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Evaluating approaches for sustaining methane production from coal through biogasification

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HIGHLIGHTS

- At 20.2% (w/v) coal loading, coal was still bioavailable after methane production ceased.
- Yeast extract and peptone were the most critical components in the nutrient solution.
- Headspace gas was not toxic to the microbial community.
- Coal degradation intermediates did not have inhibitory effect on the microbial community.
- Adding crucial nutrients periodically can sustain methane release from coal for longer time.

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ABSTRACT

Biogenic methane production from coal has been demonstrated to be a universal process at places where coal and a suitable microbial community co-exist. Through stimulating activities of in situ microbial communities, higher methane production rate can be achieved compared to those without biostimulation. However, it is commonly observed that upon stimulation either in situ or ex situ, methane production will increase but halt after certain period of time. This study was thus designed to identify reasons for this behavior and provide insight on how to sustain coal biogasification over longer durations. It was found out that after methane production rate stopped increasing, coal, at the studied loading, was still bioavailable. The headspace gas and the coal degradation intermediates were not toxic or inhibitory to the bioconversion process. Instead, lack of nutrients, especially those provided through yeast extract and peptone was critical for sustained methane release from coal. Although these two nutrients could be used as carbon sources, negligible amount of methane was observed from control reactors without coal. At least, these were true for the microbial community and the bituminous coal investigated here. Thus, to convert coal to methane continuously at a high rate that is possible, site-specific nutrient solution needs to be supplemented periodically.

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1. Introduction

During recent years, coal biogasification or bioconversion has attracted extensive interest globally among researchers and investors. Although coal is commonly recognized as recalcitrant and difficult to be degraded biologically, a wide variety of microbial communities that have the capability to gasify coal have been disclosed from different locations around the world, such as Yubai, Japan [1], Australia [2], the Waikato coalfields in New Zealand [3], the Alberta basin in Canada [4], the Eastern Ordos Basin in China [5], the Jingmen-Dangyang basin in China [6], the Illinois basin in the US [7,8] and the Powder River Basin in the US [9,10]. These communities generally include microorganisms in the two domains: Bacteria and Archaea.

Conventionally, coal biogasification is believed to require the collective actions of microorganisms encompassing three major metabolic groups: 1) hydrolytic and fermentative bacteria; 2) acetogenic bacteria, and 3) methanogenic archaea [11]. During the initial stage of gas production, complex organic compounds in coals are decomposed to simpler molecules such as acetate, long chain fatty acids, CO_2, H_2, CH_4, and HS^- by fermentative anaerobes. Fatty acids, alcohols, and some aromatic and amino acids are then converted to H_2, CO_2, and acetate by H_2-producing acetogens while H_2-using acetogenic bacteria consume H_2 and CO_2 to produce more

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acetate. Finally, simple molecules are subsequently transformed to CH_4 by methanogens belonging to the domain of Archaea [12].

Depending on the methane formation pathways, methanogens are divided into three groups: 1) acetoclastic which converts acetate to methane and CO_2; 2) hydrogenotrophic which reduces CO_2 to methane; and 3) methylotrophic which converts methylated compounds, such as methanol, methylamines and/or dimethylsulfide to methane [11]. Some methanogens, such as those within the order of Methanobacteriales [13] and Methanomicrobiales [14] can produce methane from more than one pathway. Very recently, it was reported that methanogens from the genus *Methermicoccus* can convert coal-derived methoxylated compounds directly to methane [15]. Without the presence of bacterial species, one isolate, *M. shengliensis* AmaM used more than 30 types of methoxylated aromatic compounds as substrates. When cultivated on lignite, subbituminous and bituminous coal, the methane produced was 10.8, 8.0 and 9.4 μmol/g coal, respectively [16]. The discovery of this novel pathway of methanogenesis makes research and development on coal biogasification even more interesting and exciting.

Coal biogasification can be conducted both in situ and ex situ. To study the mechanisms involved in coal bioconversion, a majority of research has been performed in a laboratory environment where in situ temperature and/or pressure may be simulated in a batch process. As reported by different researchers [9,17–24], a common phenomenon has been observed: methane production (mass of methane per mass of coal) peaked and then either slowed down or stopped increasing after certain period of time. The possible explanations could be: 1) exhaustion of nutrients in the medium and coal used; 2) product inhibition: CH_4, H_2S and NH_3 in the headspace may inhibit microbial activities; 3) accumulation of toxic or inhibitory degradation products; and 4) the residual coal was not available to microbial cells [19].

To fully understand the reasons and to sustain coal biogasification for a longer duration, in this study, we established 18 microcosms that were exactly the same at the beginning of the experiment. Out of the 18, three reactors were used as controls. After 25 days, when methane production ceased, the other 15 microcosms were divided into five groups. Each group received different treatment in order for us to pinpoint the reasons for this production halt behavior. Based upon experimental results, strategies for sustaining methane release from coal were recommended.

2. Materials and method

2.1. Coal, a microbial community and nutrient solution

Coal samples used in this study were the same as those described before [17,18,7,25]. Briefly, chunks of high volatile B bituminous coal from Illinois # 6, the Herrin seam were ground first. Those passed mesh #200 (<74 μm) were sealed in ziplog bags and stored at room temperature. A microbial community that was enriched for ex situ coal bioconversion was employed for this investigation. As described in [7], the natural community in the formation water shifted significantly after it was cultivated in the laboratory environment for a month. The enriched community, however, is stable as long as the incubation conditions remain the same. This community comprised 185 Bacteria (98.3% of the total sequences) and nine Archaea species (1.7% of the total). The dominant Bacterial species were: *Clostridium bifermentans* (15.1%), *Massilia* spp. (11.1%), *Pseudomonas putida* (11.1%), *Proteiniphilum* spp. (6.5%), *Pseudomonas stutzeri* (6.4%), *Shewanella* algae (5.7%), *Arcobacter* spp. (5.3%), *Gelria* spp. (2.8%), *Ruminococcus* spp. (2.2%), *Methylobacterium aquaticum* (2.0%), *Tindallia texcoconensis* (2.0%), and *Syntrophomonas* spp. (1.9%). The main Archaea species were: *Methanocalculus pumilus* (43.9%), *Methanocalculus taiwanensis* (42.7%), *Methanosarcina lacustris* (7.1%), *Methanomicrobium* spp. (3.5%), *Halobacterium* spp. (1.0%), *Methanosaeta spp.* (0.9%), *Thermoplasma* spp. (0.5%), *Methanocalculus halotolerans* (0.4%), and *Methanobacterium ferruginis* (0.01%). This community was stored with glycerol at −80 °C. Fresh inoculum developed from these frozen stocks was used in this study (Fig. 1). It needs to be noted that the composition of the microbial community regenerated from the same frozen stocks but different times was found to be the same according to our next generation DNA sequencing results.

The nutrient solution was made according to the MS recipe [13] except that mercaptoethanesulfonic acid (Coenzyme M, CoM) was not included. This MS medium has been demonstrated to lead to more than 10-fold increase of methane release compared to those without the addition of this solution [7]. The MS recipe contained (per L of distilled and deionized water (DDW)): 8.4 g of $NaHCO_3$, 2.0 g of yeast extract, 2.0 g of trypticase peptones, 0.25 g of $Na_2S{\cdot}9H_2O$, 1.0 g of NH_4Cl, 0.4 g of $K_2HPO_4{\cdot}3H_2O$, 1.0 g of $MgCl_2{\cdot}6H_2O$, 0.4 g of $CaCl_2$, 1.0 mg of resazurin, and 10 ml of trace mineral solution. The trace mineral solution contained (per L of DDW): 500 mg of $NaEDTA{\cdot}2H_2O$, 150 mg of $CoCl_2{\cdot}6H_2O$, 100 mg of $MnCl_2{\cdot}4H_2O$, 100 mg of $FeSO_4{\cdot}7H_2O$, 100 mg of $ZnCl_2$, 40 mg of $AlCl_3{\cdot}6H_2O$, 30 mg of $Na_2WO_4{\cdot}2H_2O$, 20 mg of CuCl, 20 mg of $Ni_2SO_4{\cdot}6H_2O$, 10 mg of H_3BO_3, 10 mg of H_2SeO_3, and 10 mg of $Na_2MoO_4{\cdot}2H_2O$.

2.2. Setting up, monitoring and modifying microcosms

A total of 18 microcosms (100 mL serum bottle) was established. Out of the 18, three microcosms served as controls where coal was not added. These three contained only 45 mL of the MS medium, 100 mM of ethanol and 5 mL inoculum developed from the microbial community aforementioned. Each of the remaining 15 microcosms contained coal at 201.98 g/L and received 45 mL of the MS solution, 100 mM of ethanol and 5 mL inoculum. After all ingredients were added, the bottles were capped with butyl rubber stoppers and sealed with aluminum crimps. All bottles were purged with N_2 completely and then incubated at 32 °C under static conditions. Starting from day 10, the headspace gas in each bottle was released and measured according to a protocol reported before [17]. Briefly, when a needle was inserted into the headspace, the pressurized gas due to gas production from coal would escape to a 50-mL gas tight syringe connected to the needle. The volume of the released gas together with gas content measured by a Gas Chromatography (GC) as detailed below were recorded for calculating cumulative methane production at different time points.

On day 25, the total nitrogen (TN) and total phosphorous (TP) content of the liquid in each bottle were analyzed according to procedures detailed below. The 15 bottles that contained coal were then divided into five groups with each group having three replicates (Fig. 1 and Table 1). The first set was kept the same with no changes. To the second group, a concentrated solution of $K_2HPO_4{\cdot}3H_2O$ was added to make the TP concentration equal to the original level. To the third group, a concentrated MS solution without yeast extract, peptone, NH_4Cl, and $K_2HPO_4{\cdot}3H_2O$ was supplemented to each bottle. This supplementation was equal to adding fresh MS medium without compounds containing N and P at 20% of the initial liquid volume. Regarding the fourth group of three, the headspace was purged with pure nitrogen to displace the whole headspace content. In terms of the fifth group, 20% of the liquid in each bottle was withdrawn followed by adding fresh MS solution at the same volume.

After these treatments, all of the 15 bottles were monitored for 10 days. On day 35, the first set of the three controls were sparged with N_2 to replace their headspace followed by adding 5 mL of fresh cells and 45 mL of MS medium to each. To the second set,