The Effects of Pretreatment and the Addition of Polar Compounds on the Production of "HyperCoal" from Subbituminous Coals

Kensuke Masaki, Takahiro Yoshida, Chunqi Li, Toshimasa Takanohashi,* and Ikuo Saito

Institute for Energy Utilization, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba 3058569, Japan

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The effects of acid and hydrothermal pretreatments and the addition of polar compounds on the production of ashless-coal (HyperCoal) from subbituminous coals using cost-effective industrial solvents were investigated. The extraction yield of Wyodak subbituminous coal (C%, 75.0%) using crude methylnaphthalene oil (CMNO) at 360 °C was increased significantly by 19% following acid pretreatment; it was 41.3% for the raw coal and 60.5% for the acid-treated coal. The addition of strongly polar compounds, such as *N*-methyl-2-pyrrolidinone (NMP), also increased the extraction yields. For Pasir subbituminous coal (C%, 73.0%) the yield increased by 10% from 54.3% for the raw coal to 64.2% when 20% NMP was added to CMNO. The highest extraction yield of 72.2% was obtained for acid-treated Wyodak coal using CMNO with 20% NMP added. The ash content in HyperCoal tended to decrease following acid pretreatment and was less than 200 ppm in some coals. Hydrothermal pretreatment had a negative effect on the thermal extraction at 360 °C, but increased the yield at extraction temperatures below 200 °C.

Introduction

Coal is an important energy source and is used extensively. There are large, widely distributed reserves, and its price is low. However, when coal is burnt directly it emits more CO_2, nitrogen oxides (NO_x), and sulfur oxides (SO_x) than other fossil fuels, such as oil and natural gas. To address environmental concerns and secure future energy demands, a more efficient way of utilizing coal must be found.

In power generation, the direct combustion of coal in a gas turbine increases power output, while reducing CO_2 emissions. However, most of the mineral matter (ash) in coal must be removed before it is injected into the gas turbines for this type of system to run successfully, without necessitating a subsequent treatment of the combustion gases, while minimizing erosion and corrosion of the turbine blades. In Australia, attempts have been made to remove the mineral matter from coals using acids or alkalies in a hydrothermal pretreatment called the Ultra Clean Coal (UCC) Project. However, the treated coal still contains 1000−5000 ppm (0.1−0.5%) ash, which exceeds the level required for direct injection of coal into gas turbines.

Unlike de-ashing with acids or alkalies, when organic solvents are used in coal extraction, only the organic components in the coals are extracted.[1] Iino et al. found that a 1:1 (by volume) mixture of carbon disulfide and *N*-methyl-2-pyrrolidinone (CS_2/NMP) resulted in extraction yields exceeding 60% for some bituminous coals, at room temperatures,[2] with almost no ash detected in the extracts.[1] Thermal extraction has also been used to produce clean, value-added coals, with 60−80% extraction yields using NMP (202 °C),[3] quinoline (350 °C),[4] 1-methylnaphthalene and tetralin (350 °C),[5,6] and carbol oil and creosote oil (350 °C).[7]

Currently, the potential of thermal extraction using cost-effective industrial solvents is being assessed in Japan with a view to producing an ashless "HyperCoal" for direct gas turbine combustion.[8−12] The target value for the extraction yield is > 60% with the HyperCoal having an ash content below 200 ppm (0.02%) in which the sodium and potassium contents are less than 0.5 ppm. HyperCoal is a powder, like the original coal, not a pitch-like material.

As reported previously, thermal extractions to produce the HyperCoal were tested on bituminous coals in

* Corresponding author. E-mail: toshi-takanohashi@aist.go.jp.

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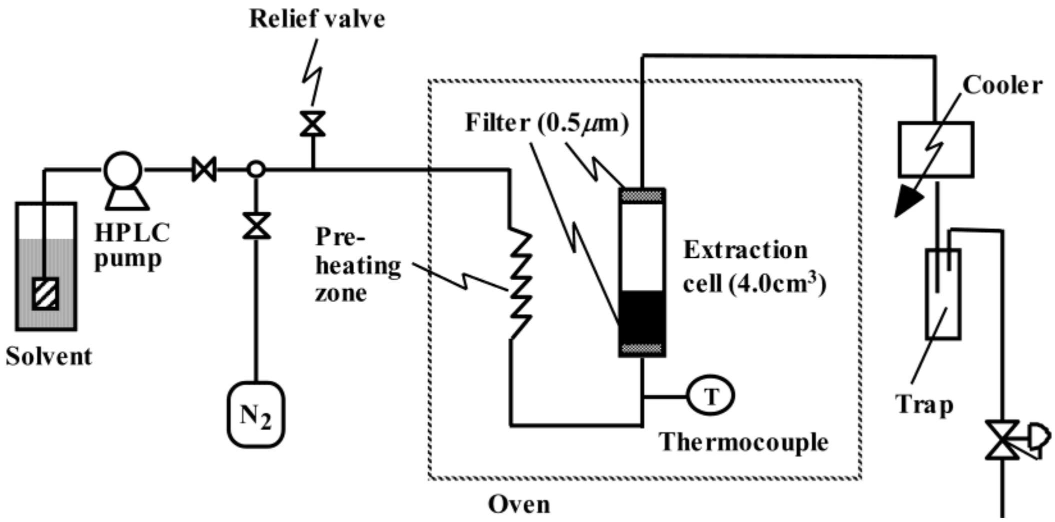

Figure 1. Schematic diagram of a flow-type extractor.

a flow-type extractor using aromatic solvents, such as 1-methylnaphthalene and two industrial solvents, light cycle oil (LCO) and crude methylnaphthalene oil (CMNO). Extraction yields of 60−80% were obtained.[11,12] These high extraction yields resulted largely from the heating and the solvent-induced relaxation of noncovalent bond interactions in the coal structure.[11,12] In addition, the extraction yields and softening temperatures of the coals were closely correlated.[11]

There are large global reserves of low rank coals, such as lignite and subbituminous coals, and these are generally cheaper than bituminous coals. However, few low rank coals can be used to make coke or generate electricity because of their poor thermoplasticity and low calorific values. Hence, the use of low-rank coals as raw materials for HyperCoal production might prove very advantageous.

The extraction yields for subbituminous coals are generally lower than those for bituminous coals under the same conditions and it is necessary to modify these coals before extraction or to alter the extraction conditions in order to enhance the extraction yield. For example, acid pretreatment enhances the extraction yields of subbituminous coals.[13,14] Opaprakasit et al. reported that with pyridine extraction (Soxhlet, 115 °C) for Wyodak subbituminous coal the yield increased from 15% for raw coal to 39% when it was acid-pretreated with 0.1 M HCl,[13] while Li et al. found an even greater increase following acid pretreatment using a high polar solvent NMP in a flow-type extractor. The maximum extraction yield was ∼80% for Wyodak subbituminous coal that was acid-treated with methoxyethoxy acetic acid.[14] Hydrothermal pretreatment of coals increases the extraction yields by 10−40% following hydrothermal pretreatment using pyridine at room temperature,[15] toluene (Soxhlet, 110 °C),[16] THF (Soxhlet, 66 °C),[17] and CS_2/NMP (1:1 by volume) at room temperature.[18]

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Table 1. Ultimate Analysis and Ash of Coal Samples

coal	symbol	ultimate analysis [wt%, daf] C	H	N	S	O[a]	ash [wt%, db]
Wyodak	WY	75.0	5.4	1.1	0.5	18.0	8.8
Adaro	AD	73.0	5.1	1.1	0.0	20.8	1.8
Pasir	PA	73.5	5.3	1.9	0.2	19.1	4.9

[a] By difference.

This study explores the effects of both acid and hydrothermal pretreatments, in which polar compounds were added to the extraction solvents, on the yield of HyperCoal from subbituminous coal using inexpensive industrial solvents.

Experimental Section

Coal Samples and Extraction Solvents. Three subbituminous coals (<150 μm) were used: Wyodak (Argonne Premium Coal Sample, WY) and Indonesian Adaro (AD) and Pasir (PA) coals. All the samples were dried in vacuo at 80 °C for 12 h. The ultimate analyses and ash contents of the coal samples are shown in Table 1.

Two industrial organic solvents were used as extraction solvents without further purification: light cycle oil (LCO) and crude methylnaphthalene oil (CMNO). LCO is a byproduct obtained from cracking vacuum gas oil to produce gasoline. The LCO used here was obtained from Petrobras-six, a Brazilian company. CMNO is derived from coal-tar distillation and was obtained from Shinnikka Environmental Engineering Co. Ltd., Japan. Both industrial solvents contain 1-methylnaphthalene and dimethylnaphthalene primarily, and CMNO also contains a small amount of quinoline and its derivatives.[12] The polar solvent NMP and the mixed polar solvent CS_2/NMP (1:1 by volume)[1,2] were also used as extraction solvents without further purification.

Acid Pretreatment. Methoxyethoxy acetic acid was used for pretreatment as it is effective for demineralizing coal.[14,19] Approximately 4.0 g of each coal sample was treated in 150 mL of 1.0 M aqueous acid with 10% ethanol at room temperature under a nitrogen atmosphere for 24 h. The treated coal was then washed with deionized water 3−5 times until the pH of the filtrate was near 6.0, when the sample was dried in vacuo at 80 °C for 12 h.

Hydrothermal Pretreatment. For hydrothermal pretreatment, 10 g of each coal sample and 20 g of deionized water

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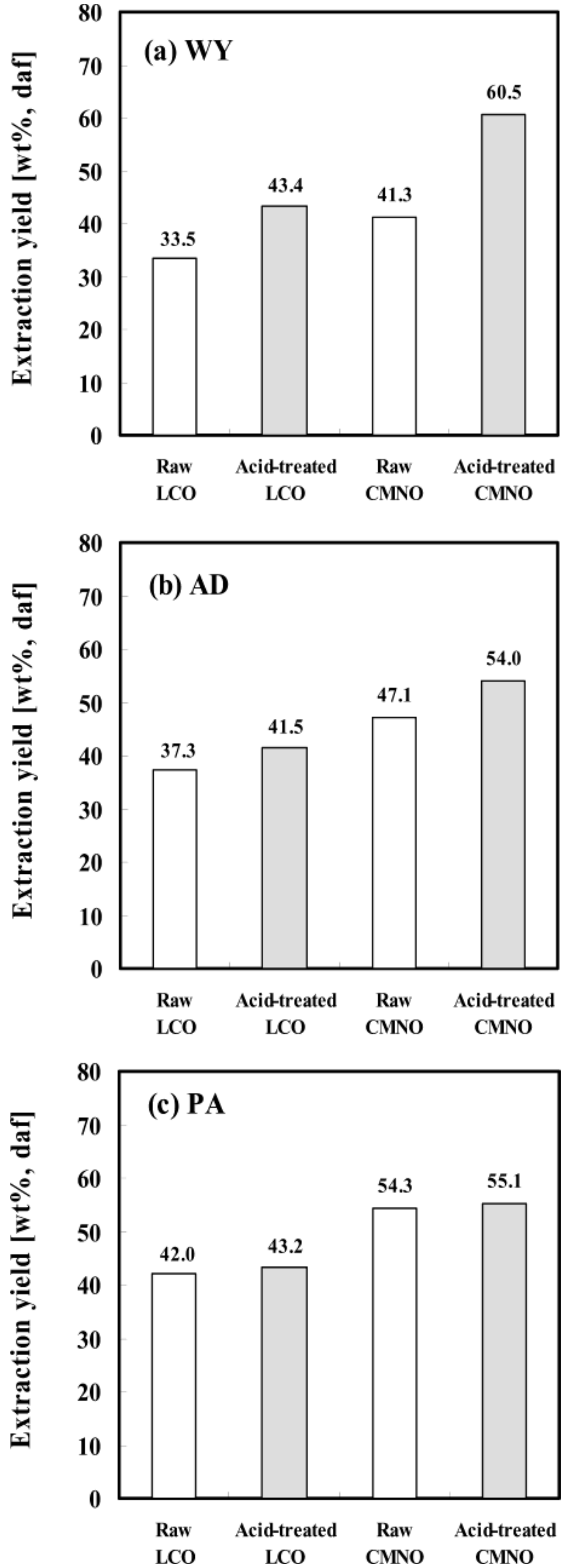


Figure 2. Extraction yields for raw and acid-treated coals using LCO and CMNO: (a) WY, (b) AD, and (c) PA coals.

were put in a stainless autoclave (ca. 50 mL), purged with nitrogen 3 times, and then pressurized with nitrogen to about 0.1 MPa at room temperature. The autoclave was then heated to 327 °C at a rate of 10 °C/min, while stirring at 500 rpm. After treatment for 1 h, the autoclave was cooled rapidly by immersion in an ice−water bath; the coal−water mixture was filtered, and the treated coal was dried in vacuo at 80 °C for 12 h.

Table 2. Ash Content of HyperCoal Obtained by Extracting Raw and Acid-Treated Coal with LCO and CMNO

	ash in HyperCoal [wt%, db]	
coal	raw	acid-treated
	LCO	
WY	0.00	0.05
AD	0.09	0.02
PA	0.05	0.00
	CMNO	
WY	0.00	0.04
AD	0.13	0.00
PA	0.21	0.00

Additives. Two polar compounds were used as additives: quinoline and NMP. Each additive (5−50%) was mixed with the extraction solvent at room temperature before thermal extraction. These additives were all high-purity reagents and were not subject to further purification.

Thermal Extraction. Thermal extraction was conducted using a flow-type extractor, as shown in Figure 1. Approximately 0.5 g of coal sample was charged into a stainless steel cell (ca. 4.0 cm^3) fitted with stainless steel filters (0.5 μm) on both sides and placed in an oven. Thermal extraction proceeded by supplying fresh solvent for 60 min at a flow rate of 0.1 mL/min under a nitrogen atmosphere of 1.0 MPa and at extraction temperatures of 200−360 °C. Following extraction, when LCO and CMNO were used as extraction solvents, an excess of *n*-hexane (400 mL) was added to the extract solution in order to precipitate the coal organic component (HyperCoal) and the mixture was filtered. When NMP was used as the extraction solvent, the extract was washed with deionized water after evaporating the NMP, and the residue was washed with NMP and then with acetone. Further, when NMP was used as an additive, the extracted solution was evaporated out at 95 °C in vacuo to remove the NMP before adding the *n*-hexane. The residue was washed with toluene and then with acetone, and then dried in vacuo at 80 °C for 12 h. The extraction yield was calculated from the weight of residue on a dry-ash-free basis using eq 1.[1] The ash content in the HyperCoal was determined by mineral analysis of a 2-mg aliquot.

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

Results and Discussion

Effect of Acid Pretreatment. Figure 2 shows the extraction yields for the raw and acid-treated coals ((a) WY, (b) AD, and (c) PA coals) extracted with LCO and CMNO. The CMNO extraction yields for the raw coals were 8−12% higher than those using LCO. For example, the extraction yields for raw PA coal were 54.3% with CMNO and 42.0% with LCO. Similar results have been found for bituminous coals, except that the extraction yields were much higher, ranging up to 80% with CMNO.[12] CMNO contains many nitrogen-containing compounds and these polar compounds might enhance the extraction yields.[12]

Figure 2a shows that the extraction yields are generally increased by acid pretreatment. For WY coal, the extraction yields of acid-treated coal increased from 33.5% for the raw coal to 43.4% with LCO, and from 41.3% to 60.5% with CMNO. Therefore, the target

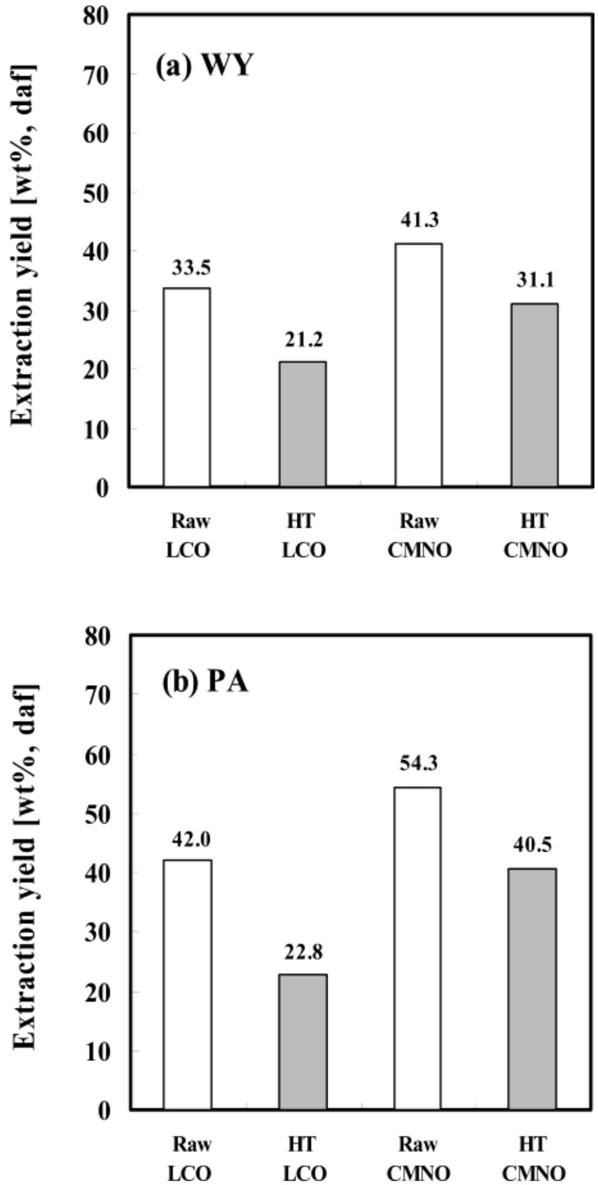


Figure 3. Extraction yields for raw and hydrothermally treated (HT) coals using LCO and CMNO: (a) WY and (b) PA coals.

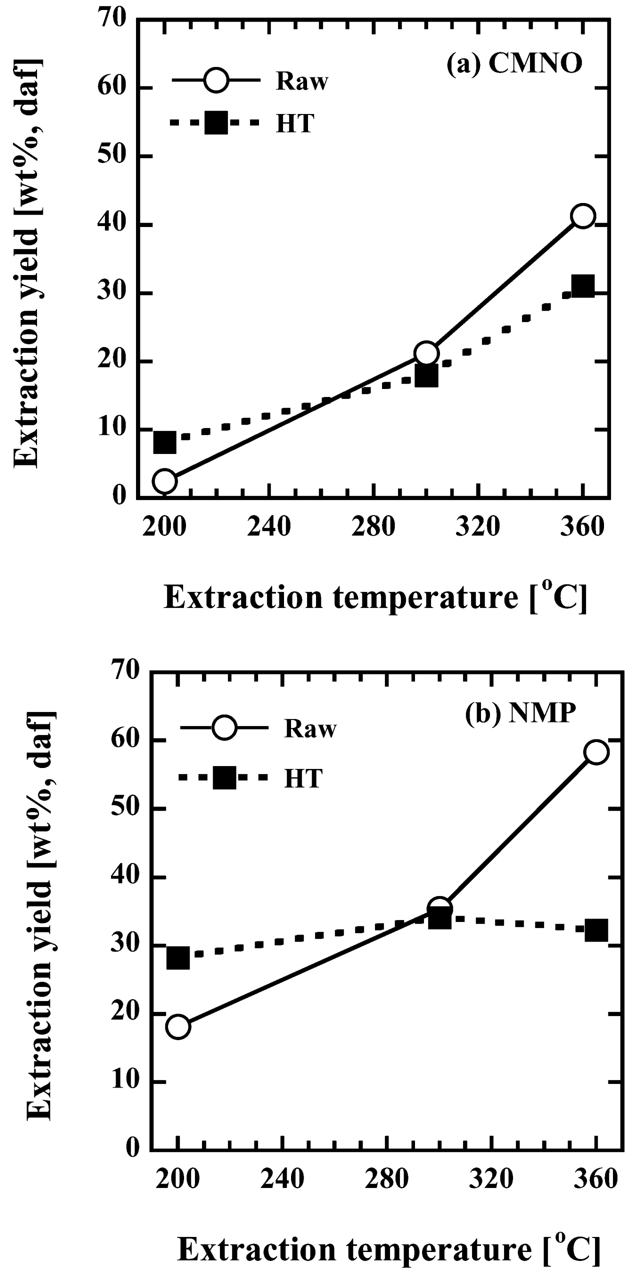
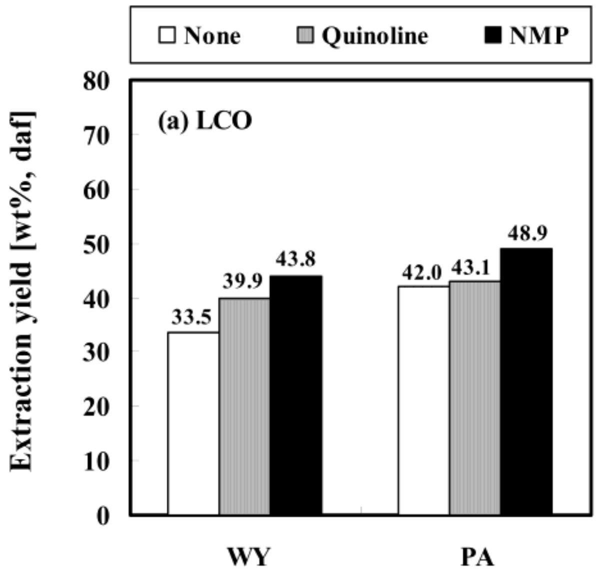


Figure 4. Extraction yields for raw and hydrothermally treated (HT) WY coal extracted using (a) CMNO and (b) NMP at various extraction temperatures.

extraction yield of 60% for HyperCoal production was achieved with acid-treated WY coal extracted with CMNO. Acid pretreatment of AD coal increased its extraction yield by 4% and 7% with LCO and CMNO, respectively. For PA coal, acid pretreatment had little effect on the extraction yields, which increased only 1% with both solvents. Clearly, the effect of acid pretreatment on the thermal extraction yield is strongly dependent on both the solvent and the coal type used.

A mechanism has been proposed to explain how acid pretreatment enhances the extraction yield during subsequent thermal extraction.[13,14] FT-IR measurements have shown that the cation-bridging cross-links that exist among metal carboxylate groups are released on removing divalent cations such as Ca^{2+} and Mg^{2+} during acid pretreatment.[13,14] The resulting carboxyl groups form new hydrogen bonds among themselves and these are readily disrupted when a polar solvent is introduced.[14] Therefore, the differences in the effects of acid pretreatment among the different coal samples can be attributed to the differences in the number of carboxylate groups or divalent cations that were originally present in each coal.

Table 2 shows the ash contents of HyperCoal obtained from extractions of raw and acid-treated coals using (a) LCO and (b) CMNO. The ash content of the HyperCoal tended to decrease in either solvent following acid pretreatment, except in the case of WY coal with LCO. The ash content of HyperCoal obtained using LCO was 0−0.09% for the raw coals and 0−0.05% for the acid-treated coals. With CMNO extraction, the ash content was 0−0.21% for the raw coals and 0−0.04% for the acid-treated coals. For acid-treated AD and PA coals, ash contents less than 0.02% (200 ppm) were obtained with both solvents. This decrease in the ash content of HyperCoal might result from the removal of metal cations, which form ion-bonds, from within the organic parts of the coal during acid pretreatment.



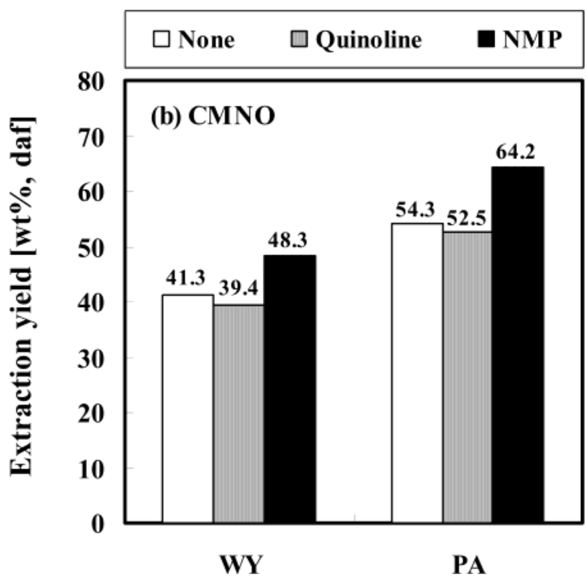


Figure 5. The effect of adding 20% quinoline or NMP on the yield of raw WY and PA coals extracted with (a) LCO and (b) CMNO.

From these results, we concluded that acid pretreatment effectively enhances the extraction yield and decreases the ash content of HyperCoal derived from subbituminous coals using inexpensive industrial solvents.

Effect of Hydrothermal Pretreatment. Numerous researchers have reported that hydrothermal pretreatment increases the extraction yields of coals.[15−18] Therefore, we investigated the effect of hydrothermal pretreatment on the thermal extraction of subbituminous coals. The extraction yields of raw coals with CS_2/NMP mixed solvent at room temperature were 9.0% and 9.4% for WY and PA coals, respectively. While, the yields of hydrothermally treated coals were 19.1% and 16.7%, respectively. Thus, the extraction yields for treated coals were 7−10% higher than for raw coals, confirming the positive effect of hydrothermal treatment on the extraction yield.[15−18] By contrast, Figure 3 shows that the thermal extraction yields of hydrothermally treated WY (a) and PA (b) coals using LCO and CMNO at 360 °C all decreased. For WY coal, the extraction yield decreased by 10−12% and for PA coal the yield decreased by 19% with LCO and 14% with CMNO.

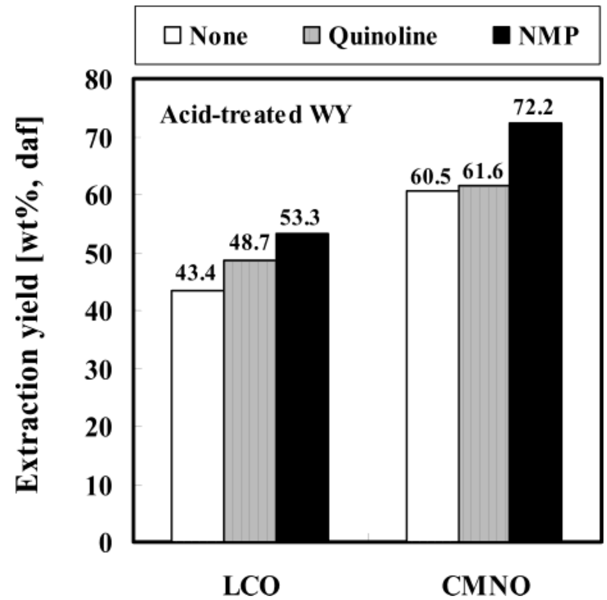


Figure 6. The effect of 20% quinoline or NMP on the yield of acid-treated WY coal extracted with (a) LCO and (b) CMNO.

To clarify the differing influences of the extraction solvents and extraction temperature on the extraction yield, extraction at temperatures from 200 to 360 °C was explored using WY coal. Figure 4 shows the extraction yields for WY raw and hydrothermally treated coal using (a) CMNO and (b) NMP, at different extraction temperatures. The extraction yields of treated coal at 360 °C were lower than those of the raw coal by ca. 10% with CMNO and ca. 30% with NMP, demonstrating that high extraction yields are not necessarily obtained from hydrothermally treated coals when polar solvents such as NMP are used. Conversely, at 300 °C, the extraction yields of the raw and hydrothermally treated coals were similar, and at 200 °C, the extraction yields for treated coal were ca. 10% higher than for the raw coal with both solvents. Therefore, hydrothermal pretreatment has a positive effect over a moderate extraction temperature range from room temperature to 200 °C.

The mechanism increasing the extraction yield with hydrothermal pretreatment may include the depolymerization of the coal by breaking covalent bonds involving oxygen functional groups or releasing hydrogen bonding during pretreatment.[15−18] The reason for the negative result at 360 °C is not yet clear, but may involve cross-linking reactions that decrease the yield during thermal extraction.

Effect of Additives. Figure 5 shows the effects of additives on the extraction yields for raw and acid-treated WY and PA coals. With LCO as the solvent, when 20% quinoline was added, the yield increased by 1−6%, but with 20% NMP the increase was 7−10% (Figure 5a). With CMNO, the extraction yields increased by 7−10% when 20% NMP was added, resulting in a 64% yield for PA coal. By contrast, quinoline had no effect with CMNO. Since NMP is strongly polar, it dissociates and disrupts the strong ionic and hydrogen bonds in the coal, which are not readily released by heat or weakly polar compounds, consequently increasing the extraction yield.[20]

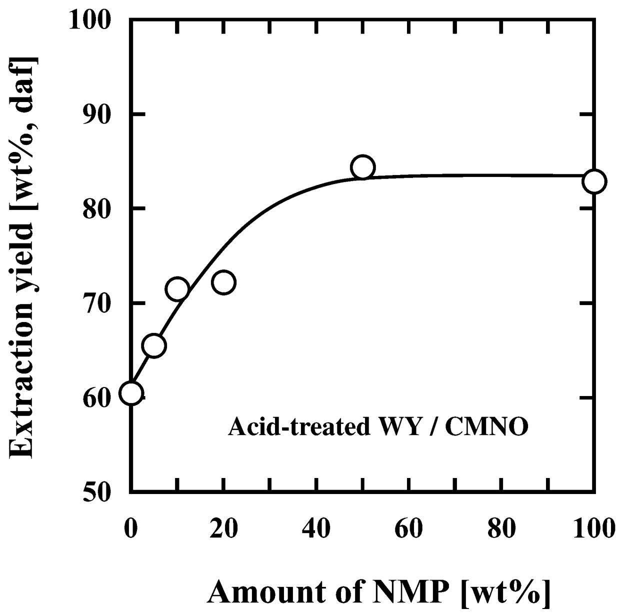


Figure 7. Extraction yields for acid-treated WY coal extracted in CMNO in the presence of different amounts of NMP.

Synergistic Effect of Acid Pretreatment Plus an Additive. Figure 6 shows the effect of the addition of 20% polar compounds on the extraction yields for acid-treated WY coal. The yields increased by 5% when quinoline was added with LCO, and by 10−12% with the addition of NMP to both solvents. The highest extraction yield of 72.2% was attained when NMP was added to CMNO.

Figure 7 shows the effect on the extraction yields with CMNO for acid-treated WY coal with varying amounts of NMP. The yield increased linearly as the NMP was increased from 5 to 50%. The yield was close to 85%, with 50% NMP, which is comparable to the result with 100% NMP. Clearly, the strongly polar solvent NMP is highly effective in the thermal extraction of subbituminous coals, especially for samples subjected to acid-pretreatment.

Conclusions

The effects of pretreatments (acid and hydrothermal), the addition of polar compounds, and of various combinations of acid pretreatment and added polar compounds on the yield of HyperCoal (ashless-coal) derived from subbituminous coals using thermal extraction with inexpensive industrial solvents were ascertained with the view of maximizing the extraction yield. Acid pretreatment and the addition of strongly polar compounds, such as NMP, increased the extraction yields markedly. Acid pretreatment increased the extraction yield by around 20%, while the addition of 20% NMP produced an additional increase of around 10%. The highest extraction yield (72.2%) was obtained for acid-treated WY coal extracted with CMNO containing 20% NMP. Following acid pretreatment, the ash content of the HyperCoal tended to decrease below 200 ppm for AD and PA coals. By contrast, hydrothermal pretreatment had little effect on thermal extraction at 360 °C, but had a positive effect at extraction temperatures below 200°C.

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