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Characterization of organic substances in lignite before and after hydrogen peroxide treatment: Implications for microbially enhanced coalbed methane

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ABSTRACT

The reaction of coal with hydrogen peroxide (H_2O_2) has been reported to accelerate the microbial transformation of coal into biogenic methane. To understand the mechanism of the increased bioavailability of coal as a result of H_2O_2 treatment, we investigated the effects of H_2O_2 reaction on humic substances of lignite by characterizing their structure and relative abundance. The H_2O_2-treated lignite, referred to as lignite-H_2O_2, was also examined in column experiments to confirm the increases in lignite solubilization and organic acids as indicators of enhanced bioavailability. The results showed that the alkali-soluble carbon content of lignite increased by 4.9 times (from 0.4 to 2.1 g C) after H_2O_2 treatment, and the humic acid (HA) content of this fraction increased by 7.7 times (from 0.2 to 1.5 g C). Previously, the enhanced solubility of lignite after H_2O_2 treatment was attributed to increased hydrophilicity of the lignite. However, we propose that this phenomenon is actually caused by chemical fragmentation (i.e., β-fragmentation) involving a radical reaction. In the column experiments, lignite treated with H_2O_2 showed higher dissolved organic carbon (up to 84.8 mg/L) and organic acid (up to 18.9 mg/L for acetic acid, and up to 19.9 mg/L for formic acid) concentrations than lignite without treatment. These results indicate the potential to optimize CH_4 production from microbially enhanced coalbed methane operations using H_2O_2.

1. Introduction

Lignite is a low-rank coal with a low calorific value, high ash content, and high water content (Bumpus et al., 1998; Chassapis and Roulia, 2008; Yan et al., 2001). It forms from the original phytomass by peatification followed by coalification, and is the intermediate between peat and bituminous coal (Doskočil et al., 2014). Currently, 90% of lignite production worldwide is used for power generation (World Energy Council, 2016), but this is environmentally problematic because combustion processes contribute to air pollution (Alpern and Lemos de Sousa, 2002; Breckenridge and Polman, 1994; Huang et al., 2013a; Kaldellis and Kapsali, 2014; Sakulniyomporn et al., 2011). At the same time, lignite has become of global interest for the generation of biogenic methane (Fallgren et al., 2013; Green et al., 2008; Huang et al., 2013b; Jones et al., 2013, 2008; Scott et al., 1994; Strapoć et al., 2008a), which is renewable and considered to be environmentally friendly energy. Compared with conventional coal mining, biogenic coalbed methane does not require the coal to be mined, processed, or transported, resulting in substantially lower capital and operating cost (Huang et al., 2013a; Yoon et al., 2016).

The process of biogenic methane production from coal can be divided into three steps: (1) soluble organics are released from the coal geopolymer, (2) biodegradation of soluble organics into substrates, and (3) methanogens consume the substrates and produce methane gas (Colosimo et al., 2016; Jones et al., 2010; Ritter et al., 2015; Strapoć et al., 2008b; Strąpoć et al., 2011). Stimulating the above processes artificially, Scott (1999) proposed the concept of microbially enhanced coalbed methane (MECBM, or MECoM) to enhance coalbed methane recovery. Under natural conditions, the activity of methanogenesis is limited by the availability of the substrates, and the generation of the substrates is limited by coal solubilization (Ritter et al., 2015). It has been suggested that enhancing the rate of coal solubilization is a key factor for successful MECBM (Green et al., 2008; Papendick et al., 2011; Park and Liang, 2016; Wang et al., 2017).

Lignite is known to be solubilized by hydrogen peroxide (H_2O_2) concomitant with the generation of methanogenic substrates such as acetic acid and formic acids under experimental conditions (Mae et al., 2001; Miura et al., 1997), which have been identified as immediate precursors to methane production (Chen et al., 2017; Papendick et al., 2011; Strąpoć et al., 2011). Aramaki et al. (2015) proposed the concept

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of subsurface cultivation and gasification (SCG), which involves the injection of hydrogen peroxide into lignite seams to generate organic acids. The biogenic production of methane from the reaction solution of lignite with H_2O_2 (by methanogens) was confirmed by Aramaki et al. (2015) in laboratory experiments (Fig. S1). More recently, Tamamura et al. (2016) verified the potential of dilute H_2O_2 (0.3%) in terms of yielding organic acids from lignite at low temperature (10 °C).

The bioavailability of lignite after H_2O_2 treatment is of interest for successful SCG. Arctech Inc. (1990) and Jones et al. (2013) showed that the rate of microbial conversion of coal into biogenic methane was higher for H_2O_2-treated coal than for untreated coal. The reaction with H_2O_2 may generate hydrophilic functional groups in the coal structure, especially O-bearing groups (e.g., hydroxyl, ketone, and carboxyl groups), which are more readily utilized by microbes for methanogenesis (Strapoć et al., 2008b). Therefore, the enhanced bioavailability of the coal after H_2O_2 treatment could reflect increased O-bearing functional groups in the coal structure. However, the effect of reaction with H_2O_2 on the content of O-bearing functional groups in lignite has not been elucidated, and the mechanism that underlies the increase in bioavailability remains unknown.

The reaction between H_2O_2 and coal has been widely investigated; yet the reaction mechanism remains uncertain. The general agreement is that the reaction generates radicals in the coal matrix either through the Fenton reaction (Doskočil et al., 2014; Huang et al., 2013b; Miura et al., 1997) or quinone reaction (Nohl and Jordan, 1987; Tamamura et al., 2016). The radicals then gradually degrade the coal substances by breaking them down into progressively smaller molecule species (Berkowitz, 1979; Martínez and Escobar, 1995). Simultaneously, the radicals may propagate a reaction to generate organic acids (e.g., acetic acids and formic acid) (Clemens et al., 1991; Fossey et al., 1995; Parsons, 2000; Wang et al., 2003). Aramaki (2016) observed an increase in organic acid concentration in a water solution in which H_2O_2-treated lignite (referred to as lignite-H_2O_2) was immersed. This observation implies the presence of reactive intermediates in the lignite-H_2O_2, which subsequently yields organic acids in pure water.

Humic substances are an essential part of natural organic matter (Jackson et al., 1996). They can be divided into fulvic acid carbon (FA) that is soluble at any pH, humic acid carbon (HA) that is insoluble at pH < 1, and humin carbon that is insoluble under all pH conditions (Kononova, 1966; Stevenson, 1994). HA and FA are regenerated in response to the natural oxidative weathering of sedimentary organic matter (Estévez et al., 1990; Klika and Kraussová, 1993; Kurková et al., 2004; Tamamura et al., 2015). However, it is not certain whether H_2O_2 treatment re-generates HA and FA with or without structural modifications.

The objectives of this study are to characterize the composition and structure of each humic fraction of lignite before and after H_2O_2 treatment, and to investigate the mechanism of enhanced bioavailability in lignite-H_2O_2. Each humic fraction is investigated because the humic composition of lignite is probably sensitive to H_2O_2 treatment, and more information is obtained in this way than by simply analyzing the bulk lignite. The properties of the humic substances are used to develop a reaction mechanism for the enhanced bioavailability of the lignite-H_2O_2 that is implied from column experiments. Finally, we discuss the implications for in situ biogenic methane production.

2. Material and methods

2.1. Lignite

A lignite sample was collected from the middle Miocene coal-bearing Soya Formation in the Tempoku Coalfield in Horonobe, northern Hokkaido, Japan. Total organic carbon (TOC) content, volatile matter content, and the calorific value of the lignite are ~69%, 47%–53%, and 6900–7200 kcal/kg, respectively, on a dry, ash-free (DAF) basis. Iron (Fe), manganese (Mn) and copper (Cu) contents of the

lignite, which can potentially affect reactions with H_2O_2 (Gierer et al., 1993), are very low (1.8% Fe, 0.029% Mn, and 0.00047% Cu), as measured by X-ray fluorescence (XRF) analysis (Table S1). Excluding quartz (SiO_2), X-ray diffraction (XRD) analysis could not detect the presence of mineral components (e.g., pyrite) in the lignite.

The field sample was prepared in two parts: original lignite (referred to as lignite-original) and lignite-H_2O_2. Both samples were dried and ground to obtain a < 106 μm diameter size fraction for humic extraction and a 0.5–1 mm diameter size fraction for column experiments. To make lignite-H_2O_2, lignite-original (50 g) was immersed in 750 mL of 3% H_2O_2 at room temperature (22 °C) for ten days (Fig. S2). The concentration of H_2O_2 used in this study was fixed at 3%. At the ratio of lignite to H_2O_2 used in this study, a higher concentration of H_2O_2 would result in over-oxidation of the lignite, while a lower concentration would result in negligible oxidation. Following H_2O_2 7treatment, the lignite solids were separated from the solution, rinsed with ultrapure water to remove residual dissolved organics and H_2O_2, and then dried.

To ensure that the lignite solids were rinsed completely, the 3% H_2O_2 solution (750 mL) was spiked with 1 mL of concentrated NaCl solution immediately after the reaction with lignite. After discarding the supernatant, the lignite was mounted on a filter paper in a funnel and rinsed with pure water repeatedly. Rinsing continued until the Cl^- concentration of solution leaching from the lignite-H_2O_2 was two orders of magnitude less than the initial chloride ion (Cl^-) concentration. The lignite-H_2O_2 was then dried in an oven at 50 °C for use in extraction and column experiments.

2.2. Extraction experiments

The humic substances were extracted from both the lignite-original and lignite-H_2O_2 samples following the method of Tamamura et al., 2015 (Fig. 1). The steps of this procedure are outlined below.

2.2.1. Lipid isolation

The lignite sample (25 g) was mixed with benzene and methanol (3:2 solution ratio) and ultrasonically treated for 20 min at 25 °C in combination with manual stirring with a glass rod. The lipid was in solution and was separated from the residue (i.e., lipid-extracted lignite) by vacuum filtration (1 μm filter paper). The residue was re-extracted under the same conditions. The mixtures (first and second extractions) were filtered again (0.50 μm PTFE filter), and the solvents were evaporated in a beaker under a vacuum. The remaining residue in the beakers was weighed as the lipid. The lipid-extracted lignite was dried at 70 °C for the subsequent alkali extraction.
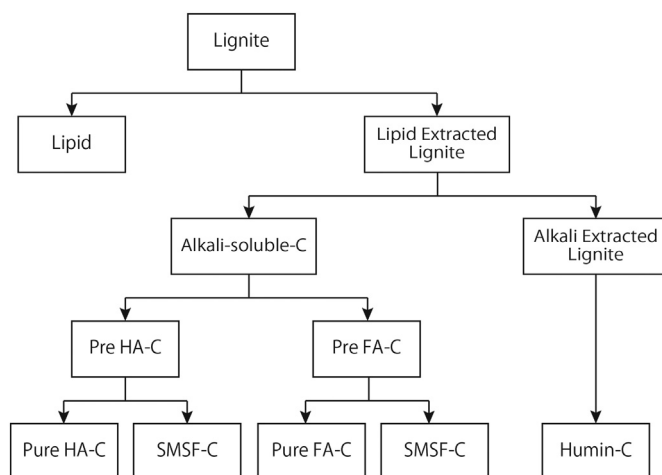

Fig. 1. Humic fractionation of lignite.