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Evaluation of methane release from coals from the San Juan basin and Powder River basin

Ji Zhang[a], Catherine Yip[b], Chunjie Xia[a], Yanna Liang[c,*]

[a] Department of Civil and Environmental Engineering, 1230 Lincoln Drive, Southern Illinois University Carbondale, Carbondale, IL 62901, USA
[b] Department of Mechanical Engineering, 235 Hopeman Building, University of Rochester, Rochester, NY 14627, USA
[c] Department of Environmental and Sustainable Engineering, 1400 Washington Ave, State University of New York at Albany, Albany, NY 12222, USA

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ABSTRACT

To enhance methane release from bituminous coal in the Illinois basin, a nutrient recipe, an adapted microbial community, and optimal biogasification condition leading to maximum methane release have been developed. To evaluate whether the developed strategy is applicable to coals from other geological settings, coal samples from the San Juan (SJ) basin and Powder River (PR) basin were investigated. This study showed that without the addition of ethanol, more methane was released from PR coal than from SJ coal. Ethanol increased and inhibited methane production from SJ and PR coal, respectively. The dominant degradation products in all microcosms were similar even though the concentrations of identified compounds were dependent on the coal samples used. The addition of 2-bromoethanesulfonate completely arrested methanogenesis and resulted in higher content of total organic carbon in fermentation broth than those without. Comparing the coals before and after biotreatment, the elemental compositions did not change much even though significant mass losses were found for both coals. This study demonstrated that a given microbial community can be used for different ranks of coals. To maximize methane release, nutrient recipes may be shared for coals with the same rank, but not for coals having different compositions.

1. Introduction

Coal is one of the largest energy resources in the United States [1]. For the purpose of utilizing this natural resource in an environmentally responsible way, biogasification has been intensively studied in recent years. This approach works by converting coal to methane through microbial activity. Even though coal has been considered a recalcitrant solid substrate, microbial communities able to degrade coal have been reported from around the world. Based on studies far from countless [2–6 5,7–11], there is no doubt that coal biogasification is a technically feasible approach for both in situ and ex situ scenarios [3].

To make this technique economically viable, a strategy termed biostimulation has been adopted broadly. This strategy seeks to stimulate microbial activities toward coal depolymerization and conversion by providing suitable nutrient solutions. Specific for the Illinois (IL) basin, we have systematically developed a nutrient recipe that brought dramatic increase of methane yield from bituminous coal [6]. The key ingredient in the recipe is ethanol at a certain concentration.

Based on our extensive studies on coal biogasification, we hypothesized that the microbial community and nutrient recipe for stimulating methane yield from the IL coal can also be applied to coals with similar properties. To test this hypothesis, we designed the study reported here. In this investigation, we compared methane yield from coals from the San Juan (SJ) basin and the Powder River (PR) basin under various conditions: with or without ethanol, with or without a methanogen inhibitor, 2-bromoethanesulfonate (BES). Besides methane yield, we also profiled and quantified coal degradation products, measured total organic carbon in fermentation broth and conducted mass balances for the studied coal samples.

2. Materials and methods

2.1. Coal, sand and graphite samples

Coal samples investigated in this study were collected from: (1) the southwest portion of the San Juan (SJ) basin located primarily in northwestern New Mexico and southwestern Colorado [12], and (2) west central Wyoming in the Powder River (PR) basin. These two samples were referred to as the SJ coal and PR coal, respectively in this study. For both coals, blocks of freshly cut coal were picked from the

* Corresponding author.
E-mail address: yliang3@albany.edu (Y. Liang).

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Table 1
Elemental composition of coals before and after biogasification.

Parameter	PR coal		SJ coal	
	Before treatment	After treatment	Before treatment	After treatment
Nitrogen	1.09 ± 0.04	1.36 ± 0.03	1.36 ± 0.01	1.63 ± 0.02
Carbon	64.19 ± 0.23	64.18 ± 0.42	70.29 ± 0.38	68.01 ± 0.36
Hydrogen	4.59 ± 0.07	4.72 ± 0.03	5.12 ± 0.05	5.03 ± 0.03
Sulfur	0.56 ± 0.01	0.55 ± 0.01	0.83 ± 0.03	0.57 ± 0.02
Oxygen	26.56 ± 0.59	27.54 ± 0.64	17.97 ± 0.06	18.09 ± 0.12

working face of underground operations. They were brought to the surface where they were sealed in boxes and kept immersed in water to prevent dehydration and exposure to sunlight. The boxes were then transported to laboratories at Southern Illinois University Carbondale and kept at room temperature. Prior to testing, the outer layers of the coal blocks were peeled away, and only the inner portion of the coal was ground. Particles that passed through a 200-mesh (< 74 μm) screen were stored in re-sealable Ziploc bags and used immediately to prevent any potential oxidation. Elemental analysis of the coal samples was conducted using a Fisher Thermo Scientific Flash 2000 Organic Elemental Analyzer (Thermo Fisher Scientific, Waltham, MA, USA). The specific composition before and after treatment is given in Table 1.

Sand (CAT#S23-3, Fisher Scientific, USA) and graphite (CAT# G67500, Fisher Scientific, USA) were also used in this study. These two solid materials were included as non-biodegradable controls for confirming the source of the biogenic methane. The sand was almost entirely naturally rounded grains of nearly pure quartz. The graphite powder was > 99% graphite. The particle sizes for both control samples were less than 200 mesh.

2.2. The microbial community and nutrient solution

A microbial community that was enriched for ex situ coal biogasification was employed for this investigation. This community was originally collected from the formation water of a coal bed methane (CBM) well in the Illinois basin. According to next generation 16S rDNA sequencing, this community comprised 185 Bacteria and nine Archaea species [13,14]. Fresh inoculum used in this study was developed from the glycerol frozen stocks stored at −80 °C.

The nutrient solution used in this work was made according to an MS recipe [15,16] except that mercaptoethanesulfonic acid (Coenzyme M, CoM) was not included. This MS medium has been demonstrated to lead to more than a 10-fold increase of methane release compared to those without. This medium contained (per L of distilled and deionized water (DDW)): 0.1 mol of $NaHCO_3$, 2.0 g of yeast extract, 2.0 g of trypticase peptones, 1.0 g of NH_4Cl, 0.4 g of $K_2HPO_4{\cdot}3H_2O$, 1.0 g of $MgCl_2{\cdot}6H_2O$, 0.4 g of $CaCl_2$, 1.0 mg of resazurin, and 10 mL of trace mineral solution. The trace mineral solution contained (per L of DDW): 500 mg of $NaEDTA{\cdot}2H_2O$, 150 mg of $CoCl_2{\cdot}6H_2O$, 100 mg of $MnCl_2{\cdot}4H_2O$, 100 mg of $FeSO_4{\cdot}7H_2O$, 100 mg of $ZnCl_2$, 40 mg of $AlCl_3{\cdot}6H_2O$, 30 mg of $Na_2WO_4{\cdot}2H_2O$, 20 mg of CuCl, 20 mg of $Ni_2SO_4{\cdot}6H_2O$, 10 mg of H_3BO_3, 10 mg of H_2SeO_3, and 10 mg of $Na_2MoO_4{\cdot}2H_2O$.

2.3. Experimental setup, monitoring, and modifying microcosms

To test biogenic methane production from the two coal samples, each coal was studied under four conditions with triplicates for each. A total of 24 microcosms (120 – mL serum bottle) was established. These microcosms were divided into four groups. The first group of six was set up according to the optimal condition we reported before for the Illinois basin coal (referred to as IL coal in the following) [6]. The coal loading was 200 g/L, coal particle sizes were < 200 mesh, the temperature was 32 °C, the nutrient solution was the MS medium with 100 mM ethanol. The second group of six had the same conditions but without ethanol. The third set of six was established in the same way as the first group, but with the addition of 2-bromoethanesulfonate (10 mM, BES). This compound was used to inhibit methanogens. The last group of six was the same as those in the second set, but with the addition of BES at 10 mM. Each microcosm contained coal at the desired loading, 45 mL of the MS medium with or without ethanol, with or without BES, and 5 mL inoculum. In addition, nine microcosms were set up to verify the source of the methane. These nine included three containing sand, three with graphite, and three with the MS medium only. All of these nine microcosms were established in the same way as those in group one.

After all ingredients were added, the bottles were capped with rubber septa and sealed with aluminum seals. All bottles including headspace and liquid were purged with N_2 completely and then incubated at 32 °C under static conditions. Starting from day 10, the headspace gas in each bottle was released and measured according to a protocol reported before [6,10,15]. Briefly, when a needle was inserted into the headspace, the pressurized gas in the bottle due to gas production from the coal would escape to a 65-mL gas tight syringe connected to the needle. The volume of the released gas was recorded and the gas content was measured by Gas Chromatography (GC), as detailed below.

After gas sampling on day 10, 15, and 30, a subsample of 1.5 mL from the liquid portion in each microcosm was collected. Upon pretreatment described below, the extracts were analyzed by Gas Chromatography – Mass Spectrometry (GC–MS) to reveal the chemicals released as a result ofcoal degradation. On day 30, the entire contents of each microcosm was centrifuged at 5000 × g for 20 min to separate the liquid from residual coal. The solid fraction was washed with DDW three to fivetimes to remove chemicals and cells associated with the coal. The washed coal was kept at 4 °C for later analysis.

2.4. Sample analysis

2.4.1. GC analysis

The methane content in the microcosm headspace was analyzed using a 17A GC (Shimadzu, Columbia, MD, USA). This GC was equipped with a 60 m × 0.53 mm RT-Msieve 5A porous layer molecular sieve (Restek, Bellefonte, PA, USA) and a flame ionization detector with argon the carrier gas at a flow rate of 10.1 mL/min. The isothermal zone temperatures for the injector and detector were set at 75 °C and 310 °C, respectively. The retention time for methane was 4.73 min. Calibration curves for methane (5–99%) were established using standard gases (Air Liquide, Plumsteadville, PA, USA).

2.4.2. GC/MS analysis

To identify potential degradation products from the coal, the liquid samples collected at different times were centrifuged at 13,000 g for 10 min and processed. Briefly, after the pH of the supernanant was adjusted to 2.0 using 12 M HCl, 5 mL dichloromethane (DCM) (99.9%, Fisher Chemical, Pittsburgh, Pennsylvania, USA) was added. The glass tube was then vortexed vigorously for 10 min. When phase separation was complete, the DCM layer was withdrawn from the bottom of the tube. The remaining aqueous phase was extracted by DCM twice. All

DCM fractions were pooled together, passed through dried sodium sulfate powder and evaporated to dryness under a gentle stream of nitrogen. Methanol was then added to dissolve the dried powder followed by transferring to a GC vial where 0.1 mL tetramethylammonium hydroxide (TMAH) stock solution (20 g/L for derivatization) was added. For selected samples, the internal standard, nonadecanoic acid ($C_{19:0}$) (98%, Acros Organics, New Jersey, USA) was also supplemented for chemical quantification.

GC/MS analysis (Agilent 7890A/5975C) was performed using helium (1 mL/min) as the carrier gas and a capillary column, HP-5MS (30 m 5% phenyl methyl siloxane * 0.25 mm i.d.; 0.25 μm film thickness, Agilent). The GC oven was heated to 50 °C for 1 min and then to 300 °C at a rate of 4 °C/min with an isothermal period of 5 min. Spectra were recorded in the EI mode (electron energy = 70 eV), with a scan range from 33 to 650 m/z in 0.42 s/scan. The injection volume was 1 μL. The identification of each compound was achieved by matching each peak's mass spectrum with that in the spectral library (NIST 11 database).

2.4.3. Total Organic Carbon (TOC) analysis

After centrifugation, the day 30 fermentation broth from microcosms without ethanol was analyzed with a TOC analyzer (TOC-5000A, Shimadzu Corporation, Kyoto, Japan). TOC was determined by performing separate total carbon (TC) and total inorganic carbon (TIC) analyses and subtracting the results. The samples were diluted by DDW with different dilution factors in order to fit the calibration range.

3. Results and discussion

As reported in our previous study, on a dry weight basis, the SJ coal and PR coal have a heating value of 12,410.65 ± 80.6 BTU/lb and 10,786.25 ± 29.80 BTU/lb, respectively [17]. These heating values place SJ coal in the category of high volatile Bituminous B which is the rank for the IL coal and the PR coal in the group of high volatile Bituminous C. However, even though the ranks are similar, the SJ coal had a black color and contained 70.3% and 18.0% carbon and oxygen, respectively which were fairly close to those of the IL coal. The PR coal appeared to be brown and had 64.2% carbon and 26.6% oxygen. Thus, these two coals are very different. When added to the MS medium with the inoculum, both coals released methane over time. By day 30, total methane from SJ coal was 174.6 ± 4.1 ft^3/ton. For PR coal, the total was 232.7 ± 11.2 ft^3/ton (Fig. 1). With the presence of ethanol, a dramatic increase of methane release was observed for SJ coal. On day 30, the cumulative methane production was 921.4 ± 1.9 ft^3/ton. Contradictory results were detected for PR coal. With ethanol addition, the final methane yield was 34.8 ± 7.4 ft^3/ton on day 30, which was much less than those without ethanol. Thus, ethanol appeared to have a stimulatory and an inhibitory effect on biogasifcation of SJ coal and PR coal, respectively.

Methane content in microcosms' headspace gas over time had a similar pattern as that of methane yield. As shown in Fig. 2, by day 30, without ethanol, the microcosms with SJ and PR coal had methane contents of 37.5 ± 0.4% and 43.2 ± 2.0%, respectively. With the presence of ethanol, methane content reached 88.7 ± 5.7% for SJ coal and 12.3 ± 2.1% for PR coal. Again, the effect of ethanol on releasing methane from these two kinds of coals was dramatically different.

The stimulating effect of ethanol on coal biogasification was first demonstrated on IL high volatile Bituminous B coal with a heat value of 12,547.50 ± 36.06 BTU/lb [17]. With the same MS medium, methane release of 172.5 ft^3/ton [15] was observed in 30 days. When ethanol was supplemented at 100 mM, methane production from the same coal during the same period was 841.0 ± 60.3 ft^3/ton [10]. These methane yields were basically the same as those for the SJ coal but very different from those for the PR coal. Therefore, our hypothesis that microbial community and nutrient recipe can be shared between coals with similar ranks was proven to be valid.

Comparing the three kinds of coals, IL, SJ and PR, it is obvious that methane yield from PR coal was larger than those from SJ and IL coal with the latter two behaving similarly in terms of methane production. This relationship correlated negatively with their heating values with PR coal having the lowest BTU/lb and negatively with their inherent color. The PR coal appeared to be brown, the SJ coal was blackish brown and the IL coal was pure black. These observations agreed well with those in the literature that reported that lower rank coals typically lead to higher methane yield [18–20]. On the contrary, Wawrik [8] reported no correlation between methane production potential and coal rank and concluded that activation of coal and the presence of a competent microbial population were the primary factors responsible for methane production rather than coal rank. In this study, the same microbial community was used for all coal samples. If Wawrik is correct, then the PR coal is relatively easier to be activated than the other two coal types.

This activation may be related to the oxygen content since there is a positive correlation between oxygen content of the coal samples and the potential for biogenic methane production (Table 1). This correlation is in line with the observation that organic oxygen content serves as an indicator of the mass of organic compounds available for microbial transformation [21].

To verify the source of methane in microcosms with ethanol addition, we set up control microcosms where sand or graphite was used to replace coal. In the third scenario as described above, the microcosms contained only the MS medium with no solid substrate. As shown in Fig. 3, only minimal volumes of methane were observed from the three sets of controls. It needs to be noted that headspace gas samples were not withdrawn from the control microcosms on day 10, 15, and 20 due to lack of overpressure. On day 30, the headspace was sampled and the measured methane content was used for calculation of methane release. Similar to what we reported before minimal volumes of methane were

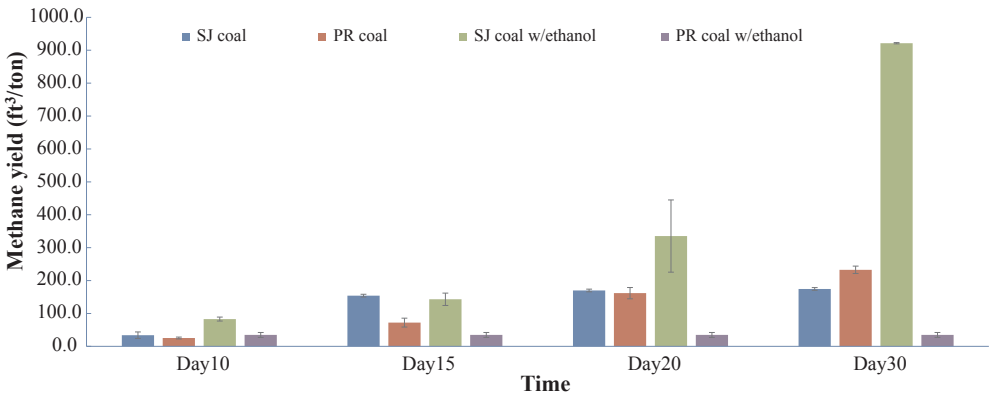

Fig. 1. Methane yield under different conditions.

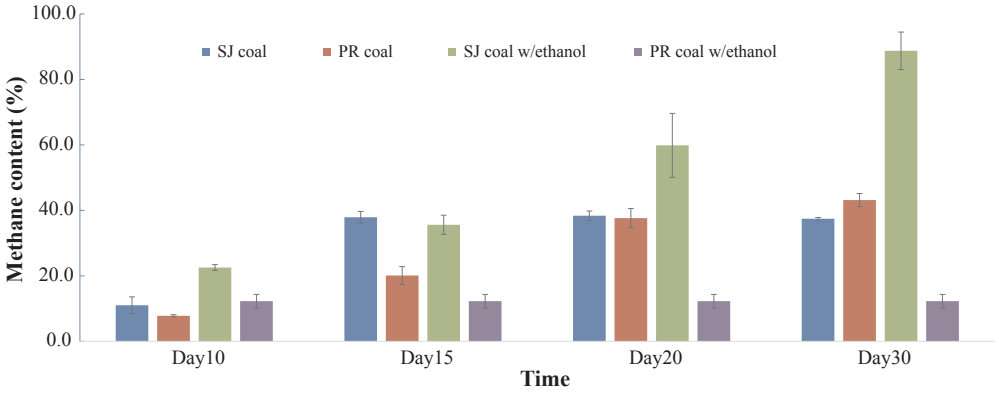

Fig. 2. Methane content under different conditions.

detected from microcosms with sand or graphite in formation water with added yeast extract and peptone [11], the majority of methane was from the coal itself rather than the MS medium and added ethanol.

During coal biogasification, ethanol could have at least three functions: (1) serving as an electron donor; (2) being used as a carbon source; and (3) behaving like an organic solvent. All three potential roles, especially the first two, could lead to increased methane production. In this study, since all control microcosms containing ethanol did not produce much methane, it is reasonable to assume that the main role of ethanol in stimulating methane release is the solvation function. It has been reported that coal consists of an immobile phase and a mobile phase [22,23]. The former may trap some organic compounds and make them non-accessible to microorganisms. The trapped organic compounds may be residual products from the original coalification process [24]. These compounds include short chain aliphatic, cyclic, and monoaromatic, all of which can be readily degraded by microorganisms once they are untrapped. This could explain the enhancing effect of ethanol on methane release for the SJ and IL coals. The reasons for the inhibitory effect of ethanol on PR coal are unknown at this point and deserve further investigation. However, at least, this study demonstrated that for different coal samples, different nutrient recipes should be developed.

With sand and graphite powder, the cumulative methane production by day 30 was 35.1 ± 4.8 ft^3/ton and 32.6 ± 3.2 ft^3/ton, respectively. These numbers were fairly close to those observed from microcosms containing the MS medium, ethanol, and microbes only, which was 40.6 ± 3.3 ft^3/ton. Thus, these control setups demonstrated that the inclusion of a solid matrix was not beneficial for methane production. It is true that the solid substrate, for instance, coal may provide a surface for biofilm formation and microorganisms bound in the biofilm may be more robust compared to planktonic cells [25]. However, based on the results from the control experiment, this was not the case in this study.

To further understand the biogasification process, we used GC/MS to profile the coal degradation products. As indicated in Fig. 4, three dominant compounds: phenylacetic acid (benzeneacetic acid), hexadecanoic acid (C16:0), and octadecanoic acid (C18:0) were extracted by DCM from samples withdrawn on day 10. Between SJ and PR coals, the percentage distribution of the three acids was different. For each type of coal, different gasification conditions: with or without ethanol, with or without BES, however, led to similar product profiles. Among the three acids, hexadecanoic and n-octadecanoic acid were also observed from degradation of sub-bituminous coal in bioaugmented microcosms [26,27]. Besides these three, minor compounds, such as undecane; heptadecanoic acid; 9,12-octadecadienoic acid; 9-octadecenoic acid; tetradecanoic acid; and phenol, were also identified based on > 90% quality matching with those in the MS database. All of these compounds also appeared in the fermentation broth for biogasifying Illinois bituminous coal [28]. The presence of aromatic compounds, such as phenylacetic acid, phenol, supported the pathway proposed by Strapoc et al. [29] where coal defragmentation by fermentation releases oxygen-containing single or polyaromatic chemicals.

The concentration changes of these compounds and two others with time in microcosms with coal, the MS medium, and the inoculum are illustrated in Figs. 5 and 6. For SJ coal, among the three observed on day 10, concentrations of hexadecanoic acid and octadecanoic acid decreased from day 10 to day 15, but remained the same by day 30 while the content of phenylacetic acid increased and then decreased in the 30-day experiment period. Two new compounds: 3-methylbutanoic acid and 1,4-benzenedicarboxylic acid appeared on day 15. The former disappeared from the day 30 samples and the latter increased with time and reached a concentration of 12.9 mg/L. A similar trend was detected for samples derived from PR coal (Fig. 6). The concentration of benzeneacetic acid was around 33.4 mg/L at day 10, but decreased to

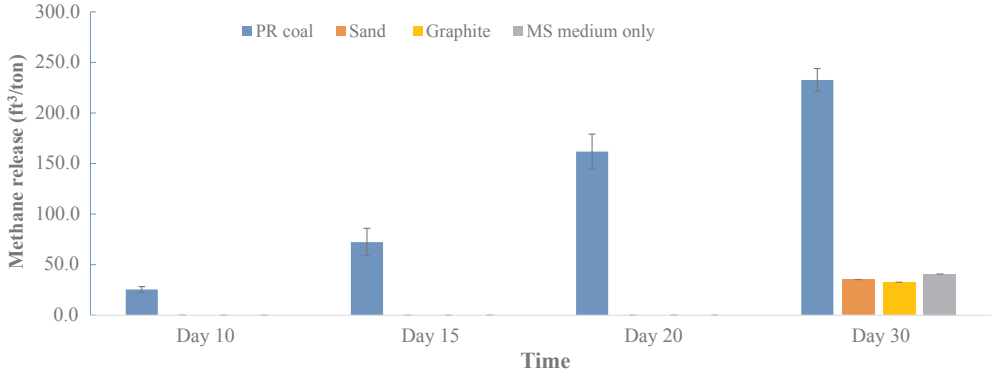

Fig. 3. Methane release under different control conditions.

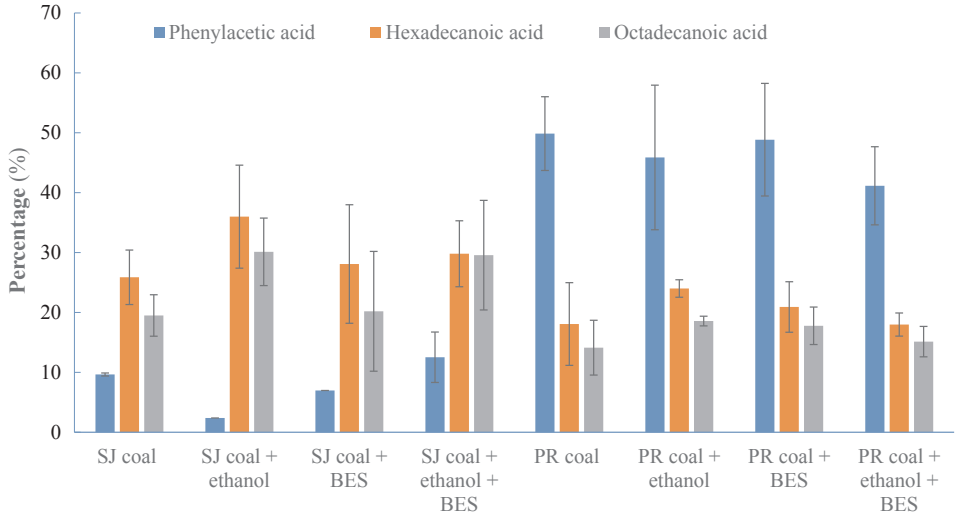

Fig. 4. Dominant compounds identified in different microcosms.

17.7 mg/L and 0.98 mg/L at day 15 and day 30, respectively, which indicated that this benzene related chemical was degraded anaerobically to different products. Nogales [30] reported that succinyl-CoA is a final product of benzeneacetic acid degradation. Succinyl-CoA could be converted into succinate and then be transformed to biogenic methane [31]. Interestingly, the final concentration of 1,4-benzenedicarboxylic acid was 75.0 mg/L which was much higher than 12.9 mg/L detected from the SJ coal. Considering the fact that high concentration of this acid could inhibit the rate of anaerobic degradation [32,33], we hypothesized that 1,4-benzenedicarboxylic acid could be one of the major factors limiting further fermentation of high molecular weight polymers in coal.

In this study, BES was added to prevent methanogenesis. As expected, for microcosms with BES addition, no methane was ever detected during the 30 days. Testing of day 30 samples revealed higher content of TOC from those microcosms with BES addition than those without (Fig. 7). Regarding the SJ coal, TOC was 207.6 ± 5.1 mg/L vs. 60.8 ± 9.3 mg/L without BES supplementation. In terms of PR coal, TOC increased from 61.8 ± 3.4 mg/L to 196.4 ± 28.6 mg/L due to the presence of BES. Thus, it appeared that the arrested methanogenesis led to higher concentrations of organic compounds.

After biogasification, the remaining coal was washed with DDW and then dried. The coal mass before and after gasification was used to calculate mass loss (Table 2). These loss percentages generally correlated well with methane yield: the higher the methane yield, the higher the mass loss. This is especially true for PR coal. For SJ coal, if ethanol was converted to methane, then the coal mass loss wouldn't be higher than those without this chemical. This supported the aforementioned observation from the control microcosms that ethanol was not a direct source of methane. These evidences led to the hypothesis that ethanol served as a solvent rather than a carbon source for microorganisms during coal bioconversion. To prove this hypothesis, studies using ^{13}C ethanol are needed. Again for the SJ coal, the high methane yield from those with ethanol did not result in dramatic increases of coal loss compared to those without ethanol. It needs to be noted, however, not all degradation products from coal were converted to methane. Some may have stayed in the headspace, for example CO_2 and some in the aqueous phase, washed off during sample preparation and counted as loss.

Even with these relatively high mass losses, the residual coal samples had similar compositions to before treatment (Table 1). This agrees well with one study investigating methane release from subbituminous coal collected from the PR basin [34]. The researchers reported that > 99.5% of BTU content remained after coalbed methane stimulation with either algal extract or yeast extract. However, with bituminous coal from the IL basin, we have observed repetitively that biogasification affects the composition of the residual coal. Upon biotreatment for 30 days, the carbon content dropped from 70.1% to 59.5% [35]. After biogasification for a year, the residual coal structure changed dramatically based upon elemental analysis, proximate analysis, and SEM imaging [28]. The difference among different coal samples could be due to different microbial actions toward coal degradation, but it definitely warrants further investigation.

In summary, this study demonstrated that: 1) the lower ranking PR

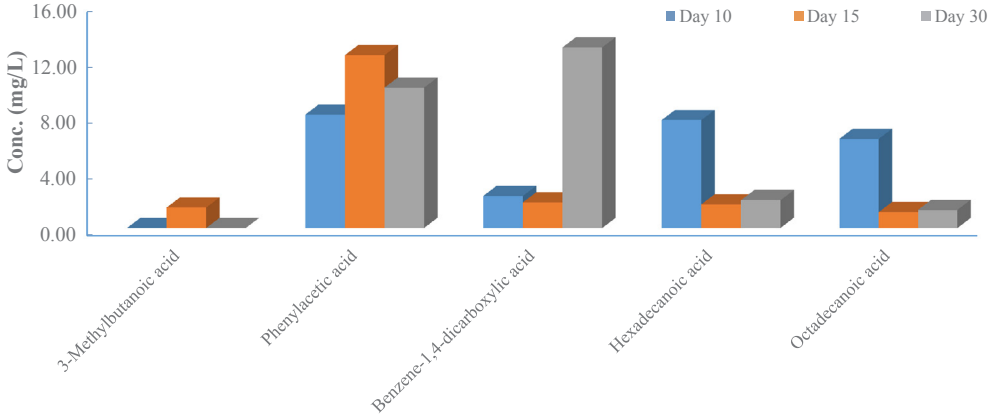

Fig. 5. Key compounds identified in microcosms with SJ coal.

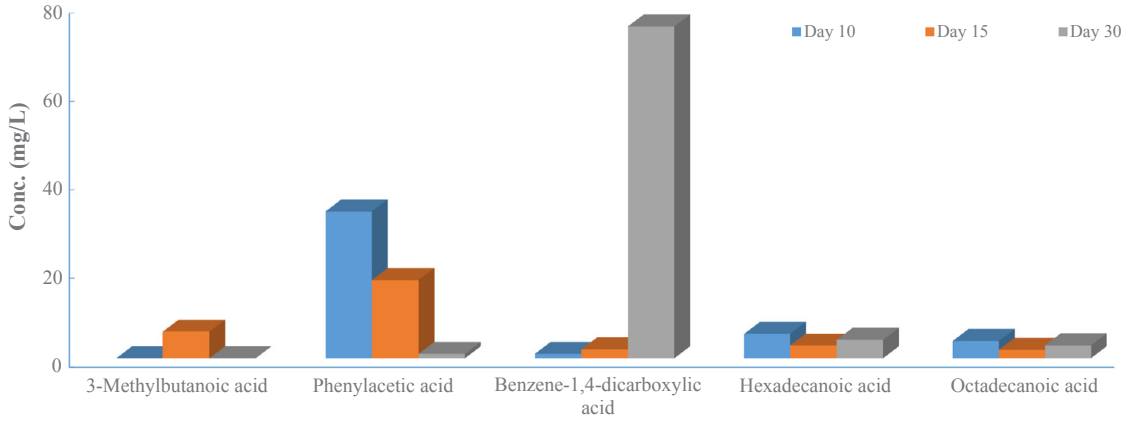

Fig. 6. Key compounds identified in microcosms with PR coal.

coal led to higher methane yield compared to SJ and IL coal by the same microbial community when a minimal medium was used; 2) ethanol, a critical chemical for stimulating methane production from SJ and IL coal was prohibitive to microbial activities on PR coal; 3) ethanol was not a direct source of methane from SJ and IL coal. Its stimulatory and inhibitive behaviors on different coals deserve further investigations which will eventually result in deeper insight of coal biogasification, creation of conceptual models for the whole process and broad application of biostimulation for producing methane from coals at different ranks.

4. Conclusion

Ethanol, which was shown to stimulate methane release from IL bituminous coal, enhanced methane yield from SJ coal having the same rank, but inhibited methane production from PR coal having a lower heating value than those of IL and SJ coals. Without the addition of ethanol, the microbial community initially collected from the IL basin resulted in higher methane yield from the PR coal than those from the SJ coal. Although similar compounds dominating the fermentation broth were identified from microcosms containing different ranks of coals, higher content of 1,4-benzenedicarboxylic acid was found to be associated with PR coal. With the supplementation of BES, no methane was observed from any microcosms. The presence of BES led to three-fold higher content of TOC compared with those without.

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Table 2
Percentage of mass loss under different conditions.

Coal	Medium used	Methane yield (ft^3/t)	Mass loss (%)
SJ coal	MS	174 ± 4.1	3.35 ± 0.05
	MS + Ethanol	921.44 ± 1.31	5.47 ± 0.24
PR coal	MS	194.1 ± 9.18	6.25 ± 0.62
	MS + Ethanol	34.8 ± 7.4	1.56 ± 0.19

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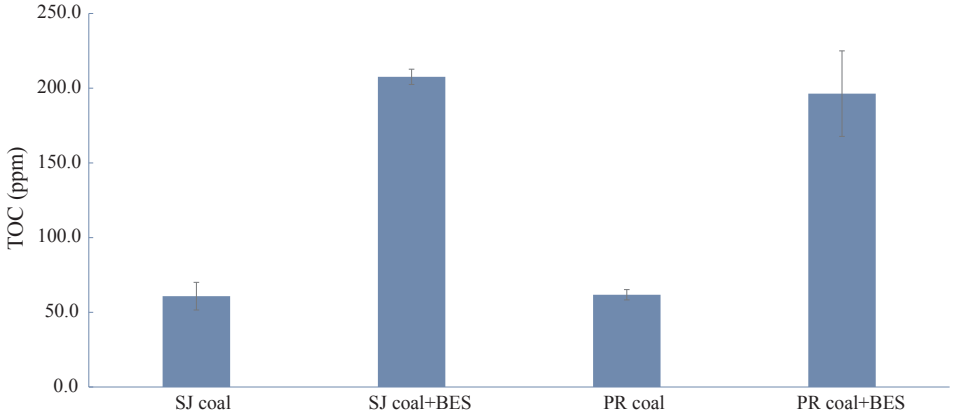

Fig. 7. Content of TOC in fermentation broth from microcosms without ethanol addition.

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