Enhanced microbial coalbed methane generation: A review of research, commercial activity, and remaining challenges

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Enhanced microbial coalbed methane generation: A review of research, commercial activity, and remaining challenges

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Abstract

Coalbed methane (CBM) makes up a significant portion of the world’s natural gas resources. The discovery that approximately 20% of natural gas is microbial in origin has led to interest in microbially enhanced CBM (MECoM), which involves stimulating microorganisms to produce additional CBM from existing production wells. This paper reviews current laboratory and field research on understanding processes and reservoir conditions which are essential for microbial CBM generation, the progress of efforts to stimulate microbial methane generation in coal beds, and key remaining knowledge gaps. Research has been primarily focused on identifying microbial communities present in areas of CBM generation and attempting to determine their function, in-situ reservoir conditions that are most favorable for microbial CBM generation, and geochemical indicators of metabolic pathways of methanogenesis (i.e., acetoclastic or hydrogenotrophic methanogenesis). Meanwhile, researchers at universities, government agencies, and companies have focused on four primary MECoM strategies: 1) microbial stimulation (i.e., addition of nutrients to stimulate native microbes); 2) microbial augmentation (i.e., addition of microbes not native to or abundant in the reservoir of interest); 3) physically increasing microbial access to coal and distribution of amendments; and 4) chemically increasing the bioavailability of coal organics. Most companies interested in MECoM have pursued microbial stimulation: Luca Technologies, Inc., successfully completed a pilot scale field test of their stimulation strategy, while two others, Ciris Energy and Next Fuel, Inc., have undertaken smaller scale field tests. Several key knowledge gaps remain that need to be addressed before MECoM strategies can be implemented commercially. Little is known about the bacterial community responsible for coal biodegradation and how these microorganisms may be stimulated to enhance microbial methanogenesis. In addition, research is needed to understand what fraction of coal is available for biodegradation, and methods need to be developed to determine the extent of in-situ coal biodegradation by MECoM processes for monitoring changes to coal quality. Questions also remain about how well field-scale pilot tests will scale to commercial production, how often amendments will need to be added to maintain new methane generation, and how well MECoM strategies transfer between coal basins with different formation water geochemistries and coal ranks. Addressing these knowledge gaps will be key in determining the feasibility and commercial viability of MECoM technology.

Keywords :

Coal
Coalbed methane (CBM)
Methanogenesis
Microbial community
Stable isotopes
Microbially enhanced coalbed methane

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1. Introduction

Coalbed methane (CBM) represents a significant portion of the world's natural gas reserves, and it has been suggested that up to 20% of the world's natural gas, including CBM, is microbial in origin (Rice and Claypool, 1981). However, drilling and maintaining microbial CBM is becoming less economical due to current, relatively low gas prices and competition from shale gas production, and due to the short life span of CBM production wells (10 years or less; Ayers, 2002; Stearns et al., 2005). Recent laboratory and field experiments have shown that not only has microbial CBM been generated in the geologic past and retained in the formation in commercial quantities, but that some sedimentary basins have active, on-going microbial methane generation (e.g., Cokar et al., 2013; Kirk et al., 2012; Martini et al., 2005; Strapoć et al., 2007; Ulrich and Bower, 2008). Because methanogenesis is an active process, it may be possible to stimulate the microbial communities that have produced CBM to generate more methane from coal biodegradation on commercially relevant timescales (i.e., years). If microbial CBM generation could be enhanced, the productive lifespans of depleted microbial CBM wells could be extended and/or new microbial methane could be generated in areas without prior history of gas production. Because existing infrastructure would be used for stimulation projects, stimulating microbial CBM generation could also reduce the environmental impact of CBM production by reducing the need to drill new wells as old wells become depleted. Enhanced microbial CBM generation could also be used to convert deep or thin, potentially unmineable coal deposits into methane, and similar strategies could be used to produce methane in gas depleted shales and from coal waste materials. The process of stimulating microorganisms to produce more methane from existing production wells is known as enhanced CBM, or microbially enhanced CBM (MECoM).

Starting about 2000, rising natural gas prices led to a rapid expansion of CBM development (drilling and production) in the United States, primarily in the San Juan, Powder River, Illinois, Gulf Coast, Black Warrior, and Appalachian basins, which is demonstrated by the increase in active production wells in the Powder River Basin (Fig. 1; www.eia.gov). Coalbed methane in the Powder River Basin (PRB) is microbial in origin, while CBM in the San Juan, Illinois, Black Warrior, Appalachian, and Gulf Coast basins is a mixture of biogenic and thermogenic gas (Strapoć et al., 2011). Development of CBM plays permitted greater access for researchers to coal formations to collect water and gas samples to study microbial CBM processes. In addition, as gas prices began to fall in summer 2008, commercial groups interested in MECoM were able to purchase wells for pilot field studies from companies that were divesting interest in CBM. Around this time, the advent and use of hydraulic

fracturing technologies opened up new petroleum and hydrocarbon reservoirs and provided the market with substantial amounts of natural gas. This has resulted in sustained low gas prices that have made it difficult for MECoM groups to continue to develop commercial technology. Shale gas wells typically cost substantially more to drill than CBM wells (several million dollars versus around half a million dollars for CBM wells, depending on depth of wells and technology used), but also produce significantly more gas per well. This means that a single shale gas well generates significantly more revenue than a CBM well. However, the process of hydraulic fracturing increases the production rate, not the ultimate supply, of hydrocarbons, and peak hydrocarbon production from hydraulic fracturing is predicted to occur around 2030, and may occur much sooner (www.eia.gov; Patzek et al., 2013). In addition, the environmental hazards associated with hydraulic fracturing are still debatable and range from ecological, water quality, and induced seismicity (Burton et al., 2014; Hallo et al., 2014; Maguire-Boyle and Barron, 2014). Increased regulation of shale gas practices could make coalbed methane production more competitive with shale gas production. Regardless of current market conditions and resources, strategies, such as MECoM, can help to fully utilize domestic energy resources.

In this paper, we review the state of scientific knowledge and major advances that have been made towards sustainable commercial MECoM technology, including what is known about coal biodegradation and methanogenesis, from both the basic research and commercial sectors. We also identify key knowledge gaps that need to be addressed to further advance MECoM technology.

Fig. 1. U.S. wellhead price of natural gas (grey, no data since December 2012; Source: US EIA, 2015) and number of active coalbed methane wells in the Powder River Basin, Wyoming (black; Source: Wyoming Oil and Gas Conservation Commission). 1 MCF is $\sim 28 \text{ m}^3$.

Fig. 2. Map showing locations where microbial production of methane from coal has been observed (for basin names and references, see Strapoć et al., 2011). Pilot tests have been performed by both Luca and Ciris in the Powder River Basin (red star). Luca has conducted tests in other basins in the United States (orange triangles). Next Fuel has conducted tests internationally (green squares), although the exact locations are unknown. All locations are approximate.

2. Natural processes and limitations on microbial methanogenesis

Since the discovery of active microbial (biogenic) gas generation in coal bed reservoirs and the development of geochemical methods to distinguish biogenic from thermogenic gas, researchers have identified coal beds around the world where microbial gas was present (Strapoć et al., 2011; Fig. 2). Widespread occurrences of microbial CBM have allowed researchers collect co-produced formation water and gas in order to investigate in situ reservoir conditions which may promote or inhibit methanogenesis, indicators of microbial methanogenesis, and metabolic pathways of coal biodegradation and methanogenesis.

2.1. Microbial pathways for coal biodegradation and community composition

Microbial conversion of coal to methane is a multi-step process that involves a consortium of bacteria and methanogenic Archaea (methanogens) (Jones et al., 2010; Strapoć et al., 2011; Fig. 3). While much of the process is poorly understood, it has been hypothesized that soluble organics (i.e., long chain fatty acids, alkanes, and low molecular weight aromatics; Orem et al., 2010) must first be released from the coal, then biodegraded by microorganisms into substrates (e.g., acetate, CO_2 and H_2 , methanol, formate) that are utilizable by methanogens prior to the onset of methanogenesis, which produces CH_4 and CO_2

(Jones et al., 2010; Fig. 3). This requires the activity of different groups of microorganisms that work together to catalyze the different steps of coal biodegradation. The solubilization and degradation of coal organic substrates can occur via aerobic or anaerobic pathways, depending on the environmental conditions, and these steps may be catalyzed by a wide variety of organisms including heterotrophic bacteria, fermenters, acetogens, syntrophs, and fungi (e.g., Beckmann et al., 2011; Fakoussa and Hofrichter, 1999; Haider et al., 2013; Jones et al., 2010; Scott et al., 1986; Silva-Stenico et al., 2007; Singh et al., 2012). In contrast, methanogenesis is carried out by microorganisms, methanogens, that are strict anaerobes (Hoehler et al., 2010; Zinder, 1993). Methanogens are found in a wide range of subsurface environments, with their distribution primarily controlled by physicochemical factors (Hoehler et al., 2010). Within coal beds, the organic-compound-degrading bacteria likely provide methanogens the necessary substrates, e.g., acetate, CO_2 and H_2 , to produce methane (Strapoć et al., 2011). The activity of methanogens is thereby limited by the availability of these substrates, and the generation of these substrates is likely limited by the rate of solubilization of coal organics, although this has not been definitively demonstrated.

Studies of microbial community composition in CBM reservoirs have identified diverse assemblages of both Bacteria and Archaea (e.g., Barnhart et al., 2013; Green et al., 2008; Klein et al., 2008; Li

Fig. 3. Steps for biodegradation of coal to methane. Figure adapted from Jones et al., 2010.

et al., 2008; Midgley et al., 2010; Penner et al., 2010; Shimizu et al., 2007; Singh et al., 2011; Strapoć et al., 2008b). DNA-based microbial community characterization studies have shown that bacterial diversity in CBM reservoirs is much higher than archaeal diversity (Barnhart et al., 2013; Penner et al., 2010). Bacterial diversity in these reservoirs tends to be dominated by organisms within the *Proteobacteria* and *Actinobacteria* phyla, with members of the *Firmicutes* often representing a minor component of the community. The *Proteobacteria* represent a vast diversity of bacterial species. However, within coal reservoirs polycyclic-aromatic-hydrocarbon (PAH)-degrading α -*Proteobacteria* and γ -*Proteobacteria*, and syntrophic δ -*Proteobacteria* have been detected and are known to be associated with methanogens (Guo et al., 2012a, 2014; Meslé et al., 2013a; Penner et al., 2010). The dominance of PAH-degrading α -*Proteobacteria* could reflect in situ physico-chemical conditions because PAHs are the main organic compound class detected in CBM produced water samples (Orem et al., 2014). *Actinobacteria* were a major component of the in situ microbial community from coal beds in China and Canada (Guo et al., 2012a, 2014; Penner et al., 2010). Many *Actinobacteria* possess the ability to degrade cellulose and hydrocarbons in aerobic environments but their role in anaerobic coal degradation has not been determined (Anderson et al., 2012; Meslé et al., 2013a). Shotgun metagenomic studies have also identified unexpectedly high proportions of genes for enzymes involved in aerobic hydrocarbon metabolism in coal and CBM produced water samples (An et al., 2013).

The association of *Actinobacteria* with aerobic hydrocarbon degradation and the detection of aerobic hydrocarbon degrading enzymes in coal beds could be the result of a greater number of studies defining enzymes involved in aerobic coal degradation (Kabe et al., 2004). It is also an indication of the need for more research investigating enzymes involved in anaerobic coal degradation (Kabe et al., 2004). Although organisms in the *Firmicutes* phylum, which include fermenters and acetogens, are often a minor component of the in situ microbial community, they may dominate in laboratory microcosm experiments (Barnhart et al., 2013; Green et al., 2008; Jones et al., 2010; Li et al., 2008; Meslé et al., 2013b; Penner et al., 2010). Fermenters and acetogens could be an important part of methanogenic community composition, but may be enriched in laboratory experiments due to the addition of supplements added to the microcosms to stimulate methane production.

Recent research has begun to use metagenomics to identify the functional composition of microbial communities associated with the process of coal biodegradation and methanogenesis (An et al., 2013; Ghosh et al., 2014). Metagenomic studies also suggest *Proteobacteria* predominate the coalbed environment and further imply biochemical capabilities to degrade coal-associated kerogen and associated solvent-extractable material (An et al., 2013; Ghosh et al., 2014). In addition, although anaerobic populations are common and expected from coal-bed environments, both pyrotag SSU rRNA gene libraries and metagenomes suggest a high proportion of sequences indicative of aerobic, hydrocarbon-degrading bacteria that include *Sphingomonads* and *Actinobacteria* (An et al., 2013). However, the gene sequences suggestive of aerobic metabolism were more prevalent in shallow CBM samples as compared to deeper CBM samples. Cultures with coal were also enriched with *Actinobacteria* compared to cultures from the same environment that did not receive coal (Barnhart et al., 2013). These results suggest an important role for the Gram-positive *Actinobacteria* in coal degradation.

As for *Archaea*, a distribution of both hydrogenotrophic and acetoclastic methanogens have been observed in pyrotag libraries. In the An et al. (2013) metagenome analysis, a distribution of sequences indicative of *Methanomicrobiales* and *Methanosarcinales* were observed. It was also noted that core samples with a mixture of sequences indicative of both aerobic and anaerobic populations had higher proportions of *Methanosarcina* sequences. The presence of *Methanosarcina* may suggest acetate-dependent methanogenesis but may also be suggestive

of intermittently oxygenated environments because these organisms can survive intermittent oxygen exposure in mixed communities. In comparison to a deep coal seam in China (Eastern Ordos Basin), the methylotrophic methanogen, *Methanobolus*, was predominant in produced water (Guo et al., 2012a, 2012b). In a separate study, enrichment cultures were compared to native coal material that was incubated down-well. The native material had a higher abundance of sequences indicative of hydrogenotrophic methanogens while stimulated enrichments contained more sequences indicative of acetoclastic methanogens (Barnhart et al., unpublished results). These results indicate that as with most other environments, the microbial populations enriched in laboratory cultures may not represent predominant populations *in situ*. Further work is needed to understand the relationship between environmental conditions, bacterial syntrophs, and potential hydrogenotrophic and/or acetoclastic methanogenesis.

Microbial community composition, function, and metabolic pathways are often distinct to a coal basin, and may even vary by location within a basin (Barnhart et al., 2013; Penner et al., 2010; Strapoć et al., 2011). For example, methanogenesis via CO₂ reduction is thought to be dominant in the Antrim Shale in the Michigan Basin (Martini et al., 1998; Waldron et al., 2007), whereas both acetoclastic and hydrogenotrophic (CO₂ reduction) methanogenesis have been detected in Powder River Basin coal beds (Barnhart et al., 2013; Flores et al., 2008; Green et al., 2008; Ulrich and Bower, 2008). In addition, pyrosequencing has shown that methylotrophic methanogenesis utilizing methanol and other methylated substrates is responsible for some microbial CBM generation in the Liulin coal beds of China (Guo et al., 2012a,b). For this reason, the ideal stimulation method for MECoM may be basin or sub-basin dependent, and nutrient treatments that are effective in one basin or area may not work in another (Mahaffey, 2012).

2.2. In situ reservoir conditions for microbial CBM generation

In situ reservoir conditions in areas of active microbial CBM generation must be understood in order to understand how changing natural conditions with MECoM projects might affect rates of methane generation. Methanogenesis occurs under anaerobic conditions (Rice and Claypool, 1981; Scott, 1999), typical of most subsurface organic-rich environments, such as coal seams, oil reservoirs, and black shales (Lovley and Chapelle, 1995). However, the matrix porosity of coals (pores typically <50 nm in diameter) is usually too small for microorganisms (typically 1000–3000 nm) to inhabit (Scott, 1999). As a result, microbial communities that degrade coal and produce methane live mainly within fractures (cleats) in the coal seams (typically 3–10 μ m wide), or at the interface of coal with overlying or underlying rock layers (Scott, 1999). This provides limited surface area for the microorganisms to interact with the coal. Increasing permeability of coal helps facilitate methane production (i.e., enhances transport of gas to the wellbore; Solano-Acosta et al., 2007), and would likely help carry injected nutrients, water, and/or microorganisms to additional coal surfaces.

Because methanogenesis only occurs in aqueous environments, injecting water may also re-wet coals that have been dewatered during methane production, allowing methanogenesis to resume. Injection of water may also help to transport nutrients and remove waste products from microorganisms (Pfeiffer et al., 2008). Nitrogen, phosphorus, and trace metals are essential nutrients for microbial generation of methane from coal, and may be limiting in methanogenic environments (Bates et al., 2011; Gilcrease and Shurr, 2007; Penner et al., 2010). Although methanogens require trace metals (e.g., Ni and Co) for enzyme function, the ideal concentration is unknown (i.e., either too little or too much may inhibit methanogenesis) (Gilcrease and Shurr, 2007; Harris et al., 2008; Ünal et al., 2012). However, the introduction of a trace metal cocktail (iron, nickel, cobalt, molybdenum, zinc, manganese, boron, and copper) in the right concentration to cultures of methanogens from CBM produced water increased rates of methanogenesis from soluble electron acceptors (acetate, methanol, and CO₂) (Ünal et al., 2012).

Recent studies have also suggested that natural groundwater recharge enhances methanogenesis by either transporting microorganisms into organic-rich reservoirs, providing moisture necessary for microbial activity, decreasing salinity, removing waste products, and/or transporting in nutrients necessary for microbial growth (Barnhart et al., 2013; Jones et al., 2013; Martini et al., 1996; McIntosh et al., 2002; Schlegel et al., 2011; Shuai et al., 2013; Strapoć et al., 2008a, 2010; Zhang et al., 2013). Reduction in salinity is key for promoting methanogenesis in basins with high salinities because these organisms prefer Cl^- concentrations <3 M (Doerfert et al., 2009; Hoehler et al., 2010; Oren, 2011; Osborn and McIntosh, 2010; Schlegel et al., 2011; Waldron et al., 2007).

Methanogenesis is frequently observed in the presence of organic-rich substrates, such as coal, although the specific fraction of organic matter utilized is not necessarily known. Microbial gas has been detected in reservoirs in source rocks with a minimum of 12–20% total organic carbon content (Martini et al., 1996; Walter et al., 2001). Laboratory studies have shown that microbial cultures produce more methane in cultures where coal is present versus cultures where it is absent (Papendick et al., 2011) and that critical microbial CBM organisms are attached to coal particles (Papendick et al., 2014). The thickness and spatial extent of organic-rich formations will also likely strongly influence gas storage capacity, as generated methane is adsorbed onto organic matter (Flores, 1998).

Several studies have also investigated how changing in-situ reservoir conditions might affect microbial methane production. Measurements of sulfate and methane concentrations in interstitial water from marine and freshwater sediments have suggested that methanogenesis and sulfate reduction are mutually exclusive due to competition for carbon substrates (Claypool and Kaplan, 1974; Hoehler et al., 2010; Kuivila et al., 1989; Lovley and Phillips, 1987; MacGregor and Keeney, 1973; Mah et al., 1977; Martens and Berner, 1974; Reeburgh and Heggie, 1977). In addition, laboratory tests on sediments in bioreactors have shown that the addition of sulfate to these reactors caused methanogenesis to cease (Abram and Nedwell, 1978; Cappenberg, 1975; Kamagata et al., 1992; Winfrey and Zeikus, 1977). Other studies have shown that, in the absence of sulfate, sulfate reducing bacteria may play a role in the breakdown of coal organics into methanogenic substrates (Bryant et al., 1977; Cappenberg, 1975; Mah et al., 1977; Raskin et al., 1996; Tasaki et al., 1993; Traore et al., 1983; Wawrik et al., 2012).

A recent study in organic-rich shale showed that aquifer conditions may shift from methanogenic to sulfate-reducing due to a pumping induced influx of sulfate-rich water from an underlying gypsum-containing carbonate formation (Kirk et al., 2012). Green et al. (2008) carried out laboratory studies that found increases in methane production when temperature was increased (from 22 °C to 38 °C), pH was lowered (from 7.4–6.4), particle size was decreased, and a solvent was added (N,N-dimethylformamide). However, another laboratory study found that methane production from coal was greatest when temperature was 35 °C, pH was 7.0–7.5, and particle size was $-60 + 15 \mu\text{m}$ (Gupta and Gupta, 2014). Laboratory studies have also found that bicarbonate did not stimulate methane production in coal slurries, but the addition of Zonyl FSN surfactant did enhance methanogenesis from coal (Papendick et al., 2011). It has also been suggested that using coal seams as CO_2 sequestration reservoirs might also increase methanogenesis (Budwill et al., 2003; Faison and Crawford, 1993; Mayumi et al., 2013; McIntosh et al., 2010; Scott, 1999; Stricker et al., 2008; Tang et al., 2012), although others have suggested that the addition of CO_2 may have no effect on methanogenesis because these systems are H_2 limited rather than CO_2 limited (Kirk, 2011; Papendick et al., 2011; Shelton et al., 2014). Research into the effect of changing reservoir conditions has been primarily laboratory based. Further laboratory and field testing is needed to determine how changing in situ conditions will affect methane generation rates at the basin scale.

2.3. Indicators of methanogenic pathway

Determining metabolic pathways is a key step in understanding MECOM processes, because understanding what microorganisms are present and producing methane is an important part of determining the best stimulation strategy. Given that the processes that convert coal to methane are difficult to observe in-situ, a major focus of basic research has been investigating tracers that can be measured in the laboratory or field as indicators of metabolic pathways of methanogenesis. Early researchers identified acetate fermentation and CO_2 reduction as the primary pathways for methanogenesis in freshwater systems, and suggested that carbon isotopes ($\delta^{13}\text{C}$) of methane and CO_2 and hydrogen isotope ($\delta^2\text{H}$) values of methane and water could be used to distinguish between these two pathways in natural gas reservoirs (Ball et al., 2005; Cheung et al., 2010; Conrad, 2005; Flores et al., 2008; McIntosh et al., 2008; Pashin et al., 2014; Strapoć et al., 2011; Wang et al., 2010; Whiticar et al., 1986; Whiticar, 1996). These isotopic indicators, especially $\delta^{13}\text{C}$ of methane and CO_2 , have subsequently been widely used in studies investigating metabolic pathways in microbial methane systems in coal and shale reservoirs (e.g., Aravena et al., 2003; Burra et al., 2014; Cheung et al., 2010; Faiz and Hendry, 2006; Gilcrease and Shurr, 2007; Golding et al., 2013; Harrison et al., 2006; Kanduć et al., 2012; Kinnon et al., 2010; Ni et al., 2013; Osborn and McIntosh, 2010; Scott et al., 1994; Smith and Pallasser, 1996; Weniger et al., 2012).

Application of isotopic indicators along with microbiology results (e.g., laboratory enrichments and DNA/RNA-based community characterization of coal samples and produced waters) in coal basins has revealed that the dominant microbial populations do not necessarily match isotopic indicators of metabolic pathways. For example, in the Gulf Coast Basin, isotopic studies have indicated that CO_2 reduction was likely the dominant pathway of methane generation in Wilcox Group coal beds (McIntosh et al., 2010; Warwick et al., 2008), yet microbiology results have suggested that methylotrophic methanogens (Doerfert et al., 2009) or acetoclastic methanogens (Jones et al., 2010) may dominate methane generation. In the Powder River Basin, isotopic studies of produced gas have suggested that hydrogenotrophic methanogenesis was the dominant pathway (Flores et al., 2008; Rice et al., 2008), while some microbial enrichments from the same area of the basin have shown a predominance of acetoclastic methanogens (Green et al., 2008).

Instead of being an indicator of metabolic pathways of methanogenesis, the relationship between carbon isotopes of CH_4 and CO_2 may more accurately describe the extent of methanogenesis (i.e., how much of the organic matter has been converted into methane versus alternative electron acceptor processes, such as sulfate reduction) (Bates et al., 2011; Brown, 2011; Hamilton et al., 2014, 2015; Vinson et al., 2012). Future work is needed to pair produced gas isotopic signatures, isotopes of acetate, and head space gas from laboratory experiments of various pathways of methanogenesis, with genomic data on microbial function to better constrain potential indicators of methanogenic pathways (e.g., Akob et al., 2014).

3. Potential MECOM methods

While there are a number of potential MECOM techniques that could be applied, Jones et al. (2013) identified four main categories of MECOM techniques: microbial stimulation, microbial augmentation, physically increasing microbial access to coal and distribution of amendments, and increasing the bioavailability of coal organics. These approaches could be used separately or in combination to achieve continued generation of microbial CBM from existing CBM installations.

3.1. Microbial stimulation

Microbial stimulation involves the addition of nutrients (such as nitrogen and phosphorus) and/or micro-nutrients (such as vitamins

and trace metals) to coal seams to stimulate methane production from microorganisms that are indigenous to the coal formations. Nutrients may be added to coal to stimulate microbial growth where microbial methane generation is active in order to increase methane production, or added to areas where there is no history of methane production in an attempt to stimulate the growth of methanogenic communities and shift redox conditions to methanogenesis (Barnhart et al., 2013; Fallgren et al., 2013b; Jones et al., 2010). Although methanogens could be stimulated to produce more methane by simply adding acetate and/or CO₂ and H₂, the primary goal of microbial stimulation is to stimulate coal-dependent methanogenesis. Therefore, it has been suggested that MECOM injections should target the colonizers and degraders of coal (i.e., “first biters”; Mahaffey, 2012; Schlegel et al., 2013) to degrade the coal and produce intermediary products that can be converted to methane by methanogens. In the context of coal-dependent methanogenesis, one of the main amendments studied has been cell extracts, e.g., yeast extract (Gilcrease and Shurr, 2007). While these types of cell extracts have high levels of nitrogenous compounds (e.g., amino acids), the extracts are a complex mixture of nitrogen, phosphorus, carbon, and other micronutrients. Therefore, it is difficult to identify the exact stimulants that impact the microbial communities. Adding nutrients seems to be the primary approach of current commercial MECOM projects (See Supplementary Table 1 for patents; see also Luca: Mahaffey, 2012; Next Fuel: Fallgren et al., 2013b; Ciris: Ciris Energy, 2013).

3.2. Microbial augmentation

Microbial augmentation is the process of adding new or additional microorganisms to coal in order to enhance or initiate microbial CBM production. Additions may consist of a single microorganism or a consortium of microorganisms (i.e., Bacteria and Archaea) with variable functions selected for in laboratory cultures. Microorganisms may be added because they are seen as more productive than the current active microorganisms in the coal beds, or because microbial CBM is not currently being produced due to a lack of microbial communities present in the coal. In addition to adding microorganisms to the coal bed, redox conditions or salinity of the coal bed may have to be adjusted to optimize the growth of native or exotic consortia. For example, methanogenesis may be limited in certain locations because of high (inhibitory) sulfate or chloride concentrations, which would need to be adjusted in conjunction with adding methanogenic populations. It may also be difficult to get permission from regulatory agencies to inject microorganisms into the subsurface, especially into aquifers, which are used for drinking water. Very few research groups have pursued the microbial augmentation approach at the field scale (see <http://www.arctech.com/micgas.html>).

3.3. Physically increasing microbial access to coal and distribution of amendments

Because microorganisms are typically too large for the pore matrix of coal (Scott, 1999) and are limited to coal fractures (cleats), one MECOM technique is to increase the surface area available for microbial colonization. This may be accomplished through grinding of coal (typically ex-situ), creating a chamber in the coal seam through burning, fracturing the coal (e.g., hydraulic fracturing), dissolving coal using underground solution to create cavities or increase porosity, or other methods (Green et al., 2008; Scott, 1999). Coal cleat area could be used to estimate the available surface area of coal (Papendick et al., 2011; Scott, 1999), allowing for an estimation of how increasing coal surface area might increase in situ methane generation rates. While this approach might be useful on its own, it is more likely to be used in conjunction with microbial stimulation or augmentation in order to promote the colonization of newly exposed coal surfaces.

3.4. Increasing the bioavailability of coal organics

The approach of increasing the bioavailability of coal organics involves chemically breaking down the coal geopolymers so that microorganisms along the pathway of generating methane from coal can use the byproducts. The biotic and abiotic process of breaking down coal into intermediates that methanogens can use to make methane is often considered a rate-limiting step in methanogenesis (Scott, 1999; Strapoć et al., 2011; Wawrik et al., 2012). Using a solvent or some other means (e.g. alcohols or esters of phosphorus: Downey, 2013; Downey and Verkade, 2012; surfactants: Papendick et al., 2011; biosurfactants: Singh and Tripathi, 2013; emulsified soybean oil: Akob et al., 2014) to increase the bioavailability of coal organics could potentially bypass this rate-limiting step. There has been some concern that this could alter the quality (i.e., BTUs; 1 BTU is ~1055 joules) of the coal (Patriot Energy Resources, 2011), although laboratory studies have reported a maximum fraction of coal converted to methane of 0.44 wt.% (Papendick et al., 2011). It is also possible that amendments could include chemicals that are harmful to the methanogens or that could contaminate drinking water resources. Chemically increasing the availability of coal organics could be accomplished through adding chemicals to dissolve the coal matrix (Scott, 1999). Laboratory studies have suggested that the addition of a strong oxidant, such as potassium permanganate or hydrogen peroxide, may help to convert coal carbon to organic acids (KMnO₄: Huang et al., 2013; H₂O₂: Jones et al., 2013). It has also been suggested that oxidation of coal during dewatering may increase the bioavailability of the coal, although laboratory studies have not clearly established whether this type of oxidation is beneficial (Gallagher et al., 2013; Jones et al., 2013).

4. Commercial approaches to MECOM

Rising natural gas prices around the year 2000 (Fig. 1) led to the formation of several companies, including Luca Technologies, Inc., Ciris Energy, and Next Fuel, Inc., whose primary objective was to stimulate MECOM production (See also: Luca Technologies: Ulrich and Bower, 2008, Next Fuel: Fallgren et al., 2013a,b; Fallgren et al., 2013b). Several other groups have some current interest in MECOM, even though it is not a primary business objective. At present, the primary focus of MECOM projects is adding nutrients to stimulate indigenous microorganisms, but all have looked into other strategies for MECOM, including bioaugmentation, and increasing microbial access to coal organics through chemical or physical processes. Most MECOM projects are focused on trying to generate additional gas in areas where microbial CBM production is already present, because these areas already have important infrastructure in place (Fig. 4). Additionally, existing methane means that MECOM projects have to generate less methane in order return treated wells to economic production levels. One exception is Next Fuel, Inc., which has moved to trying to generate new methane from areas where no microbial methane has previously been found. It should be noted that all information contained in this section is information that has been made public by the companies, and is often presented by companies in a purposefully vague manner to protect intellectual property.

4.1. Companies with primary investments in MECOM technology

4.1.1. Luca Technologies, Inc.

Luca Technologies, Inc. was founded in April 2003 as Clearflame Resources, and officially became Luca Technologies, Inc. in July 2004. In 2006, Luca began field testing its proprietary coalbed natural gas farming technology (Fig. 5). Luca owned and operated over 1,350 wells in the Powder River Basin in Wyoming, and also conducted field tests on wells owned by other parties in the Uinta Basin (Utah), San Juan Basin (New Mexico), and Black Warrior Basin (Alabama) (Fig. 2; see also <http://www.lucatechnologies.com/>). In July 2013, Luca filed

Fig. 4. Hypothetical gas (red) and water (blue) production curves for a typical coalbed methane well. The goal of microbially enhanced coalbed methane (MECoM) is to increase gas production during the decline phase, as illustrated in green. Figure adapted from Nuccio, 2000.

for bankruptcy due to financial struggles brought on, in part, by an inability to obtain a commercial scale permit for MECoM in the Powder River Basin from the Wyoming Bureau of Land Management (BLM). Transworld Technologies, Inc. has since purchased Luca's intellectual property.

Luca held at least 13 patents related to its MECoM process (Supplementary Table 1). While the patents cover methods for all of the MECoM stimulation strategies mentioned above, Luca's laboratory and field tests showed that its primary strategy was microbial stimulation through the addition of nutrients to coal seams in areas of commercial microbial CBM production. Luca's primary goal was to acquire CBM production wells near the end of their economic production life in order to stimulate production of new gas with minimal drilling of new wells (Mahaffey, 2012; Fig. 4). Luca began research by developing several amendment mixtures in the laboratory that were found to stimulate methanogenesis of native microorganisms. Luca's amendment mixtures were made up of vitamins and minerals, multi-nutrients, cell vitality enhancers, and tracers (Patriot Energy Resources, 2011; Table 1). Once the best amendment mixtures were identified from laboratory studies, Luca tested their efficacy in Powder River Basin field tests. The most productive amendment mixtures were those that produced the most gas, and these successful amendments were used for further field studies (Mahaffey, 2012).

Luca started a large scale pilot field test in 2006 on 260 wells in the Powder River Basin (named South Kitty unit). The wells had 40 or 80

acre spacing ($\sim 162,000 \text{ m}^2$ or $\sim 324,000 \text{ m}^2$) and amendments were added to wells using gravity (i.e., water level in the wellbore was increased to increase static pressure head and allow nutrients to flow down gradient into the coal seam). Amendment mixtures were added using coal formation water from other parts of the field in a recirculation process (i.e., water was pumped from one set of wells to produce gas and then used to add amendments to other wells, thereby having little to no net water removal from the formation; Fig. 6A). Treatments were added to wells for 1–2 months, and then allowed to “soak” (i.e., incubate) for an additional 1–2 months to allow the microorganisms to use added nutrients. Luca predicted it would take months or years for new gas to then be seen in treated wells (DeBruyn, 2012). Of the 260 wells treated by Luca in the South Kitty pilot test, 58 had increased methane production in response to the nutrient mixtures added to them over the course of the pilot study. In order to determine whether their amendment mixtures had been successful, Luca used the production histories of all of their pilot wells to produce an expected production curve, and then measured the gas produced above this expected baseline to determine their estimated new gas produced (Mahaffey, 2012). Gas output was increased by an average of $\sim 45 \text{ MCF}$ ($\sim 1260 \text{ m}^3$) per successfully treated well above expected production. Successfully treated wells returned to about 50% of original peak productivity (DeBruyn, 2012). After ~ 5 years, the amount of additional gas in successfully treated wells began to decrease, indicating that amendments would need to be re-injected at roughly 5-year intervals, although this could vary in different coal seams and basins (DeBruyn, 2012).

One of Luca's major objectives in adding nutrients was to shift the methanogenic community from one that was dominantly hydrogenotrophic to one that was dominantly acetoclastic. Luca did not give justification for changing the microbial community in their publications or publicly available presentations, but it was asserted that the greatest success in converting coal to methane was through acetoclastic methanogenesis in laboratory experiments. This corresponds to the findings of Jones et al. (2010), where an increase in acetoclastic *Methanosarcina* and/or *Methanosaeta* were associated with methane production from coal. Measurements of microbial populations from their pilot study indicated that Luca was successful in shifting the methanogenic community in-situ in response to the nutrient amendments. The bacterial community also changed, but not necessarily in predictable or yet understandable ways. This may be a reflection of the greater natural diversity of the bacteria compared to the Archaea (methanogens) (Mahaffey, 2012).

4.1.2. Next Fuel, Inc.

Next Fuel, Inc. was founded in 2007 and is headquartered in Sheridan, Wyoming. Next Fuel currently has operations in China and Inner Mongolia, Indonesia, and India (Fig. 2). Next Fuel has also carried out

Fig. 5. Timeline of commercial microbially enhanced coalbed methane milestones (Abbreviations used: MECoM-microbially enhanced coalbed methane; PRB-Powder River Basin, Wyoming; BLM-Bureau of Land Management).

Table 1
Composition of possible amendment ingredients by company.

Company	Named amendment constituents
Luca Technologies, Inc.	Vitamins and minerals: calcium(CaCl_2); magnesium(MgCl_2); phosphate($\text{Mg}_3(\text{PO}_4)_2$, H_3PO_4 , $\text{Ca}_3(\text{PO}_4)_2$, Na_3PO_4 , K_3PO_4 , or $\text{Na}_5\text{P}_3\text{O}_{10}$); potassium(KCl); vitamin B-12; niacin; thiamin; riboflavin; biotin; pantothenic acid; folate Multi-nutrients: casein hydrolyzates; yeast extract; brewer's yeast; soy protein; peptones Cell vitality enhancers: glycerol; weak organic acids: formic, acetic propionic, butyric, lactic, decanoic; glyceryl triacetate; ethyl lactate; polyoxyethylene Tracers: potassium iodide; sodium chloride; potassium chloride; sodium bromide; potassium bromide
Next Fuel, Inc.	Nutrients: ammonium chloride (NH_4Cl); potassium phosphate monobasic (KH_2PO_4); sodium nitrite (NaNO_2); milk; NaCl ; NH_4Cl ; KCl ; KH_2PO_4 ; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ Trace metals: nitrilotriacetic acid; $\text{MnSO}_4 \cdot \text{H}_2\text{O}$; $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$; Na_2SeO_4 ; Na_2WO_4 Vitamins: pyridoxine $\cdot \text{HCl}$; thiamine $\cdot \text{HCl}$; riboflavin; calcium pantothenate; thioctic acid; p-aminobenzoic acid; nicotinic acid; vitamin B12; mercaptoethanesulfonic acid (coenzyme M); biotin; folic acid
Ciris Energy	Amendments: oxoacid ester of phosphorus; thioacid ester of phosphorus and/or hydrogen; carboxylic acids; esters of carboxylic acids; salts of carboxylic acids; oxoacids of phosphorus; salts of oxoacids of phosphorus; vitamins; minerals; mineral salts; metals; yeast extracts
Synthetic Genomics	Amendments: yeast extract; NH_4Cl ; NaNO_3 ; K_2HPO_4 ; Coenzyme M; PO_4 ; Vitamin mix minus phosphate; Trace metals; O_2 ; H_2 ; Phosphorus compounds; Lactic acid; Mineral amendments (such as chloride, ammonium, phosphate, sodium, potassium, magnesium and calcium); Metal amendments (such as Mn, Fe, Co, Zn, Cu, Ni, Se, W, or Mo); Vitamin amendments
ExxonMobil	Major nutrients containing nitrogen and phosphorus: NaNO_3 ; KNO_3 ; NH_4NO_3 ; Na_2HPO_4 ; K_2HPO_4 ; NH_4Cl Vitamins: folic acid; ascorbic acid; riboflavin Trace elements: B; Zn; Cu; Co; Mg; Mn; Fe; Mo; W; Ni; Se Buffers for environmental controls Catalysts, including enzymes Natural and artificial electron acceptors: SO_4^{2-} ; NO_3^- ; Fe^{3+} ; humic acid; mineral oxides; quinone compounds; CO_2 ; O_2

tests in the Powder River Basin in Wyoming, but does not currently appear to be testing stimulation techniques there (<http://www.next-fuel.com/>; Next Fuel Quarterly Report, 2013).

A patent search does not bring up any granted patents belonging to Next Fuel, but does show two recent patent applications. The most

pertinent application to MECOM is a system for introducing nutrients to a coal seam (Jin and Craig, 2012), although the nutrients to be used are not listed. Injection of nutrient-rich fluid may be accomplished using gravity, similar to Luca's approach, or through a series of pumping and injection wells, similar to Ciris Energy's approach. Next Fuel appears to be focused solely on microbial stimulation as an MECOM strategy, with its primary targets being lignite coal seams in which there is no past history of microbial methane production (Next Fuel Quarterly Report, 2013).

Next Fuel's strategy of targeting non-productive lignites is justified by lab experiments showing that coal with no prior history of commercial microbial methane production could be used to generate methane when nutrients are added (Fallgren et al., 2013b; see also Jones et al., 2008, 2010). These experiments were performed on coal from three regions of the world, and while all samples produced measureable methane, some samples were more productive than others (Fallgren et al., 2013b). It is important to note that their process does not involve bioaugmentation; rather, microorganisms that are apparently already present in coal, but relatively inactive, are stimulated to convert coal to methane by the addition of nutrients (Fallgren et al., 2013b). The nutrient mixture is not publicly available, but is reported to have no carbonaceous constituents and to include basic chemical macronutrients (e.g., ammonium and phosphate) and micronutrients (e.g., vitamin mix) (Fallgren et al., 2013b). Amendments are said to be similar to those added in Green et al. (2008) (Minerals: NaCl ; NH_4Cl ; KCl ; KH_2PO_4 ; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Trace metals: nitrilotriacetic acid; $\text{MnSO}_4 \cdot \text{H}_2\text{O}$; $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$; Na_2SeO_4 ; Na_2WO_4 . Vitamins: pyridoxine $\cdot \text{HCl}$; thiamine $\cdot \text{HCl}$; riboflavin; calcium pantothenate; thioctic acid; p-aminobenzoic acid; nicotinic acid; vitamin B12; mercaptoethanesulfonic acid (coenzyme M); biotin; folic acid.) and Jin (2007) (several different microcosm experiments, with various mixtures of ammonium chloride, potassium phosphate monobasic, sodium nitrite and milk used as stimulants) (Table 1).

Next Fuel is currently performing nutrient injections in 16 wells in Indonesia, and has licensed MECOM technology to other companies for use in China (Future Fuel Limited) and India (unspecified). Injections have not commenced in India, and injections in Indonesia and China have not yet produced commercial volumes of gas (defined in the license agreement as 2 million m^3 of gas per 40,000 m^2 of gas producing material of a specified thickness) (Next Fuel Quarterly Report, 2013). Next Fuel recently sold licensing rights to their technology in China,

Fig. 6. Schematic diagrams of Luca Technologies' approach (A) to Microbially Enhanced Coalbed Methane (MECOM) versus Ciris Energy's approach (B).

and currently has no plans for MECOM projects in areas where it controls the license for its technology (Next Fuel Quarterly Report, 2014).

In addition to commercial MECOM technology, Next Fuel has published a paper from a laboratory study looking at microbial methane production related to coal rank (Fallgren et al., 2013a). This study showed higher rates of microbial methane production from coals of higher rank. This result is contrary to all other studies on microbial methane production and coal maturity (Strapoć et al., 2011), and seems contrary to Next Fuel's interest in targeting low-rank lignites for its stimulation procedure.

4.1.3. *Ciris energy*

Ciris Energy was founded in 2007 and is headquartered in Centennial, Colorado. Ciris has projects in Australia and the Powder River Basin in Wyoming. Ciris began a pilot scale field test, known as the Antelope Project, in fall 2012 in the Powder River Basin (Fig. 2). Ciris' website also indicates that it has commercial projects in Australia (see <http://cirisenergy.com>).

Ciris holds at least five granted patents, with several other patent applications appearing in the public record. As with Luca, Ciris' patents and applications cover multiple potential MECOM stimulation strategies (Downey, 2013; Downey and Verkade, 2012). Ciris' process seems to differ from Luca's in that fluid is continuously circulated under pressure through the coal seam. Ciris' pilot test in the Powder River Basin shows that it is primarily focused on microbial stimulation through the addition of nutrients, while also possibly increasing microbial access to coal by controlling reservoir pressure (i.e., fluid is injected at pressure slightly higher than reservoir pressures, which may increase the size of fractures and cleats) (Ciris Energy, 2013; Downey and Verkade, 2012).

Ciris' MECOM approach introduces nutrients to the coal bed through a continuous-flow injection process. Nutrients are injected into the coal seam with water through an injection well under pressure, and the same amount of water is removed from the coal seam by production wells to continuously supply microorganisms with nutrients. This process circulates 1000–2000 barrels of water per day through the coal seam. The pilot project uses 4 injection wells surrounded by 13 production wells with 10 acre (~40,500 m²) spacing (Ciris Energy, 2013; Downey and Verkade, 2012; Fig. 6B). All of Ciris' wells are on private property, and were drilled as part of the Antelope Project. As of December 2013, no additional gas had been produced from Ciris' pilot injections, although likely not enough time had passed to determine whether or not the injections were successful. Tracer tests performed by Ciris have indicated that injected nutrients are being consumed (Ciris Energy, 2013). As of July, 2014, Ciris had been awarded another 10 year permit to continue its MECOM operation in Wyoming (see press release at www.cirisenergy.com).

The exact composition of the nutrient mixture that Ciris uses has been kept confidential. Patents mention that amendment mixtures may contain one or more of the following: oxoacid ester of phosphorus, thioacid ester of phosphorus and/or hydrogen, carboxylic acids, esters of carboxylic acids, salts of carboxylic acids, oxoacids of phosphorus, salts of oxoacids of phosphorus, vitamins, minerals, mineral salts, metals, and yeast extracts (Downey, 2013; Table 1). Esters would likely be used as solvents to break down coal, while other ingredients are likely used for microbial stimulation.

4.2. Other companies with minor interest in MECOM

4.2.1. *Arctech*

Arctech was founded in 1988 and is based in Chantilly, Virginia. Arctech has projects that provide products to the agricultural, energy, and environmental market sectors. Arctech produces a variety of products from organic materials, consisting of fertilizers and products used for remediation of waste. These products are manufactured at a plant in South Boston,

Virginia. Arctech holds patents for an in-situ and/or ex-situ MECOM process it calls MicGAS technology, although it is unclear if it is currently producing any methane utilizing this technology (<http://www.arctech.com/micgas.html>). Arctech has also partnered with Verso Energy and proposed a pilot study in Gippsland, Australia. This pilot study would convert coal to acetate in situ, then bring the acetate to the surface for conversion to methane (<http://www.versoenergy.com/>).

Arctech's MicGAS technology utilizes microorganisms from both tree-eating and humus-eating termites. These microorganisms are adapted to effectively convert coal to methane in a step wise process in which a culture of microorganisms is grown in increasing amounts of coal substrate (Srivastava and Walia, 1997). The process of converting coal to methane involves first converting coal to volatile organic compounds, followed by exposing these volatile organic compounds to microorganisms, which are naturally adapted in the laboratory, to convert the compounds to methane (Srivastava and Walia, 1997). Leftover coal is then converted to humic matter for other products (<http://www.arctech.com/micgas.html>). Arctech claims that the process can be done in-situ, but it is unclear whether any tests have been conducted to verify this claim. One patent (Srivastava and Walia, 1997) mentions that coal is ideally crushed and mixed with water to form a slurry, suggesting an ex-situ process.

4.2.2. *Synthetic Genomics, Inc.*

Synthetic Genomics, Inc. was founded in 2005 and is headquartered in La Jolla, California. In June 2007, Synthetic Genomics partnered with BP to investigate microbially enhanced conversion of subsurface hydrocarbons. Synthetic Genomics appears to be primarily responsible for laboratory studies, with BP likely handling any field-scale testing of technology that is developed. To date, it does not appear that any field tests have taken place (<http://www.syntheticgenomics.com>).

Synthetic Genomics has two patents and two published patent applications related to MECOM. The first patent (Toledo et al., 2011) describes using microbial nucleic acid sequencing to determine gene products that are enzymes in a variety of pathways involved in the conversion of hydrocarbons to methane. This can then be used to determine stimulants, which can enhance methane production from hydrocarbon deposits, such as coal. The other published patent (Toledo et al., 2013) is an update of this material. One of the patent applications (Venter et al., 2010) is for a device for sorting cells in anaerobic environments which could potentially be used to sort cells for enhanced methane production from coal beds. The other patent application (Clement et al., 2012) discusses adding stimulants to enhance CBM production either in-situ or ex-situ. The nutrients listed in the patent are yeast extract, sulfur compounds (e.g., thiosulfate, sodium thiosulfate, potassium thiosulfate, sulfuric acid, disulfuric acid, peroxymonosulfuric acid, peroxydisulfuric acid, dithionic acid, thiosulfuric acid, disulfurous acid, sulfurous acid, dithionous acid or polythionous acid), NH₄Cl, KCl, vanadium and vanadium compounds (VCl₃, VCl₂, VCl), Na₂SO₃, MnCl₂, Na₂MoO₄, FeCl₃ or Na₂SO₄. The preferred stimulant is vanadium or vanadium compounds, sulfur, thiosulfate or sodium thiosulfate.

4.2.3. *ExxonMobil*

ExxonMobil holds one patent that is potentially related to MECOM. Its patent (Converse et al., 2003) describes stimulating microorganisms in underground hydrocarbon bearing formations to produce methane from hydrocarbons left behind after traditional production techniques have been completed. ExxonMobil proposes doing this by controlling chemistry, salinity, temperature and pressure, with the possibility of adding nutrients to enhance production. Nutrients included in ExxonMobil's patent are major nutrients containing nitrogen and phosphorus, vitamins, trace elements, buffers for environmental controls, catalysts, including enzymes, and both natural and artificial electron acceptors (Table 1). Once again, many of these nutrients are similar to those listed by other companies, although many of the electron acceptors are not listed in any other patents. ExxonMobil's

process is mainly designed for use in recovery of methane from depleted oil reservoirs, although the processes may also be used for microbial stimulation in coal beds. ExxonMobil is also primarily concerned with altering reservoir environmental conditions, which is not the primary focus of other MECoM projects. It is unclear to what, if any, extent ExxonMobil has utilized the technology described in the patent.

4.3. Non-technological obstacles to commercial MECoM implementation

In addition to scientific considerations relating to MECoM approaches, MECoM projects face other obstacles that ultimately play a major role in determining their commercial viability, such as implementation costs, natural gas prices, and the regulatory environment of the specific field/basin areas. The viability of stimulation methods is inextricably tied to the cost of implementation and price of natural gas. Most methods of stimulation likely fall in an area where they are feasible only if the price of gas is favorable and the infrastructure exists (e.g., existing CBM production wells and pipelines). After decades of somewhat stable prices, the wellhead price of natural gas increased significantly beginning in the year 2000, but then experienced a sharp decline in recent years (Fig. 1). Where the price of natural gas settles in the future is likely to determine how viable certain MECoM methods are. Much of the recent drop in North American gas prices is related to the introduction of significant amounts of shale gas to the market. The price of natural gas in the future will depend on how much of this shale gas continues to come to the market, along with potential gas from other technologies that may not have been developed yet. Depending on the approach used, MECoM could be relatively inexpensive, especially in areas where existing infrastructure can be utilized (e.g., Powder River Basin), when production water is recirculated, and when injected nutrient amendments are comprised of readily available ingredients.

The regulatory environment also plays a strong factor in whether or not a MECoM strategy can be implemented. For instance, as Luca Technologies prepared to transition from a field scale pilot test to commercial scale production, it was unable to implement its process due to U.S. BLM concerns about the impact of its process on the coal resource (Patriot Energy Resources, 2011). Any effective MECoM technology must be able to meet the demands of regulators. In addition, in an area like the Powder River Basin, where MECoM targets are shallow, near surface coal mines, and in areas that may be used for drinking water, it would have to be shown that MECoM processes are not harming drinking water supplies or significantly degrading coal quality. It is also important to consider that Luca and Ciris have been able to claim that the nutrients being injected are all food quality. Other MECoM methods, such as injecting microorganisms or solvents, are unlikely to be able to make a similar claim and may therefore face stricter regulations than nutrient stimulation (Supplementary Table 1).

5. Remaining knowledge gaps

While MECoM companies and basic research groups have all made significant progress in understanding the process of microbial CBM generation and moving MECoM technology toward commercial implementation, there are still several significant knowledge gaps remaining (Fig. 7). For example, key questions remain about the mechanisms of coal biodegradation and methanogenic processes. Little is understood regarding microbial processes upstream of methanogenesis, especially what microorganisms are responsible for breaking down the coal, what fraction of the coal is most susceptible to microbial degradation, and how this process might be stimulated, including making less labile coal fractions more bioavailable. Studies are needed to determine the function of microorganisms found in association with methanogens in CBM reservoirs. In addition, methods need to be developed for

Proposed Questions to be Addressed by Future Research

Methanogenic process knowledge gaps

- What bacterial species are the most important for coal biodegradation and what is their function? What are the best methods for stimulating the bacterial community to help facilitate the breakdown of coal to products that methanogens can use to make methane?
- What fraction of the coal is bioavailable? What constituents of the coal are the most biodegradable now, and how might the other, less labile coal constituents be accessed?
- Is coal being significantly biodegraded by stimulation processes, and if so, to what extent? What are the best methods for measuring if coal is being biodegraded by MECoM processes?

Gaps regarding transfer of technology and commercial viability

- What are the best methods for distributing water and nutrients/amendments into the coal seams to access the greatest surface area?
- How will stimulation technology be affected as pilot tests are scaled up to commercial production scale?
- What is the optimum frequency/duration of addition of nutrient amendments and recirculation of water to coal seams to produce the most gas?
- What methods can be used to verify new microbial methane generation as a result of stimulation? Who owns the methane generated (i.e., coal rights versus oil and gas rights)?
- How transferable are MECoM approaches to other coal basins with different microbial populations and environmental conditions?
- What will the permitting environment be like in other basins? In the future?

Fig. 7. Proposed questions to be addressed by future research.

quantifying if and how much coal is biodegraded by MECoM processes. It will be important to see if proxies can be developed for biodegradation (e.g., the presence of specific organic constituents in coal waters) that are more cost effective to measure than extracting intact cores. Among other things, this would help to address regulatory concerns about stimulation processes lowering coal BTU content (Patriot Energy Resources, 2011). It will also need to be determined who owns the methane generated from MECoM processes (i.e., is it a coal right or an oil and gas right).

Further research also should focus on issues related to implementation and sustainability of MECoM processes. All of the projects examined have different methods of delivering nutrient amendments to microorganisms in coal seams. Companies must determine which amendments are the most effective, and find ways to efficiently deliver a sufficient amount of nutrients to the greatest area of coal possible. More work needs to be done to determine how effective each method is and what may be the best method of nutrient delivery. It will also be important to find a way to directly measure the amount of new methane produced by MECoM processes versus microbial methane that would have been produced without amendments. Luca used an expected production curve to show generation of new gas, but this may not be the best or most accurate method of measuring if and how much new methane has been produced, as it relies on estimation of how much gas a well would have produced without stimulation. Using tracers (e.g., stable isotopes) to label injected nutrients could help prove production of new gas as a result of nutrient injections. Pilot tests have also only been conducted in a limited number of coal basins, and the heterogeneous nature of coal seams makes it difficult to tell how well stimulation processes will work in different parts of coal basins and in different coal basins. While Luca was able to carry out a pilot test over several years, this represented only one nutrient injection cycle, so it remains to be seen how often nutrients need to be added to coal seams to sustain economic methane production, and if nutrient injections are as effective after the first injection period. Pilot tests will also need to be scaled up to commercial scales to test the viability and sustainability of MECoM as a commercial process.

6. Conclusions

Basic and commercial research into MECoM technology has significantly increased our knowledge about the processes that lead to microbial generation of methane from coal. Basic research has provided insight into locations and environments where microbial CBM accumulations are present, what microorganisms may be producing methane in coal seams, what metabolic pathways may be utilized for producing methane, what hydrogeochemical indicators can tell us about methanogenic processes, and what conditions are most favorable for methane generation. Commercial research has shown that microbial methane production can be stimulated and has provided a template for moving laboratory experiments to the field.

The amendment package used by Luca Technologies has proven to be effective in shifting the in situ coal methanogenic community to one dominated by acetoclastic methanogens, which Luca reported led to increased methane production rates in laboratory and field experiments. Field tests conducted by Luca Technologies produced new CBM in areas where methane production from existing wells had slowed. Luca's tests were limited in scale, since it was unable to implement larger-scale studies (i.e., commercial-scale) due to regulatory and economic hurdles. There was also little research completed on what effect Luca's amendments, or the amendment mixtures of other projects, had on the composition and function of microbial communities which provide substrates for methanogens. It is possible that the processes which provide substrates for methanogens could be further stimulated as well, leading to even more effective microbial methane generation from coal. Research into rate limiting steps and stimulation of these processes could significantly improve MECoM technology. Overcoming

these obstacles and increasing the scale of successful pilot tests is a crucial next step in validating and implementing MECoM technology.

Several key questions about methanogenic processes and the implementation of MECoM technology need to be addressed to demonstrate the viability of MECoM. In order for MECoM processes to be effective on a commercial scale, an understanding of what specific microbial communities are present and how they work in consortium to degrade coal must be developed. Once the microbial processes are understood and stimulation techniques are developed, research will need to focus on determining how well MECoM injections work over time and in different basins so that the most effective and economical MECoM processes can be implemented.

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Appendix A. Supplementary data

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