



## Methanogenic fermentation of lignite with carbon-bearing additives, inferred from stable carbon and hydrogen isotopes

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### ABSTRACT

Lignite from the Konin area (Poland) was used as a substrate for incubation experiments to evaluate its potential for simulation of biogenic methane production. Lignite was incubated with a bacterial inoculum enriched from lake sediments, mineral media, and various supplemental components for microbial life. Additives, such as acetate, methanol, glucose, nutrient broth, and yeast extract, can significantly increase methane production. At the same time, biodegradation of these additional carbon sources leads to overestimation of methane yield. In this paper, selected geochemical properties (total organic carbon content; stable isotopic composition of carbon  $\delta^{13}\text{C}$ ) were analyzed in order to evaluate changes in the organic matter of fermented lignite. Stable isotope analysis of carbon and hydrogen was applied in order to identify sources of methane and carbon dioxide formation. TOC decreased in range from 1.4 to 9.6% in lignite after fermentation. The  $\delta^{13}\text{C}$  value of lignite used in the experiments ( $-25.2\text{‰}$ ) decreased after incubation to values in range from  $-27.1$  to  $-26.2\text{‰}$ . Methane yield per g of TOC (lignite + organic carbon in nutrients) ranged from 0.47 to 2.60 mM/g. Glucose, acetate, and methanol significantly increased biogas production. Nutrient broth and yeast extract were not a source of organic carbon for methane formation, but their presence enhanced biogas production. Values of  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^2\text{H}(\text{CH}_4)$  across incubation conditions ranged from  $-70.2$  to  $-24.2\text{‰}$  and from  $-396.6$  to  $-290.5\text{‰}$ , respectively. Values of  $\delta^{13}\text{C}(\text{CO}_2)$  ranged from  $-55.2$  to  $45.0\text{‰}$ . The high level of variation of  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^{13}\text{C}(\text{CO}_2)$  suggests mixing of gases from different carbon sources during incubation, but can also be caused by mixing of metabolic modes by the microbial community. Understanding the  $\delta^2\text{H}(\text{CH}_4)$  variation is even more difficult than the  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^{13}\text{C}(\text{CO}_2)$ , since many substrates often contain exchangeable hydrogen (e.g. in water, lignite, and elements of nutrients). The combined values of  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^{13}\text{C}(\text{CO}_2)$  suggests that the dominant methanogenesis pathway in our experiments may be acetate fermentation. In biodegraded lignite, high relative concentrations of *p*-cresol (one of the most abundant in the sample) and *n*-(2-acetylphenyl)formamide were identified. These compounds are most probably lignin decomposition products, or, in the case of the latter, bacterial by-products or remnants. Organic compounds with low molecular weights, *n*-alkanes, and biomolecules including ferruginol, sugiol, and 6,7-dehydroferruginol, as well as amyrins and tocopherols, were preferentially degraded. The potential for methane production from lignite spiked with carbon-bearing additives is at least one magnitude lower than that from agricultural wastes. The lignite utilization as the single substrate for methanogenic fermentation is economically unprofitable. Mixing of lignite with the external substrate as biomass may be an alternative for consideration and future research.

### 1. Introduction

Lignite (brown coal) is commonly used in the power industry, mostly in Europe. Conventional technologies for lignite exploitation and processing, especially opencast mining and combustion, have a

significant negative impact on the environment (Fabbri et al., 2008, 2009; Krzywański et al., 2013). These processes, due to the formation of a large cone of depression, result in changes to the landscape and surface and groundwater regimes. Thus, finding clean lignite management technologies is an extremely important task.

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Poland is the second largest (after Germany) producer of lignite in the European Union. In Poland, 91 deposits of lignite have been documented; currently exploitation is being carried out in 5 open pit mines (locations: Adamów, Bełchatów, Konin, Sieniawa, and Turów). Today, approximately 99% of lignite extracted from mines is burned as fuel in power plants. Many lignite beds are not suitable for traditional opencast mining due to the coalbed's insufficient thickness or too high ash or sulfur content. For these reasons, they are currently not recognized as lignite resources in the balance sheet of mineral resources (Polish Geological Institute, 2016). Nevertheless, lignite can be regarded as a raw material for biotechnological and chemical processes as thermal and microbial gasification, extraction of humic acids, hydrothermal and enzymatic liquefaction (Catcheside and Ralph, 1999; Patel et al., 2017; Srivastava and Walia, 1997; Vasireddy et al., 2011; Wang et al., 2014; Wise, 1990).

Organic matter in lignite consists of residual components which are relatively resistant to microbial decomposition under geological conditions. These consist particularly of biopolymers or residues of substances such as lignin, cellulose, and hemicellulose, as well as other components which are resistant to degradation, such as humins and humic acids (Diessel, 1992; Killops and Killops, 2005). The latter are considered to be constituents of plants or their diagenetic products (e.g., Bechtel et al., 2007, 2008; Fabbri et al., 2009). Furthermore, carbohydrates and amino acids can be found following hydrolysis of lignite (Fabbri et al., 2009; Killops and Killops, 2005). These compounds, if bioavailable, are readily metabolized by microorganisms. Degradation of lignite under aerobic conditions can occur with the participation of white or brown rot fungi (Catcheside and Ralph, 1999), whereas under anaerobic conditions lignite can be a source of energy for anaerobic microbial communities consisting of Archaea and fermenting microorganisms (Beckmann et al., 2011a, 2011b; Krüger et al., 2008; Midgley et al., 2010; Strapoć et al., 2011).

Biogasification, or microbial conversion of organic-rich sedimentary rocks into clean fuels (methane and hydrogen), is one of the lignite utilization technologies discussed recently (Park and Liang, 2016; Ritter et al., 2015; Strapoć et al., 2011). Biogasification could exert an influence on the reduction of harmful emissions of gases (CO<sub>2</sub>, CO, SO<sub>x</sub>, NO<sub>x</sub>) and dust into the atmosphere, water, and soil resulting from storage and combustion. There have been extensive debates as to whether clean coal technologies can significantly reduce the greenhouse effect. The current state of knowledge has apparently revealed an opportunity to convert lignite to biogas in bioreactors (Ritter et al., 2015; Wise, 1990). However, recent and future research may provide valuable input for the biogasification of lignite directly in the deposit. For this purpose it is necessary to accurately identify this process and control it under laboratory conditions (Ritter et al., 2015).

Microbially formed methane is present in many lignite deposits around the world, e.g., in Australia, China, Germany, Poland, Slovenia, and the USA (Baublys et al., 2015; Butland and Moore, 2008; Krüger et al., 2008; Green et al., 2008; Kanduč et al., 2012; Papendick et al., 2011; Shimizu et al., 2007; Strapoć et al., 2008; Strapoć et al., 2011; Ulrich and Bower, 2008; Wang et al., 2013). Furthermore, activity of sulfate-reducing bacteria has been observed in lignite deposits, though sulfate is, for the most part, not very abundant in lignite. The source of sulfates in lignite deposits is mostly pyrite weathering, which starts when oxygen penetrates the coal bed strata. The growth of sulfate-reducing bacteria could result in the inhibition of methanogenesis through outcompeting methanogens during consumption of hydrogen (Jędrysek, 2005). However, in this case, methyl-type or acetate fermentation is possible (Strapoć et al., 2011).

In the past years many studies have been carried out on the methanogenic biodegradation of different types of coal (e.g., Fallgren et al., 2013; Krüger et al., 2008; Midgley et al., 2010; Opara et al., 2012; Robbins et al., 2016; Daisuke Mayumi et al., 2016). Often, these studies have concentrated on the identification of microbial species which can convert material originating in coal into methane and the elucidation of factors which enhance or limit methanogenesis. Methanogenic biodegradation of lignite requires appropriate conditions for microorganisms, such as an anoxic environment, suitable salinity and pH, a moderate temperature, the presence of biodegradable compounds, and the availability of macro- and micronutrients (Flores et al., 2008; Orem et al., 2010). Degradation of coal material is also possible with the use of simple chemical reagents, thermal conversion technologies, and enzymes (Strapoć et al., 2011).

Methanogenic biodegradation of lignite under laboratory conditions can be enhanced by the addition to the mineral medium of a direct substrate for methanogenesis. Such compounds as glucose, acetate, methanol, yeast extract, and nutrient broth are widely used as carbon sources for the cultivation of microorganisms as well in batch experiments with coal material. Their addition often causes overestimation of produced biogas and complicates the interpretation of obtained data (Jones et al., 2008, 2010; Opara et al., 2012; Wang et al., 2016; Yoon et al., 2016). These problems can be solved by the use of an isotope tracer experiment using labeled components (Conrad, 2005; Feisthauer et al., 2010).

Most studies of Polish lignites have concentrated on geology, tectonics, petrography, organic geochemistry, and palynology. The data in the literature contains mentions of biogenic methane in the Bełchatów (Macuda et al., 2011) and Konin (Strapoć et al., 2010, 2011) regions, but it has not been definitely proven that biogenic methane is being formed today. It is possible that methane present in coalbed strata was formed in the geological past and that methane has been emitted from the outcrop into the atmosphere for as long as open pit mines have been active.

In this paper we attempt to prove that lignite from the Konin region can be degraded to methane by microorganisms under laboratory conditions. Unlike many other studies, this research does not focus on the identification of microbial communities growing on coal material. Rather, it examines changes in organic matter in lignite caused by microbial activity, as well as the effect of carbon-bearing additives on methane production in batch experiments using lignite as the main substrate. Moreover, it estimates yields of methane production for lignites from the Konin region. The main geochemical tool applied in this work was stable isotope mass spectrometry; however, a preliminary molecular study of biodegradation products was performed as well.

## 2. Materials and methods

### 2.1. Collection and processing of samples

Lignite for incubation experiments was collected in the Konin area, located in central Poland. Currently, exploitation of lignite is carried out by the company PAK Kopalnia Węgla Brunatnego Konin S.A. from three open pits (Drzewce, Józwin IIB, Tomisławice). Lignite for our research was collected in the Józwin IIB open pit. Lignites from the deposits of the Konin region are characterized by a low degree of maturity. The deposits, formed in the Middle Miocene (Badenian stage), are in the early to late stages of diagenesis. Biogenic methane has been observed in the mine (Strapoć et al., 2011). The deposit contains different coal lithotypes described by several authors (Fabińska, 2007;

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