



## Improving coal bioavailability for biogenic methane production via hydrogen peroxide oxidation



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### ABSTRACT

Hydrogen peroxide solution was used to pretreat coal samples for the purpose of improving bioavailability for methanogenesis. Crushed coals of subbituminous (PEN9-003) and medium-volatile-bituminous (C.D.) ranks were oxidized with three different dosages of H<sub>2</sub>O<sub>2</sub> solution over four time periods (1, 4, 7, and 30 days) in the presence of UV light. Bioassays were set up using the oxidation products as the sole carbon substrates for biomethane production. To characterize the change in coal composition after oxidation, concentrations of volatile fatty acids (VFAs) and total organic carbon (TOC) in the filtered liquid sample of the pretreatment reactor were measured. The solid phase was dried and solvent-extracted with a mixture of dichloromethane and methanol. Compounds in the organic extract were analyzed using a GC–MS. H<sub>2</sub>O<sub>2</sub> oxidation has managed to boost the biomethane yield in the subbituminous PEN9-003 coal by a maximum 10 times to 223.7 μmol/g. Production of methane was found to increase exponentially with the concentration of H<sub>2</sub>O<sub>2</sub> relative to coal, but less significantly with pretreatment length. In contrast, the bituminous C.D. coal was barely affected by pretreatment. In addition, oxidation has considerably enhanced solubilization of PEN9-003 coal in water, with contents of VFAs and dissolved TOC surged by up to 28.2 and 22.3 times. The pretreatment has also increased the abundance of solvent-extractable matter in PEN9-003 coal. Oxygen-containing compounds, including aliphatic carboxylic acids, alcohols, ethers, ketones, and oxygenated monocyclic aliphatic and aromatic hydrocarbons were the most affected. The enrichment was due both to formation of new chemical species and an increase in the abundance of existing compounds. In comparison, oxidation of C.D. coal failed to generate any new organic species, nor did it increase the content of dissolved TOC. Biodegradation has resulted in depletion of all dissolved organic carbon, suggesting water-soluble compounds are highly bioavailable. Bioconversion of solvent-extractable matter in PEN9-003 has been improved by a maximum 29.5% upon pretreatment, while that of C.D. coal was lowered. Molecules with heterogeneous moieties, especially those that have been enriched after pretreatment demonstrated the highest bioavailability. Thermal maturation of coal from subbituminous to medium-volatile bituminous rank has been associated with a decrease in extractable matter contents, liptinite proportion, H/C ratio, elemental oxygen, heterogeneous moieties, as well as physical accessibility to microorganisms. They are thought to be responsible for the poor bioavailability and amenability of C.D. coal to H<sub>2</sub>O<sub>2</sub> oxidation. Application of the pretreatment is only likely to be ex-situ, in which coal beneficiation waste may be used as a feed to bioreactors. The study offers a good basis for further process optimization and upscaling.

### 1. Introduction

As a most common type of fuel, coal is an important resource in meeting our demand for energy, contributing to about 70% of total electricity generation in Australia and 40% worldwide (Saunders, 2015). However, direct combustion of thermal coals may cause environmental issues due to emission of toxic gases such as sulfur dioxide and nitrogen oxides, heavy metals such as mercury, and particulates. A possible strategy of mitigation is to transform coal to a cleaner form of

fuel as a way of balancing the energy need and environmental stress. Natural gas (mainly methane) from coal seams is such a type of coal derivative that offers high calorific value and is clean upon burning as it releases only water and carbon dioxide, with lower emission of the latter than for equivalent energy from burning coal and petroleum. Microbially-enhanced production of secondary natural gas (mainly methane) from coal has gathered tremendous interest in the past decades, and has been shown to be a primary source of coalbed methane from Walloon coals in Surat Basin, Queensland (Draper and Boreham,

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2006; Hamilton et al., 2014). Numerous studies have proved the feasibility of the process through laboratory enhancement, such as nutrient stimulation, and microbial augmentation (through addition of inocula) on crushed coals with higher physical accessibility (Chen et al., 2017; Colosimo et al., 2016; Fallgren et al., 2013a; Fallgren et al., 2013b; Green et al., 2008; Harris et al., 2008; Jones et al., 2013; Jones et al., 2010; Jones et al., 2008; Papendick et al., 2011; Park and Liang, 2016; Ritter et al., 2015; Robbins et al., 2016; Susilawati et al., 2013). However, the majority of methane yields reported in the research area are low, ranging from  $< 5 \mu\text{mol/g}$  (Fallgren et al., 2013a; Formolo et al., 2008; Jones et al., 2008) up to about  $140 \mu\text{mol/g}$  (equivalent to  $3.43 \text{ m}^3/\text{t}$ , Green et al., 2008). In most experiments, methane production plateaued within 1 year with a final conversion (of coal to methane) below 1%. This elicits the needs for a potential pretreatment method that could effectively increase coal bioavailability to make the process more commercially viable.

A typical strategy is to use chemicals that react with coal, breaking down cross-linked structures, converting large molecules to smaller fragments, and modifying functional groups in a way that increases bioavailability. Oxidizing agents such as nitric acid, potassium permanganate, chromic acid, and hydrogen peroxide have been commonly used for this purpose (Hayatsu et al., 1981; Huang et al., 2013a; Huang et al., 2013b; Jones et al., 2013). They are capable of introducing heteroatoms to coal hydrocarbon, forming activation sites that lower the bond dissociation energy of neighboring chemical bonds, thereby facilitating microbial cleavage (Oyeyemi et al., 2015; Oyeyemi et al., 2014a; Oyeyemi et al., 2014b). Low rank coals treated with  $\text{H}_2\text{O}_2$  show increased content of water-soluble matter, particularly low-molecular-weight fatty acids and alcohols (Mae et al., 2001; Miura et al., 1996; Pietrzak and Wachowska, 2003; Yu et al., 2014). Similar compounds have also been reported in potassium permanganate oxidized lignites, such as  $\text{C}_4 - \text{C}_{18}$  branched and unbranched carboxylic acid, dicarboxylic acid, and tricarboxylic acid (Hayatsu et al., 1981), which have demonstrated high bioavailability to methanogenic consortia (Chen et al., 2017; Jones et al., 2013; Jones et al., 2010; Orem et al., 2010). The benefit of chemical oxidation on coal bioavailability has also been directly evidenced by Huang et al. (2013a), Huang et al. (2013b), and Jones et al. (2013), who observed significant increase in biogas production after oxidation.

A common challenge with chemical pretreatment is, however, the need to condition the pretreatment product in order to make it amenable to anaerobes. This includes removal of residual oxidants, adjustment of pH and salinity, and detoxification of foreign ions such as  $\text{Mn}^{2+}$  if potassium permanganate is used (Altug and Balkis, 2009; Cheung et al., 1982; Gadd and Griffiths, 1977), resulting in extra cost and complexity in terms of application. On this ground, hydrogen peroxide is deemed to be a more suitable reagent since it has mild effect on pH and salinity without introducing foreign chemical species (except for the hydroxyl free radical, which is reacted away). Reaction with hydrogen peroxide takes place in two steps, starting with formation of hydroxyl free radicals in a UV-catalyzed chain reaction, followed by interaction between the radicals and coal moieties. The reduction potential ( $E^0$ ) of hydroxyl free radical is  $2.02 \text{ V}$ , higher than that of permanganate  $1.507 \text{ V}$  (when converted to  $\text{Mn}^{2+}$ ) and nitrate  $0.957 \text{ V}$  (when converted to  $\text{NO}$ ) (Haynes, 2017), suggesting a strong capacity of the oxidant.

Application of chemical pretreatment is, however, only feasible for an ex-situ process as injection of oxidants underground may contaminate local aquifers, and pose safety hazards when oxidants interact with combustible gases in coal seam. It is also hard to implement a stable supply of UV light deep underground if  $\text{H}_2\text{O}_2$  is used. For an ex-situ process, coal beneficiation waste or surface coal may be used as a source of substrate having low or zero mining cost. Zheng et al. (2017) reported a compatible level of biomethane production from a Jameson Cell reject with that of raw coals, confirming the biomethane potential of coal wastes.

Although earlier studies have demonstrated the feasibility of improving coal bioavailability by  $\text{H}_2\text{O}_2$  oxidation (Huang et al., 2013a; Jones et al., 2013), knowledge on how the treatment alters coal composition, especially within the hydrophobic fraction, and how the oxidation products contribute to bioavailability is still preliminary and lacking. This study aims to provide a more comprehensive picture of coal compounds formed after hydrogen peroxide oxidation and their biodegradability when being used as substrates for methanogenesis. The study engages the following objectives: 1) investigate the effect of peroxide oxidation on biomethane yield; 2) characterize the change in composition of coal solvent-extractable matter upon oxidation; 3) characterize the bioavailability of oxidation products; and 4) investigate the effect of coal rank on the amenability to  $\text{H}_2\text{O}_2$  oxidation and biodegradation.

## 2. Method

### 2.1. Sample information

Two coal samples of different ranks were investigated in this study. The subbituminous Walloon coal: PEN9-003 was a coal core sample collected from the Juandah Coal Measure in the central-north Surat Basin, Queensland, a spot with active microbial production of coalbed methane (Draper and Boreham, 2006; Hamilton et al., 2012; Hamilton et al., 2014). Previous studies have found the coal has a vitrinite reflectance  $R_r\% = 0.45$ , and is rich in liptinite (32.7% by volume on as-received basis, a.r.) and perhydrous vitrinite (48.8% vol. a.r.), a characteristic of high bioavailability (Chen et al., 2017). The remainder of the coal is composed of 16.2% vol. (a.r.) mineral matter and 2.4% vol. (a.r.) inertinite. The higher rank bituminous coal was taken from the Carborough Downs underground mine (abbreviated as C.D.), Rangal Coal Measures, Bowen Basin, Queensland. The sample is richer in vitrinite (55.2% vol. a.r.) and inertinite (39.6% vol. a.r.) but has a low liptinite content (4% vol. a.r.) and little mineral matter (1.2% vol. a.r.). The vitrinite reflectance of the C.D. coal is  $R_r\% = 1.13\%$ . After being transported to the laboratory, the coals were crushed anoxically in an anaerobic chamber into fine grains. Experiments in this study were carried out on the size portion that passed  $300 \mu\text{m}$  sieve.

To prepare samples for coal characterization, the coal powder was passed through a metal splitter that evenly divides the material into two subsets of homogeneous composition. The same process was repeated on one subset (randomly chosen) from each generation until roughly 20 g of sample was achieved. The samples were then sealed in a bag and sent to the ALS Laboratory, Brisbane, Australia for proximate and ultimate analysis (Table 2), following Australian Standards AS 1038.3 (for proximate composition, StandardsAustralia, 2000), AS 1038.6.4 (for carbon, hydrogen and nitrogen, StandardsAustralia, 2005) and AS 1038.6.3.3 (for total sulfur, StandardsAustralia, 1997).

### 2.2. Coal oxidation

Hydrogen peroxide has been chosen as the pretreatment reagent for the reasons that 1) it is potent oxidant and can form free radicals in the presence of UV light; 2) it does not introduce foreign ions that might be inhibitory to microorganisms; and 3) it has minor effect on the salinity and pH of culture solution. The standard concentration of  $\text{H}_2\text{O}_2$  used was calculated assuming complete conversion from coal to acetate. To do so, the formula of the organic part of coal was firstly approximated using the elemental composition shown in Table 2. This gives a formula for PEN9-003:  $\text{CH}_{0.973}\text{O}_{0.139}\text{N}_{0.013}\text{S}_{0.00213}$ , and that for C.D.:  $\text{CH}_{0.664}\text{O}_{0.0552}\text{N}_{0.0153}\text{S}_{0.0019}$ . Since the contribution of N and S is relatively insignificant compared to the rest, the formula can be further simplified to:

- 1) PEN9-003:  $\text{CH}_{0.973}\text{O}_{0.139}$
- 2) C.D.:  $\text{CH}_{0.664}\text{O}_{0.0552}$

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