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Molecular composition of extracts obtained by hydrothermal extraction of brown coal

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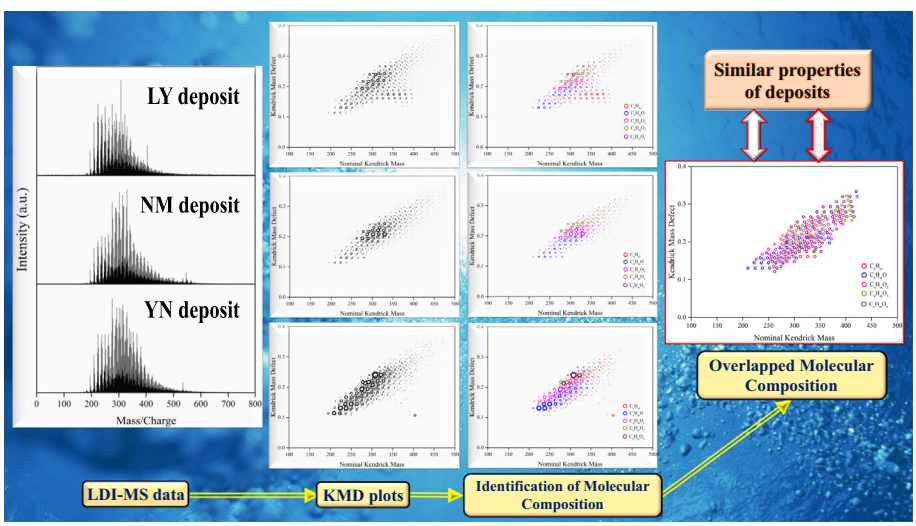
GRAPHICAL ABSTRACT



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ABSTRACT

Three brown coals were extracted by a hydrothermal method at 350 °C and 20 MPa for 90 min, and the molecular compositions of the deposit extracts were analyzed in detail by high-resolution mass spectrometry measurements. The extract yields were as high as ~30% for all brown coals, indicating that hydrothermal extraction is applicable to brown coals with differing ash and sulfur contents. The high-resolution mass measurements with Kendrick mass analyses identified the chemical compositions and clarified the abundance of common molecular species in all the extracts prepared from the three brown coals. The sum of mass intensities of overlapped C_nH_m, C_nH_mO, $C_nH_mO_2$, $C_nH_mO_3$, $C_nH_mO_4$, and C_nH_mN species in the mass spectra of LY, NM, and YN extracts were 37.0%, 35.9%, and 50.8%, respectively, indicating the presence of abundant compounds with similar molecular compositions in all of the extracts, regardless of the parent coal.

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1. Introduction

Although the use of brown coals has been hindered by their high moisture content, low heating value, due to intrinsic oxygen functional groups, and high spontaneous combustibility after drying, brown coals still attract much attention and are expected to be useful not only as a fuel but also as a chemical feedstock because there are abundant minable reserves worldwide and the price is low versus high-rank coals [1]. There have been many studies applying extraction methods to recover useful components from brown coal, such as supercritical gas extraction [2], supercritical fluid extraction [3,4], alkali extraction [5], solvent extraction [6–8], and hydrothermal extraction [9–15].

Among these methods, hydrothermal extraction using subcritical or supercritical water as the reaction/extraction medium has been shown to be an effective and suitable method because during the process, the inherent water in brown coals can be used as a reactive medium and removed, and many of the oxygen functional groups decompose [14]. Such hydrothermal extractions convert brown coal into four fractions: extraction residue (upgraded coal, UC), gaseous product (gas), solid extract (deposit), and water-soluble extract (soluble) [13,14]. In a previous study, we clarified that the deposits obtained at 350 °C from various coals were similar in elemental composition, molecular weight distributions, pyrolysis behavior, and softening/melting behavior, and had an interesting thermoplastic property under mild conditions, which made possible their use as an effective binder for metallurgical coke [15]. This result suggested that the deposits might be the most valuable product from the hydrothermal extraction of coal, due to their potential applications and multiple sources. Further identification requires characterizing the molecular compositions in detail.

Laser desorption/ionization mass spectrometry (LDI-MS) is an important tool in characterization of compounds, and Kendrick mass defect (KMD) analysis is an effective method for identifying the chemical composition of homologous series [16]. High-resolution LDI-MS with KMD analysis has been used to characterize petroleum [17], natural organic matter [18], and polymers [19], but not coal or extracts therefrom. Although the MS intensity does not directly reflect the amount of a molecule in the target sample (i.e., MS is not a quantitative analytical method), the molecular compositions identified by the technique provide valuable information about a sample's properties. The "Kendrick mass" is a new mass scale designed to supersede the International Union of Pure and Applied Chemistry (IUPAC) mass scale. Typically, the Kendrick mass of CH_2 is defined as exactly 14, but the Kendrick mass of a given compound can be obtained by multiplication of the mass values by 14/14.01565, where 14.01565 is the IUPAC mass of CH_2. KMD is defined as the difference between the exact Kendrick mass and the nominal Kendrick mass (NKM). Two-dimensional plots of KMD as a function of NKM display the distribution of components, in which the components with common repeat units line up in the horizontal direction, whereas the components having different structures shift in the vertical direction.

Here, three brown coals – one Australian and two Chinese brown coals – were extracted at 350 °C and 20 MPa for 90 min by a hydrothermal method. Then, high-resolution LDI-MS measurements with KMD analyses were used to characterize for the first time the deposits obtained from the various brown coals in molecular detail.

2. Material and methods

2.1. Coal samples

One Australian brown coal, Loy Yang coal (LY), and two Chinese brown coals, Inner Mongolia coal (NM) and Yunnan coal (YN), were used without drying or grinding. Table 1 shows the ultimate and proximate analyses of these three brown coals, including elemental compositions, fixed carbon (FC) and volatile matter (VM) contents, ash content, water content (moisture), and aromatic carbon percentage (f_a). LY, NM, and YN had high moisture contents of 58.0%, 31.2%, and 48.2%, respectively, and high oxygen contents of 27%, 23%, and 32%, respectively. The ash content of LY was only 1.5%, much lower than the two Chinese brown coals: 9.2% and 10.9% for NM and YN, respectively. NM had the highest sulfur content of 4.4%, while those of LY and YN were below 0.5%.

2.2. Apparatus and experimental procedure

Fig. 1 shows a schematic diagram of the semi-continuous extractor used. About 1.5 g of brown coal was used and placed on a filter (filter 1 in Fig. 1, Swagelok, SUS316, 11.2 mm outer diameter and 0.5 μm pore size) in the extractor. Distilled water was supplied continuously into the system with a flow rate of 1 mL/min using a high-performance liquid chromatography (HPLC) pump, and the pressure was kept at 20 MPa, which is above the saturated vapor pressure at the extraction temperature of 350 °C. After the extractor was heated to 350 °C at a rate of 30 °C/min using a fluidized sand bath, the hydrothermal extraction process was carried out for 90 min. During the extraction process, the components dissolved in the hot water passed through filter 1, and flowed out of the extractor. A fraction deposited by cooling with an ice bath was trapped on filter 2 (the pore size and material were the same as those of filter 1); another fraction was separated into gas and solution at the final volumetric flask. After the experiment, the system was cooled to room temperature and the pressure was released after flushing the system with nitrogen.

Gaseous product was collected in a gas bag and its volume was measured with a cylinder. The extractor, filter 2, and connection tubes were dried in vacuum at 80 °C for 12 h and weighed. The amounts of product in the extractor and filter 2 were calculated by subtracting the blank weights. The product recovered in the volumetric flask was filtered and separated into solid extract and a yellow transparent aqueous solution using a membrane filter (0.45 μm pore size). This part of the solid extract was dried and weighed. To recover the extract from the aqueous solution, water was removed using a vacuum rotary evaporator at 60 °C, and then the solid-state product was weighed after further drying in a vacuum at 60 °C for 24 h. Thus, through the hydrothermal extraction, brown coal was converted into four fractions: the residual solid product in the extractor (upgraded coal, UC), the solid extract on filter 2 and in the volumetric flask (deposit, D), the solid-state product obtained from the transparent aqueous solution (soluble, S), and the gaseous product from the gas bag (gas). The difference between the sum of the four fractions and 100% is considered to correspond to water formed in the reaction and low-boiling-point products removed with water during the rotary evaporation. The experiment under each condition was repeated three times to examine the deviation in product yields, and the elemental analysis and the LDI-MS measurement were performed using one representative sample for each experimental condition.

2.3. Product analysis

The composition of the gas fraction was analyzed with a natural gas analyzer (GL Science Inc.) with two columns of 3 m packed with Porapak Q and Molecular Sieve 5A for CO_2, CO, H_2, and CH_4. The elemental composition of the solid product was determined using a CHNS analyzer (FLASH 2000, Thermo Scientific). VM, FC, and ash contents were measured using a thermogravimetric analyzer (TGA-50, Shimadzu). The value of f_a was determined by