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Optimization of methane production from bituminous coal through biogasification

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HIGHLIGHTS

- Among 12, coal loading, temperature, particle size and ethanol were statistically significant on methane production.
- The optimal conditions for producing methane from bituminous coal were determined.
- Under optimal conditions with a fed-batch scheme, 2900 ft^3 methane/ton was observed in 55 days.

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ABSTRACT

To optimize methane production from bituminous coal through use of a well-studied microbial community derived from the same Illinois basin in USA, a total of 12 parameters were first evaluated by setting up 64 reactors following a 2-level factorial design. Among the 12 parameters, temperature, coal loading, particle size and ethanol were found to have statistically significant effects on methane content and yield from coal. Following screening, to identify optimal value for each significant factor, a Box-Behnken design necessitating 29 reactors was adopted. Optimal conditions provided by the Design of Expert software for the highest methane yield were: temperature, 32 °C; coal loading, 201.98 g/L; coal particle size, <73.99 μm; and ethanol at 300 mM. Under these optimum conditions, the predicted methane yield and content was 2957.4 ft^3/ton (83.7 mm^3/ton) and 74.2%, respectively. To confirm the predicted results, a verification experiment was conducted, where a methane yield of 2900 ft^3/ton (82.1 mm^3/ton) with a methane content of 70% was observed. Thus, models developed from this study can be used to predict methane content and yield from bituminous coal through biogasification ex situ.

1. Introduction

The global coal reserve is estimated to be 1,000 Gt [1]. As an abundant and inexpensive resource, coal has been investigated extensively for generating fuels and chemicals through various conversion technologies besides the conventional combustion for power generation. Conversion techniques that attempt to circumvent the negative environmental impacts associated with coal combustion, such as carbon fuel cell [2], coal to synthetic natural gas (SNG) [3], pyrolysis [4] and underground coal gasification [5] typically employ thermal and/or chemical processes under high pressures and/or temperatures with high capital and operating costs [6,7]. To alleviate these problems, coal bioconversion or biogasification has been studied intensively during recent years.

Biogasification transforms solid coal to methane gas through actions of microorganisms. Different from in situ gasification where syngas is produced from controlled combustion of coal [8] or ex situ gasification which is generally performed at temperatures higher than 800 °C [9], biogasification can be conducted under mild environmental conditions. In addition, coal does not need to be cleaned before biogasification like those prepared for power generation [10]. This technology can be used for both in situ (abandoned or unmineable coal seams) and ex situ (coal wastes or mined out coal) scenarios [11]. Considering the U.S. coal resource of 6 trillion tons [12], if a methane content of 200 ft^3/ton could be achieved, then the total methane from coal would be 1,200 trillion cubic feet (Tcf). This volume of methane is much higher than 158.2 Tcf, estimated by the potential gas committee as of year-end 2012 for coalbed gas resources and would be

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53.9% of 2226 Tcf of gas potentially recoverable from traditional reservoirs, such as conventional, tight sands and carbonates and shales [13]. Hence, if methane production from coal through biogasification is successful, it would generate the same volume of methane as that produced from shale gas in 2012, 1,073 Tcf. Considering the fact that coal seams are located at much shallower depth than shales, recovery of methane from charged coalbeds would be relatively inexpensive compared to that from shale.

To harness this natural process and make coal biogasification a commercial reality and a clean coal technology [14,15], huge amounts of efforts have been dedicated to microbially enhanced coal bed methane (MECBM). Specifically, these efforts have spanned from understanding the coal conversion pathways [16,17]; improving methane production rate by investigating different microbial communities [18,19], different nutrient solutions [11], different testing conditions; and conducting pilot scale tests by several companies [20]. Under different testing conditions, evaluating effects from different parameters have been investigated intensively. Factors, such as coal loading, medium pH, coal particle size and temperature [21–23], surfactants [24], solvents [22,25] and salinity [23] have been optimized for different coal samples.

Although excellent studies have been conducted on elucidating the key factors for increasing methane production rate, all researches so far have only evaluated the effect from variation of single parameters. For example, effect of temperature was detected in cultures having the same pH or effect of pH was studied for cultures at one temperature. Combined effects from multiple parameters, though critical, have not been investigated to the best of our knowledge. In addition, no such studies have been carried out for bituminous coal. Thus, for this study, we conducted experiments designed by the use of Design of Expert (DOE) software to: (1) evaluate effects from single and multiple factors simultaneously; and (2) identify the optimal conditions for achieving maximal methane yield. To achieve this purpose, we started with a 2-level factorial design to screen the most important parameters affecting methane productivity. Once significant parameters were identified, we used response surface methodology (RSM) to identify the optimal conditions for obtaining the highest methane yield.

A total of 12 parameters were evaluated in this study. These 12 factors were chosen based on their reported effects on methane production from coal. It needs to be noted that these parameters are strongly tied to ex situ coal bioconversion although valuable information can be applied to in situ scenarios. The selected parameters were: (1) particle size (<420 μm, mesh size 40); (2) pH (6.0–8.0). As demonstrated by our previous study [26], in our enriched microbial consortium, the order of Methanomicrobiales was 90.4% of the methanogenic population. For this order, the optimal pH ranges from 6.0 to 8.0 [27]; (3) temperature (20–40 °C). With two exceptions that can tolerate temperatures up to 60 °C, the majority of the Methanomicrobiales are mesophiles and have optimal temperatures from 20 to 40 °C; (4) mixing (0–75 rpm). As almost all studies on coal biogasification are conducted under static conditions, effect from mixing is unknown. On one hand, mixing can enhance the contact and interaction between coal and microorganisms. On the other hand, mixing may damage the attachment of cells to coal; (5) inoculum size (10–20% of final liquid volume in each reactor). An inoculum size of 10% has been commonly used. But it is unknown whether increased initial cell numbers will enhance methane release from coal; (6) coal loading (200–700 g/L). Different studies have reported different coal loadings ranging from 25 to 800 g/L [28]. Low coal loading requires large consumption of nutrient solutions while high loading may render some coal un-accessed by medium and microbes; (7) mercaptoethanesulfonic acid (coenzyme M, CoM, 0–0.25 g/L). This compound is generally included in nutrient media for anaerobic cultures. It is a reducing agent and also required by an enzyme: methyl-coenzyme M reductase in the final step of methane formation from various substrates in anaerobic environments [11,29]. This chemical accounts for approximately 75% of the total medium cost when used at 0.5 g/L; (8) two surfactants (30–50% of critical micelle concentration (CMC)). Triton X-100 is nonionic and was reported to exert no effect on enhancing methane production from subbituminous coal while its effect on bituminous coals are unclear [24]. Sodium dodecyl sulfate (SDS), is anionic and has not been evaluated in terms of impact on methane production. These two surfactants were chosen due to their low toxicity and low cost. Cationic surfactants were not selected since their solutions can interact with coal and result in decreased pH [30]; and (9) three carbon sources (each at 100 mM). Members of the order of Methanomicrobiales grow by reducing CO_2 with H_2 and some strains can use formate and alcohols as electron donors. Since H_2 is a cleaner fuel than methane, it does not make sense to add large amount of H_2 (80% of headspace gas) for the purpose of producing methane, especially considering large scale applications. Thus, in the reported study here, we did not attempt to supply H_2 in the headspace. To reduce CO_2, we investigated effects from sodium formate, 2-propanol and ethanol. It needs to be noted that: (a) like H_2, the two alcohols are also biofuel molecules. But their concentrations in this study were only 100 mM; (b) the two alcohols either being miscible with or having high solubility in water might also serve as solvents to increase coal solubility.

2. Materials and methods

2.1. Coal samples

For the current study, the coal samples used were the same as what were studied and reported before [26]. Coal blocks were collected from the Herrin Seam, #6 in the Illinois basin. This coal contained 70.1% of carbon, 1.4% of nitrogen, 5.2% of hydrogen, 0.6% of sulfur, 15.4% of oxygen, and 7.5% of ash (dry weight basis). Contents of volatile matter and fixed carbon were 49.9% and 42.6% (dry weight basis), respectively. The high content of volatile matter and a heating value of 12,548 BTU/lb put this coal in the category of high volatile B Bituminous. Immediately before use, a block of coal was broken into lumps approximately 1.3 cm in size. The coal lumps were subsequently ground and sieved to obtain coal samples at different particle sizes as discussed below. Ground coal samples were stored in re-sealable plastic bags at room temperature in order to prevent moisture loss.

2.2. A microbial community and nutrient solution

The microbial community used in this study was developed from microorganisms initially present in the formation water collected from an on-going coal-bed methane operation in southern Illinois, USA. Through cultivating on ground bituminous coal detailed above in a MS medium [31] and after four transfers, the final enriched community comprised a total of 185 bacterial species and nine species of archaea. The abundant bacterial species were: *Clostridium bifermentans* (15.1%), *Massilia spp.* (11.1%), *Pseudomonas putida* (11.1%), *Proteiniphilum spp.* (6.5%), and *Pseudomonas stutzeri* (6.4%). The majority of archaea belonged to the *Methanocalculus* genus and the *Methanomicrobiales* order [26]. From this enriched consortium, frozen stocks were made and stored at −80 °C for later use. All inocula used in this study were developed from the same frozen stocks.

The MS 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, 0.5 g of mercaptoethanesulfonic acid (Coenzyme M, CoM), 0.25 g of $Na_2S{\cdot}9H_2O$, 1.0 g of NH_4Cl, 0.4 g of K_2-

$HPO_4 \cdot 3H_2O$, 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 [31]. 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. Two-level factorial design - experiment 1

To identify critical factors that affect methane yield and understand the interactions among different parameters, a two-level factorial design through using Design of Expert (DOE, Stat-Ease, Inc. Minneapolis, MN) was adopted. A total of 12 parameters were evaluated (Table 1). These parameters included: (1) coal particle

Table 1
2-Level factorial design with results.

No	Particle size (mm)	Temp. (°C)	Inoculum size (%)	Coal loading (g/L)	pH	Mixing (rpm)	Coenzyme M (g/L)	Triton X (% of CMC)	SDS (% of CMC)	Ethanol (mM)	2-Propanol (mM)	Sodium formate (mM)	Methane yield (ft^3/ton)	Methane content (%)
1	0.074–0.42	40	10	200	8	100	0	30	50	100	100	100	25.6	10.3
2	0.074–0.42	40	20	700	6	0	0.25	50	30	0	100	100	23.8	27.0
3	0.074–0.42	28	10	200	8	0	0.25	50	50	0	100	100	7.8	3.0
4	0.074–0.42	28	20	200	6	0	0	50	50	100	0	100	39.5	14.0
5	<0.074	40	10	200	8	100	0.25	50	30	0	0	100	24.6	9.2
6	<0.074	40	20	700	6	100	0	30	50	0	100	0	5.1	10.0
7	<0.074	40	20	200	8	100	0	50	50	100	0	0	65.6	18.0
8	<0.074	28	20	200	6	0	0.25	30	30	0	100	100	263.3	60.0
9	<0.074	28	20	700	8	0	0.25	50	30	100	0	100	243.2	66.0
10	0.074–0.42	40	20	700	8	0	0.25	50	50	0	0	0	48.2	40.0
11	<0.074	40	20	700	8	100	0	30	30	0	0	100	4.5	7.5
12	0.074–0.42	40	10	200	6	0	0	30	30	0	100	100	74.3	25.0
13	0.074–0.42	40	20	200	6	0	0.25	30	50	100	100	0	102.5	34.0
14	<0.074	40	10	200	6	0	0.25	50	50	100	0	100	193.3	38.0
15	0.074–0.42	40	20	700	8	100	0.25	50	50	100	100	100	52.1	38.0
16	<0.074	28	20	200	6	100	0.25	30	30	100	0	0	880.1	64.0
17	0.074–0.42	40	20	200	8	100	0.25	30	30	0	100	0	54.9	19.2
18	0.074–0.42	28	20	700	8	0	0	30	50	0	100	100	68.1	69.0
19	0.074–0.42	28	20	700	6	0	0	30	30	0	0	0	51.0	41.0
20	<0.074	28	10	200	8	100	0	30	30	0	100	0	255.4	55.0
21	<0.074	40	10	700	6	100	0.25	30	30	100	100	100	131.1	76.0
22	<0.074	28	10	700	8	100	0	50	50	100	100	100	242.6	69.0
23	0.074–0.42	40	10	700	8	0	0	50	30	100	0	100	214.4	66.0
24	0.074–0.42	40	10	700	8	100	0	50	30	0	100	0	20.1	24.0
25	<0.074	40	20	700	8	0	0	30	30	100	100	0	105.4	65.0
26	0.074–0.42	28	10	700	6	100	0.25	30	50	0	100	0	38.6	38.0
27	0.074–0.42	28	10	200	8	100	0.25	50	50	100	0	0	32.0	12.3
28	<0.074	40	10	700	8	100	0.25	30	50	100	0	0	141.4	61.0
29	<0.074	28	10	200	8	0	0	30	30	100	0	100	979.4	76.0
30	<0.074	28	20	700	6	0	0.25	50	50	100	100	0	230.5	74.0
31	0.074–0.42	40	20	200	6	100	0.25	30	50	0	0	100	33.9	14.0
32	0.074–0.42	40	20	200	8	0	0.25	30	30	100	0	100	142.0	36.0
33	0.074–0.42	28	20	200	6	100	0	50	50	0	100	0	46.8	19.0
34	<0.074	40	10	700	6	0	0.25	30	30	0	0	0	23.8	19.0
35	0.074–0.42	28	20	700	6	100	0	30	30	100	100	100	264.4	77.0
36	<0.074	28	20	200	8	0	0.25	30	50	0	0	0	18.6	7.0
37	0.074–0.42	28	10	700	6	0	0.25	30	50	100	0	100	126.3	69.0
38	<0.074	28	10	700	6	0	0	50	30	0	100	100	73.4	50.0
39	<0.074	28	20	700	6	100	0.25	50	50	0	0	100	77.8	51.0
40	0.074–0.42	28	20	700	8	100	0	30	50	100	0	0	193.2	62.0
41	<0.074	28	20	200	8	100	0.25	30	50	100	100	100	84.6	27.0
42	<0.074	28	20	700	8	100	0.25	50	30	0	100	0	59.9	44.0
43	0.074–0.42	28	10	700	8	0	0.25	30	30	100	100	0	231.1	73.0
44	<0.074	28	10	700	8	0	0	50	50	0	0	0	30.4	29.0
45	0.074–0.42	28	10	700	8	100	0.25	30	30	0	0	100	46.5	42.0
46	<0.074	40	10	200	8	0	0.25	50	30	100	100	0	225.0	46.0
47	<0.074	28	10	200	6	100	0	30	50	0	0	100	101.0	35.0
48	0.074–0.42	28	20	200	8	100	0	50	30	0	0	100	21.2	9.4
49	<0.074	40	20	200	8	0	0	50	50	0	100	100	75.5	25.0
50	<0.074	40	20	200	6	0	0	50	30	0	0	0	336.6	52.0
51	<0.074	40	10	700	8	0	0.25	30	50	0	100	100	20.1	24.0
52	0.074–0.42	28	20	200	8	0	0	50	30	100	100	0	69.2	28.0
53	0.074–0.42	40	10	200	8	0	0	30	50	0	0	0	26.9	10.3
54	0.074–0.42	40	10	200	6	100	0	30	30	100	0	0	30.0	10.0
55	0.074–0.42	40	10	700	6	100	0	50	50	0	0	100	10.5	15.2
56	0.074–0.42	28	10	200	6	100	0.25	50	30	100	100	100	514.9	76.0
57	0.074–0.42	40	10	700	6	0	0	50	50	100	100	0	37.3	41.0
58	<0.074	28	10	200	6	0	0	30	50	100	100	0	57.2	21.0
59	<0.074	40	20	700	6	0	0	30	50	100	0	100	186.1	50.0
60	<0.074	40	20	200	6	100	0	50	30	100	100	100	335.9	15.0
61	<0.074	28	10	700	6	100	0	50	30	100	0	0	97.6	51.0
62	0.074–0.42	40	20	700	6	100	0.25	50	30	100	0	0	203.3	58.0
63	<0.074	40	10	200	6	100	0.25	50	50	0	100	0	65.5	21.0
64	0.074–0.42	28	10	200	6	0	0.25	50	30	0	0	0	125.5	34.0

size, <0.074 mm (200 mesh) or 0.074–0.42 mm (100–200 mesh); (2) temperature, 28 or 40 °C; (3) inoculum size, 10% or 20% of the final total volume in each bioreactor; (4) coal loading, 200 or 700 g/L; (5) MS medium pH, 6 or 8; (6) mixing, 0 or 100 rpm; (7) CoM, 0 or 0.25 g/L; (8) Triton X-100, 30% or 50% of critical micelle concentration (CMC, 0.23 mM); (9) SDS, 30% or 50% of its CMC of 7 mM; (10) ethanol, 0 or 100 mM; (11) 2-propanol, 0 or 100 mM; and (12) sodium formate, 0 or 100 mM. The responses were methane yield (ft^3/ton) and methane content (%).

According to this design, a total of 64 reactors were set up. Each reactor (125 mL serum bottle) contained a total of 50 mL of MS medium (without CoM) plus the same inoculum at different sizes, coal at different loadings and other additions defined by the matrix (Table 1). All reactors after being capped by butyl rubber septas and sealed by aluminum crimps were maintained under different cultivation conditions (Table 1). Headspace gases were withdrawn at day 10, 15, 20, 25 and 30 for measuring newly produced gas volume and gas content through use of a gas chromatograph (GC) as described below. The final cumulative methane yield and final methane content at day 30 was presented in Table 1. These data were then subjected to statistical analyses through use of the DOE software.

2.4. Box-Behnken design - experiment 2

After analyzing results generated from the 64 reactors, four out of 12 parameters were identified to be statistically significant for the two responses. These four parameters were: temperature, particle size, coal loading and ethanol. To further determine optimal value for each, a total of 29 reactors were established based on the Box-Behnken design (Table 2). The upper and lower limit was 32 and 24 °C for temperature, <74 µm (200 mesh) and <37 µm (400 mesh) for coal particle size, 300 mM and 100 mM for ethanol concentration, and 400 g/L and 200 g/L for coal loading. Once the range for each parameter was provided, the software automatically generated a median value (Table 2). Similar to the 64 reactors described above, each of the 29 bioreactors consisted of a total of 50 mL of MS medium (without CoM) plus the same inoculum at 10% of the final liquid volume. pH of the MS medium was 7.0. All reactors were kept under different conditions (Table 2). No shaking or mixing was provided to the reactors. Headspace gas in each serum bottle was monitored at the same time interval as detailed above for the 64 reactors. Similarly, both gas volume and gas content were measured, recorded and used for calculating the final methane yield (ft^3/ton) at day 30 (Table 2). Results obtained from this experiment were analyzed by using the DOE software.

2.5. Verification of methane production under conditions provided by the model – experiment 3

Once the optimal value for each parameter was given by the software, a verification experiment was conducted. A total of five bottles were established for this purpose. Each bottle contained coal at 200 g/L with a particle size of <74 µm; and ethanol, 300 mM in the same MS medium but without the presence of CoM. The same inoculum at 10% of the final total volume was used for each bottle. All reactors were kept at 32 °C without shaking and monitored over time for headspace gas content. In another experiment, we set up three serum bottles under the same conditions except that the initial ethanol concentration was 100 mM. Ethanol at 100 mM was added to each microcosm at two other time points. In addition, another three microcosms which contained no coal, but 100 mM ethanol were established under the same cultivation conditions to test methane yield from ethanol only. Results from these experiments were compared with those predicted by the software.

2.6. Sample analysis

Headspace gas analyses were conducted in the same way as reported before [11]. Briefly, to maintain a 1 atm pressure in each

Table 2
Box-Behnken design with results.

Run	Temp. (°C)	Particle size (µm)	Ethanol (mM)	Coal loading (g/L)	Methane yield (ft^3/ton)	Methane content (%)
1	24	74	200	300	32.4	18.0
2	28	37	200	400	19.1	14.8
3	28	37	100	300	304.1	72.0
4	28	55.5	200	300	149.9	47.0
5	28	74	100	300	58.8	27.0
6	24	55.5	200	200	50.6	17.0
7	28	55.5	200	300	1074.6	74.0
8	32	55.5	100	300	619.6	72.0
9	32	37	200	300	23.5	12.0
10	28	55.5	300	200	112.4	28.0
11	28	55.5	100	200	152.8	37.0
12	28	55.5	200	300	740.4	82.0
13	28	55.5	300	400	43.3	28.0
14	24	55.5	300	300	19.8	12.0
15	24	37	200	300	24.9	15.0
16	28	74	200	200	100.4	24.0
17	24	55.5	100	300	26.5	15.0
18	28	55.5	200	300	65.9	32.0
19	32	55.5	300	300	98.8	36.0
20	28	74	200	400	9.9	10.0
21	28	37	300	300	19.9	11.0
22	28	55.5	200	300	58.4	28.0
23	32	55.5	200	200	367.2	73.0
24	32	74	200	300	1079.8	75.0
25	32	55.5	200	400	284.7	74.0
26	24	55.5	200	400	25.3	21.0
27	28	55.5	100	400	15.9	13.0
28	28	37	200	200	46.1	15.0
29	28	74	300	300	158.8	64.0

reactor and release overpressure caused by microbial activities, a stainless steel needle was inserted to each microcosm headspace at different time points. The needle was connected to a 50-mL gas tight syringe. Gas volume in the syringe was recorded and used for calculation of methane yield. The molar contents of methane in the reactor headspace were analyzed through 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 being the carrier gas with 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%) was established using standard gases (Air Liquide, Plumsteadville, PA, USA).

Table 3
Main effects from different parameters for methane yield.

Term	Standardized effect	Sum of squares	% Contribution
A-Particle size	−0.469	3.516	4.310
B-Temperature	−0.529	4.469	5.478
C-Inoculum size	0.112	0.201	0.246
D-Solid loading	−0.256	1.046	1.282
E-pH	−0.305	1.493	1.830
F-Mixing	−0.233	0.866	1.061
G-Coenzyme M	0.205	0.669	0.820
H-Triton X-100	−0.016	0.004	0.005
J-SDS	−0.669	7.162	8.778
K-Ethanol	1.19305	22.774	27.913
L-2-Propanol	0.0209669	0.0070338	0.009
M-Sodium formate	0.0659437	0.0695771	0.085

3. Results

As discussed above, different cultivation conditions, such as medium pH, temperature, coal particle size, coal loading, with or without shaking, inoculum size have been reported. Different chemicals, such as surfactants, solvents and carbon sources have been studied. To determine the best condition for achieving the highest methane production from bituminous coal, here we took the most comprehensive three-step approach. First, we used a two-level factorial design to evaluate the effects of 12 parameters on methane yield and methane content. Second, for those that were statistically important to the desired responses, a Box-Behnken design was employed. Third, the optimal conditions given by the DOE software were confirmed by a verification experiment.

3.1. Two level factorial design

Based on the half-normal probability plot (Fig. 1), five parameters: inoculum size, CoM, ethanol, 2-propanol and sodium sulfate had positive while the other seven parameters had negative effects on methane yield (ft^3/ton). The largest positive effect came from ethanol with 27.913% of relative contribution (Table 3). The largest negative effect was from SDS with a relative contribution of 8.778%. Analysis of Variance (ANOVA) indicated that five parameters, particle size, temperature, pH, SDS and ethanol, had statistically significant effects with $p < 0.05$ (Table 4). In addition, interactions between some parameters, such as particle size and coal loading (AD), coal loading and SDS (DJ), and coal loading and ethanol (DK) have statistically signficant effects on methane production.

In terms of methane content (%) (Fig. 2), five parameters: inoculum size, solid loading, CoM, ethanol and propanol had positive effects. Solid loading which was negative on methane yield had the highest relative contribution of 17.703% toward methane content followed by ethanol of 13.733% (Table 5). This difference on solid loading is reasonable considering: (1) more coal should theoretically result in higher methane being produced and (2) methane yield (ft^3/ton) was calculated by dividing total methane volume by total mass of coal. Among seven parameters that did not enhance methane content, temperature and SDS had the highest negative contribution of 5.547% and 5.257%, respectively. ANOVA analysis (Table 6) indicated that seven parameters: particle size,

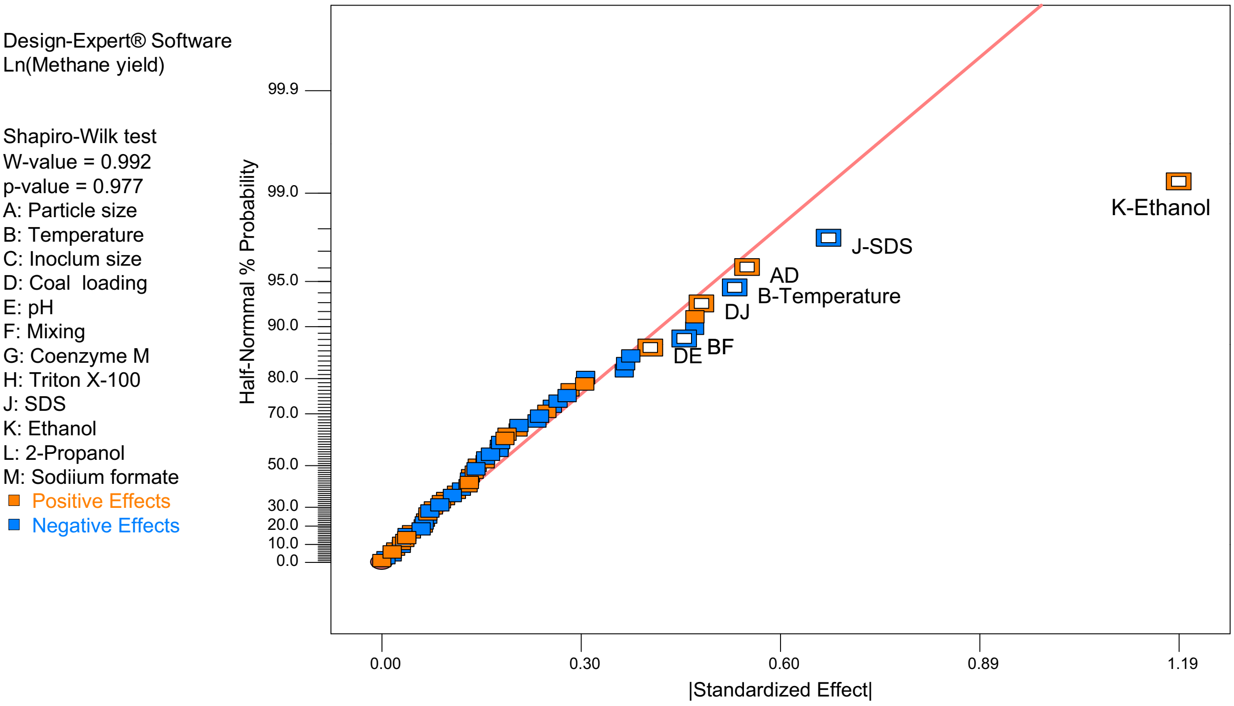

Fig. 1. Half normal probability plot for methane yield (ft^3/ton).

temperature, coal loading, pH, mixing, SDS and ethanol had statistically significant effects on methane content, each with a *p* value of less than 0.05. In addition, interactions between some parameters were significantly important, too (Table 6).

Thus, considering results for the two responses: methane yield (the primary) and methane content (the secondary), we concluded that among 12 parameters, temperature, particle size, coal loading and ethanol were the most important ones. Other signficant factors, such as mixing and SDS, were not considered in further studies due to their negative effects. Higher pH between 6 and 8 was demonstrated to exert negative impacts on the two responses. Therefore, in the following studies, pH of 7.0 of the MS medium was adopted. Non-significant factors, CoM, 2-propanol, sodium formate, Triton X-100 were eliminated from further investigations while inoculum size was kept at 10% of the final total volume in reactors. To further identify the optimal value for each critical parameter, we used the Box-Behnken Response Surface Methodology and designed another matrix (Table 2).

Table 4
Analysis of variance for methane yield.

Source	Sum of squares	df	Mean square	F value	p-Value Prob > F
Model	70.92	26	2.73	9.46	<0.0001 significant
A-Particle size	3.52	1	3.52	12.2	0.0013
B-Temperature	4.47	1	4.47	15.5	0.0004
C-Inoculum size	0.2	1	0.2	0.7	0.4092
D-Solid loading	1.05	1	1.05	3.63	0.0646
E-pH	1.49	1	1.49	5.18	0.0287
F-Mixing	0.87	1	0.87	3	0.0914
G-Coenzyme M	0.67	1	0.67	2.32	0.1361
H-Triton X-100	4.07E-03	1	4.07E-03	0.014	0.906
J-SDS	7.16	1	7.16	24.84	<0.0001
K-Ethanol	22.77	1	22.77	79	<0.0001
L-2-Propanol	7.03E−03	1	7.03E−03	0.024	0.8767
M-Sodium formate	0.07	1	0.07	0.24	0.6261
AD	4.79	1	4.79	16.61	0.0002
AH	2.11	1	2.11	7.33	0.0102
BF	3.28	1	3.28	11.39	0.0017
DE	2.59	1	2.59	8.99	0.0048
DJ	3.67	1	3.67	12.73	0.001
DK	3.52	1	3.52	12.21	0.0013
EG	2.13	1	2.13	7.4	0.0099
FL	1.48	1	1.48	5.13	0.0294
GM	1.23	1	1.23	4.28	0.0455
ACH	2.23	1	2.23	7.73	0.0085
Residual	10.67	37	0.29		
Cor total	81.59	63			

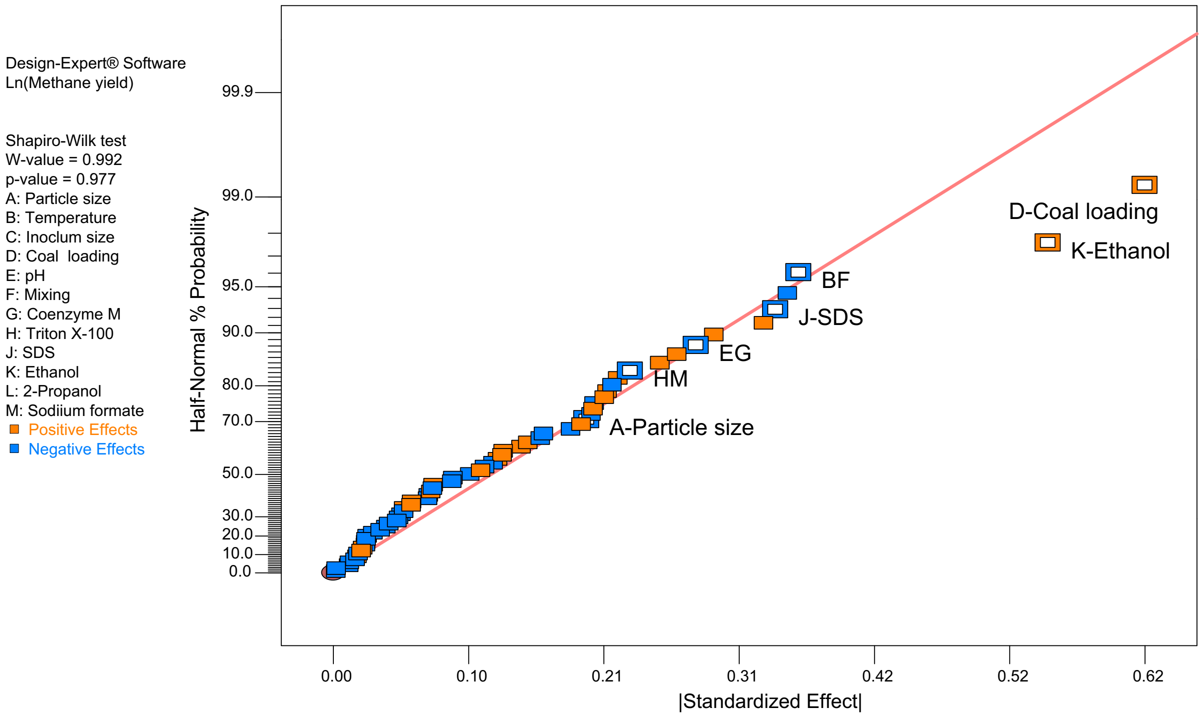

Fig. 2. Half normal probability plot for methane content (%).

Table 5
Main effects from different parameters for methane content.

Term	Standardized effect	Sum of squares	% Contribution
A-Particle size	−0.195	0.608	1.726
B-Temperature	−0.350	1.955	5.547
C-Inoculum size	0.025	0.010	0.029
D-Solid loading	0.625	6.240	17.703
E-pH	−0.199	0.631	1.790
F-Mixing	−0.201	0.647	1.834
G-Coenzyme M	0.145	0.335	0.951
H-Triton X-100	−0.073	0.086	0.244
J-SDS	−0.340	1.853	5.257
K-Ethanol	0.550	4.841	13.733
L-2-Propanol	0.131	0.275	0.780
M-Sodium formate	−0.0121663	0.002368	0.007

3.2. The Box-Behnken design

For the four most important parameters, different ranges were used in the Box-Behnken design. The rationale for the selected range of each parameter was: (1) temperature we tested in the screening experiment was either 28 or 40 °C. Since temperature had a negative effect, lower temperatures than 40 °C should be beneficial for the biogasification process. So, in this design, we chose 24 and 32 °C; (2) in the experiment 1, particle size was studied at 0.074–0.42 mm and <0.074 mm. Since effect from this factor was also negative, the smaller the coal particles, the higher methane yield should be. In this new design, we selected <0.074 mm (200 mesh) and <0.037 mm (400 mesh); (3) coal loading investigated in experiment 1was 200 g/L and 700 g/L. Since coal loading had a negative effect on methane yield but positive on methane content, in this new design, we set 200 g/L and 400 g/L; and (4) ethanol at 100 mM was positive on both methane yield and content. Thus, we intended to test its effect at 300 mM. Once the lower and upper values were set, the software automatically added a middle value for each parameter. Therefore, in the matrix (Table 2), every parameter was tested at three levels.

Analysis of variance (ANOVA) for methane yield (Table 7) revealed that: (1) the reduced 2FI model was statistically significant with a *p* value of 0.0052; and (2) both temperature and coal loading were statistically significant with *p* values less than or equal to 0.05. ANOVA of methane content (Table 8) was a little different in that coal loading was not statistically significant. It needs to be noted that the ranges tested in the Box-Behnken design were different from those in the 2-level factorial design. Thus, though ethanol and particle size were statistically significant as disclosed in the factorial design, they were not so in the later design. The equation that fit all experimental data for methane yield was:

$$\begin{aligned}\text{Log (Methane yield)} = {} & 9.787 - 0.176 \times \text{Temp} - 0.181 \\ & \times \text{particle size} - 0.0132 \times \text{Ethanol} \\ & - 0.00266 \times \text{Coal loading} + 0.00526 \\ & \times \text{Temp} \times \text{Particle size} + 0.000218 \\ & \times \text{Particle size} \times \text{Ethanol}\end{aligned}$$

And the mathematical expression of methane content was:

$$\begin{aligned}\text{Square root(Methane content)} = {} & -12.580 + 0.408 \times \text{Temp} \\ & + 0.187 \times \text{Particle size} - 0.063 \\ & \times \text{Ethanol} + 0.0586 \\ & \times \text{Coal loading} + 0.001 \\ & \times \text{Particle size} \times \text{Ethanol} \\ & - 0.0033 \times \text{Particle size}^2 \\ & - 0.0001 \times \text{Coal loading}^2\end{aligned}$$

The 3-D response surface clearly demonstrated that the methane yield can reach to 2996 ft^3/ton (84.8 m^3/ton) with the increase of particle size and temperature when ethanol concentration was fixed at 300 mM and coal loading was set at 200 g/L (Fig. 3a). The 3-D graph on methane content indicated that methane content can be close to 80% when the conditions were the same as those for methane yield (Fig. 3b). Based on these analyses, the optimal condition given by the DOE software was: temperature: 32 °C; coal particle size, 73.99 μm; ethanol

Table 6
Analysis of variance for methane content.

Source	Sum of squares	df	Mean square	F value	p-Value Prob > F
Model	31.25	32	0.98	7.58	<0.0001 significant
A-Particle size	0.61	1	0.61	4.72	0.0376
B-Temperature	1.96	1	1.96	15.17	0.0005
C-Inoculum size	0.01	1	0.01	0.079	0.7803
D-Solid loading	6.24	1	6.24	48.4	<0.0001
E-pH	0.63	1	0.63	4.89	0.0345
F-Mixing	0.65	1	0.65	5.02	0.0324
G-Coenzyme M	0.34	1	0.34	2.6	0.117
H-Triton X-100	0.086	1	0.086	0.67	0.4198
J-SDS	1.85	1	1.85	14.37	0.0007
K-Ethanol	4.84	1	4.84	37.55	<0.0001
L-2-Propanol	0.27	1	0.27	2.13	0.1544
M-Sodium formate	2.37E-03	1	2.37E-03	0.018	0.8931
AC	0.64	1	0.64	4.98	0.0331
AD	1.76	1	1.76	13.62	0.0009
BF	2.05	1	2.05	15.92	0.0004
DE	1.01	1	1.01	7.85	0.0087
DJ	1.37	1	1.37	10.66	0.0027
DK	0.7	1	0.7	5.41	0.0267
EG	1.25	1	1.25	9.67	0.004
EK	0.58	1	0.58	4.53	0.0414
FG	1.12	1	1.12	8.69	0.006
HM	0.84	1	0.84	6.48	0.0161
ACH	0.74	1	0.74	5.72	0.023
Residual	4	31	0.13		
Cor total	35.25	63			

Table 7
Analysis of variance for methane yield obtained from Box-Behnken design.

Source	Sum of squares	df	Mean square	F value	p-Value Prob > F
Model	27.03	6	4.5	4.29	0.0052
A-Temp	13.26	1	13.26	12.64	0.0018
B-particle size	1.8	1	1.8	1.71	0.2043
C-ethanol	0.83	1	0.83	0.79	0.3827
D-solid loading	4.51	1	4.51	4.3	0.05
AB	3.18	1	3.18	3.03	0.0958
BC	3.46	1	3.46	3.29	0.0832
Residual	23.08	22	1.05		
Lack of fit	15.73	18	0.87	0.48	0.877
Pure error	7.34	4	1.84		
Cor total	50.1	28			

Table 8
Analysis of variance for methane content obtained from Box-Behnken design.

Source	Sum of squares	df	Mean square	F value	p-Value Prob > F
Model	8.52	7	1.22	4.75	0.0025 significant
A-Temp	3.62	1	3.62	14.12	0.0012
B-particle size	0.69	1	0.69	2.68	0.1162
C-ethanol	0.17	1	0.17	0.68	0.4196
D-solid loading	0.24	1	0.24	0.95	0.3406
BC	1.88	1	1.88	7.34	0.0132
B^2	1.35	1	1.35	5.28	0.0319
D^2	0.82	1	0.82	3.21	0.0878
Residual	5.38	21	0.26		
Lack of fit	4.45	17	0.26	1.13	0.5076 not significant
Pure error	0.93	4	0.23		
Cor total	13.9	28			
Cor total	16.33	28			

concentration, 300 mM; and coal loading; 201.98 g/L. Under these conditions, the predicted methane yield was 2957 ft^3/ton (83.7 m^3/ton) with a methane content of 74.2%.

3.3. Verification experiments

The five bottles which had an initial ethanol concentration of 300 mM produced no methane over 40 days. In contrast, the three reactors, each with an initial 100 mM ethanol proceeded normally as what we observed from experiment 1 and 2. At day 10, the standard deviations among the three replicates were large for both methane yield and content (Fig. 4). But as time went by, the one reactor which was not very active at the beginning caught up with the other two and resulted in similar methane content and yield. Methane production rate of 56.1 ft^3/ton-day (1.6 m^3/ton-day) was the highest during the first 15 days. After that, methane content decreased from 69.7% to 63.3% and released gas volume in the reactors decreased significantly. At day 25, as a result of addition of 100 mM of ethanol, methane production resumed again. Within 10 days, the methane production rate was 94.6 ft^3/ton-day (2.7 m^3/ton-day) and methane content reached 77.6% at day 35. After this time, however, methane release slowed down. At day 40, the third dose of ethanol at 100 mM was supplemented and increased methane yield was detected. Between day 40 and 50, the methane production rate was 91.3 ft^3/ton-day (2.6 m^3/ton-day) with a methane content of 77.3%. Overall, the total methane yield was 2900.1 ± 170.6 ft^3/ton (82.1 ± 4.8 m^3/ton) in 55 days. The final methane content in the reactors was 70 ± 1%. These results were fairly close to those predicted by the software: methane yield of 2958 ft^3/ton (83.7 m^3/ton) and a methane content of 74%. Therefore, the models we developed from this study can be used to predict methane yield and content as long as the conditions were within the ranges detailed above. Regarding the three microcosms which contained 100 mM ethanol but without coal, the total methane volume after 25 days was 6.9 ± 1.7 mL, which was 2.35% of 255.3 mL released from those with coal and 100 mM ethanol during the same time period. Thus, the majority of methane detected from the microcosms was from coal, not ethanol.

3.4. Time series data

To understand the methane production process better, time series data for the top three performing reactors (Table 2) were summarized. For the top #1 (#29) and #2 (#16) reactors, methane content increased with time during the first 20 days to 81.3% and 74.0%, respectively (Fig. 5a). After that time, however, methane content in the headspace stopped increasing and decreased after day 25. For the top #3 (#56) reactor, methane content increased with time to a final level of 76.0% during the 30-day experimental period.

In terms of methane yield, a similar trend to methane content was observed. For the top #1 and #2 reactors, the majority of methane was released during the first 20 days (Fig. 5b). Methane production after that time was minimal. In 30 days, methane production in the top #1 and #2 reactors were 979.43 and 880.13 ft^3/ton (27.7, 24.9 m^3/ton), respectively. Regarding the top #3 bioreactor, methane productivity increased with time during 30 days. The final methane yield was 514.93 ft^3/ton (15.3 m^3/ton). Based on these observations, we concluded: (1) methane release under different conditions may have different production rates and (2) for the best-performing reactors, what happened after day 20 needs to be investigated. If this bottleneck

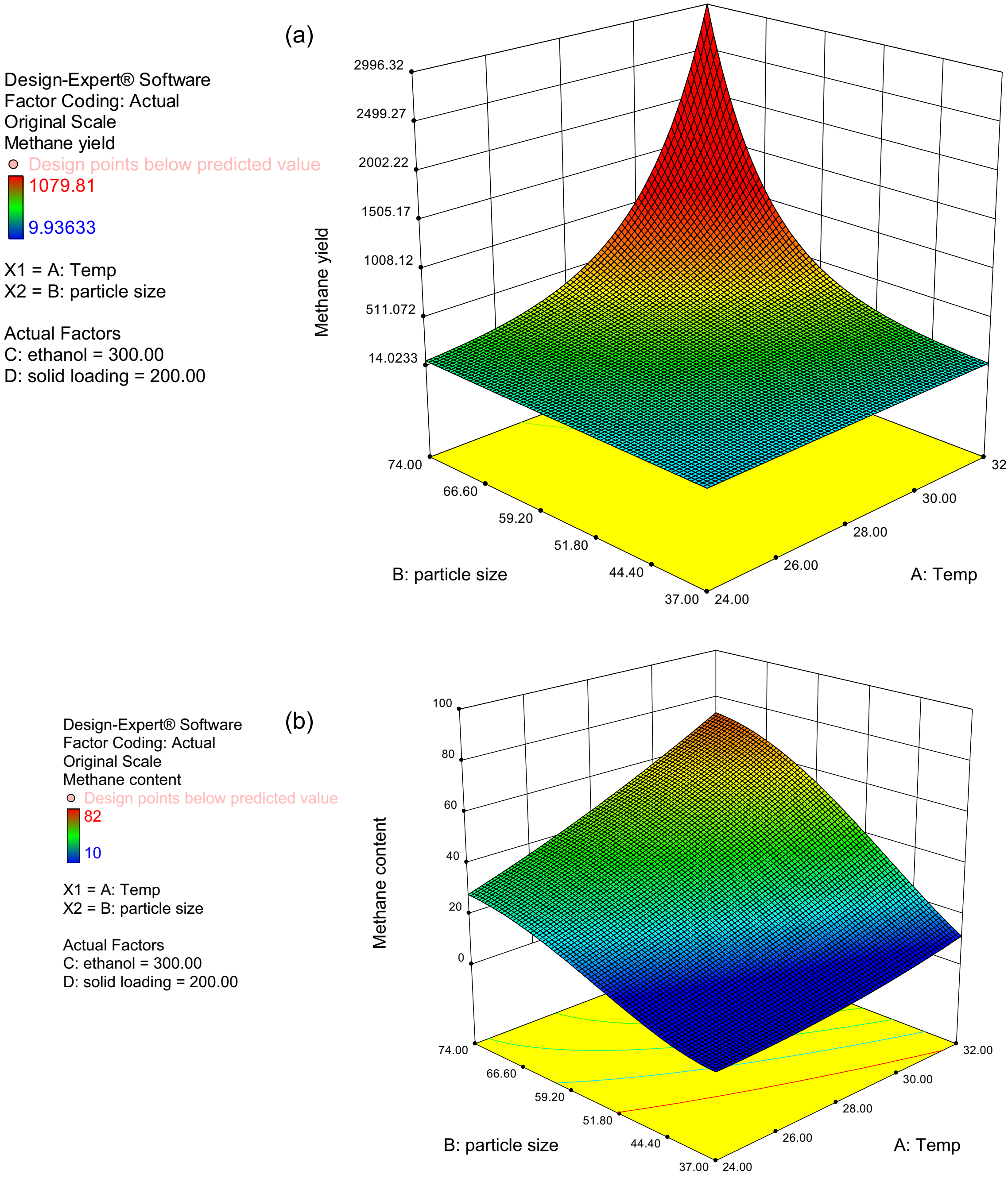

Fig. 3. 3-D response surface for methane yield (a) and methane content (b).

can be resolved, methane production will be sustained continuously and enhanced dramatically.

4. Discussion

As revealed above, parameters, such as shaking, inoculum size, CoM, 2-propanol, and sodium formate did not have significant effect on methane production. Thus, for ex situ application of coal bioconversion, shaking is not needed and inoculum size at 10% should be sufficient. For both ex situ and in situ coal conversion, the latter three chemicals do not need to be considered. These factors were not further discussed here.

Temperature is critical for microbes who perform the best at optimal temperature range. For the microbial community used in this study, the higher end of temperature close to 40 °C was proven to be detrimental to methane production. Within the range of 24–32 °C, methane yield increased with increased temperature. This is in agreement with what was reported for a microbial community collected from the Fort Union Formation in the Powder River Basin. When the incubation temperature was increased from 22 to 38 °C, the rate of methane production increased by 300% [22]. Higher temperature may enhance cell metabolism and growth kinetics, increase coal solubility and increase the rate and extent of substrate mass transfer from the coal solids [22]. However, if the temperature is too high, certain microbes may be negatively affected. As of now, optimal temperature has been reported as 35 °C for a community isolated from mine water in Jitpur, India for converting left over coal remains at the same place [21]; 60 °C for a thermophilic methanogenic consortium enriched from Banaskantha coal mine in Western India [23].

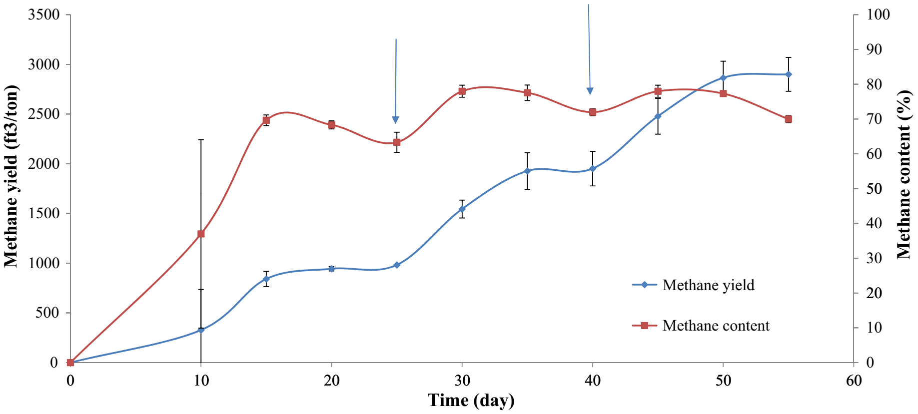

Fig. 4. Methane production as a result of ethanol supplementation. The two arrows indicate when ethanol (100 mM) was added.

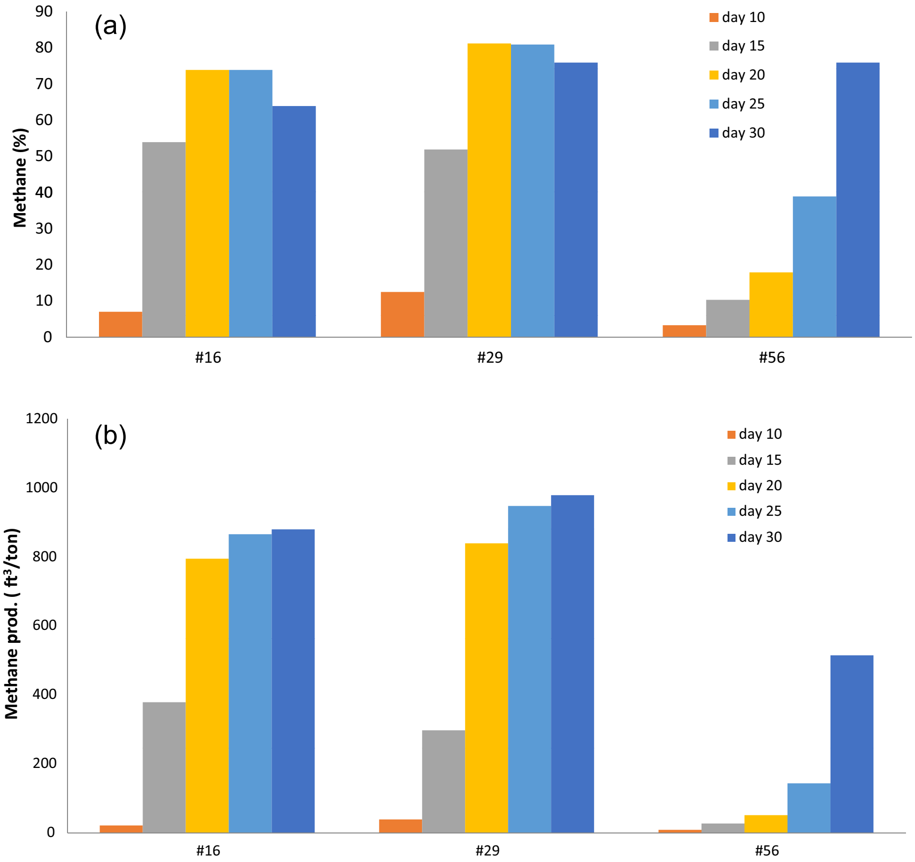

Fig. 5. Time series data for methane content (a) and methane yield (b).

Particle size is also an important parameter affecting methane yield since coal degradation is generally a mass-transfer limited process and small particles having large surface areas are more accessible to microorganisms [17]. Results from the 2-level factorial design agrees with this common recognition. However, the Box-Behnken results demonstrated that methane yield had not much difference between coal particles less than 74 μm and those less than 37 μm. Thus, for bioconverting Illinois bituminous coal to methane, coal particle size of <74 μm is optimal. This is similar to a range of 25–60 μm optimal for Indian coal wastes [21].

In this study, lower pH between 6 and 8 was proven to be beneficial for coal biogasification. This agrees with what was observed for subbituminous coal. The explanation was that lower pH may enhance coal solubility [22], hydrolyze ester or ether bonds within coal matrix and acids may enter the coal pore structure and interact with ion-exchangeable cations, resulting in limited dissolution of the coal via disruption of ionic bridges [32].

For ex situ setups, these three parameters can be easily modified. For in situ applications, manipulation of these parameters, though difficult, is still achievable. For example, particle size and surface area may be altered by hydraulic fracturing and pH and temperature may be changed by adding acid and injecting steam, respectively.

Regarding coal or solid loading, it had a *p* value of 0.0646 on methane yield and <0.0001 for methane content. Thus, it is an important parameter affecting methane production. Based on our observations, when coal loading was close to 700 g/L, a significant amount of coal was not completely wetted by the nutrient solution. However, microbes may still be able to penetrate and degrade coal as coal associated microbes have been identified in our previous study [26]. During data analysis for finalizing the best coal loading, 201.98 g/L was predicted to be the optimal if a preference was given to methane yield instead of methane content.

Surfactants that can enhance the aqueous solubility of coal have been tested on improving methane yield from subbituminous coal. But they are like double-edged swords. The obvious negative impact is that they are toxic to microbial cells at concentrations above certain levels. Among three non-ionic surfactants (Zonyl FSN, Triton X-100, and Brij 35) studied, only the first one at 50% of its CMC produced 93% and 57% more methane than no-surfactant controls and cultures with 100% CMC Zonyl FSN [24]. In this study, when used at 30 or 50% of respective CMCs, both Triton X-100 and SDS has negative effects on methane production. Effect from the former was not, but from the latter was statistically significant. Thus, both surfactants do not need to be supplemented to the nutrient solution.

Similar to surfactants, solvents are also used to enhance coal solubility. In one study, where three solvents were tested, methanol, pyridine, and N,N-dimethylformamide (DMF), only DMF at 0.25 vol.% produced 346% more methane than the no-solvent control cultures. However, the researchers were unable to conclude whether the enhanced methane production in the presence of DMF was due to enhanced coal utilization or direct degradation of DMF [22]. In another study, where ethanol served as the solvent, enhanced methane production was observed only when ethanol was added in the amount of 5 or 10 mg to 10 g coal from Power River Basin [25]. In our study, ethanol was shown to have the highest positive effect on methane yield and the second highest on methane content.

Based on experimental results, the DOE software predicted that 300 mM was the optimal concentration for ethanol. However, during verification experiments, when this concentration was added to reactors containing all needed components, only negligible amount of methane was released. When the total 300 mM ethanol was divided into three equal portions and supplemented at three time points, then indeed the final methane yield and content matched those predicted. These results may indicate ethanol toxicity to the studied microbial community at 300 mM.

Besides being a solvent, ethanol can serve as a carbon source and electron donor to microorganisms through various pathways. Through reaction with bicarbonate, sulfate, or acetate, ethanol can be degraded to acetate, butyrate and propionate. Through ^{13}C tracer tests, ethanol was found to account for 6%, 14%, and 2.5% of the total carbon flux to methane in anoxic environments of Lake Mendota, Knaack Lake and sewage digester sludge, respectively [33]. Fate of ethanol in our reactors are not known at this time and deserves further investigation. Additionally, the observed phenomenon of methane content decreasing after certain time warrants further study. Furthermore, the interactions among different parameters that were revealed only in this study need to be studied further in terms of their combined effects on methane yield from coal. However, although this study leads to deep research of coal biogasification, the models developed from this study can be used to predict methane content and yield from bituminous coal through biogasification ex situ. In addition, the methodology presented in this manuscript can certainly be adopted to study bioconversion of coal with different ranks and using different microbial communities.

5. Conclusion

Through this comprehensive study involving 12 parameters and three steps, statistically significant factors were identified for methane yield and content. The optimal condition for biogasifying Illinois bituminous coal to methane was: temperature, 32 °C; coal loading, 201.98 g/L; coal particle size, <73.99 μm; and ethanol at 300 mM. Under these conditions, the predicted methane yield and content was 2957.4 ft^3/ton (83.7 m^3/ton) and 74.2%, respectively. Results from experiments conducted under these conditions led to a methane yield of 2900 ft^3/ton (82.1 m^3/ton) with a methane content of 70%. Thus, experimental data matched those predicted perfectly.

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