Final Scientific/Technical Report

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ABSTRACT

To increase our understanding of coal biogasification and move this technology closer toward field scale demonstration, we have thoroughly investigated coal bioconversion both ex situ and in situ. Specifically, we have screened a total of 12 parameters and identified those that exert statistically positive influence on coal biogasification. Based on these evaluations, a recipe for a nutrient solution was developed. With the addition of this nutrient solution, methane yield from Illinois coal was enhanced dramatically. In addition, we have demonstrated that coal bioconversion can be sustained over a long period of time as long as suitable conditions were maintained. Furthermore, biogasification of coal was tested under pressure simulating in situ conditions. Surprisingly, pressure was found to have no negative effects on microbial activities. Thus, the same recipe developed for ex situ may be used in situ as well.

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EXECUTIVE SUMMARY

Biological coal conversion (BCC) has attracted extensive attention during recent years. Production of methane through BCC has been a commercial reality in several parts of the world. In the United States, the two most prolific coal-bed methane (CBM) producing basins are the Powder River and Sun Juan, contributing 80% of the total CBM production in the US. Both basins located in states west of the Mississippi river, are featured by having coals with low rank and high permeability. In states east of the Mississippi river, where > 95% of coal is bituminous, CBM has not been as successful.

At the beginning of this project, little work has been done on methane production from bituminous coal. Among the few studies, the results contradict each other. In addition, all reported studies have been conducted at microcosm scale under static conditions. And the majority of them have been carried out in a delicate environment, such as a glove box. Thus, the applicability of these laboratory investigations is questionable. The proposed project, however, seeks to maximize methane productivity from bituminous coal in a dynamic system adopting parameters optimized at batch modes.

At the conclusion of this project, we have accomplished all proposed tasks. The major accomplishments from this project are:

(1) We have simplified and reduced cost of a standard nutrient medium by eliminating expensive but not very useful ingredients.

(2) We have identified optimal conditions for converting bituminous coal to methane ex situ. To optimize methane production from bituminous coal through use of a well-studied microbial community derived from the same Illinois basin in the 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^{o}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 2,957.4 ft^3/ton (83.7 m^3/ton) and 74.2%, respectively. To confirm the predicted results, a verification experiment was conducted, where a methane yield of 2,900 ft^3/ton (82.1 m^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;

(3) We have found solutions on how to sustain methane release from coal. Coal biogasification typically follows a trend of increased methane release within certain time followed by decreased methane production. To identify reasons for this behavior and provide insight on how to sustain coal biogasification over longer durations, we studied coal bioconversion under fed-batch conditions. It was discovered that after methane production rate stopped increasing, coal, at the studied loading, was still bioavailable. The headspace gas and the coal degradation intermediates were not toxic or inhibitory to the bioconversion process. Instead, lack of nutrients, especially those provided through yeast extract and peptone was critical for sustained methane release from

coal. Although these two nutrients could be used as carbon sources, negligible amount of methane was observed from control reactors without coal. At least, these were true for the microbial community and the bituminous coal investigated here. Thus, to convert coal to methane continuously at a high rate that is possible, site-specific nutrient solution needs to be supplemented periodically.

To prove this strategy, we established a 3-liter fermentor to evaluate coal biogasification over a longer duration as compared to studies reported so far. During the one-year study, a nutrient recipe was added three times to sustain methane release from Illinois bituminous coal. After the fermentation was terminated, the residual coal and fermentation broth were characterized in detail. The cumulated methane production was 5,171 ft^3/ton with a methane content of 75.36%. Throughout the experimental duration, methane release continued to increase over time.

(4) We elucidated pressure effect on coal biogasification. For this purpose, we set up four reactors. Two reactors contained coal core and the other two contained powdered coal. Once the reactors were added with a microbial community, a formation water-based nutrient recipe and coal at desired sizes, the reactors were kept at 450 psi by purging with nitrogen. Results from this study did show that the developed recipe could be used for coal core and coal powder. Coal particle size and pressure had no negative effects on methane release.

After biogasification, compared to the untreated coal, the coal residue after treatment appeared to be finer and highly degraded with less carbon but more sulfur and ash. Based on mass balance, volatile and fixed carbon decreased 15.9% and 29.6%, respectively, using the untreated coal as the baseline. According to GC/MS analysis, the fermentation broth contained mainly three groups of compounds: fatty acids, aromatics, and hydrocarbons.

Comparison of actual accomplishments with the goals and objectives of the project.

The major goals of this project are to: (1) maximize methane productivity from bituminous coal ex situ and (2) demonstrate the feasibility of enhanced methane production in situ. Table 1 compares our overall progresses made at the conclusion of this project with the proposed milestones.

Table 1: Comparison between actual accomplishments with proposed tasks.

Task	Milestone title/Description	Planned completion date	Actual completion date	Verification method	Comments
Task 2.0	**Simplify the composition of the nutrient medium**				
Subtask 2.1	A medium with half of its original cost is identified.	12/29/2014	02/30/2015	Economic analysis	We have developed two nutrient solutions that have half of the original cost of the medium.
Subtask 2.2	Proximate and elemental analyses of coal is finished	12/29/2014	12/29/2014	Comparison with literature data	This subtask was accomplished.
Task 3.0	**Investigate individual and interactive effects from different parameters**				
Subtask 3.1	Screen important parameters	6/29/2015	6/29/2015	By experimental results	This subtask was accomplished.
Subtask 3.2	Identify optimal conditions	9/29/2015	11/30/2015	By experimental results	This subtask was accomplished.
Task 4.0	**Optimize methane yield in fed-batch systems**				
Subtask 4.1	Test different schemes	12/29/2015	12/31/2015	Experimental results	This subtask was accomplished.
Subtask 4.2	Run the fed-batch for 6 months	9/29/2016	4/19/2017	Experimental results	This subtask was accomplished.
Task 5.0	**Bioconversion under pressurized conditions**				
Subtask 5.1	Test BCC under high pressure	8/29/2016	9/30/2016	Experimental results	This subtask was accomplished.
Subtask 5.2	Evaluate changes in coal properties	9/29/2016	9/30/2017	Experimental results	This subtask was accomplished.

REPORT DETAILS

All Experimental methods, Results and discussions and Conclusion were clearly described in the publications listed below. Copies of these papers are available upon request.

Journal Articles generated from this project

1. Zhang, J., Bi, Z., **Liang, Y.-N**. Development of a nutrient recipe for enhancing methane release from coal in the Illinois basin. International Journal of Coal Geology. In revision.
2. Bi, Z., Zhang, J., Park, S., Harpalani, S., **Liang**, **Y.-N**. 2017. A formation water-based nutrient recipe for maximizing methane release from coal in the San Juan Basin. Fuel. 209: 498-508.
3. Zhang, R., Liu, S-M., Bahadur, J., Elsworth, D., Wang, Y., Hu, G., **Liang**, **Y.-N**. 2017. Changes in pore structure of coal caused by coal-to-gas bioconversion. Scientific Reports. 7:3840-3853.
4. Zhang, J., **Liang**, **Y.-N**. 2017. Evaluating approaches for sustaining methane production from coal through biogasification. Fuel. 202: 233–240.
5. Xia C., Wiltowski, T., Harpalani, S., **Liang**, **Y.-N**. 2016. Coal depolymerization using permanganate under optimal conditions. International Journal of Coal Geology. 168: 214–221
6. Zhang, J*., **Liang, Y.-N.** Harpalani, S. 2016. Optimization of methane production from bituminous coal through biogasification. Applied Energy, 183:31–42.
7. Pandey R*; Harpalani, S., Feng, R*., Zhang, J*., **Liang, Y.-N.** 2016. Changes in gas storage and transport properties of coal as a result of enhanced microbial methane generation. Fuel, 179. 114–123.
8. Zhang, J.*, Park, S., **Liang, Y.-N**., Harpalani, S. 2016. Finding cost-effective nutrient solutions and evaluating environmental conditions for biogasifying bituminous coal to methane ex situ. Applied Energy. 165:559–568.
9. Park, S., **Liang, Y.-N**. 2016. Biogenic methane production from coal: A review on recent research and development on microbially enhanced coalbed methane (MECBM). Fuel. 166. 258–267.
10. Zhang, J.*, **Liang, Y.-N**., Yau, P.M., Pandey, R.*, Harpalani, S. 2015. A metaproteomic approach for identifying proteins in anaerobic bioreactors converting coal to methane. International Journal of Coal Geology. 146, 91–103.
11. Zhang, J.*, **Liang, Y.-N**, Pandey, R.*, Harpalani, S. 2015. Characterizing a microbial community dedicated for converting coal to methane *in situ* and *ex situ*. International Journal of Coal Geology. 146, 145–154.

Conference proceedings generated from this project

1. **Yanna Liang**. 2017. Bioleaching of Rare Earth Elements from coal-based products. Pittsburgh Coal Conference. Sep. 4-7. Pittsburgh.
2. **Yanna Liang**. 2016. Converting bituminous coal to methane: approaches to maximizing methane yield ex situ and in situ. The first CBM meeting at Jincheng, Shanxi, China. June 20-22.
3. Ji Zhang, **Yanna Liang**, Satya Harpalani. 2016. Identifying optimal parameters for converting bituminous coal to methane through biogasification. The fourth E^2E Energy Conference. Beijing, China. July 6-8.
4. Ji Zhang, **Yanna Liang**, Satya Harpalani. 2016. Optimizing microbial coal conversion to methane for ex situ applications. 21st annual conference of Institute of Biological Engineering, Greenville, SC, April 7-9.
5. Satya Harpalani, Rohit Pandey, **Yanna Liang** and Ji Zhang. 2016. Bioconversion of Coal Waste to Natural Gas: Conversion of a Liability to an Asset. 3rd International Conference

on Chemical, Biological and Environmental Sciences, December 31, 2015 – January 1, 2016, Bangkok, Thailand.

6. Stephen Park. 2015. Maximizing methane yield from bituminous coal through biostimulation under optimal conditions. 2015 Mid-American Environmental Engineering Conference. Columbia, MO. October 24.
7. **Yanna Liang***, Ji Zhang, Stephen Park, Satya Harpalani. 2015. Microbially enhanced coalbed methane (MECBM): identifying optimal conditions for maximizing methane yield. BIT's 4th Annual International Symposium of Clean Coal Technology. Xian, China. September 24-26.
8. **Yanna Liang***, Ji Zhang, Stephen Park, Satya Harpalani. 2015. Biostimulation for biogasification for converting coal to methane. International Pittsburgh Coal Conference, Pittsburgh, PA, USA. October 5 - 8.
9. **Yanna Liang**, Ji Zhang, Satya Harpalani. Peter Yau, Rohit Pandy. Bioconversion of coal to methane – study of microbial community, conversion pathway and property of the residual coal. The 40th International Technical Conference on Clean Coal & Fuel Systems. May 30-June 4^{th}. 2015. Clearwater, FL.
10. Ji Zhang, **Yanna Liang**, Robit Pandey, Satya Harpalani. Using selective bio-catalytic activities as a new route for conversion of waste coal to methane. IBE 20^{th} Annual Conference, March 6-8th, 2015, St. Louis, MO.