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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（工学） 氏名 Shofa Rijalul HAQ

学 位 論 文 題 名

Biogenic Methane Generation from Lignite with Hydrogen Peroxide for Subsurface Cultivation and Gasification

(地層内メタン生産技術確立のための過酸化水素を用いた褐炭のバイオメタン化)

Increasing energy requirements and decreasing conventional hydrocarbon reserves have led to the development of unconventional hydrocarbon, including biogenic coal bed methane (CBM). Lignite production for power generation is environmentally problematic because the combustion processes contribute to air pollution (e.g., CO₂, SO_x, NO_x, particulate matter, and Hg). However, the lignite has become of global interest for the generation of biogenic CBM via microbial transformation, which is renewable and considered to be environmentally friendly energy. Previous studies have indicated that lignite is solubilized by hydrogen peroxide (H₂O₂) concomitant with the generation of methanogenic substrates (e.g., acetic acid and formic acid). More recently, the concept of subsurface cultivation and gasification (SCG) was proposed to produce biogenic methane by injecting hydrogen peroxide into lignite seams to generate methanogenic substrates. Although this concept has a great promise, its applicability in the field remains uncertain, as only batch experiments have been conducted in the laboratory. Therefore, the biogenic methane generations using solution from column reactions of lignite with H₂O₂ was studied to demonstrate the potential for the successful in situ microbially enhanced CBM generation using H₂O₂.

Chapter 1 gives the motivation, importance, and objectives of this study. The recent studies and remaining knowledge gaps regarding biogenic CBM were also discussed.

In Chapter 2, an indigenous microbial consortium associated with coal from the coal-bearing Soya Formation in the Tempoku Coalfield (northern Hokkaido, Japan) was applied to reaction solutions of lignite and H₂O₂ (i.e., chemically solubilized lignite) to evaluate in situ biogenic methane generation. Column experiments using such reaction solutions achieved maximum concentrations of dissolved organic carbon, acetic acid, and formic acid of 6,330, 612, and 1,810 mg/L, respectively. Cultivation experiments using the above reaction solution as a substrate for methanogens produced nearly 6 cm³ CH₄ per g lignite with a maximum rate of 0.14 cm³ per g per day without additional amendments such as minerals or reducing agents. These findings present a great opportunity to produce biogenic CH₄ from the world's lignite seams by injecting H₂O₂ into its lignite seams without additional microorganisms (bio-augmentation) or minerals (bio-stimulation).

After confirming the methane production from the reaction solution of lignite with H₂O₂, an indigenous microbial consortium associated with coal from the coal-bearing Soya Formation in the Tempoku Coalfield was identified and discussed in Chapter 3. Pyrosequencing analysis of the microbial consortium after cultivation showed diverse archaeal and bacterial cultures in the vials that would lead to the generation of CH₄. The operational taxonomy units (OTUs) affiliated with the class *Deltaproteobacte-*

ria, *Bacteroidetes*, *Betaproteobacteria*, *Clostridia*, and *Methanomicrobia* were major microbial. These results revealed that the biogenic methane was produced through hydrogenotrophic (CO_2 reduction), acetoclastic (acetate fermentation), and formate-utilizing methanogenesis pathways, partly following bacterial activities of fermentation, homoacetogenesis, and syntrophic acetate oxidation.

In Chapter 4, 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. 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 when reacted with ultrapure water under the column reaction. These results demonstrated enhanced solubility of lignite after H_2O_2 reaction, as well as the generation of reactive structures (e.g., peroxy acids), resulting in the production of organic acids (e.g., acetic acid and formic acid). Thus, the enhanced bioavailability of lignite from reaction with H_2O_2 would enhance the biogenic CH_4 yield from lignite- H_2O_2 reaction solution, which is encouraging for the field application of microbially enhanced CBM generation using H_2O_2 .

Finally, in Chapter 5, to understand the mechanism of the increased bioavailability of lignite as a result of H_2O_2 treatment, the effects of H_2O_2 reaction on humic substances of lignite were investigated by characterizing their structure and relative abundance. 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). The main cause of the increase in alkali-soluble contents in lignite- H_2O_2 could be the breakage of bonds in the lignite macromolecular network, yielding HA, small molecule size fraction (SMSF), or fulvic acid (FA). Specifically, the H_2O_2 yields peroxide structures (i.e., ROOH) in lignite, from which alkoxyl radicals ($\text{RO}\bullet$) are formed either by homolytic cleavage or are radical-induced. In HA, which is the dominant regenerated component in the alkali-soluble fraction, O-alkyl-C content decreased while carbonyl-C content increased in response to the H_2O_2 reaction. Therefore, instead of attributing to increased hydrophilicity of the lignite, the enhanced solubility of lignite after H_2O_2 treatment might be caused by chemical fragmentation (i.e., β -fragmentation) of the alkoxyl radicals ($\text{RO}\bullet$), converting O-alkyl-C to carbonyl-C.

In chapter 6, the contents of this research are summarized, and the conclusions are presented.