Solubilization of a Brown Coal in a Solvent Mixture of Methanol and a Non-polar Solvent at Room Temperature

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A new method was developed for solubilizing a brown coal in a conventionally used solvent at room temperature. The coal pretreated with hydrogen peroxide in liquid phase at 60 °C for 2 h was extracted by solvent mixtures of methanol and a non-polar solvent by the conventional method. In the solvent consisting of methanol and 1-methyl-naphthalene (0.54:0.46 volumetric ratio), surprisingly, 84 wt% of the pretreated coal were extracted.

Low rank coals such as brown coal and lignite are most abundant fossil resources, but they have not been utilized in a large amount. This is mainly due to their low calorific values. One of the inherent drawbacks for utilizing the coal lies in the difficulty of handling such as transportation and storage. Therefore, the low value coals will not be utilized widely without some method that merits the utilization of such coals. Low rank coals are not suitable for the preparation of coal-water mixture (CWM), because they have lots of hydrophilic functional groups such as -COOH and -OH. Liquefaction is another means to fluidify the low rank coals, but it is a technology of the next generation. Solubilization of coals into various solvents have also been performed for decades, but only the coals of a certain rank can be extracted by 70 wt% or so with a special solvent.[1,2] Extraction yield of low rank coals has been less than 10 wt% even in a highly polar solvent. Therefore, it has been desired to develop the method for fluidifying low rank coals under mild conditions.

An Australian brown coal, Morwell coal (MW), was used as a sample of low rank coals. Two grams of the finely ground coal (less than 74 μm) were mixed with 3 ml of MeOH, then 20 ml of 30 wt% aqueous hydrogen peroxide were added to the mixture. After treating the mixture for 2 h in a water bath kept at 60 °C, an excess of cold water was added to the mixture to terminate the oxidation pretreatment.

The ultimate analysis and the atomic H/C and O/C values of the treated coal are given with those of the raw coal in Table 1. The solid yield was 0.79, and 0.08 kg/kg-coal of CO_2 were found to be formed through this treatment. The rest of the coal was found to be converted into water soluble organic acids from the analysis of the liquid phase. Since the evolution of CO_2 of this amount is inevitable in any coal conversion processes and the water soluble organic acids can be recovered, the loss of the carbon during this treatment is unimportant. Both H/C and O/C values of the coal increased through the treatment. The peculiarity of the oxidation by H_2O_2 lies in the introduction of hydrogen as well as oxygen.

Figure 1 compares the F.T.i.r. spectra of the treated and the raw coals. For the treated coal, the peak at 1710 cm^{-1} which is assigned to carboxyl groups increased by the oxidation. This clearly shows that a large amount of carboxyl groups were formed in the coal through the treatment by H_2O_2. These results suggest that the covalent bondings in the coal are partly decomposed. The carboxyl groups introduced would form the hydrogen bondings in the pretreated coal.

Table 1. Ultimate analyses of the raw coal and the coal treated with H_2O_2 for MW

	Ultimate analysis[wt% on sample basis]				mol ratio	
	C	H	N	S+O	O/C	H/C
Raw coal	64.0	4.7	0.7	30.6	0.359	0.881
Treated coal	60.1	4.9	0.7	34.3	0.428	0.978

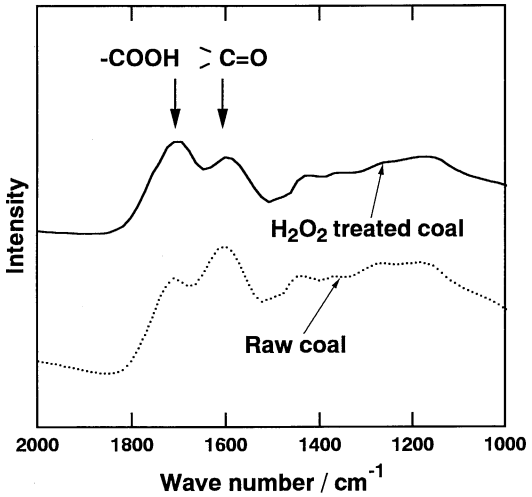

Figure 1. Comparison of the F.T.i.r. spectra between the oxidized coal and the raw coal

The raw coal and the treated coal were extracted at 25 °C in the binary solvent of methanol and a non-polar solvent chosen from 1-methylnaphthalene (1MN), 2-methylnaphthalene (2MN), or xylene (Xy) by the conventional method.[1] Two hundred mg of the coal sample were mixed with 6 ml of solvent and were kept for 3 h at 25 °C under the irradiation of an ultrasonic wave. After centrifuging the mixture and removing the extract, 6 ml of fresh solvent were added to the residue and the mixture was treated for 3 h at 25 °C under the irradiation of the ultrasonic wave. This centrifugation-extraction cycle was repeated three times. The residue was then washed with an excess of methanol and evacuated for 24 h at 60 °C. The extraction yield was calculated from the weight difference between the coal sample and the residue.

Figures 2a to 2c show the extraction yields against the volumetric fraction of MeOH in the solvent for the three binary solvent systems. In the MeOH-1MN mixture the extraction yield of the raw coal was 10 wt% at most at the MeOH fraction of 0.6. On the other hand, the extraction yield of the

treated coal was 13 wt% even in pure methanol, and the yield surprisingly reached 84 wt% at the MeOH fraction of 0.54. The value of 84 wt% on the treated coal basis corresponds to 66 wt% on the raw coal basis. Even this value of the extraction yield is marvelously large as compared with the values reported by now. If we can add the water soluble organic acids recovered during the pretreatment to the extraction yield, the extraction yield reaches more than 80 wt% on the raw coal basis. In the MeOH-2MN mixture the extraction yield of the treated coal also reached 82wt% at the MeOH fraction of 0.54. In the MeOH-Xy mixture the extraction yield of the treated coal was 37wt% at the MeOH fraction of 0.78.

Since the coal treated by H_2O_2 could be extracted by 84 wt% with the mixture of MeOH and 1-MN, the extract was dissolved in an excess of dimethylformamide, then was served to GPC analysis using a RI detector. The calibration curve was constructed using several phenol formaldehyde resins of known molecular weight. Figure 3 shows the molecular weight (number basis) distribution of the extract. The molecular weight ranged from 200 to 10000 kg/kmol, and the average molecular weight (number basis) was found to be 837 kg/kmol.

It was found that a brown coal treated with H_2O_2 could be extracted by 84 wt% at room temperature with a binary solvent of MeOH-1MN. The proposed method succeeded to fluidify the lower rank coals under mild conditions for the first time. Since this is peculiar phenomenon to the lower rank coals as will be reported in later works and since 1MN is involved in coal derived liquids and MeOH is one of most popular solvents, the proposed method will surely enhance the utilization of the lower rank coals. The method will also enable to elucidate the molecular structure of the lower rank coals as an additional merit, because the extract is easily served to various spectroscopic measurements.

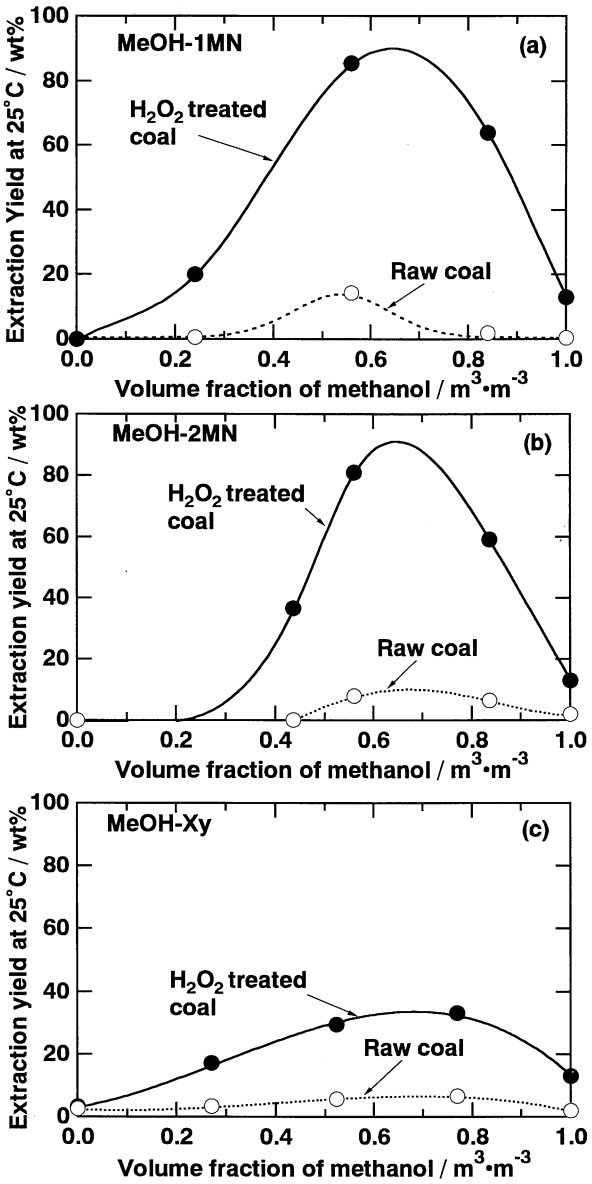

Figure 2. Extraction yields of the raw coal and the H_2O_2 treated coal measured at 25 °C in the mixtures of methanol and non-polar solvent of several volumetric ratios

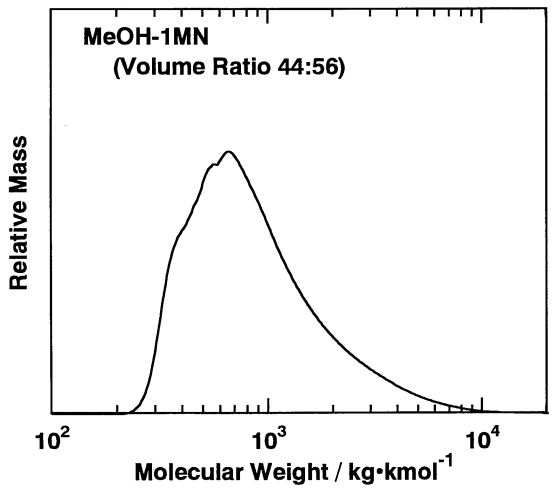

Figure 3. The molecular weight distribution of the MeOH-1MN extract of the H_2O_2 treated coal

References

1 T. Takanohashi and M. Iino, *Energy & Fuels*, **4**, 452(1990).
2 M. Nishioka, *Fuel*, **70**, 1413(1991).