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Experimental simulation of biogenic coalbed gas generation from lignite and high-volatile bituminous coals

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ABSTRACT

To deeply understand the formation of biogenic gas and develop evaluation methods of coalbed methane resources, it is important to clarify the influence mechanism of coal on the formation of biogenic coalbed methane. This paper selected lignite samples from Longkou coalfield and high-volatile bituminous coal samples from the Huainan coalfield, China as substrates of biogenic gas generation in simulation experiment, and aimed to investigate the characteristics of biogas formation from two different coal ranks. The experiments lasted for 90 days, and the results showed that both low rank coals (lignite) and higher rank coals (bituminous coal) can be utilized by methanogenic bacteria to produce biogas. Lignite, which has a greater abundance of hydrogen and oxygen atoms, had a greater potential for biogas production than bituminous coal. However, the maximum generation rate of bituminous coal groups was higher than that of lignite groups in the initial stage. The whole process of biogas generation can be divided into the following three stages: 1) a rapid growth stage; 2) slow descent stage; and 3) inhibition stage, which was consistent with the fluctuant change of the CH_4 and CO_2 contents in headspace gas, indicating that CO_2-utilizing methanogens are present in all experimental groups throughout the process, especially in the first stage in the lignite groups. The gas components from the bituminous coal groups consisted of CH_4, CO_2, and small amounts of heavy hydrocarbons (but H_2 not ruled out), suggesting the presence of acetoclastic methanogenesis, which was also confirmed by more positive $\delta^{13}C$ values of CH_4 and CO_2 (−39.2‰ to −30.2‰ and −20.6‰ to −19.2‰, respectively) and more negative δD-CH_4 values (−334‰ to −325‰, except for lignite groups on the 20th day of the experiment). However, more positive δD-CH_4 values for the lignite groups (−244‰ and −239‰) demonstrated the occurrence of hydrogenotrophic methanogenesis, which coincided with a high CO_2 content and low CH_4 content on the 20th day of the experiment.

1. Introduction

Coal bed methane (CBM), also referred to as coal bed natural gas, originates from both thermogenic and microbial processes [1]. Biogenic gas is generated at low temperatures from organic matter in coal by anaerobic micro-organisms [2–5]. Biogenic gas resources are significant, accounting for 20% of the conventional natural gas reserves in the world [4,6]. Published studies have reported the presence of the biogas reservoir in many countries, including the USA [7,8], New Zealand [9], Australia [10], and China [11–13].

Biogas is characterized by low development costs and fewer environmental impacts. It has received significant attention from mainly in situ biogas reservoir and laboratory conditions. In situ research mainly focuses on two aspects including the evaluation of hydrocarbon generation potential of gas source rocks [4,13–20] and geochemical characteristics of typical biogenic coalbed gas reservoir [2,12,21–26]. The geochemical properties of gas can effectively separate biogenic coalbed gas from thermogenic coalbed gas. Widely used geochemical and isotopic evidence of the microbial origin of gas includes: (1) ratios of methane to ethane and propane ($C_1/(C_2 + C_3)$), typically > 1000 in samples of microbial gas and (2) $\delta^{13}C$-CH_4 values generally less than approximately −55‰ expected for biogenic gas [27–30].

To better understand the biogenetic mechanism, increasing attention has been paid to the simulation of biogas generation in laboratory conditions, and many scholars have also made many breakthroughs. Microbial conversion of coal to methane may be controlled by a combination of factors, such as the bioavailability of coal carbon, presence of a microbial community to convert coal carbon to methane, and an environment supporting growth, especially methanogenesis [31]. The substrate type, an important factor for biogas generation, is given more

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attention on how to enhance microbial activity and increase gas production. Huang et al. stimulated the generation of methane from a subbituminous coal that was treated with potassium permanganate ($KMnO_4$) as a depolymerization agent, enhancing the bioavailability of coal [32]. Yoon et al. [33] found that cumulative amount of biogas generation was increased by 199.7 mL with adding 6 g of rice straw. Wang et al. [34] combined the effects of exogenous aerobic and anaerobic microflora to more effectively convert lignite to methane. Low rank coals, such as lignite, and high-volatile subbituminous coal have lower calorific value, but they are more easily degraded biologically [35]. Therefore, they are commonly used as raw materials for simulation experiments of biogas generation [33,36–41]. However, with growing focus on environmentally clean energy, higher rank coals will be made more available to microbial degradation in the future.

In using organic matter with a high maturity as a carbon and energy source, the microbial community can also generate biogas under suitable conditions [42,43]. In the USA, CBM is identified as biogenic gas in some coalfields, which are dominated by high volatile bituminous coal [7,44,45]. In laboratory conditions, Opara et al. [37] examined microbial methane and carbon dioxide production from bituminous coal waste, lignite, and bituminous coal materials by adding different types and levels of nutrient amendments for 30 days. Fallgren et al. [46] determined the potential for stimulating microbial methane production in lignite, subbituminous and bituminous coals, and the authors found that the potential for biogenic gas production has a poor relationship with coal rank. Robbins et al. [47] cultured microorganisms with different rank (peat to bituminous) coals as the sole carbon and energy source to provide insight into how methanogenic consortia and gas production are influenced by coal rank. The studies noted above are mainly concerned with the effects of coal rank on microorganisms and the potential for biogas generation. However, the biogas generation process and gas geochemical characteristics from different rank coals remain unclear.

Using lignite and high-volatile bituminous coal as biological substrate, this paper periodically detected the geochemical characteristics of biogenic gas in experimental simulation of biogas generation, including biogenic gas component and carbon- and hydrogen-isotopic characteristics. The results contribute to a comprehensive understanding of the formation mechanism of biogenic gas as well as provide theoretical guidance for developing and utilizing in-situ biogas reservoirs.

2. Experimental materials and methods

2.1. Coal sample collection and processing

The coal samples used in this study were two pieces of lignite and four pieces of bituminous coals. The lignite samples were collected from sites from Beizao and Liangjia mines of Longkou coalfield, Shandong Province and the bituminous coal samples were obtained from Panyi, Pansan, Xinji, and Zhangji mines of Huainan coalfield, Anhui Province, China (Fig. 1). Fresh coal samples were collected by groove method on the working face of coal mines, and each sample weighs about 2 kg. Collected coal samples were immediately wrapped to prevent oxidation. Coal samples are indicated as L-BZ, L-LJ, B-PY, B-PS, B-XJ, and B-ZJ, respectively.

Preliminary smashed coal samples were put into a flask, which was linked to the beaker with water by a glass catheter. The flask was placed in a constant temperature water bath (at 60 °C) for 7 days to desorb gas filled in coal core pores. No bubble in the water was regarded as completion of degassing. After degassing, coal samples were crushed and ground to −200 mesh particle size in an anaerobic incubator (model SYQX-II).

Proximate analysis was conducted using ASTM Standard D3173-11, D3175-11, and D3174-11. ASTM Standard D5373-08 was used to conduct coal element analysis. For the maximum vitrinite reflectance ($R_{o,\ max}$), the measurement was conducted on a Zeiss Imager Mim microscope at 50 points on all samples. Maceral contents were determined on a mineral-matter basis by petrographic analysis, which was conducted with a Zeiss Imager Mim microscope equipped with white light photometer, and 500 points were recorded and assigned to the corresponding maceral, which contains vitrinite (huminite), exinite, inertinite, and various minerals. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the concentrations of trace elements in samples. These results were listed in the Tables 1 and 2.

All coal samples are of high-volatile content (37.81% to 45.17%) and low-ash (9.69% to 12.94%) according to Chinese coal industry standard MT/T 849-2000 (coal with 37% to 50% volatile matter is high-volatile coal) and GB 15224.1-2004 (coal with < 16% ash yield is low-ash coal). Compared to lignite, the high-volatile bituminous coals have lower moisture content and higher fixed carbon content. In terms of elemental analysis, the lignite has a lower carbon content and higher oxygen content compared to high-volatile bituminous coals. Furthermore, based on the atomic ratio, the molecular structure of lignite contains more hydrogen and oxygen atoms, indicating that lignite has more aliphatic hydrocarbon chain or heteroatom groups.

All coal samples have a similar maceral composition in which vitrinite (huminite) is the main component, which is followed by exinite and inertinite. Inorganic matter mainly consists of clay mineral (2.60% to 7.62%) and tiny levels of pyrite (less than 2.5%).

2.2. Microbial samples and culture medium

Microbial consortia were acquired from mine water in the Dananhu mine of Hami coalfield, Xinjiang Province, China, which was supplied by the Chinese Academy of Sciences. The mine water was kept in a portable incubator (model FYL-BW-11L) with a constant 7 °C, and immediately transported to laboratory. Published literature has demonstrated the presence of methanogens in the mine water [48].

Strictly following the technical process, the 3L culture medium was prepared in a glass container, which was put into the vertical pressure steam sterilizer (model LDZX-75KBS) at a temperature of 121 °C for half an hour for sterilization. The culture medium was formulated as follows.

A trace element solution consisted of 6.0 g of $FeCl_2{\cdot}4H_2O$, 5.0 g of $MgCl_2{\cdot}6H_2O$, 5.0 g of $MnCl_2{\cdot}4H_2O$, 0.64 g of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 0.45 g of $Ni_2SO_4{\cdot}6H_2O$, 0.15 g of $CoCl_2{\cdot}6H_2O$, 0.1 g of $ZnSO_4{\cdot}7H_2O$, 0.05 g of $CuSO_4{\cdot}5H_2O$, 0.1 g of H_3BO_3, 0.001 g of resazurin, and 1 L of distilled water [49].

Nutrient solution consisted of 4.27 g of $MgCl_2{\cdot}6H_2O$, 3.32 g of $CH_3COONa{\cdot}3H_2O$, 0.55 g of $K_2PO_4{\cdot}6H_2O$, 2.0 g of NaCl, 1.0 g of NH_4Cl, 0.4 g of KH_2PO_4, 0.2 g of KCl, 1.0 g of yeast extract, 0.5 g of cysteine, 0.001 g of resazurin, 10.0 mL of trace element solution, and 1 L of deionized water [50]. The pH value of the solution was adjusted to 7.0 using 1.0 mol/L HCl and 1.0 mol/L NaOH solution.

2.3. Enrichment culture

Microbial inoculation was performed in the anaerobic incubator mentioned above, which was in an anaerobic environment through replacement of air by nitrogen. The environment inside the incubator had a temperature of 25 °C and pressure of 0.1 MPa. A serum bottle (Vol. 500 mL) was used as a bioreactor for biogenic gas generation. Additionally, 380 mL of culture medium, 6 mL of sodium acetate solution (2.5 mol/L), and 50 mL of mine water were added into the serum bottle. The serum bottle was plugged using a butyl rubber stopper and finally sealed by paraffin for good airtightness. The inoculated serum bottle was placed in a stability temperature oscillated incubator (model HZQ-F160), which was kept at a constant temperature of 37 °C and shaken at a frequency of 50 rounds per minute for 30 days. At the end of the 30-day incubation period, the chromatographic analysis result of the gas collected from the serum bottle showed the generation of CO_2,