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Full Length Article

A formation water-based nutrient recipe for potentially increasing methane release from coal in situ

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ABSTRACT

Biogasifying coal to methane represents an environmentally benign way to utilize the abundant and inexpensive coal resource. To increase methane yield from coal, numerous studies have investigated the approach of biostimulation through finding the best nutrient solutions to enhance microbial activities. Toward this end, however, almost all studies have adopted laboratory made medium that is tap water- or deionized and distilled water-based. As a matter of fact, this water is dramatically different from formation water in coal basins. Thus, in order to enhance methane release from coal in situ, this study aimed to design a formation water-based recipe. To accomplish this objective, the chemical and microbial compositions of the formation water collected from the San Juan basin were analyzed first. Equipped with this fundamental knowledge, a screening test was conducted to evaluate nine parameters to identify statistically significant ones affecting methane yield from coal. For those critical parameters, the optimal value for each was determined through response surface methodology. Finally, the predicted results by the models were verified by an experimental study adopting all optimum conditions. This study demonstrated that microbes capable of converting coal to methane were present at the San Juan basin and the developed recipe increased methane yield 24.3-fold compared to those without.

1. Introduction

It has been suggested that up to 20% of the world's natural gas is microbial in origin [1]. Specific to coal bed methane (CBM), biogenic methane production has been observed as a significant source in nearly every shallow coal seam at temperatures less than 80 °C [2]. In some basins, like the Illinois basin except the southeastern part in western Kentucky, methane gas is formed primarily through biogenic rather than thermogenic process [3]. In the US, the coal resources are estimated at 6 trillion tons, and 90% of it is currently unmineable due to seam thickness, depth, and structural integrity [4]. To convert these unmineable coals to methane through the biogenic pathways, four potential techniques, such as physically increasing microbial access to coal and distribution of amendments, increasing the bioavailability of coal organics, microbial augmentation, and microbial stimulation, can be applied [5,6].

The first two approaches can be achieved by hydraulic fracturing, a technique commonly used for releasing natural gas from shales [7,8]. The latter two deal with the microorganisms that initiate the coal conversion process. Regarding microbial augmentation, the purpose is to supplement a coal basin where coal-degrading microbes are not present. This could be needed for non-productive CBM wells as reported [9]. But the majority of recent studies have shown that indigenous microbes capable of gasifying coal to methane are present in coal seams. And this observation has been reported for coal basins across the globe. Representative examples include: the Powder River basin [10–12], the San Juan basin [13], the Illinois basin [14], the Indio formation [9], the Alberta coalbeds in western Canada [15], the Jiuligang formation in the Jingmen-Danyang basin in Hubei, China [16], the south Sydney basin [17] and the others listed in the review [18]. Since microbes co-exist with coal and/or inhabit the formation water, the last approach of biostimulation is the most reasonable one.

Methane yields in different basins are disclosed at different levels. It is 67 ft^3/ton for the Illinois basin [19], 50–70 ft^3/ton for the Powder river basin [20], 70–106 ft^3/ton for the Springfield (Indiana) [21], and 115–263 ft^3/ton for the Paleocene Fort Union coals in south-central Wyoming [22]. To further increase methane production from coal, different studies have evaluated effects of different recipes/chemicals on coal conversion to methane. These recipe/chemicals include, but not limited to: trypticase soy broth [23], a MS medium for methanogens

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[24], a commonly used anaerobic medium [25], non-ionic surfactants (Zonyl FSN, Triton X-100, and Brij 35) [26], and solvents (ethanol, methanol, pyridine, and N,N-dimethylformamide (DMF) [20] [27]. Besides these studied in the academic labs, other recipes have been tested at pilot scales by different companies [28]. However, except our previous study targeting developing a nutrient solution for biogasification of Illinois coal ex situ [24], none of the reported studies focused on finding the most suitablenutrient recipes for a specific coal basin. To fill this gap, this study was designed to identify the optimal nutrient recipe for the San Juan basin. Specifically, this recipe is aimed for in situ application. For this purpose, the formation water collected from the coal seam was used as the basis for developing the nutrient solution. The basin specific recipe was developed through a systematic approach considering the chemical and microbial composition of the formation water and the in situ temperature. To determine the optimal nutrient solution, a three-step methodology: screening, optimization and verification was adopted as detailed below.

2. Materials and methods

2.1. Coal and formation water sample collection and preparation

Chunks of coals were collected from a coal mining site at southwest of the San Juan basin in the United States (US). This seam is well known as the oldest natural gas production area in the US from both conventional and unconventional tight sand, CBM, and shale formations. The collected coal samples were immersed in water in a bucket at room temperature in darkness. Prior to use, the surface layer of the coal chunk was peeled off. The remaining coal was ground and only the portion that passed through a 40 mesh (< 0.42 mm) screen was kept in Ziploc bags and maintained in a humidity chamber to avoid water loss. Prior to use, the coal samples were subject to elemental and proximate analysis as reported before [29]. From the former, the percentage of carbon, nitrogen, hydrogen, sulfur, and oxygen was found to be 70.29 ± 0.38; 1.36 ± 0.01; 5.12 ± 0.05; 0.83 ± 0.03 and 17.97 ± 0.06, respectively. From the latter, the coal had 5.09 ± 0.00% of ash, 44.15 ± 0.09% of volatile carbon and 50.76 ± 0.1% of fixed carbon. The heat content was 12,410.65 ± 80.6 BTU/lb [29].

From a CBM well that is in the same seam as where the coal was collected, the formation water samples were gathered from a depth of 3000 ft. At the sampling site, temperature was measured immediately after the formation water came to the surface. Fresh formation water was handled differently depending on their final use. Regarding those for chemical analysis, no chemicals were added. For analysis of total organic carbon (TOC), the formation water was added to glass vials containing HCl. On the way from the San Juan basin to our laboratory in Carbondale, IL, water samples dedicated for chemical composition analysis were kept on ice. In terms of those dedicated for microbial analysis, the formation water was supplemented with sodium sulfide (Na_2S) at 0.25 g/L and resazurin at 1 mg/L to maintain anaerobic conditions. During transportation back to our lab, these water samples were not put on ice for the purpose of keeping the microbes alive.

Once the samples reached our labs in Carbondale, the on-ice samples were transferred to the Carbondale Central Laboratory (CCL, Carbondale, IL, USA) immediately for chemical analysis. Samples for microbial analysis were treated in two ways. First, nine one-liter samples were filtered through 0.2 μm membrane filters (90 mm, Whatman™, Freiburg, Germany). Three resulting membranes were used for DNA extraction using Powerwater DNA extraction kit (Mo Bio, Carlabad, CA, USA) following manufacturer recommended procedures. These DNA samples were stored at −20 °C before use. The remaining six membranes were used to set up microcosms as described in the following. Some water samples were used to make glycerol frozen stocks. Briefly, the formation water was concentrated 80 times through centrifugation at 4 °C. The concentrated samples were then used to make frozen stocks with glycerol at 20%. These stocks were stored at −80 °C before use. The remaining water samples were kept at −20 °C for later use.

Table 1
Chemical composition of the formation water.

Parameter	Unit	Formation water	Filtered formation water
Temperature	(°C)	41–44	NA
pH		8.19	NA
Free ammonia	mg/L	0.23	NA
Total ammonia	mg/L	1.78	NA
Total Nitrogen-N	mg/L	2.4	NA
Chemical oxygen demand (COD)	mg/L	2497	NA
Hydrogen sulfide	mg/L	33	NA
Fluoride	mg/L	4	NA
Nitrite	mg/L	< 0.5	NA
Nitrate	mg/L	0.2	NA
Phosphate	mg/L	< 0.75	NA
Total phosphate-P	mg/L	0.171	NA
Sulfate	mg/L	< 0.75	NA
Chloride	mg/L	161	NA
Iron	mg/L	1.11	NA
Total dissolved organic carbon	mg/L	1.15	NA
Alkalinity as $CaCO_3$	mg/L	1280	NA
Aluminum	μg/L	86.7	25
Boron	μg/L	971	875.1
Cobalt	μg/L	< 1	< 1
Copper	μg/L	4.3	< 1
Manganese	μg/L	22.3	12
Molybdenum	μg/L	6.6	3.2
Nickel	μg/L	4.2	< 1
Selenium	μg/L	< 1	< 1
Tungsten	μg/L	7.2	6.3
Zinc	μg/L	21.1	1.6
Magnesium	mg/L	1.1	< 1
Sodium	mg/L	721	703
Calcium	mg/L	13.6	12.5
Potassium	mg/L	6	5.3

2.2. Chemical analysis

At CCL, concentrations of dissolved metals, such as: Na, K, Ca, Mg, Fe, Al, Co, Mn, Zn, W, Cu, Cu, Ni, Se, B, Mo were analyzed according to EPA method 200.8 through use of Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Table 1). Concentrations of anions, such as: Cl^-, SO_4^{2}, PO_4^{3-}, NO_3^- were determined according to EPA method 300.0 through use of Ion Chromatography (IC). HCO_3^- concentration was determined following SM320B. TOC content was measured according to SM5310B. In addition, since nitrogen is especially important for microbial activities, ammonia-nitrogen concentration was determined by using an ion selective ammonia electrode following EPA method 350.3. Total nitrogen concentration was measured by using a Hach Kit TNT827 (Hach, Inc.). Furthermore, since dissolved sulfide above certain concentrations may be toxic to microbes, content of dissolved H_2S was determined according to EPA 376.2.

2.3. DNA sequencing

Following DNA extraction, DNA samples were quantified using a Nanodrop spectrophotometer. Those with excellent quality (A_{260}/A_{280}: 1.8–2.0) and high concentrations (30–50 ng/μl) were sent for sequencing according to procedures reported by our lab [25]. In short, to determine the overall diversity of the microbial population, the 16 S rRNA gene V4 variable region PCR primers F515 (5′-CACGGTCGKCGGCGCCATT-3′) and R806 (5′-GGACTACHVGGGTWTCTAAT-3′) [30,31] were used. Single-step PCR using the HotStarTaq Plus Master Mix Kit (Qiagen, Valencia, CA, USA) was performed under these conditions: