal paraffins.

The higher boiling point of SBCL-B contained much complex heteroatoms and mostly refractory species. 4-methylthiophene (61ppm) and 4,6-dimethyl thiophene (12 ppm) of refractory sulfur species were clearly identified. Benzoquinoline and its derivative also identified as the major nitrogen species. Such complex heteroatom compounds with three or more benzene ring believed to be difficult to remove by catalytic up grading, using conventional commercial catalyst. Inhibitor such oxygen compound and basic nitrogen species in CLOs, forces us to design better catalyst and better process for up-grading such a crude in a current transportation fuel.

Conclusions

- Gas chromatography with atomic emission detector is very powerful for characterization and identification heteroatom species of whole molecular species in petroleum and coal liquid oil.
- Thiophenes, benzothiophene as sulfur compound, pyridine, aniline as nitrogen compounds, phenols as oxygen compound were identified in CLOs of lighter boiling point. Dibenzothiophene, quinoline, indole, dibenzoquinoline, dibenzofuran and their derivatives were only found in SB due to its higher cutting boiling range.

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Table 1. Ultimate analyses of CLOs

CLO	Process	b.p.(°C)	C ^a	H ^a	N ^a	S ^a	O(diff)	H/C
South Banko (SBCL-A)	NBCL	< 300	84.97	10.37	0.84	0.09	3.74	1.46
South Banko (SBCL-B)	NBCL	300-420	87.89	9.29	0.77	0.07	1.98	1.27
Adaro (ADCL)	NEDOL	<260	87.78	10.16	0.35	0.10	1.61	1.39
Tanitotharum (THCL)	NEDOL	<260	86.84	10.84	0.84	0.05	2.23	1.50
Ikejima (IJCL)	NEDOL	<260	88.48	9.94	0.51	0.10	0.97	1.35

a : wt% ; diff : differences

Table 2. Analyses of raw coals

Coal	C ^a	H ^a	N ^a	S ^a	O(diff)	H/C
South Banko coal	71.3	5.4	1.3	0.5	21.5	0.91
Adaro coal	74.2	5.2	0.9	0.0	19.7	0.84
Tanitotharum coal	75.9	5.8	1.8	0.2	16.3	0.92
Ikejima coal	81.8	6.1	1.4	1.4	9.3	0.89

a : wt% ; diff : differences

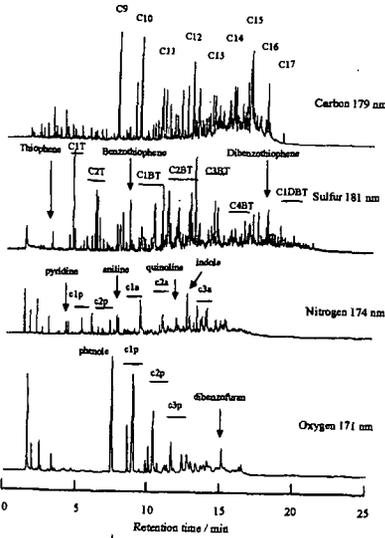


Figure 1 : chromatograms of carbon, sulfur, nitrogen and oxygen species in SBCL

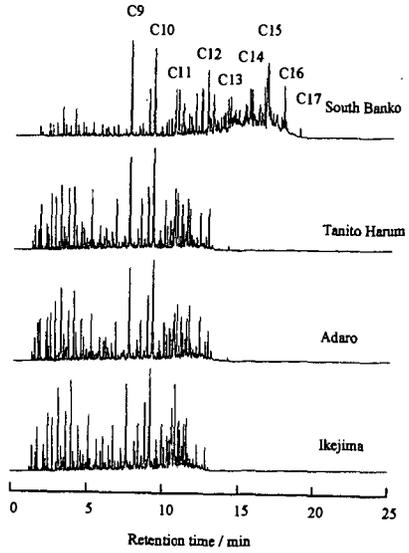


Figure 2 GC-AED chromatograms of carbon in CLOs

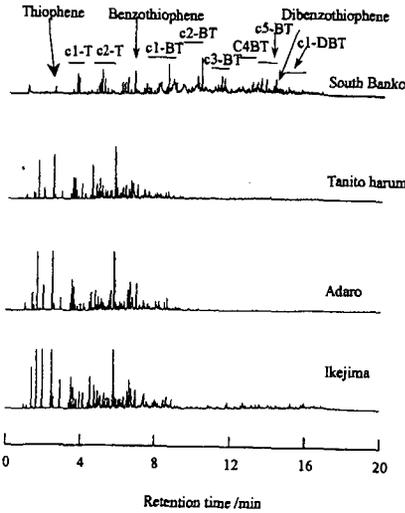


Figure 3 GC-AED chromatogram of sulfur in CLOs

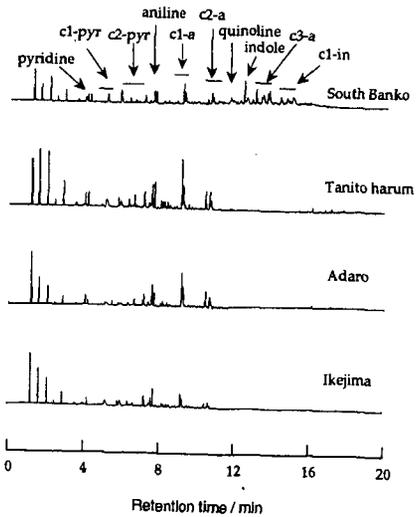


Figure 4 GC-AED chromatograms of nitrogen in CLOs

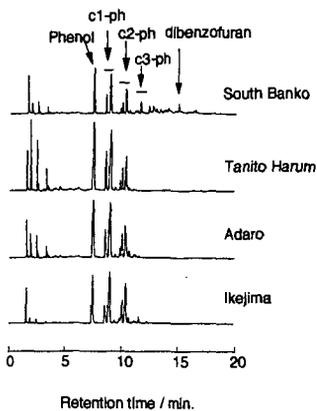


Figure 5 GC-AED chromatograms of oxygen in CLOs

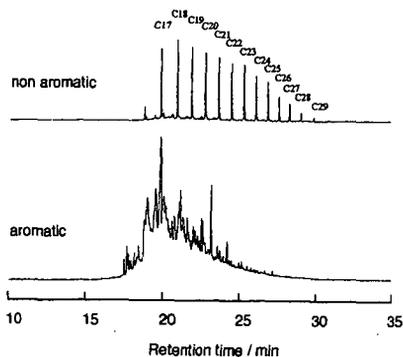


Figure 6 AED chromatograms of aromatic and non aromatic hydrocarbon in SBCL-B

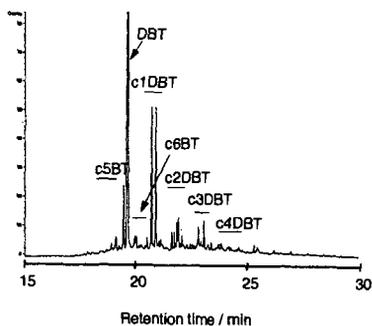


Figure 7. AED chromatograms of Sulfur compounds in SBCL-B

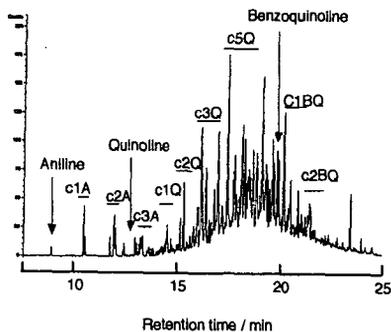


Figure 8. AED chromatograms of basic nitrogen compounds in SBCL-B

Behavior of additives on the coal solubility and aggregation

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Abstract

A very small amount of additives significantly increases the extraction yield of Upper Freeport coal in NMP/CS₂ mixed solvent from 63% to 78–84%. Twenty additives were tested. The most effective ones are TCNE, TCNQ, PDA, 1,1,2,3,3-pentacyanopropenide (PCNP) and acetate anion. In addition, the effect of PCNP anion and acetate anion on the aggregation of coal extract was observed by Size Exclusion Chromatography. The result indicates that anions prevent the aggregation of the coal extracts.

Introduction

NMP/CS₂ mixed solvent has good extractability for some bituminous coals, e.g., ~60% for Upper Freeport coal and Zao Zhuang coal¹. The purpose of adding additives into this mixed solvent is to further increase the coal solubility. Some of them increase the extraction yield of Upper Freeport coal from ~60% to ~80%^{2,3}. Unfortunately, only a few additives are effective among the twenty additives we tested. In addition to their effect on coal extractability, some additives also prevent the aggregation coal molecules in solution, which was investigated by Size Exclusion Chromatography (SEC). The effect of TCNE on coal aggregation is hard to observe by SEC because of the strong interaction of TCNE with the polystyrene column⁴. Some anionic additives significantly increase coal extractability. They do not strongly interact with the column⁵. Their effect on coal aggregation was investigated by comparing the SEC eluted by NMP or NMP/anionic additive.

Experimental

Extraction of coal with NMP/CS₂ containing additive was carried out according to the method described in ref. 1. All the additives are commercial product except for NMP-1,1,2,3,3-pentacyanopropenide (PCNP), which was prepared by the author³.

SEC was run on the polystyrene column (7.8_300mm, particle size 13μm, TOSOH Co., Japan) and eluted by NMP and additive modified NMP with a flow rate of 1.0ml/min.

The effect of anionic additives on pyridine-phenol hydrogen bond was observed by ¹H-NMR in CDCl₃.

Results and discussion

Table 1 presents the extraction yield of Upper Freeport coal extracted by NMP/CS₂ with or without additives. Some of these additives are strong electron acceptors or donors. In previous works, the charge-transfer interaction between coal and additive was considered to be responsible for breaking coal-coal interaction. However, the correlation of the electron acceptability or donate ability with coal extractability did not support this assumption⁶. In addition, TCNE was found converted to PCNP anion in NMP. This anion was as effective as TCNE, although it is not an electron acceptor³. The result rules out the formation of a charge-transfer complex between coal and TCNE as a main route to break coal-coal interaction.

TCNQ is another effective additive. The pathway of its interaction with coal is probably related to the interaction of TCNQ with solvent⁷. It is found that TCNQ forms radical anion in NMP but does not in THF and chlorobenzene. TCNQ is also effective in NMP but not in THF and chlorobenzene. TCNQ radical anion formed in NMP may have some relations with its effect on coal solubility. The mechanism is under investigation.

Aniline and *p*-dimethyl-aniline(PDA) are also very effective in increasing coal extractability as shown in table 1. Their electron donating ability with increased coal extractability was also not well correlated⁸. Instead, the hydrogen bonding formed between additive and coal was thought to be a factor. Comparing the effect of aniline and dimethylaniline; PDA and TMPDA, methylated amines are less effective. The result indicates that hydrogen bonding formation may affect the extraction of coal, because dimethylaniline and TMPDA have weaker ability to form hydrogen bonds with coal.

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Anion is an effective additive found recently^{3,5}. The most effective ones are PCNP anion and acetate anion. They increase UF coal extractability from 62% to 78~84%. Hydrogen bonding with coal may also be a factor to break coal-coal interaction, which will be discussed later.

These additive are also effective in increasing the solubility of PI fraction, which is a fraction from coal extract that dissolves in NMP/CS₂ but not in pyridine. Two PI fractions were prepared by different method. PI(1) was prepared by washing extract with pyridine under ultrasonic radiation at room temperature, while PI(2) was washed by pyridine with Soxhelt extraction, in which more pyridine solubles were removed(unfortunately, the accurate weight loss was not measured, roughly estimated about 10~20%). The solubility of the two PI in NMP/CS₂ is significant different as shown in table 2. The more pyridine solubles is removed the lower solubility is. It seems that the PI(2) becomes more associated. Both PI fractions are associated by non covalent bonding, but the effect of these additive on them is different. TCNE is always the most effective one. Over 90% of PI was dissolved in NMP/CS₂ with addition of TCNE for the two PI fractions. However, TCNQ, DDQ and others become less effective for PI(2). Some of them even cause stronger association of coal, and decrease the solubility of PI(2). The difference between PI(1) and PI(2) is that PI(1) still has more pyridine solubles which is difficult to remove at room temperature. In other words, PI(2) is heavier than PI(1). The major structure difference between PS and PI is that PI has higher heteoatom, OH content. Accordingly, PI(2) should have higher heteoatom, OH content and aromaticity, which may give rise to the stronger non-covalent interaction in PI(2). If the additive breaks the covalent bond to increase the coal solubility, their effect will not be so dependent on the lighter fraction(pyridine soluble) reminded in PI. These results demonstrate that additives break the non-covalent interaction but not the covalent bond in coal.

Based on the observation of the structure of additives listed in Table 1, the effective ones usually have symmetrical and delocalized structure. Most anionic additives are effective. Among those effective additive, TCNE, TCNQ and aniline, PDA were well discussed. Here, we force our interest on organic anion, e.g., PCNP anion and acetate anion.

The behavior of the two anionic additives on coal molecular aggregation was investigated by SEC. The use of NMP as an eluent minimized the sample adsorption on the polystyrene column⁹⁻¹¹. The separation is mainly size based¹⁰. The SEC chromatogram of coal extract exhibits bimodal peaks. The first one appearing near exclusion limit of the column is assigned to those stronger aggregated molecules⁵. Another one resolved by the column eluting at longer retention time corresponds to the less aggregated portion⁵. Addition of small amount of PCNP or acetate anion into the NMP eluent results in the disappearance of the peak near exclusion limit of the column, but no effect on the peak at longer retention time. This change indicates the size of coal molecular aggregates decreased. The effect of anion on coal molecular aggregation depends on the nature of the anion. Addition of LiBr into NMP eluent shifts all the peaks to longer retention time, which was considered due to the decrease of solvent solubility because some precipitates appeared in NMP/LiBr¹². Addition of PCNP anion and acetate anion increases the Upper Freeport coal solubility in NMP/CS₂ from 60% to 78% and 84%, respectively, but addition of same amount of LiBr does not increase coal solubility at all. Accordingly, the change of SEC behavior by adding PCNP and acetate anion is due to the disruption of the coal molecular aggregation. The reversible effect of additive on SEC was also found. Some materials eluted near exclusion limit still appear when injection of the sample containing anion additive onto the column eluted by NMP. The result indicates a partial reversible aggregation of coal extracts.

The mechanism of anion increasing coal extractability is under investigation. We are not very sure whether the new hydrogen bonds formed between coal molecules and anion will break the coal-coal interaction or not. The change of OH proton signal in NMR spectrum of pyridine-phenol mixture by addition of 0.1% PCNP anion may provide some information for better understanding the mechanism of PCNP anion increasing coal extractability. As described in figure 2, for the pyridine-phenol mixture, hydrogen bonded OH proton shows a broad peak in low field. Addition of 0.1% PCNP anion (NMP-1,1,2,3,3-pentacyanopropenide) shifts of this proton signal up field appearing as a sharp peak. The result indicates that the chemical environment of this proton changed. Pyridine-phenolic OH hydrogen bond is a major hydrogen bond in coal. NMR result

indicates that PCNP anion affects this hydrogen bond. If this is related to coal solubility increase is awaiting further investigation.

Acknowledgment

The authors are grateful to the JSPS for financial support of this work.

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Table 1 Extraction yield of Upper Freeport coal from NMP/CS₂^a

Additives ^b	Structure	Extraction yield wt%	Additives ^b	Structure	Extraction yield wt%
PCNP anion		84.1			53.9
TCNE		81.3			60.2
TCNQ		80.0	TTF		61.9
PDA		78.6	TMPDA		60.4
Aniline		71.7			60.1
Acetate		78.6			61.8
		75.0			49.7
		69.5			49.8
		68.0			39.3
	OH ^d	66.1			

^a) extraction yield with no additive added, 62.8%; ^b) amount of additive, ~0.2mmol/g-coal; ^c) from NMP-1,1,2,3,3-pentacyanopropene ^d) tetrabutylammonium salt.

Table 2. Solubility of PI fraction in NMP/CS₂ with or without additive

Additive (~0.2mmole/g-coal)	Solubility of PI (wt%)	
	PI(1)	PI(2)
No	66.4	20.8
TCNE	99.5	89.5
TCNQ	94.3	52.9
DDQ	88.8	6.9
1,2,4,5-Tetracyanobenzene	71.2	10.5
Benzoquinone	76.1	10.2
2,6-Dichloro- <i>p</i> -benzoquinone	67.4	8.5

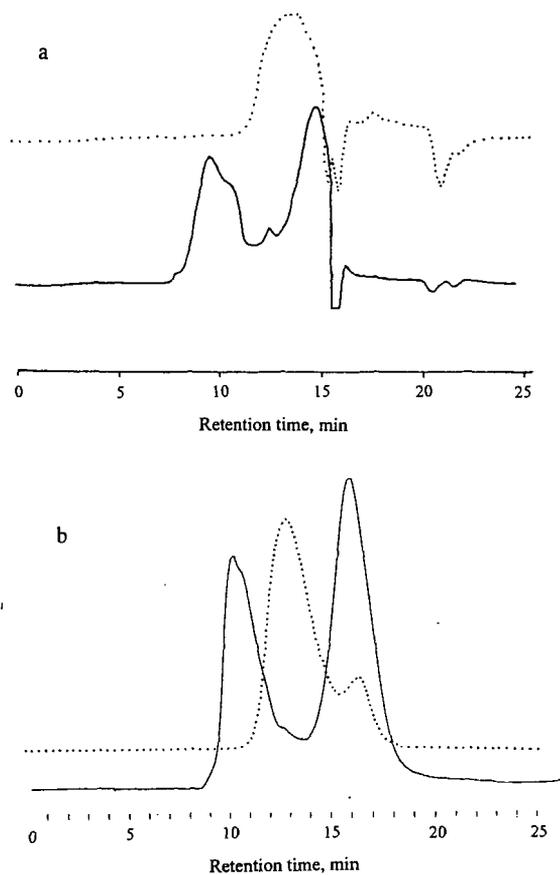


Figure 1. Size Exclusion Chromatograph of UF coal extract eluted by NMP (solid line) and NMP containing anion additive (dot line). (a) additive, 5mM NMP-PCNP; detected by RI detector; (b) additive, 10mM Tetrabutylammonium acetate, detected by UV at 300nm

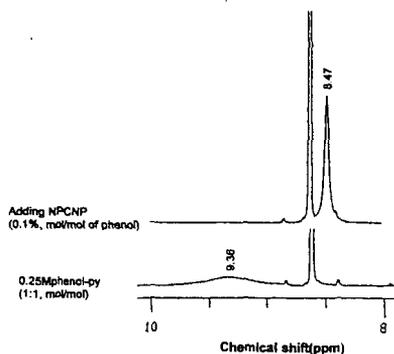


Figure 2. Shift of hydrogen bonded proton (phenol-pyridine) by adding NMP-PCNP. Solvent, CDCl_3