Methanogenesis

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Coal bed methane (CBM) extraction has astounding effects on the global energy budget. Since the earliest discoveries of CBM, this natural gas form has witnessed ever-increasing demands from the core sectors of the economy. CBM is an unconventional source of energy occurring naturally within coal beds. The multiphase CBM generation during coal evolution commences with microbial diagenesis of the sedimentary organic matter during peatification, followed by early to mature thermogenic kerogen decomposition and post-coalification occurrences. Indeed, the origin of the CBM and, moreover, its economically valuable retention within coal seams is a function of various parameters. Several noticeable knowledge gaps include the controls of coal make-up and its physicochemical position on the CBM generation and genetic link through fossil molecular and stable isotopic integration with the parent coal during its evolution.

Keywords: methanogenesis ; microbially enhanced–coalbed methane ; molecular signals

1. Origin of Methane in Coal Beds

The origin of coal bed methane (CBM) can be distinguished broadly into (a) primary microbial (PM), (b) thermogenic (T), and (c) mixed sources [1][2][3][4][5][6][7]. Meanwhile, microbial methane is present primarily in low-rank coals, while high-rank coals often comprise secondary late mature microbial gas [2][6][7][8][9][10][11][12]. Thermogenic gas can also be divided into early mature thermogenic gas (EMT) and late mature thermogenic gas (LMT) [9] based on its mode of origin. The origin of CBM can be evidenced by (a) the gas molecular ratio (methane/(ethane + propane): $CH_4/(C_2H_6 + C_3H_8)$); (b) the stable carbon and deuterium isotopes of methane ($\delta^{13}C–CH_4$ and $\delta D–CH_4$); (c) the stable carbon isotope of carbon dioxide ($\delta^{13}C–CO_2$); (d) the stable deuterium and oxygen isotopes of coal seam water ($\delta D–H_2O$ and $\delta^{18}O–H_2O$); (e) the stable carbon isotopic discrimination factor ($\alpha_{CO2–CH4}$); and (f) the carbon isotopic difference between CO_2 and CH_4 ($\Delta^{13}C_{CO2–H4}$), [2][3][4][7][9][11][13][14][15][16].

2. Microbial Methanogenesis: An Overview

Microbial methanogenesis is the ultimate phase of organic matter biodegradation, which yields methane and carbon dioxide [5]. The microbial decomposition of organic matter involves geopolymer conversion to low-molecular-weight hydrocarbons (C_{LMW}) within the coal beds. Microbially mediated transformations of the C_{LMW} compounds yield methane precursors, i.e., methanol, formate, H_2, acetate, carbon monoxide, etc. [12][17]. The obligate anaerobes, such as methanogenic archaea, facilitate the final stage of biodegradation and yield methane. Carbon dioxide is a subsidiary product of microbial methanogenesis that is required by the electron balance of the C_{LMW} compounds [5][9]. The methane precursor compounds donate an electron to the methanogenic archaea in a syntrophic association in the final stage of biodegradation. However, direct electron transfer from microbes to methanogens may also occur without requiring the intermediary H_2 precursor [18][19]. Methanogens, including *Methanospirillum*, *Methanococcus*, and *Methanobacterium*, can utilize the H_2 and CO_2 precursors, whereas only *Methanosaeta* and *Methanosarcina* archaea can utilize the acetate. *Methanosarcina* utilizes either acetate or $CO_2 + H_2$ [17]. Assessments based on the DNA of the microbial communities suggest that their archaeal diversity is less than that of the bacteria in unconventional reservoirs [20][21][22]. Proteobacteria, Bacteroidetesm, Firmicutes, and Actinobacteria are abundant in coal beds [22][23][24][25][26], and are capable of metabolizing and decomposing kerogen and hydrocarbons. Meanwhile, *Methanobacteriales*, *Methanomicrobiales*, and *Methanosarcinales* reflect the archaeal diversity in CBM basins [27][28].

3. Pathways of Primary Microbial Methanogenesis

Methanogenic archaea proliferate in oxygen-poor anoxic redox conditions. In addition, thermogenic constraints influence microbial methanogenesis. Competitive substrates, such as formate, acetate, and H_2 [7], are scavenged by heterotrophic microbes that intercede in the iron, nitrate, and sulfate reduction pathways. These non-methanogenic pathways produce more free energy per mole of the substrate than the methanogenic route [5]. Microbial methanogenesis takes place

primarily through two ways in water free of alternative electron acceptors (such as sulfate): (a) the hydrogenotrophic or CO_2-reduction pathway (Equation (1)), which involves H_2 as an electron donor and CO_2 as an electron acceptor; and (b) acetate fermentation, or the acetoclastic route (Equation (2)), which is characterized by the reduction of a methyl group to methane and the oxidation of a carboxylic group to carbon dioxide [2][5][16][17][29].

$$CO_2 + 4H_2 = CH_4 + 2H_2O \quad (1)$$

$$CH_3COOH = CH_4 + CO_2 \quad (2)$$

The hydrogenotrophic and acetoclastic methanogenesis involve terminal enzymatic activities, and these pathways engage the methyl–coenzyme M reductase. Meanwhile, during hydrogenotrophic methanogenesis, primary activation and transfer of the C1 unit from the substrate uses the methanofuran coenzyme [17]. Further, in the acetoclastic pathway, methane production from acetate is activated by acetyl–coenzyme A. Subsequent enzymatic procedures form methyl–coenzyme M, which is further reduced to methane. The presence of transition metals, such as cobalt and nickel, also influences the enzymatic activities during methanogenesis [30][31]. These two transition metals are present as trace elements in coal beds, and, thus, may have a considerable effect on CBM production. Both of these methanogenic pathways are exogenic and yield free energy, and the gain in free energy is used to synthesize adenosine triphosphate (ATP). Oremland et al. [32] reported that the free energy yield during hydrogenotrophic methanogenesis (−135 kJ mol^{-1}) is much higher compared to acetoclastic methanogenesis (−31 kJ mol^{-1}). This free energy gain during hydrogenotrophic methanogenesis is sufficient to synthesize at least one molecule of ATP. The terminal enzymatic activities involving the methyl–coenzyme M reductase help to conserve energy. These enzymatic activities are crucial for preserving the methanogenic society, and also favor energetically efficient metabolisms in energetically inadequate environments [17].

Methanogenesis using methylamines and methanol by *Methanolobus* has also been reported in addition to the acetoclastic and hydrogenotrophic pathways. Demethoxylation produces ranges of methylated compounds, which can be utilized as non-competitive substrates [12][21][33][34]. Meanwhile, in the presence of microbially-reducible iron oxides or sulfates, methylated substrates are used by methylotrophs when bacteria surpass the methanogens in utilizing the competitive substrates. Sulfate abundance may adversely affect methanogenesis by restricting the methanogens from utilizing the competitive substrates. In the presence of sulfur, sulfate-reducing microbes efficiently scavenge the acetate, making hydrogenotrophic methanogenesis the dominant pathway in marine sediments. On the other hand, acetoclastic methanogenesis is dominant in freshwater sediments that lack sulfur [7][16][17][35]. A lack of sulfate-reducing microbes promotes the formation of short-chain-length volatile fatty acids and acetate, which offer a proper substrate for acetoclastic methanogenesis in a freshwater environment [6][7]. In addition, the methylotrophic pathway is also considered to be dominant in marine sediment due to the abundance of sulfate in seawater [36][37]. Furthermore, salinity and temperature control the growth, proliferation, and extent of biodegradation of organic matter. Methanogenic activities are hindered at temperatures > ~80 °C [38]. Further, freshwater recharge can induce methanogenesis in coal beds [10][39][40][41]. Salinity may also influence the archaea, as the energy needed to remove salts from bacterial cells alleviates the methanogenic potential [5]. Hydrogenotrophic methanogenesis can tolerate higher salinity, while acetate precursor is scavenged at lower salinity conditions by methanogens [42][43]. Meanwhile, methylotrophic methanogenesis that utilizes a methylated substrate persists at a greater level of salinity than acetoclastic and even hydrogenotrophic methanogenesis [44]. Moreover, it is also observed that hydrogenotrophic methanogenesis tolerates more salt compared to the acetoclastic pathway at low temperatures (≤30 °C), while at 60 °C, both methanogenic routes become less tolerant to salt [38].

4. Secondary Microbial Methanogenesis

Secondary microbial gases may occur in the medium- to high-rank coals and may alter the primary thermogenic methane isotopic fingerprints if mixing occurs [2][11]. The secondary microbial methanogenesis may occur either by the hydrogenotrophic or acetoclastic pathway. Weathering of coal seams, atmospheric exposure, and mixing between meteoric water and coal bed formation water may introduce microbes into the coal beds, which metabolize residual kerogen and have previously produced wet gases to generate methane. In hydrogen-rich coals or petroliferous coal reservoirs, the biodegradation of liquid hydrocarbons may also generate secondary microbial gases. The carbon dioxide formed along with these gases shows ^{13}C enrichment and is, thus, isotopically heavier than primary microbial gases [45]. Low-rank coals often possess higher gas content than high-rank coals, which may further indicate a plausible influence of secondary microbial methanogenesis. The microbial communities introduced into coal beds through the aforementioned pathways may utilize the hydrocarbons and residual labile kerogen to yield methane. If this secondary microbial methane is present in considerable abundance, it may re–saturate the coal to adsorption isotherm [46]. The stable isotopic

differences between the primary and secondary microbial methane (discussed in the following sections) were documented by Milkov and Etiope [47] in their proposed gas genetic diagrams.

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