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Hydrous pyrolysis of two kinds of low-rank coal for relatively long duration

Koh Kidena *, Ryoko Adachi, Satoru Murata, Masakatsu Nomura

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

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Abstract

Brown coal samples were treated with hot water in a stainless steel batch reactor at 623 K for 2–72 h. After this hot hydrous treatment, gas, oils, and residues were recovered. The resulting residues were chemically analyzed in detail to understand the reaction chemistry during hydrous pyrolysis. Oxygen functionalities were analyzed chemically with the titration method and carbon types in the residue were examined by solid-state ^{13}C NMR measurement. Elemental analyses showed that the oxygen atoms in the residue decreased markedly up to 2 h while treatments longer than 48 h were also very effective in removing oxygen functionalities from brown coal. The detailed chemical analyses revealed that alcoholic hydroxyl and carboxyl groups were decomposed in the earlier stages of the treatment, and that ether bonds may be cleaved during the latter stages of the hot hydrous pyrolysis. Experiments using two kinds of brown coal gave very different results. A comparison of the chemical structure of these two coals revealed the origin of the difference; one of them has a greater amount of hydroaromatic moieties than the other, which act as a hydrogen source even during hydrous pyrolysis occurring at temperatures as low as 623 K.

Keywords: Brown coal; Hydrous pyrolysis; Structural changes; Long duration

1. Introduction

Brown coal is the most abundant among the coals in the world, however, it contains many oxygen atoms, which may be one of the reasons for its high affinity with moisture. The moisture in the brown coal lowers its transport efficiency and also the calorific value. Furthermore, when the coal is stacked or stored outside, oxidation reactions which originate from the oxygen in the air sometimes occurs at the very bottom of the coal layer. The exothermic properties of the oxidation reactions can lead to spontaneous heating and/or self ignition. Therefore, brown coal is generally difficult to handle in any process or transport from the mining site, therefore, its utilization is relatively limited. For the effective use of brown coals as a fuel resource, this problem must be solved. Another strategy for the utilization of brown coal as a chemical resource is the depolymerization of coal molecules to obtain low-molecular weight components.

In order to remove the oxygen functionality from brown coal and/or depolymerize brown coal, much investigation has been carried out to date from various viewpoints. This study focuses on the hydrous treatment of brown coal since water has some advantages; the physical and chemical properties of water molecules change drastically at its critical point (647 K, 22.1 MPa), that is, its affinity for organic molecules becomes higher than that at room temperature, and its acidity (and basicity) is also higher [1]. Such properties may have an effect on the role of water as a solvent, catalyst, and reactant in the coal–hot water system. In addition, use of water makes ecological sense since it is abundant and non-polluting.

Supercritical or subcritical water is often applied in the treatment of brown coal [1–5]. For example, extraction of

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* Corresponding author. Tel.: +81 3 3599 8553; fax: +81 3 3599 8554.
E-mail address: k-kidena@aist.go.jp (K. Kidena).

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brown coal with supercritical water to obtain low-molecular weight components has been examined on a number of occasions [6–12]. In the reaction process of brown coal with water, the cleavage of ether bonds to give phenols, which are frequently found in brown coal, was reported in the treatment with supercritical or subcritical water [9]. Other types of oxygen functionalities could also be decomposed in supercritical or subcritical water. Subcritical water has frequently been used in the reforming process of brown coal. One example is the pre-treatment of brown coal with steam at 613 K and 51 atm resulting in an improvement in reactivity for hydrocracking reactions [13]. On the other hand, moisture retained in brown coal could be removed rapidly by treatment with steam at 453–533 K and 1–2.5 MPa [14,15]. At slightly higher temperatures, it was reported that added water might promote the decomposition of carboxylic groups and cleavage of arylether bonds in the hydrocracking reaction of low-rank coals at 558–603 K [16]. However, detailed structural changes in the presence of water have not yet been clarified.

Treatment with subcritical water was also applied in the artificial maturation process of kerogen samples. Kerogen is a kind of rock which is a source of petroleum, and its maturation under certain temperatures and pressures produces oil [17,18]. The maturation process was simulated at 623 K for 72 h in the presence of hot (subcritical) water to give liquid products [18–20]. Artificial maturation of brown coal was also examined under similar conditions [21,22]. Thus, water at a subcritical point such as 623 K or lower temperature behaves differently from supercritical water, and treatment for long duration is effective in the maturation process. In fact, ether bond-containing compounds were treated at around 623 K for 72 h to give hydrolyzed products of ether bonds [23,24].

In this study, hydrous pyrolysis of two Indonesian brown coals was performed at 623 K for 2–72 h. The chemical structure of the resulting products was analyzed to investigate the structural changes that had occurred during the long duration hydrous treatment. The differences between the short and long duration treatments are also discussed.

2. Experiments

Two kinds of Indonesian brown coal, named ‘A coal’ and ‘B coal’, were used in the present study. The analytical data are shown in Table 1. The coal samples were pulverized into less than 100 mesh for use.

Table 1
Elemental composition of the sample coals

Coal	C	H	N	S	O	Ash	Atomic ratio	
	(wt%, daf.)					(wt%, db.)	H/C	O/C
A coal	72.7	5.4	1.0	0.1	20.8	1.0	0.89	0.21
B coal	73.3	5.1	1.5	0.6	19.5	4.0	0.83	0.20

Hydrous treatment (treatment with hot water) of the brown coals was conducted in a stainless steel batch container, whose inner volume was 12 mL. One gram of pulverized coal sample and 5 mL of deionized water were put in the stainless steel reactor, which was purged with nitrogen. The heat treatment was started by transferring the stainless steel reactor into a sand bath (Techne Inc.) heated up to the determined temperature (from 598 to 673 K, mainly, 623 K). In order to stop the heat treatment, the reactor was removed from the sand bath then cooled down in a water bath after the predetermined time elapsing (from 2 to 72 h). Gaseous products were collected in an evacuated glass tube before the reactor was opened. Then, liquid products along with water and treated coal were recovered by filtration with ether and additional water. The treated coal was extracted with tetrahydrofuran (THF) at room temperature under ultrasonic irradiation to obtain THF-soluble and -insoluble fractions. Light fractions such as benzene or hexane were lost during the recovery procedure, therefore, the yield of the recovered products (gases, liquids including oily products and THF-soluble fraction, and solids) did not reach 100%. The difference corresponds to the volatile products and water produced from brown coal during hydrous pyrolysis.

Analyses of the products were performed by elemental analysis. Solid-state ^{13}C NMR measurement of treated coals and THF-insoluble fractions were taken, oxygen functionalities such as hydroxyl and carboxylic groups were estimated, and the gas yields were evaluated with a gas chromatograph. Details of the solid-state NMR measurements have been described elsewhere [25]. NMR spectra were recorded on a Chemagnetics CMX-300 spectrometer with SPE/MAS (single pulse excitation/magic angle spinning) and SPE/DD (dipolar dephasing)/MAS methods, and the data were treated with GRAMS/AI software to obtain the carbon distribution. Such data treatments may include a maximum of 5% of each value. However, increased/decreased tendency can be identified from data so that it endures comparing. Analyses of oxygen functional groups were performed by the following conventional titration methods: ion exchange with $NaHCO_3$ for carboxyl groups and acetylation followed by hydrolysis and titration of resulting acetic acid for hydroxyl groups. These titration experiments were performed at least three times to test reproducibility.

3. Results and discussion

3.1. Hydrous treatment of A coal

3.1.1. Effect of treatment time

Before detailed structural changes of hydrous treated coal samples are analyzed, the effect of temperature and treatment time on the yield and elemental composition of treated coal was examined for A coal. First, the A coal sample was treated in the presence of water at various temperatures for 2 h. The results are summarized in Table 2.