

## Coal and solvent properties and their correlation with extraction yield under mild conditions

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**Abstract**—Coal solvent extraction is a clean coal technology that involves the extraction of organic matter from coal using solvents. In this study, the effects of various coal and solvent properties on extraction yield were studied and their correlations were observed. Solvent extraction was performed for fifteen coal samples of different ranks with eight solvents under mild conditions. Statistical analyses were then conducted to find correlations between the extraction yields and the coal and solvent characteristics. The extraction yield was strongly correlated with the atomic H/C ratio or volatile matter content. Among the solvent properties, the correlation between the electron donor, acceptor number (DN-AN) and yield was confirmed to be high. The results of multiple regression showed that positive correlations were found with the content of volatile matter of coal and polar force, DN-AN of solvent. Whereas negative correlations were found with the Ca/Mg content of coal and dispersion force, hydrogen bonding force of solvent. The regression-equation-calculated value was similar to the experimental value.

Keywords: Coal, Solvent Extraction, Extraction Yield, Extraction Factor, Multiple Regression

### INTRODUCTION

Coal solvent extraction is a conversion process that extracts organic components from coal. Initially intended for the study of coal structure or composition, it became a major research topic in the wake of Bedson's 1902 discovery that bituminous coals were substantially soluble in hot pyridine [1]. However, recent investigations of coal solvent extraction have focused mainly on the manufacture of clean coal. For example, the hyper-coal process [2-4] is currently being studied in Japan. The principle of such an extraction is simple. Coals may be considered as cross-linked macromolecules consisting of large heterocyclic monomers held together by both covalent bonds and noncovalent interactions [1]. When a solvent is introduced, swelling occurs in the coal due to the disruption of the noncovalent interactions, such as H-bonds in the case of polar solvents and dispersion forces in the case of nonpolar solvents. The swelling of coal is followed by the solubilization of coal molecules if the coal-solvent interactions are stronger than the coal-coal interactions [5]. However, it is difficult to predict the extraction yield due to the complexity of the coal molecular structures, which cannot be determined exactly.

A number of studies have correlated the extraction yield with the properties of the coal or solvent. In earlier studies, solvent behavior with coal was examined in terms of solvent properties such as dipole moment, dielectric constant, and surface tension, without success [1]. Van Krevelen attempted to express the solvent potency in terms of a solubility parameter ratio, suggesting that good solu-

bility requires the square of the solubility parameter ratio to be less than 1 [6]. In 1979, Marzec et al. attempted to find a correlation between the extraction yield and the electron donor-acceptor properties of the solvent [7]. Several solvents whose electron donor number (DN) and electron acceptor number (AN) had been quantified by the electron donor-acceptor number theory [8,9] were used. As a result, a high correlation between the extraction yield and DN of the solvent was revealed, particularly the difference between DN and AN (DN-AN). In the extraction mechanism, the solvent interaction process was expressed as "substitution" since electron-donating solvent molecules are substituted for the electron-donating fragments of coal [10]. Also, the results suggested that a higher extraction yield would be obtained for a solvent with higher electron-donating ability, since more electron-donating fragments of the coal would be substituted. Similar correlations were reported by Chawla and Davis [11], who conducted coal extraction tests using eighteen different solvents under mild conditions. In 1988, Iino et al. performed coal solvent extractions with 56 coal samples using a mixed solvent of CS<sub>2</sub> and *N*-methyl-2-pyrrolidone at room temperature [12]. Regression analysis was applied to correlate the coal properties with extraction. The carbon content of the coal and the volatile matter ratio to the sum of the oxygen and sulfur contents (VM/(O+S)) were predictor variables that determined the extraction yield. The highest extraction yield obtained was 85-87% of the carbon content. The report suggested that the extraction yield was probably related to the crosslinking density [13], which has a minimum value at 85-87% of the carbon content of the coal. However, the correlation coefficients of the regression were high enough to be statistically significant. There have often been cases in which the extraction yield increased significantly with mixed solvents such as CS<sub>2</sub>/NMP. NMP affords extraction yields of 60-70%, even with-

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out thermal decomposition at room temperature, when mixed in a 1 : 1 ratio with CS<sub>2</sub>. In 1989, Iino et al. studied the effects of NMP and CS<sub>2</sub> mixtures [5]. The high viscosity of pure NMP was reduced from 1.69 mPa to 0.62 mPa when NMP mixed with CS<sub>2</sub> in a 1 : 1 ratio. It was proposed that extraction occurred more extensively because the mixture was more permeable due to the reduced viscosity. In 1996, Aida et al. proposed the “wedge effect” for a CS<sub>2</sub>/NMP mixture, wherein the small CS<sub>2</sub> molecules assist NMP to extract more coal by disrupting the cross-links within the coal fragments [14]. In 2006, Shui et al. analyzed the FTIR spectra of 1 : 3, 1 : 1, and 3 : 1 mixtures of CS<sub>2</sub>/NMP [15]. A strong peak was found at 1,508 cm<sup>-1</sup> when NMP and CS<sub>2</sub> were mixed in a 1 : 1 ratio, whereas that peak did not appear in pure NMP, CS<sub>2</sub>, or the 1 : 3 and 3 : 1 mixtures. Therefore, they estimated that a mixture of NMP and CS<sub>2</sub> with the ratio of 1 : 1 would result in greater extraction by forming a specific bond that would reduce the viscosity of NMP. In 2006, Kashimura et al. studied the effects of the carboxyl groups in coal on extraction yield [16]. The content of carboxylates (-COOM) bonded with Ca<sup>2+</sup> and Mg<sup>2+</sup> in the coal was measured by ion exchange, and the relationship between the extraction yield after extracting with crude methylnaphthalene oil (CMNO) was analyzed. The extraction yield decreased with increasing quantities of -COOM. In addition, the extraction yield declined with reductions in the Ca<sup>2+</sup> and Mg<sup>2+</sup> content after acid treatment. Thus, we concluded that large quantities of Ca<sup>2+</sup> and Mg<sup>2+</sup> carboxylates would impede extraction by solvents. One recent study focused on the relationship between petrographic properties and extraction yield [17], which was observed by analyzing the extracts after the solvent extraction of two coals with opposite maceral compositions (vitrinite-rich coal and inertinite-rich coal). It was found that the mean random vitrinite reflectance (Rm) was lower with the more extract. These results were tentatively rationalized to be related to changes in complex factors such as structure, elemental composition, and surface properties, as observed in other studies. There also have been several studies on the effects of the caking [18] and

caking [19] properties of the coal and the molecular structure of the solvent [20].

However, it was assumed that the properties of both coal and solvent affect extraction at the same time. Therefore, in this study, the properties of both coal and solvent were studied simultaneously to identify important factors in coal solvent extraction using multiple regression analysis. To collect statistical data and information about the relationship between the coal and solvent properties and the extraction yield, coal solvent extraction was carried out with fifteen coal samples in eight solvents. The extractions were conducted under mild conditions in order to allow only interactions between coal and solvent and avoid coal pyrolysis.

## EXPERIMENTAL

### 1. Materials

#### 1-1. Coal Samples

Of the fifteen coal samples in this study, many are used in power plants in Korea and are from Indonesia. Most were supplied in the form of raw coal; thus, the samples went through several pre-treatments. First, the coals were dried for 4 h at 110 °C in a vacuum oven under nitrogen to prevent oxidation. After crushing with a jaw crusher and disk mill, the samples were pulverized with a ball mill to <200 mesh. The recovered coals (97% after 200 mesh sieve) were vacuum-packed to prevent oxidation. The proximate and ultimate analyses of the coal samples are shown in Table 1, and the van Krevelen diagram [21] by H/C and O/C atomic ratios is in Fig. 1. A wide distribution was observed in the diagram. The rank of each coal was classified by ASTM D388-8, as listed in Table 2. There were three ranks: two samples of anthracite, eleven samples of bituminous, and two samples of subbituminous coal. The petrographic analyses of the coals are shown in Table 3, and the X-ray fluorescence (XRF) analyses of the ash are listed in Table 4. The raw coal must be at least 30 mm in diameter for petrographic analysis. However, seven coal samples were supplied in the form of fine particles,

**Table 1. Proximate and ultimate analysis of coal samples**

Sample	Proximate analysis (wt%, db)			Ultimate analysis (wt%, daf)					Atomic ratio	
	Volatile matter	Fixed carbon	Ash	C	H	O	N	S	H/C	O/C
EC	54.26	41.22	4.52	71.60	5.79	21.70	0.88	0.03	0.97	0.23
SM	51.37	45.45	3.18	67.94	4.92	26.08	1.05	0.02	0.87	0.29
RS	49.93	47.05	3.02	69.50	4.90	24.65	0.92	0.03	0.85	0.27
LG	48.29	45.41	6.30	69.47	4.85	24.62	1.03	0.02	0.84	0.27
TA	44.87	49.86	5.27	72.36	5.20	20.48	1.58	0.37	0.86	0.21
BE	44.14	48.48	7.38	71.29	5.23	20.89	1.63	0.95	0.88	0.22
AR	42.21	43.42	14.36	75.11	5.82	16.75	1.47	0.85	0.93	0.17
KI	35.18	58.76	6.07	76.69	4.70	17.38	1.01	0.22	0.74	0.17
IN	38.30	51.21	10.50	80.25	5.84	11.48	1.73	0.70	0.87	0.11
SH	32.42	56.83	10.75	78.12	4.71	15.90	1.06	0.22	0.72	0.15
AN	31.67	49.35	18.98	80.81	5.44	10.75	1.93	1.08	0.81	0.10
CA	30.55	52.04	17.41	81.00	5.41	10.94	2.01	0.64	0.80	0.10
AT	26.73	54.48	18.79	80.37	4.31	13.51	1.37	0.43	0.64	0.13
A1	6.42	75.88	17.70	88.95	1.56	8.06	0.86	0.09	0.21	0.06
A2	5.59	79.18	15.23	89.64	1.54	7.55	0.85	0.08	0.21	0.07

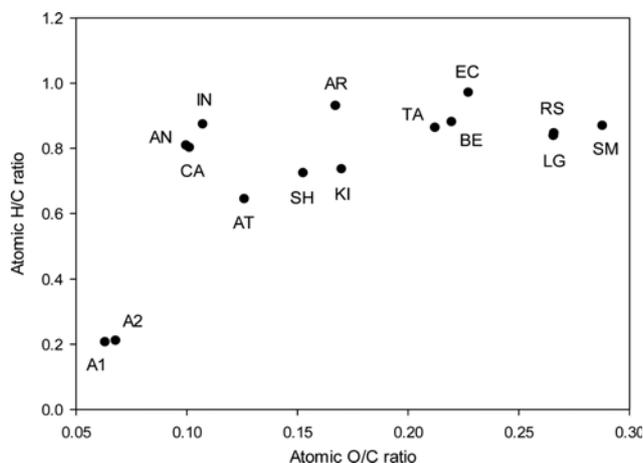


Fig. 1. Van Krevelen diagram of coal samples.

and thus were excluded from the analysis. In addition, the limited quantities of these seven coal samples necessitated their exclusion from XRF analysis.

#### 1-2. Solvents

Eight solvents were examined: tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMS), ethylenediamine (EDA), pyridine (PRD), quinoline (QNL), and a mixed solvent of *N*-Methyl-morpholine-*N*-oxide (NMMO) and NMP. These solvents have produced extraction yields exceeding 10% in previous coal solvent extraction studies. All the solvents purchased from Sigma-Aldrich were reagent grade with more than 99.5% purity (except QNL, 98%), and were used without further purification. The general properties, electron donor-acceptor properties, and solubility parameters of the solvents were obtained from the literature [8,9,22,23]; these are summarized in Tables 5 and 6. QNL, which has previously exhibited high extraction yields, was used, even though the information on DN, AN, and solubility parameters was not available. NMMO was also used in the mixed solvent with NMP, as an alternative to CS<sub>2</sub>.

Table 2. Rank of coal samples classified by ASTM D388-84

Sample	Volatile matter (wt%, daf)	Fixed carbon (wt%, daf)	Calorie (kcal/kg, daf)	Rank
A1	7.8	92.2	6,800	Anthracite
A2	6.6	93.4	6,900	Anthracite
AT	32.9	67.1	8,040	High-volatile A bituminous coal
CA	37.0	63.0	8,643	High-volatile A bituminous coal
IN	42.8	57.2	8,192	High-volatile A bituminous coal
SH	36.3	63.7	7,857	High-volatile A bituminous coal
AN	39.1	60.9	7,436	High-volatile B bituminous coal
KI	37.5	62.6	7,189	High-volatile C bituminous coal
AR	49.3	50.7	7,113	High-volatile C bituminous coal
TA	47.4	52.6	7,050	High-volatile C bituminous coal
BE	47.7	52.3	7,157	High-volatile C bituminous coal
SM	53.1	46.9	7,160	High-volatile C bituminous coal
LG	51.5	48.5	6,480	High-volatile C bituminous coal
RS	51.5	48.5	6,270	Subbituminous A coal
EC	56.8	43.2	5,313	Subbituminous B coal

Table 3. Petrographic analysis of eight coal samples

Sample	Mean random vitrinite reflectance	Maceral composition		
		Vitrinite (%)	Liptinite (%)	Inertinite (%)
IN	0.62	76.2	4.0	19.8
KI	0.53	52.4	0.4	47.2
SH	0.51	54.2	0.6	45.2
RS	0.43	87.4	5.2	7.4
LG	0.43	89.0	6.4	4.6
TA	0.43	89.0	3.6	7.4
BE	0.41	90.6	3.0	6.4
EC	0.40	89.6	5.4	5.0

## 2. Methods

### 2-1. Solvent Extraction

The coal samples were extracted by Soxhlet extraction. A coal sample (3 g) was placed in a thimble filter (PTFE/silica fiber) and then dried overnight at 105 °C, whereupon the mass of filter was measured. Extraction was performed continuously for 72 h with the selected solvent (200 mL) by heating the vessel to the solvent boiling point. Because of high boiling points of NMP, DMS, DMF, and QNL, heating tapes were used around the Soxhlet column to ensure smooth circulation of the solvent without premature condensation. Afterwards, the samples were further extracted by the Soxhlet method with acetone for 3 h to wash the remaining solvent from the residue. The residue remaining in the thimble filter were dried overnight at 120 °C under vacuum. The weight of the residue was calculated by deducting the filter weight from the total weight of the thimble filter containing the residue. The extraction yield was determined from the weight of the residue using Eq. (1). The equation includes the assumption that the mineral matters in coal may not be extracted by organic solvent. Each extraction was repeated three times since extraction yields varied despite the use of identical conditions, coal samples, and solvents. Mean values were

**Table 4. XRF data of ash in coal samples**

Formula	EC	SH	IN	BE	LG	RS	TA	KI
SiO <sub>2</sub>	57.32	55.10	52.14	50.29	50.02	49.97	43.87	47.07
Al <sub>2</sub> O <sub>3</sub>	21.64	20.48	32.18	22.08	23.31	24.02	20.47	18.72
TiO <sub>2</sub>	0.55	0.69	0.91	0.87	1.18	1.54	0.51	0.68
Fe <sub>2</sub> O <sub>3</sub>	7.49	6.85	8.02	8.01	8.70	9.23	4.35	11.42
MgO	5.11	2.24	1.82	6.43	6.41	5.69	18.29	2.64
CaO	4.25	11.86	1.00	9.64	8.52	7.49	10.76	16.55
Na <sub>2</sub> O	1.50	0.92	1.28	1.04	0.23	0.42	1.07	1.89
K <sub>2</sub> O	1.78	1.36	2.38	1.32	1.41	1.41	0.42	0.46
MnO	0.18	0.14	0.03	0.12	0.08	0.12	0.07	0.24
P <sub>2</sub> O <sub>5</sub>	0.15	0.33	0.20	0.16	0.09	0.07	0.17	0.27
LOI	0.03	0.03	0.04	0.04	0.05	0.04	0.02	0.06
Total	100	100	100	100	100	100	100	100

Unit: wt%, db

**Table 5. General properties of solvents**

Solvent	Molecular weight	Boiling point	Specific gravity	Viscosity	Polarity
THF	72.12	66 °C	0.88	0.48 cp	Polar
DMS	78.13	189 °C	1.10	2.47 cp	Polar
DMF	73.09	153 °C	0.95	0.80 cp	Polar
QNL	129.16	237 °C	1.09	3.36 cp	Polar
PRD	79.10	115.3 °C	0.98	0.88 cp	Polar
NMP	99.13	202 °C	1.03	1.69 cp	Polar
EDA	60.10	116 °C	0.90	1.70 cp	Polar
NMMO	117.15	-	-	2.50 cp	Polar

used for statistical analysis.

$$\text{Extraction yield (\%)} = \frac{1 - \frac{\text{residue (g)}}{\text{feed coal (g)}}}{1 - \frac{\text{ash (wt\%, db)}}{100}} \times 100 \quad (1)$$

where, residue: the weight of the residue of coal after extraction

feed coal: the weight of the feed coal sample

ash: the weight percentage of the ash component in coal sample

**2-2. FTIR and <sup>13</sup>C-NMR Measurements**

To obtain chemical structure information regarding some coal

samples, FTIR and <sup>13</sup>C-NMR measurements were conducted in this study. FTIR was measured using a Thermo Scientific Nicolet 6700 spectrometer; 32 scans were carried out at a resolution of 8 cm<sup>-1</sup>. 400 MHz <sup>13</sup>C-NMR were measured using a Bruker Advance 400WB spectrometer with 13 kHz spinning rate.

**RESULTS AND DISCUSSION****1. Variation in Extraction Yields with Time**

The extraction was performed a total of 11 times over 144 hours, in 4 h intervals for the first 24 h, and in 24 h intervals thereafter. EC and AT were selected as coal samples, because EC was expected to be highly extractable as opposed to AT, based on the pre-test of 48 hours extraction for all of coal samples with each solvent. The solvent EDA was chosen based on its high extraction yields in previous studies [7,11]. The results of the experiments are summarized in Fig. 2. Both samples show rapid yield increases initially, and achieve nearly steady yields after 48 h. As mentioned previously, the extraction yields varied even with the same coal and solvent. Considering that the deviation was 5%, the maximum yield was considered to be reached after ~48 h. The maximum extraction yield for EC was ~45% which was more than twice that of AT (~20%). With respect to the time required to reach the maximum extraction yield, AT, with its lower yield, was faster. Based on these results, it was determined that 72 h would be a suitable extraction time for the triplicate experiments that follow.

**Table 6. Solubility parameter and Electron donor-acceptor number of solvents**

Solvent	Hildebrand solubility parameter	Hansen parameter			Electron donor-acceptor number		
		Dispersion force	Polar force	Hydrogen bonding	DN	AN	DN-AN
DMS	26.7	18.4	16.4	10.2	29.8	19.3	10.5
EDA	25.3	16.6	8.8	17.0	55.0	20.9	34.1
DMF	24.8	17.4	13.7	11.3	26.6	16.0	10.6
NMP	22.9	18.0	12.3	7.2	27.3	13.3	14.0
RPD	21.8	19.0	8.8	5.9	33.1	14.2	18.9
THF	19.4	16.8	5.7	8.0	20.0	8.0	12.0

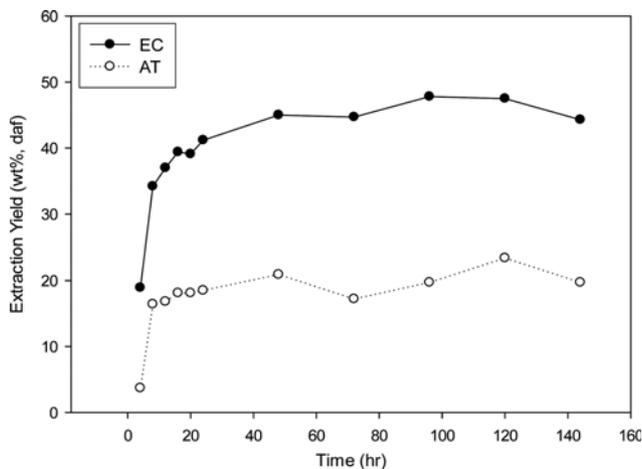


Fig. 2. Extraction yields of EC and AT by time with EDA.

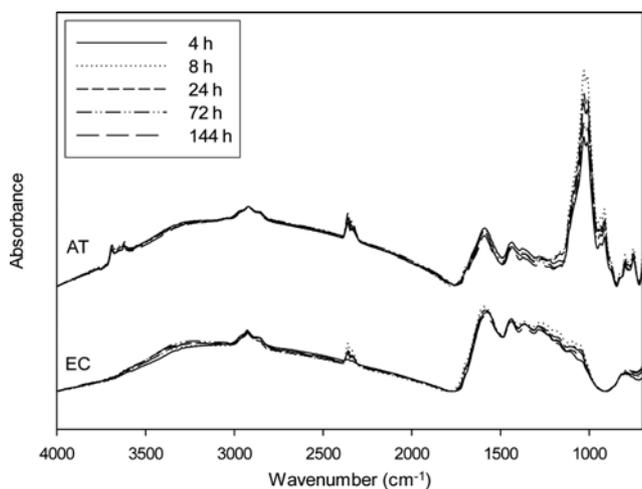


Fig. 3. FTIR spectra of residue with different extraction time.

## 2. Variation in Chemical Structure of Coal Before and After Extraction

To investigate any changes in coal structure after solvent extraction, the residue was analyzed by FTIR after extraction intervals of 4, 8, 24, 72, and 144 h. It is possible to observe the overall structural changes by FTIR through the changes in the peaks. The exact same amount of each residue was sampled using random sampling method for analysis. Fig. 3 presents the overlapped FTIR spectra of the residual EC and AT coals at each time point. No structural change was observed for either EC or AT, even though nearly half of the material was extracted in the case of EC. Fig. 4 shows the FTIR spectra in which Damin et al. compared a raw coal sample with extract [24]. The spectra of the raw and extracts were almost the same, except that the peak at  $2,900\text{ cm}^{-1}$  corresponding to aliphatic C-H bonding was reduced slightly in the extract compared to the raw sample. Based on this change, it was assumed that the aliphatic structure was reduced more in the extract than the raw

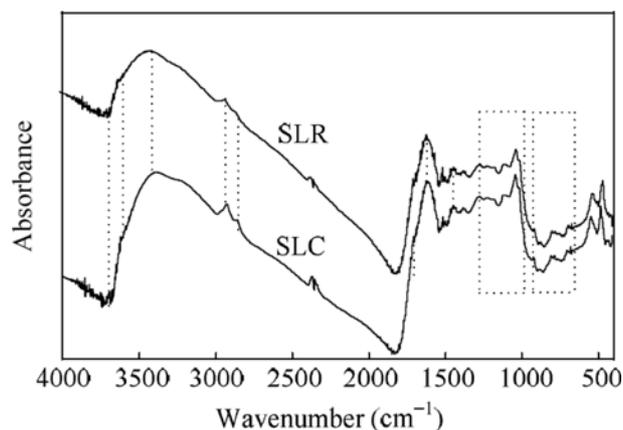


Fig. 4. FTIR spectra of raw coal sample (SLC) and extract (SLR) analyzed by Damin [24].

Table 7. Mean yield of extraction repeated three times for each coal sample and solvent

Samples	NMMO	EDA	NMP	PRD	QNL	DMF	DMS	THF	Average
EC	50.27	47.01	34.04	28.98	27.06	20.95	20.25	19.72	31.03
SM	46.79	45.31	30.12	23.58	23.07	18.25	16.87	16.35	27.54
IN	46.61	37.40	32.40	24.58	25.12	18.62	17.50	15.23	27.18
RS	46.82	42.78	28.34	23.42	22.51	16.37	15.94	14.66	26.36
LG	44.76	41.15	27.41	23.04	22.48	15.45	14.87	13.96	25.39
BE	40.14	38.03	25.40	22.71	21.43	12.72	13.92	12.56	23.36
AR	39.70	36.01	24.72	22.19	20.24	11.68	13.62	11.09	22.41
KI	29.89	27.68	21.21	20.01	17.64	10.46	9.58	8.97	18.18
CA	31.08	28.92	20.58	17.56	16.75	8.88	8.88	7.06	17.46
TA	30.48	26.04	19.24	16.32	16.24	8.85	8.74	8.80	16.84
SH	28.17	22.42	19.45	18.49	17.01	9.23	9.83	8.10	16.59
AN	27.98	20.70	17.49	15.63	15.22	8.23	7.82	7.41	15.06
AT	24.63	18.95	15.80	10.26	9.65	4.52	4.93	4.10	11.60
A2	5.85	5.14	4.49	4.58	3.72	2.42	1.18	0.00	3.42
A1	5.07	4.89	3.98	4.43	3.17	1.23	1.17	0.00	2.99
Average	33.22	29.49	21.64	18.39	17.42	11.19	11.01	9.87	19.03

(Unit: wt%, daf)

sample, and there would be a significant relationship between extraction and the aliphatic structure of coal. However, additional studies to quantitatively analyze the chemical bonding motifs of coal are considered necessary since the extent of peak reduction was slight and there were almost no changes in the other peaks.

### 3. Mean Extraction Yields of Three Times Extractions

To obtain accurate data, triplicate experiments were conducted under the same conditions and the mean extraction yields were calculated and summarized in Table 7. The highest yield was 50% when extracting EC with the NMMO/NMP mixed solvent, whereas the lowest yields (0%) were obtained when extracting the two anthracites A1 and A2 with THF. In terms of the mean extraction yield for each coal, EC was the highest with 31%, and followed by SM, IN, RS, LG, BE, AR, KI, CA, TA, SH, AN, and AT in the range 28–12%. The extraction yields of A2 and A1 were the lowest at ~3%. As for solvent, the NMMO/NMP mixed solvent exhibited the highest extraction yield, with a mean extraction yield of 33%, followed by EDA, NMP, PRD, QNL, DMF, and DMS in the range 29–11%. The solvent having the lowest mean extraction yield was THF (9.87%), which has the only value below 10% out of the eight solvents.

The trend that is evident from the experimental results is that slight changes might occur when the extraction yield is low; however, the order of extraction for each of coal and solvent is nearly fixed. For the coals, extraction yields from the highest to the lowest are observed in the order EC, SM, IN, RS, LG, BE, AR, KI, CA, TA, SH, AN, AT, A1, and A2 for almost all the solvents. In the case of the solvents, the maximum yields from highest to lowest are obtained in the order NMMO, EDA, NMP, PRD, QNL, DMF, DMS, and THF for almost all the coals. Based on these trends, it was expected that the extraction results would supply appropriate statistical data by which to ascertain via multiple regression analysis the key factors affecting extraction.

### 4. Variation in Extraction Yields with Coal Properties

Pursuant to identifying the extraction factors related to coal properties, correlations between the extraction yield of each coal and their various properties were sought on the basis of the coal sample analyses and mean extraction yields. Since the order of extraction yield

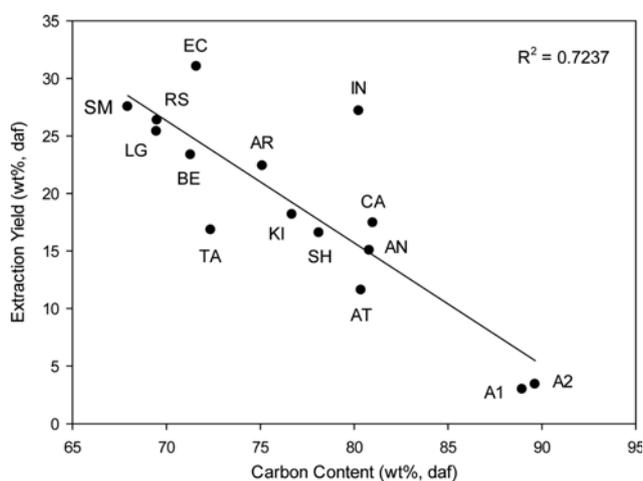


Fig. 5. Correlation between extraction yield and carbon percentage of coal samples.

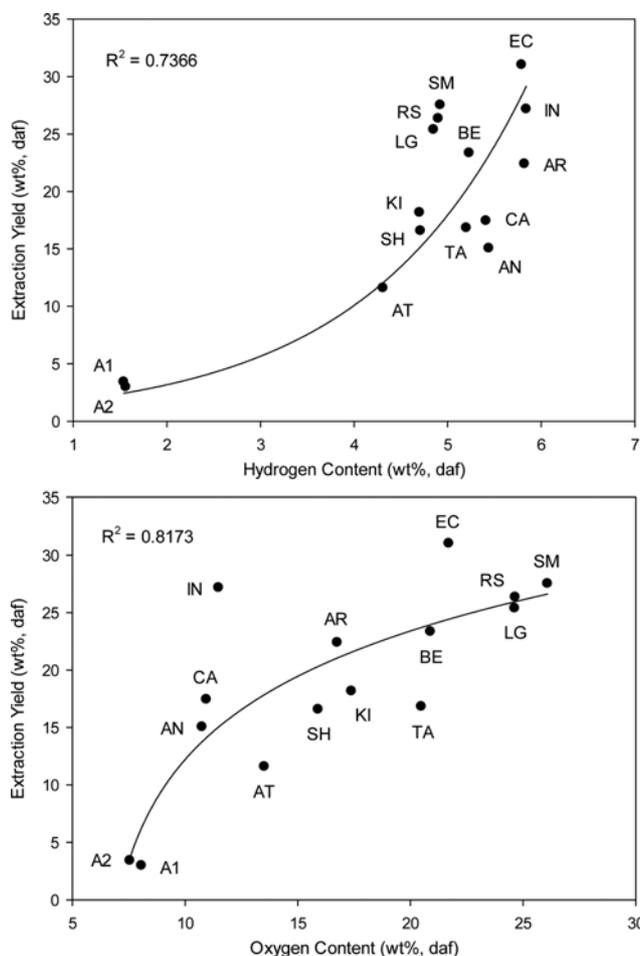


Fig. 6. Correlation between extraction yield and hydrogen, oxygen percentage of coal samples.

in accordance with the solvents appeared to be nearly the same for all the coal samples, their mean extraction yields were used.

#### 4-1. Variation in Extraction Yields with Elemental Composition of Coal

Figs. 5 and 6 present the mean extraction yields of each coal as functions of the contents of the main elements of coal (C, H, and O). The extraction yields increase as the carbon content of the coal decrease and the hydrogen and oxygen contents increases. The trend in terms of carbon content is found to be somewhat linear, with a coefficient of determination ( $R^2$ ) of 0.7237, whereas changes with respect to hydrogen are better described by an exponential function with  $R^2=0.7366$ . For oxygen, the changes can be described by a log function with the highest  $R^2$  value, 0.8173. The tendency of the extraction yield to increase with less carbon and more hydrogen and oxygen can be considered as related to the fact that extraction yields increase with coals of lower rank.

The atomic ratios of the hydrogen and oxygen content to carbon have a closer relationship to the rank of the coal rather than the direct contents. Fig. 7 presents the extraction yields in terms of the H/C and O/C ratios. The O/C ratio does not have a significant difference with the correlation ( $R^2=0.8173$ ) of the oxygen content; however, it does have an  $R^2$  of more than 0.8. The highest

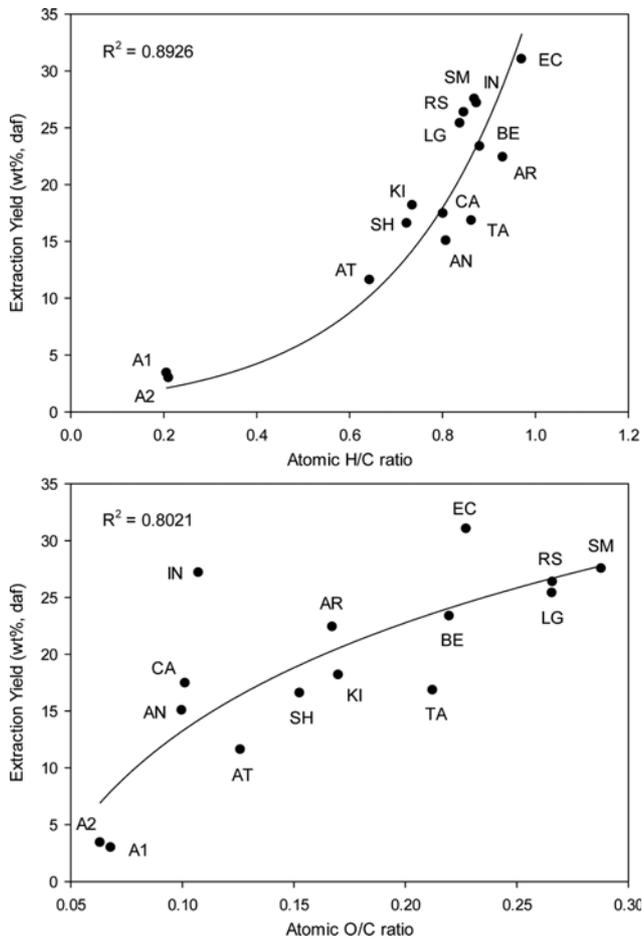


Fig. 7. Correlation between extraction yield and atomic hydrogen, oxygen ratio of coal samples.

correlation of quadratic equation with extraction yield is observed in the case of the atomic H/C ratio, for which  $R^2$  increases to 0.8926. The atomic H/C ratio is an index that can indirectly represent the aromaticity of the coal [25,26]; thus, the aromaticity of the coal and the extraction yield should be related. Finally, it was not possible to determine any relationship with the extraction yield in the cases of nitrogen and sulfur content (Fig. 8).

#### 4-2. Variation in Extraction Yields with Proximate Composition of the Coal

The proximate analysis components were highly correlated with the rank of the coal, similarly to the elements. Fig. 9 reveals the extraction yields as functions of the volatile matter and fixed carbon contents of each coal. In coal, solvent extraction theoretically targets only the organic components and excludes ash. Thus, the dry ash-free basis was used as for the volatile matter and fixed carbon. Based on the figure, it should be possible to confirm that the extraction yield increases as the volatile matter increases and the fixed carbon decreases. In dry ash-free basis, two ingredients of volatile matter and fixed carbon exist. Therefore, the coefficient of determination was found to be 0.8701, which was sufficiently high to indicate a strong correlation with the extraction yield, despite the linear regression fit. On the other hand, it was not possible to find any relationship between the extraction yield and the ash

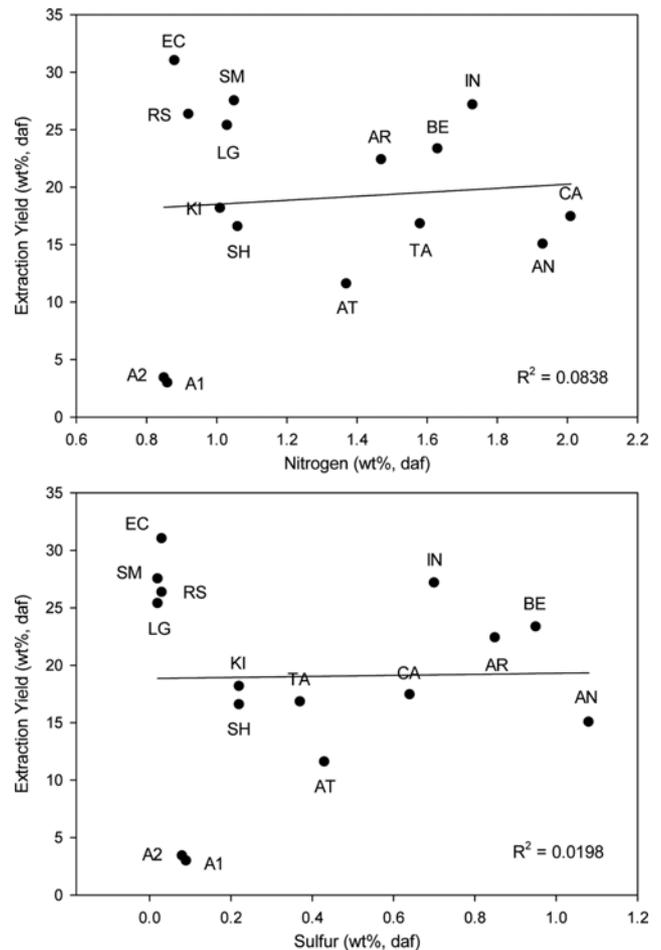


Fig. 8. Plot of extraction yield versus nitrogen, sulfur percentage of coal samples.

content of the coal (Fig. 10).

The following facts may be inferred from these results. A larger quantity would be extracted from lower rank coal during solvent extraction. The extraction yield is highly correlated with the volatile matter content of the coal, which can be verified indirectly via the C, H, and O content. In fact, the volatile matter fraction of coal has more hydrogen and oxygen than general coal, and is a source for the discharge of such hydrocarbon gases as methane, ethane, olefins, and paraffins at high temperature. Moreover, volatile matter has more aliphatic than aromatic structure.

#### 4-3. Variation in Extraction Yields with Maceral Composition and the Vitrinite Reflectance of Coal

The maceral components have varying degrees of chemical reactivity (general reactivity that is not directly associated with extraction yield), depending on the type. Vitrinite has a high degree of reactivity, whereas liptinite (ecgenite) and inertinite have intermediate and low degrees of reactivity, respectively. Niekerk et al. showed that the extraction yield was higher with lower vitrinite reflectance [17]. Thus, the relationships between the maceral composition and the vitrinite reflectance with the mean extraction yield can be verified by the results of the petrographic analysis.

Fig. 11 displays the extraction yield as a function of the vitrinite, liptinite, and inertinite contents. The vitrinite and liptinite had



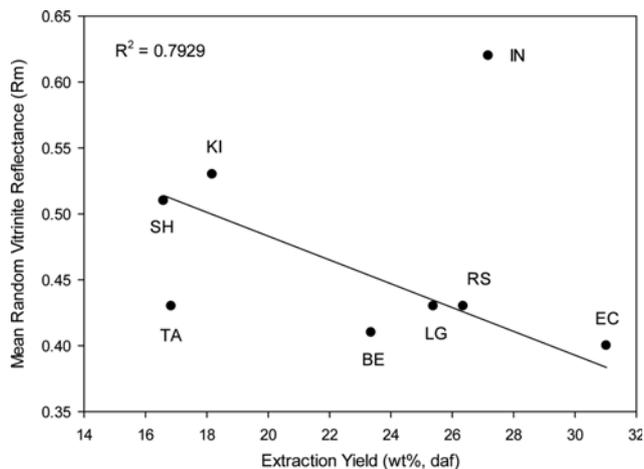


Fig. 12. Correlation between extraction yield and mean random vitrinite reflectance of coal samples.

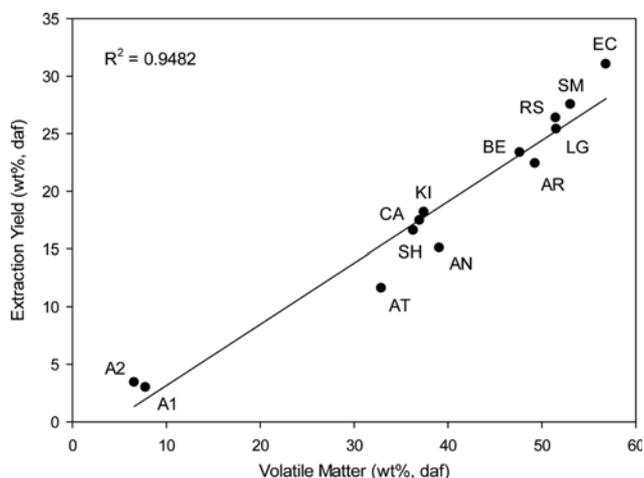


Fig. 13. Correlation between extraction yield and volatile matter percentage of coal samples except IN, TA.

that excludes the results from IN and TA from Fig. 9 reveals an increase in  $R^2$  from 0.8701 to 0.9482.

Also, with respect to the deviations for IN and TA, structural specificity may be a factor. Fig. 14 compares the FTIR spectra of IN, BE, and TA. IN has a mean extraction yield of 27%, which is the third highest; the mean extraction yield of BE is intermediate at 23%, and TA has a relatively low extraction yield at 17%. The most prominent difference in the FTIR spectra of these three coals, with the exception of the peak ( $1,050\text{ cm}^{-1}$ ) attributed to minerals, is the peak spanning  $2,800\text{--}3,000\text{ cm}^{-1}$  corresponding to aliphatic C-H bonds. The mean extraction yield and the peak size have a proportional relationship. In addition, it is possible to corroborate the trend using the  $1,300\text{--}1,400\text{ cm}^{-1}$  interval corresponding to  $\text{CH}_2$  and  $\text{CH}_3$  group. The peak sizes tend to decrease in the order IN, BE, and TA.

It is also possible to observe a similar trend in the  $^{13}\text{C}$  NMR spectra. The relative amounts of aliphatic structures and aromatic structures are able to compare with  $^{13}\text{C}$  NMR spectroscopic analysis [27–30]. Fig. 15 presents the spectra of the three coal samples in the

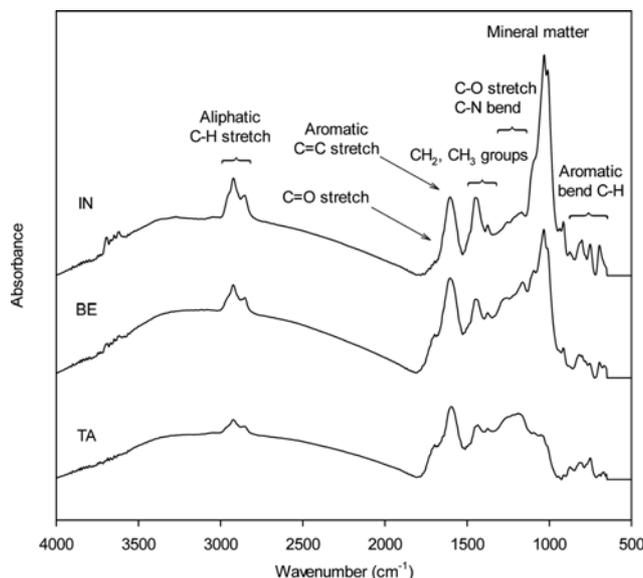


Fig. 14. FTIR spectra of three coal samples (IN, BE, TA).

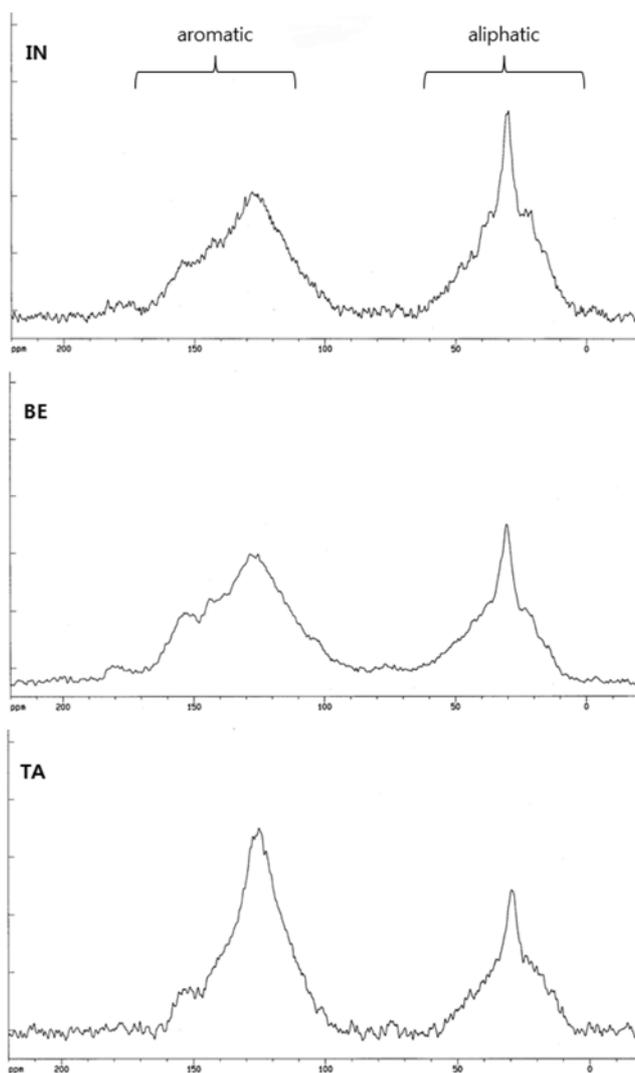


Fig. 15.  $^{13}\text{C}$ -NMR spectra of three coal samples (IN, BE, TA).

order of extraction yield. For IN, the peak hill at 10-50 ppm representing the aliphatic structure is more prominent than the peak hill at 100-150 ppm representing the aromatic structure. On the other hand, the heights of the two peak hills appear to be similar in the case of BE, and the peak hill due to aromatic structure appears to be higher than that due to aliphatic structure in TA.

The results of these spectral analyses enabled us to estimate that IN has more aliphatic structure relative to the other coals, and that TA has a more aromatic structure. The aliphatic structure is easily disrupted relative to that of the aromatic structure, and it has often been reported that coals with higher aliphatic content afford higher extraction yields [17,30,31]. However, the difference between the peaks of the IN and TA coal samples and that of the other coal samples is not large, and the spectra of all the coal samples generally have a similar shape. Moreover, the atomic H/C ratios for the two coals are neither significantly high nor low in terms of an H/C ratio that would represent the aromatic nature of a coal in a direct or indirect way. Therefore, it was determined that it is somewhat inadequate to predicate the structural specificity and aromatic nature of a coal only based on the aforementioned results. Thus, follow-up studies to quantitatively analyze the aromatic nature of coal are required.

#### 4-5. Variation in Extraction Yields with Ca and Mg Content in Ash of Coal

Kashimura et al. [16] argued that the extraction yield would decrease with increasing content of Ca and Mg associated in carboxyl group. The Ca and Mg content refers to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions that are integrated with organic components in the coal rather

than Ca and Mg present as minerals. This study could not directly measure the Ca and Mg content that were bound to organic components; however, we did examine the effects of Ca and Mg contained in the coal ash on extraction yield. Inorganic elements inside coal structures seem to come from outside minerals during coalification [1,32,33]. It was assumed that there is a correlation between the amount of Ca and Mg in organic structures and those in mineral matters in coal. Fig. 16 shows the correlation between the sum of the CaO and MgO content and extraction yield. The graph

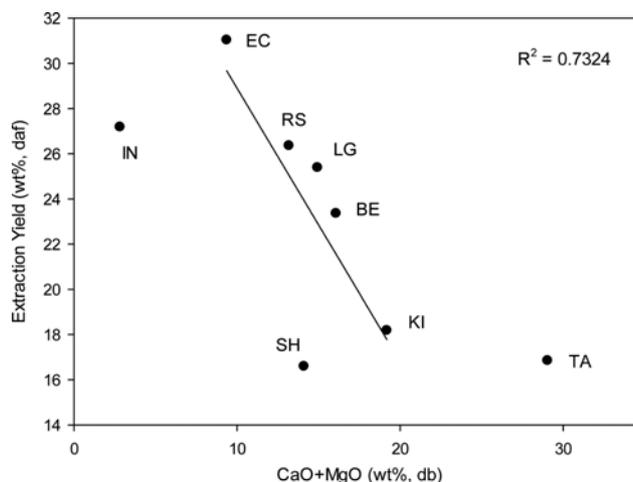


Fig. 16. Correlation between extraction yield and CaO, MgO percentage of ash of coal samples from XRF data.

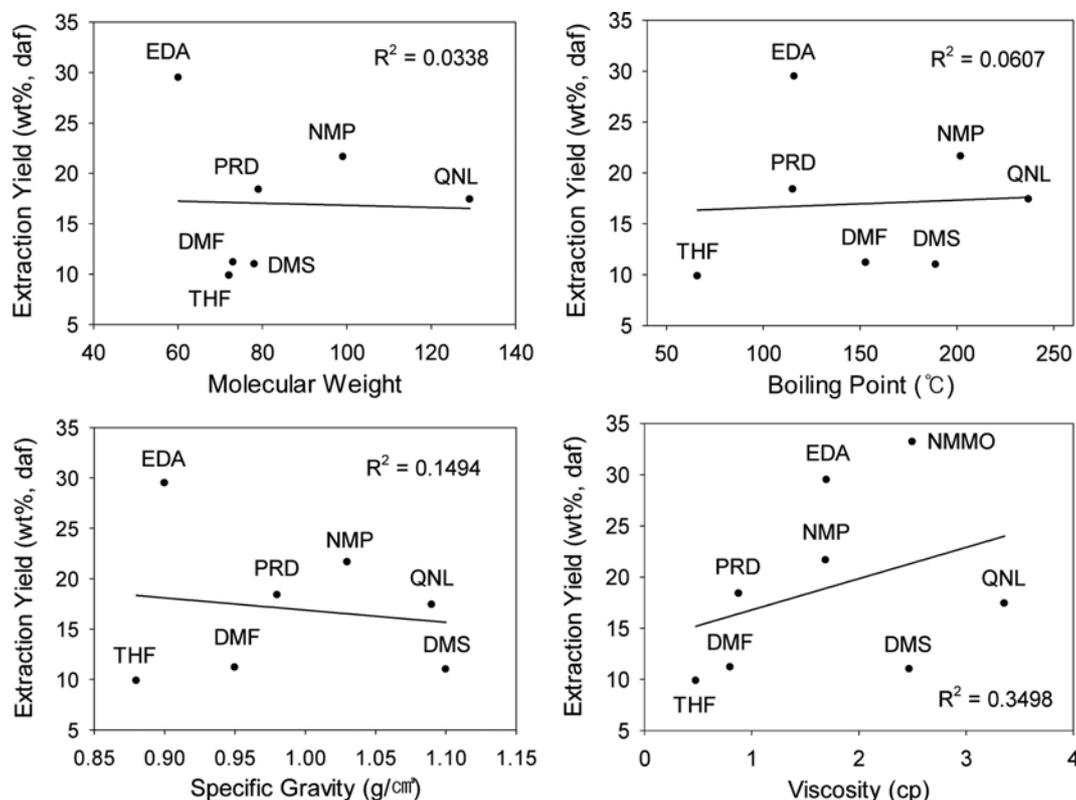


Fig. 17. Plot of extraction yield versus general properties (molecular weight, boiling point, specific gravity, viscosity) of solvent.

allows us to discern that the extraction yield decreases as the Ca and Mg content in the ash increases. Based on this finding, Ca and Mg in mineral matter are believed to flow to the inside of organic matter of coal in the course of formation or solvent extraction. In the case of IN, the CaO and MgO content is significantly lower than in the other coals, but significantly higher for TA. Therefore, the extraction specificity in these two samples might be related to the structure as well as the Ca and Mg content.

## 5. Variation in Extraction Yields with Solvent Properties

### 5-1. Variation in Extraction Yields with General Solvent Properties

A correlation between the general solvent properties (molecular weight, boiling point, specific gravity, and viscosity) and extraction yields was identified. The mean extraction yield for the four properties was used since the extraction ranks of the coals were similar in all the solvents. Fig. 17 plots the extraction yield as a function of the four solvent properties. However, no relationship to the extraction yield could be found for any of the four properties. Shui et al. [15] suggested that adding CS<sub>2</sub> to NMP would reduce viscosity, thereby increasing the extraction yield; however, we did not observe any significant relationship between viscosity and extraction yield. Furthermore, the viscosity increased substantially from 1.69 to 2.50 when adding NMMO as an alternative to CS<sub>2</sub>; however, the extraction yield also increased substantially from 22% to 33%.

### 5-2. Variation in Extraction Yields with Solubility

The Hildebrand solubility parameter of a solvent represents its solubility as a function of molecular cohesion. Although it is not an indicator of the intensity, its correlation with extraction yield is summarized in Fig. 18 to verify the changes in extraction yield with respect to the parameter. However, a relationship between the parameter and extraction yield could not be found.

The Hildebrand solubility parameter is sub-divided into three components: the dispersion, polar, and hydrogen-bonding forces; these are known as the Hansen parameters. The sum of their respective squares is equivalent to the sum of the squares of each Hildebrand solubility parameter. The extraction yield versus each of the three components is shown in Fig. 19. A clear relationship could not be found, as was the case for the Hildebrand solubility param-

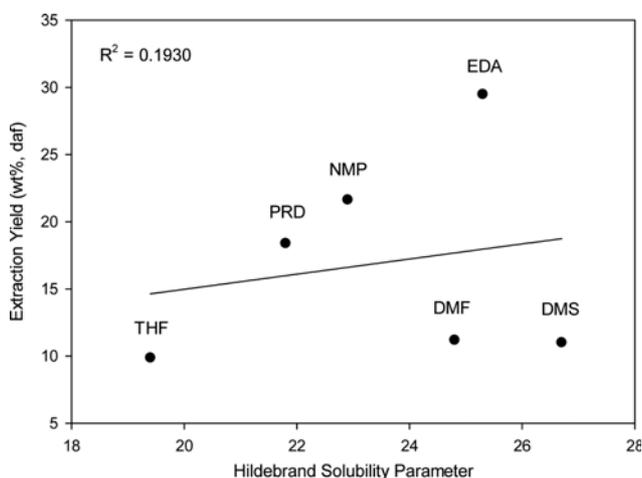


Fig. 18. Plot of extraction yield versus Hildebrand solubility parameter of solvent.

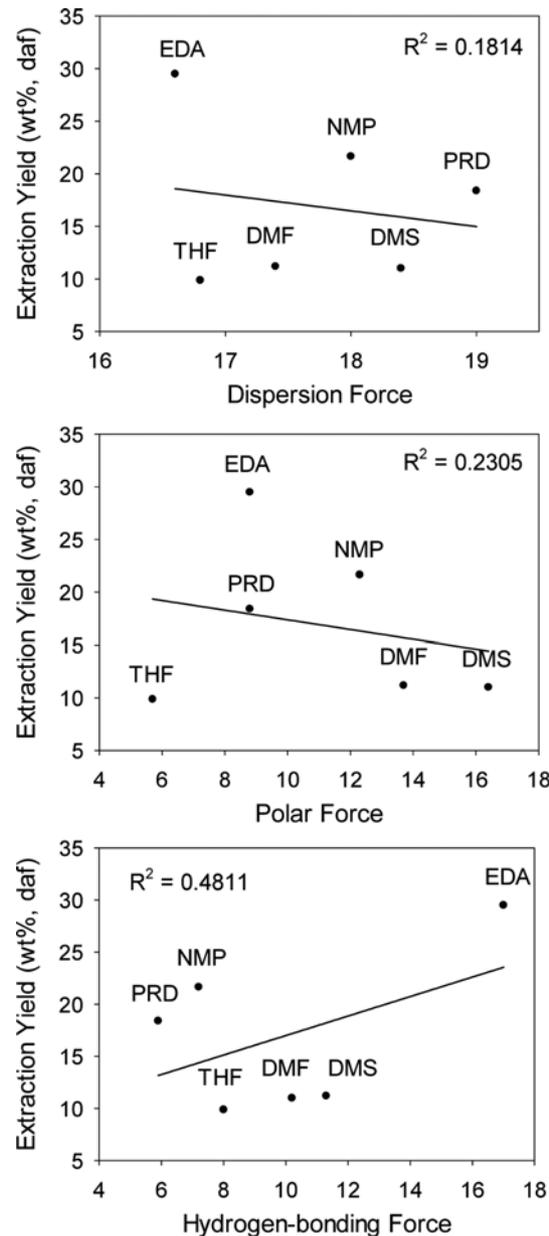


Fig. 19. Plot of extraction yield versus Hansen parameter of solvent.

eter. However, the polar force exhibited a trend similar to the Hildebrand solubility parameter.

The Hansen parameters can be represented by a Teas triangular graph, using the ratio of each element to the total sum of the three elements. The location of each solvent is shown in Fig. 20 in the triangular graph. The extraction yields of these solvents are all different; thus, the correlations between the three elements of the Hansen parameters and the extraction yields are represented by the heights of the extraction yields by using contour lines, as in a map. Each line of circles represents 5% increments of extraction yield from outside to inside. The outermost line refers to 5%, while the innermost line refers to 20%. As a result, the contour line for the extraction yield based on NMP was drawn, as shown in the graph; however, EDA was found to be an outlier. This result shows a trend

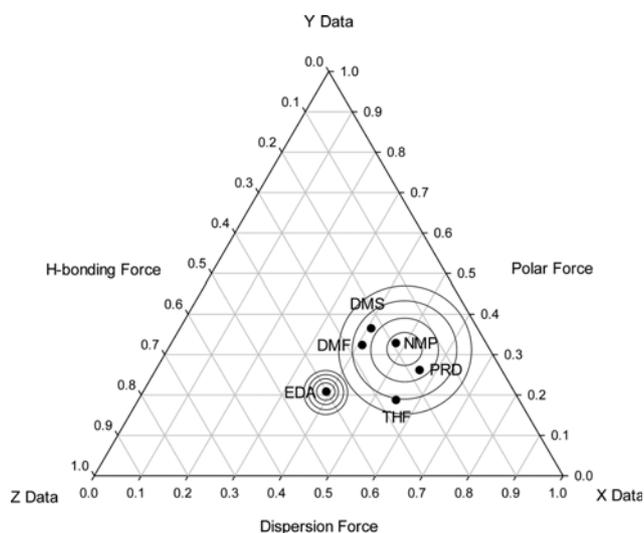


Fig. 20. Teas triangular graph of solvents used in this study with contour line of extraction yield.

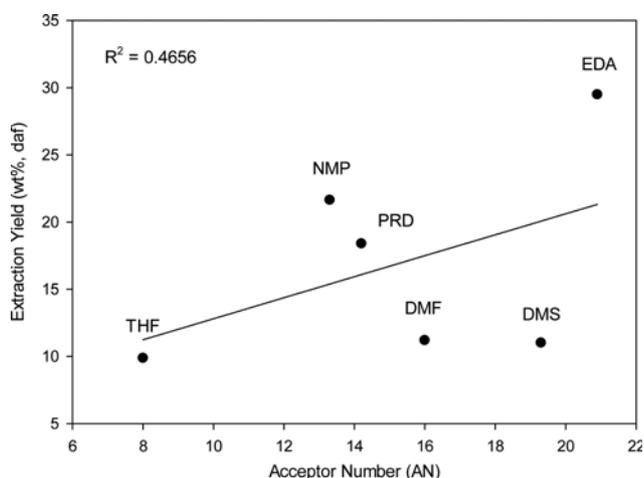


Fig. 21. Plot of extraction yield versus acceptor number of solvent.

similar to the second assumption of the Hildebrand solubility parameter. The deviation by EDA may be related to its significantly higher hydrogen bonding force than those of the other solvents.

### 5-3. Variation in Extraction Yields with Electron Donor-acceptor Properties

DN and AN are the properties that are believed to have the highest level of correlation with extraction yield. To verify such relationships, the mean extraction yields as functions of the DA, AN, and DN-AN of the six solvents are displayed in Figs. 21 and 22. Unlike AN (Fig. 21), which showed no correlation, DN and DN-AN (Fig. 22) clearly exhibited a proportional relationship wherein the extraction yield increases as these values increase.  $R^2$  was 0.7199 for DN and 0.7964 for DN-AN; thus, their degree of correlation with extraction yield was found to be higher than that of AN. The solvent NMP demonstrated a slight degree of deviation; however, it was significant enough to be considered as an exception like EDA in Hildebrand solubility parameter. The correlation between the DN-AN and the extraction yield, which agreed with the results of

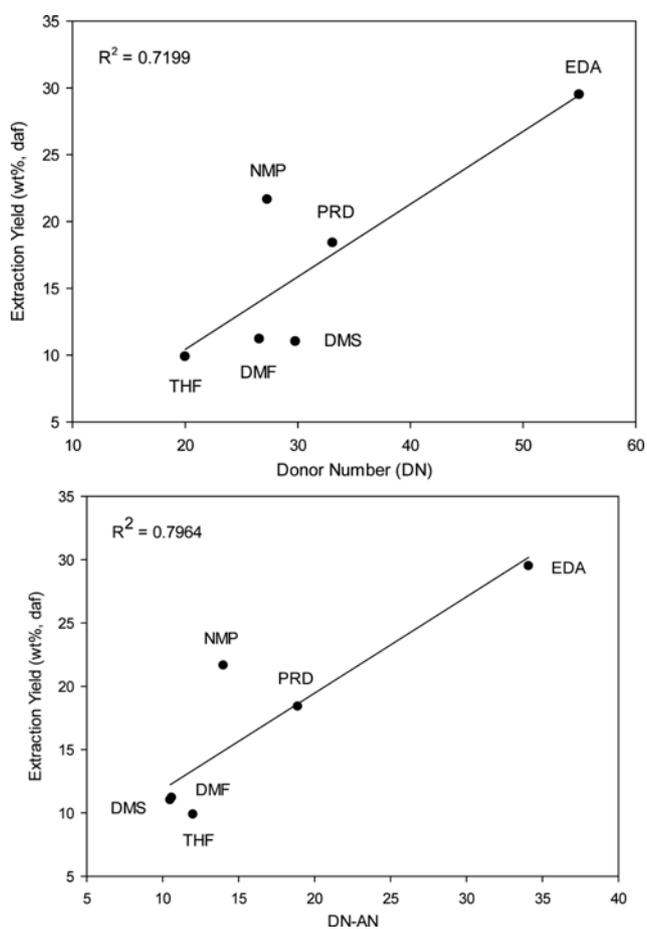


Fig. 22. Correlation between extraction yield and DN, DN-AN of solvent.

Marzec et al. [7], allowed us to reconfirm that the extraction factor had the largest effect on the solvent properties.

## 6. Characterization of Coal Solvent Extraction Using Multiple Regression

### 6-1. Multiple Regression with Fifteen Coal Samples

This section statistically analyzes by multiple regression analysis how and which of the properties of the coals and solvents affect extraction yield. For coal, the elemental components of C, N, S, and the H/C and O/C atomic ratios were considered, and among the technical analysis components, the volatile matter was taken into account. Fixed carbon was excluded since it was the value obtained by subtracting volatile matter from 100 in dry ash-free base. In the case of the maceral ingredient, the vitrinite reflectance and the Ca and Mg contents of the ash are first excluded, but will be discussed later, because these values were determined for only eight of the fifteen coals. In terms of solvent properties, the three contributions (DE, PE, and HB) to the Hildebrand solubility parameter (HSP) and Hansen parameters, as well as the DN-AN values, were considered.

Setting independent variables is very important for conducting multiple regression analysis; if done incorrectly, odd results may obtain even though there is no statistical error. One of the most important aspects for setting independent variables is to ensure

**Table 8. Setting of dependent, independent variables for multiple regression No. 1 to 8**

Regression no.	Dependent variable (y)	Independent variable (x)	
		Coal	Solvent
1	Yield	C, N, S	HSP, DN-AN
2	Yield	C, N, S	DF, PF, HB, DN-AN
3	Yield	H/C, N, S	HSP, DN-AN
4	Yield	H/C, N, S	DF, PF, HB, DN-AN
5	Yield	O/C, N, S	HSP, DN-AN
6	Yield	O/C, N, S	DF, PF, HB, DN-AN
7	Yield	VM, N, S	HSP, DN-AN
8	Yield	VM, N, S	DF, PF, HB, DN-AN

**Table 9. Results of multiple regression No. 1 to 8**

Regression no.	Coefficient of determination (R <sup>2</sup> )	Standard error	F ratio
1	0.8467	7.5733	108.7631
2	0.8919	6.2405	120.4442
3	0.9173	5.3612	233.9625
4	0.9360	4.5905	232.6425
5	0.8838	6.5156	152.9079
6	0.9038	5.8411	139.1516
7	0.9169	5.3760	232.5754
8	0.9344	4.6593	225.4772

that they are not related to any other independent variable. From the data for the regression analysis as above, the C, H/C, O/C, and VM values for the coals are closely related to the ranks of the coals. Thus, only one of these four properties should be considered. Even among the solvent properties, the Hansen parameters are a property derived from the HSP, and thus, should not be set as independent variables. Therefore, multiple regression analysis was conducted with the eight cases as shown in Table 8. The dependent variable, the extraction yield, was set as the *y*-axis, and the *y*-intercept was set to zero, since the extraction yield should be zero when there is no coal.

The results of multiple regression analyses for the eight cases are summarized in Table 9. The coefficients of determination ranged from 0.8467 to 0.9360, and the *F*-ratios had sufficiently large values in all cases. Therefore, it was possible to ensure that there were no statistical issues for the eight multiple regression models. Based on the results of each analysis, the atomic H/C ratio and volatile matter had the largest coefficients of determination as for the properties of coal. For the solvents, higher coefficients of determination were found when considering the three Hansen parameters and DN-AN. The results of a detailed analysis of two regression models (No. 4 and No. 8) having high coefficients of determination are summarized in Table 10.

A variable whose *t*-statistical value is the closest to zero and has the highest *P*-value from the results of a multiple regression analysis would have the least effect in the regression model. Based on

**Table 10. Statistics of multiple regression No. 4 and No. 8**

Regression no. 4				
R-squared		0.9360		
Residual sum of square		1749.0273		
F ratio		232.6425		
X	Coefficient	Standard deviation	t-Statistics	P-value
N	-4.6447	2.6428	-1.7575	0.0825
S	-2.3504	2.7814	-0.8450	0.4005
H/C	34.0793	2.3520	14.4897	0.0000
DF	-1.1683	0.2031	-5.7538	0.0000
PF	0.9084	0.1954	4.6480	0.0000
HB	-1.1173	0.2159	-5.1756	0.0000
DN-AN	1.2101	0.1053	11.4966	0.0000
Regression no. 8				
R-squared		0.9344		
Residual sum of square		1801.8312		
F ratio		225.4772		
X	Coefficient	Standard deviation	t-Statistics	P-value
N	-1.7499	2.6347	-0.6642	0.5084
S	-0.6942	2.8349	-0.2449	0.8072
VM	0.4936	0.0348	14.1903	0.0000
DF	-1.0857	0.2047	-5.3029	0.0000
PF	0.8923	0.1983	4.4996	0.0000
HB	-1.0929	0.2190	-4.9902	0.0000
DN-AN	1.2033	0.1068	11.2654	0.0000

the analysis results, S had the smallest absolute *t*-statistical value and the highest *P*-value in all cases; thus, the S variable was determined to have the lowest effect on extraction yield. Therefore, multiple regression analysis was conducted with the remaining variables after excluding the S term (Table 11).

For removing invalid variables from a multiple regression analysis, the *F*-test verifies whether it would be justifiable to remove the relevant variable or not. When excluding S from the two models, the *F*-values are calculated to be 0.7141 and 0.0600, respectively. *F*-values corresponding to the number of variables (1) excluded from the *F*-statistics at a 5% significance level and the value (83) obtained by subtracting the number of *x* variables (7) of unrestricted formula from the number of analysis data (90) ranged from 3.92 to 4.00; thus, it is justifiable to exclude S since the obtained *F*-values are smaller than 4. N was similarly removed from the two models by this method; the results are summarized in Table 12.

On removing N from the two models, the *F*-value becomes 23.7525 for No. 4, whereas it becomes 3.3100 for No. 8. The *F*-value surpassed 4 for No. 4; thus, it would not be appropriate to remove N. No. 4-2, wherein only S was removed, became the final model. In the case of No. 8, it would be appropriate to remove N and No. 8-3 would become the final model since the *F*-value did not surpass 4. In other words, N should be taken into consideration due to the extraction influencing factors in the case of the

**Table 11. Statistics of multiple regression No. 4-2 and No. 8-2**

Regression no. 4-2				
R-squared	0.9363			
Residual sum of square	1764.0751			
F ratio	272.2238			
X	Coefficient	Standard deviation	t-Statistics	P-value
N	-6.5649	1.3470	-4.8737	0.0000
H/C	34.2362	2.3406	14.6269	0.0000
DF	-1.0828	0.1758	-6.1610	0.0000
PF	0.8917	0.1941	4.5941	0.0000
HB	-1.0920	0.2134	-5.1165	0.0000
DN-AN	1.2031	0.1047	11.4852	0.0000
Regression no. 8-2				
R-squared	0.9351			
Residual sum of square	1803.1328			
F ratio	266.0238			
X	Coefficient	Standard deviation	t-Statistics	P-value
N	-2.3140	1.2719	-1.8193	0.0724
VM	0.4946	0.0343	14.4046	0.0000
DF	-1.0611	0.1773	-5.9857	0.0000
PF	0.8875	0.1962	4.5228	0.0000
HB	-1.0856	0.2157	-5.0316	0.0000
DN-AN	1.2013	0.1059	11.3438	0.0000

atomic H/C ratio; however, it would be fine to remove N for volatile matter. The coefficients of determination of these two final models were not very different; thus, the No. 8-3 model, which had one less variable, was determined to be a more effective model for calculating extraction yield. A summary of the extraction yield calculation formula using the No. 8-3 model based on the analysis results is as follows:

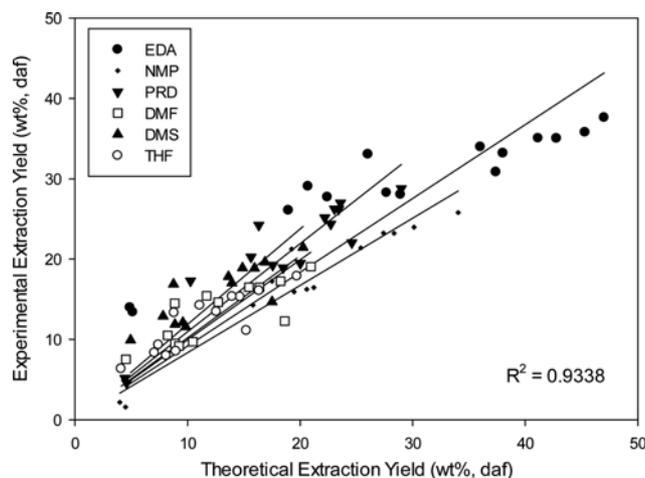
$$y=0.4819x_1-1.2059x_2+0.9157x_3-1.1284x_4+1.2131x_5 \quad (2)$$

where, y: extraction yield (wt%, daf)  
 $x_1$ : volatile matter of coal (wt%, daf)  
 $x_2$ : dispersion force of solvent  
 $x_3$ : polar force of solvent  
 $x_4$ : hydrogen bonding force of solvent  
 $x_5$ : DN-AN of solvent

From the extraction yield calculation formula, it was possible to observe that the volatile matter content of coal, and the polar force and DN-AN of the solvent would have a positive effect on the extraction yield, whereas the dispersion and hydrogen bonding force of the solvent would have a negative effect on extraction yield. Fig. 23 is the graph for comparing the theoretical values calculated using the above formula with the experimental values.

#### 6-2. Multiple Regression with Eight Coal Samples

Due to the sample issue, the maceral and XRF analysis of ash could not be conducted for all the coals; thus, multiple regression analysis for the 15 kinds of coal was conducted by excluding the



**Fig. 23. Correlation between experimental extraction yield and the theoretical extraction yield of regression No. 8-3.**

maceral ingredients, vitrinite reflectance, and Ca and Mg contents of ash. As a result, the extraction yield calculation formula having a high correlation (0.9338) with the coefficient of determination was deduced. However, there was only one property of coal in the calculation formula, which was volatile matter, so it would be unreasonable to assess the influencing factors for coal extraction using only volatile matter. Also, the maceral composition, vitrinite reflectance, and Ca and Mg content were found to have a correlation, to some extent, with the extraction yield from the aforementioned results of this study. Multiple regression analysis was again conducted by additionally taking them into consideration. Among the properties of coal, H/C atomic ratio, volatile matter, mean vitrinite reflectance ( $R_m$ ), the three maceral ingredients (VI, LI, IT), and the Ca+Mg content were found to have a high correlation with the extraction yield in the previous regression analysis and were taken into account. Among the solvent properties, the Hildebrand solubility parameter, Hansen parameter and DN-AN were taken into account, as previously considered.

In the case of the eight kinds of coal, the number of analysis data by the six solvents was just 48. There were too many variables for 48 data and setting too many independent variables can lead to wrong analysis results; thus, vitrinite reflectance, which was related to the rank of coal, was first reviewed. This study also verified which properties would have the highest coefficient of determination, by setting the H/C atomic ratio, volatile matter, and vitrinite reflectance separately, which were found to have high correlation in the regression model on the fifteen kinds of coal as shown in Table 13. It would be imperative to consider only one as an independent variable, since all of them were related to the rank of coal. On the other hand, the three maceral components and the Ca+Mg content were not directly related to the rank of coal; thus, they were excluded for the meantime.

The results of regression analysis for No. 9 to 14 are summarized in Table 14. The analysis results allowed us to observe that the correlation between the vitrinite reflectance and extraction yield turned out to be lower than that for the H/C atomic ratio and volatile matter content, since its coefficient of determination was found

**Table 12. Statistics of multiple regression No. 4-1 to 4-3, No. 8-1 to 8-3**

Regression	No. 4-1	No. 4-2	No. 4-3
R-squared	0.9360	0.9363	0.9225
Residual sum of square	1749.0273	1764.0751	2262.8996
X	P-value		
N	0.0825	0.0000	-
S	0.4005	-	-
H/C	0.0000	0.0000	0.0000
DF	0.0000	0.0000	0.0000
PF	0.0000	0.0000	0.0000
HBF	0.0000	0.0000	0.0000
DN-AN	0.0000	0.0000	0.0000
F-value	-	0.7141	23.7525
Regression	No. 8-1	No. 8-2	No. 8-3
R-squared	0.9344	0.9351	0.9338
Residual sum of square	1801.8312	1803.1328	1874.1837
X	P-value		
N	0.5084	0.0724	-
S	0.8072	-	-
VM	0.0000	0.0000	0.0000
DF	0.0000	0.0000	0.0000
PF	0.0000	0.0000	0.0000
HBF	0.0000	0.0000	0.0000
DN-AN	0.0000	0.0000	0.0000
F-value	-	0.0600	3.3100

**Table 13. Setting of dependent, independent variables for multiple regression No. 9 to 14**

Regression no.	Dependent variable (y)	Independent variable (x)	
		Coal	Solvent
9	Yield	H/C	HSP, DN-AN
10	Yield	H/C	DF, PF, HB, DN-AN
11	Yield	VM	HSP, DN-AN
12	Yield	VM	DF, PF, HB, DN-AN
13	Yield	Rm	HSP, DN-AN
14	Yield	Rm	DF, PF, HB, DN-AN

**Table 14. Results of multiple regression No. 9 to 14**

Regression no.	Coefficient of determination (R <sup>2</sup> )	Standard error	F ratio
9	0.9136	5.8380	229.2006
10	0.9410	4.3579	254.3494
11	0.9183	5.6212	248.3949
12	0.9361	4.6480	222.5481
13	0.9002	6.2026	186.9193
14	0.9063	6.1188	124.7780

**Table 15. Statistics of multiple regression No. 10 and No. 12**

Regression no. 10				
R-squared	0.9410			
Residual sum of square	816.6174			
F ratio	254.3440			
X	Coefficient	Standard deviation	t-Statistics	P-value
H/C	53.8855	8.2662	6.5188	0.0000
DF	-2.6637	0.4426	-6.0176	0.0000
PF	1.2643	0.2633	4.8020	0.0000
HB	-1.6251	0.2996	-5.4232	0.0000
DN-AN	1.4848	0.1399	10.6149	0.0000
Regression no. 12				
R-squared	0.9361			
Residual sum of square	928.9678			
F ratio	222.5481			
X	Coefficient	Standard deviation	t-Statistics	P-value
VM	0.5648	0.0996	5.6705	0.0000
DF	-1.5495	0.3295	-4.7028	0.0000
PF	1.0475	0.2730	3.8370	0.0004
HB	-1.2956	0.3036	-4.2681	0.0001
DN-AN	1.3936	0.1466	9.5061	0.0000

**Table 16. Setting of dependent, independent variables for multiple regression No. 10-2 to 12-3**

Regression no.	Dependent variable (y)	Independent variable (x)	
		Coal	Solvent
10-2	Yield	H/C, Ca+Mg	DF, PF, HB, DN-AN
12-2	Yield	VM, Ca+Mg	DF, PF, HB, DN-AN
10-3	Yield	VM, VI, LI, IT	DF, PF, HB, DN-AN
12-3	Yield	H/C, VI, LI, IT	DF, PF, HB, DN-AN

to be low. The solvent properties were found to have a higher degree of correlation when setting the Hansen parameter and DN-AN as before than when taking the Hildebrand solubility parameter and DN-AN into account. The results of the detailed analysis of the No. 10 and No. 12 regression models to represent the highest coefficients of determination are summarized in Table 15.

It was determined that it would not be required to remove additional variables since the P-value of the coefficient of the two models was close to zero. Therefore, this study reviewed how the coefficients of determination and P-value of each coefficient would be changed by adding the Ca+Mg content and maceral composition separately to the two models as shown in Table 16.

The analysis results indicate that the P-value of all the coefficients is close to zero, while the coefficient of determination increased substantially to 0.95 when adding the Ca+Mg content (No. 10-2 and No. 12-2); thus, they are statistically significant (Table 17). On the other hand, adding the three maceral ingredients (No.

**Table 17. Statistics of multiple regression No. 10-2 and No. 12-2**

Regression no. 10-2				
R-squared	0.9510			
Residual sum of square	562.6189			
F ratio	303.6535			
X	Coefficient	Standard deviation	t-Statistics	P-value
H/C	45.9115	7.1799	6.3944	0.0000
Ca+Mg	-0.3362	0.0772	-4.3544	0.0000
DF	-1.9816	0.4034	-4.9120	0.0000
PF	1.1316	0.2232	5.0694	0.0000
HB	-1.4234	0.2559	-5.5623	0.0000
DN-AN	1.4290	0.1182	12.0920	0.0000
Regression no. 12-2				
R-squared	0.9529			
Residual sum of square	519.5338			
F ratio	329.4160			
X	Coefficient	Standard deviation	t-Statistics	P-value
VM	0.5232	0.0757	6.9111	0.0000
Ca+Mg	-0.4146	0.0721	-5.7532	0.0000
DF	-1.0783	0.2624	-4.1088	0.0002
PF	0.9558	0.2072	4.6132	0.0000
HB	-1.1562	0.2310	-5.0060	0.0000
DN-AN	1.3550	0.1111	12.1930	0.0000

10-3, 12-3) reduced the coefficient of determination substantially to 0.85-0.86, thereby allowing us to observe that the correlation with extraction yield was not as high as the Ca+Mg content (Table 18). A summary of the extraction yield calculation formula based on the analysis results of the No. 12-2 model having a higher coefficient of determination would be as follows:

$$y = 0.5232x_1 - 0.4146x_2 - 1.0783x_3 + 0.9558x_4 - 1.1562x_5 + 1.3550x_6 \quad (3)$$

where, y: extraction yield (wt%, daf)

$x_1$ : volatile matter of coal (wt%, daf)

$x_2$ : sum of CaO and MgO content in ash of coal (wt%, db)

$x_3$ : dispersion force of solvent

$x_4$ : polar force of solvent

$x_5$ : hydrogen bonding force of solvent

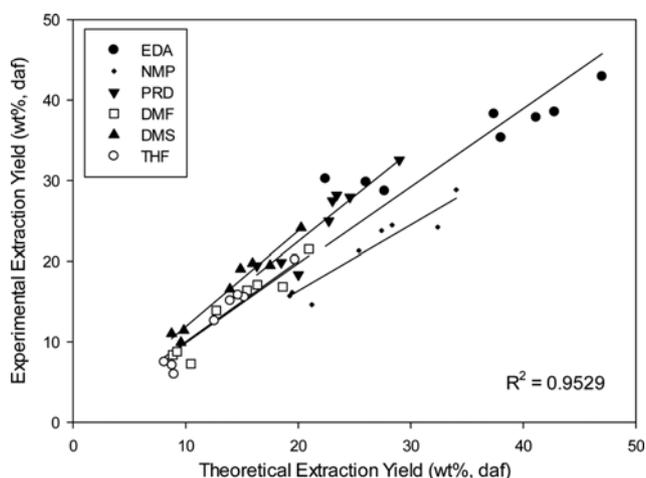
$x_6$ : DN-AN of solvent

Examining each coefficient of the calculation formula would allow us to observe that volatile matter would have a positive effect on the extraction yield, while the Ca+Mg content would have a negative effect on extraction yield for the properties of coal. For the solvent, it could be confirmed as before the fact that the polar force and DN-AN would have a positive effect, whereas the dispersion and hydrogen bonding would have a negative effect. In other words, the extraction yield would increase with the lower rank of coal; this could be verified through the volatile matter content. Moreover, extraction would be impeded more as there was

**Table 18. Statistics of multiple regression No. 10-3 and No. 12-3**

Regression no. 10-3				
R-squared	0.8578			
Residual sum of square	567.1876			
F ratio	234.9965			
X	Coefficient	Standard deviation	t-Statistics	P-value
H/C	60.4316	10.9767	5.5054	0.0000
VI	1.0068	0.2839	1.5463	0.1010
LI	3.3567	0.5164	6.5002	0.0000
IT	1.3158	0.2727	4.8248	0.0000
DF	-9.6686	1.5475	-6.2481	0.0000
PF	2.6275	0.3473	7.5659	0.0000
HB	-3.6965	0.4945	-7.4754	0.0000
DN-AN	2.0579	0.1577	13.0534	0.0000
Regression no. 12-3				
R-squared	0.8489			
Residual sum of square	554.1955			
F ratio	220.2680			
X	Coefficient	Standard deviation	t-Statistics	P-value
VM	0.5594	0.2180	1.5660	0.1141
VI	1.3041	0.3410	3.8244	0.0304
LI	2.8465	0.7417	3.8376	0.0304
IT	1.5020	0.3315	4.5312	0.0021
DF	-9.6686	1.9011	-5.0858	0.0000
PF	2.6275	0.4267	6.1584	0.0000
HB	-3.6965	0.6075	-6.0848	0.0000
DN-AN	2.0579	0.1937	10.6252	0.0000

more Ca and Mg in ash. Among the solvent properties, more extraction would be achieved with greater DN-AN and polar force, whereas extraction would be impeded upon increasing the disper-

**Fig. 24. Correlation between experimental extraction yield and the theoretical extraction yield of regression No. 12-2.**

sion force and hydrogen bonding force. Fig. 24 is the graph that compares the theoretical values of the No. 12-2 model with the actual.

## CONCLUSIONS

Coal solvent extraction with various coal samples and solvents was performed to study the effects of coal and solvent properties on the extraction yield. The following conclusions may be drawn.

1) The effect of coal rank: For 15 kinds of coal with various ranks, the extraction yields increased with lower degrees of carbon content, fixed carbon content, mean vitrinite reflectance, and higher degrees of hydrogen and oxygen contents (particularly the H/C and O/C ratios) and volatile matter. Lower ranks of coal were shown to be more highly extractable, possibly because they contain more components that would be easily extracted by solvents. Also, the fact that the properties having the highest correlation with extraction yield were the H/C atomic ratio and the volatile matter content allowed us to confirm this finding indirectly.

2) The effect of coal structure: Coals containing more aliphatic than aromatic structures afforded higher extraction yields. Moreover, based on the decreasing of peak corresponding to the aliphatic structure from the extracts, the extracted amount is expected to be high when there is a greater proportion of aliphatic structures. However, follow-up studies such as quantitative analysis would be required on the nature of the aromatic materials, since the relationship between the H/C ratio (representing the aromatic nature of the coal) and those coals having structural specificity has not yet been confirmed.

3) The effect of Ca and Mg content: The extraction yield decreased when there were larger amounts of Ca and Mg in the coal ash. In addition, the extraction yield appeared to be higher or lower than the conventional extraction yield trend when the Ca and Mg content was significantly higher or lower than the other coals. Such trends allowed us to infer that extraction by solvents would be more impeded when there were larger amounts of Ca and Mg in the ash. However, follow-up studies would be necessary to establish a path of Ca and Mg from mineral matter to the functional group such as carboxylic acid inside coal.

4) The effects of solvent properties: By using the eight solvents with different properties, it was possible to verify that the extraction yield was more closely correlated with DN and AN than the solubility parameters of the solvents. In particular, the highest degree of correlation was found with the DN-AN values of the solvents; this finding could be explained by Marzec's extraction mechanism [7]. Solvent molecules can easily disrupt the internal associations with coals only if the solvent DN is larger than the DN of the coal, and the solvent AN of similarly exceeded that of the coal.

5) Multiple regression analysis: Conducting a multiple regression analysis on the extraction yield based on the coal and solvent properties allowed us to develop a formula to calculate the extraction yield. The coefficients of the deduced formula enabled us to confirm that the volatile matter content of the coal, polar force of the solvent and DN-AN of the solvent would have positive effects on the extraction yield; however, the Ca and Mg content of the coal, and the dispersion and hydrogen-bonding forces of the solvent

would have negative effects on extraction yield. The deduced formula afforded coefficients of determination of 0.95 or higher, which was close to the experimental value.

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