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**DEVELOPMENT OF BIOLOGICAL COAL GASIFICATION
(MicGAS PROCESS)**

14th Quarterly Report

DOE-METC Contract No. DE-AC21-90MC27226

Submitted to:

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DEVELOPMENT OF BIOLOGICAL COAL GASIFICATION (MicGAS PROCESS)

1. CONTRACT: For the DOE contract # DE-AC21-90MC27226 MOD A006 following tasks were completed:

Task 1. NEPA Compliance and Updated Test Plan

This task has been completed.

Task 2. Enhance Methane Production

Subtask 2.1 Bacterial Strain Improvement. One of the important factors to enhance methane production from low rank coals is to study the process parameters such as substrate concentration, pH of the medium, temperature, etc. Process parameters, on the other hand, have a direct influence on the microorganisms involved in the process. In order to better understand the effect on some parameters (such as solids loadings and pH of the medium) and to improve the CH₄ production from coal, several experiments have been conducted. As it was mentioned before (6th Quarterly Report), the pH of the medium does not significantly influence at solids loadings up to 5% (w/v). At higher solids loadings (10% TxL and higher), however, pH of the reaction broth decreases sharply after the addition of TxL and ranges from 6.6 to lower values.

An experiment to study the mechanism of lowering the pH during biomethanation of Texas lignite (TxL) at higher solids loadings was conducted in 60-mL vials containing 40 mL of 0.2% SNTM and 10% TxL. The initial pH of the medium in both control and experimental vials was corrected with 1 N HCl or 1 N NaOH to the following values: 6.5, 7.0, 7.5, 7.8 (no correction), 8.0, 8.5, and 9.0. Every seven days the control and experimental vials were monitored for total gas production, gas composition, COD, VFA, and pH changes. At 10% TxL (or higher) solids loadings, even the pH of the medium was corrected to 8.5 - 9.0, and an hour after the start of the experiment the pH to the reaction mixture decreased to 6.6 - 7.6. This is interpreted as the effect of TxL addition. The different initial pH of the medium in both control and experimental vials did not significantly influence CH₄ production. Cumulative CH₄ production in the experimental vials containing 10% TxL at different pH values varied from 10 to 22 cc after 21 days of static cultivation (Fig. 1). The highest CH₄ production was observed in the experimental vials without additional correction of initial pH of the medium and was 53% from the CH₄ produced in the control vials. The COD measured in all experimental sets were significantly higher (1725 mg O₂/L when the initial pH of the medium was corrected to 9.0) as compared to the controls (58-93 mg O₂/L, Fig. 2). This is interpreted as a presence of more carbon source in the medium released from the TxL biodegradation. When initial pH of the medium was adjusted to 9, the COD/CH₄ ratio was in excess of 440 in the experimental vials containing TxL. In contrast, the COD/CH₄ ratio for the control vials was 13-19. This indicates that

correction of the initial pH of the medium can help for better biomethanation of TxL by releasing more soluble compounds in the medium and enhancing the growth of microorganisms. The changes in the pH after the initial correction were not significant and varied from 7.0 to 7.2 (Fig. 3).

Another avenue for improvement of the bacterial consortium used in this process is to isolate and study the most productive bacterial strains. The experiment to evaluate the isolates from Mic-1 and Mic-4 consortia described in the 13th Quarterly report was completed. After 28 days of static cultivation at 37°C, when all vials were inoculated with 10% mixture of methanogenic consortium, each combination of isolates showed different capabilities for biomethanation of TxL. Combinations D and G were found to be the most promising (Figure 4). Further, these combinations will be used together with Mic-1 consortium to evaluate the effect of the new consortia on the biomethanation process.

Subtask 2.2 Addition of Co-Substrates. An experiment to study the effect of co-substrate addition was conducted in 100-mL vials containing 50 mL 0.2% SNTM and 1% TxL. Citrate, oxalate and methanol were used as a co-substrate at different concentrations (10 mM, 1 mM and 0.5%, respectively). The experiment was carried out under static conditions at 37°C for 28 days. Maximum methane production was obtained from the vials that contained 0.5% methanol and 1% TxL (174 cc), while in the control vials CH₄ production was only 123 cc (Table 1). This can be explained with the fact that methanol is one of the simplest substrates for CH₄ formation and acts as an additional donor of protons necessary for the biomethanation process. These results support our previous data obtained in fluidized bed reactors and reported in the 10th Quarterly Report.

Citrate and oxalate are important mediators for the formation of acetate (main precursor for CH₄ formation) in the glyoxylate cycle. At the same time, citrate also has sequestering properties for metal ions. The hypothesis to be tested was that the metals (such as Fe³⁺, Mn²⁺, Mg²⁺, etc., present in the coal structure) are chelated/sequestered by addition of citrate, and therefore, facilitate coal carbon to CH₄ conversion by the microorganisms. The results from this experiment show that there was no significant difference in the amounts of CH₄ produced in the control vials. The increased concentration of citrate (10 mM) induced more CO₂ production, compared to the rest of the control vials containing 1 mM citrate or oxalate. In the presence of 1% TxL, however, a significant increase in CH₄ and CO₂ production was observed. The highest CH₄ production was obtained in the treatment with 10 mM citrate (Figure 5), while the amount of CO₂ produced varied slightly (121 -132 cc for all experimental vials). This phenomenon can be explained by the leaching of the inhibitory compounds from TxL and their subsequent sequestration by the citrate, thereby allowing the bacteria to convert TxL to CH₄ more efficiently. Mass balance calculations show that CH₄ production is due to the biomethanation of TxL and not from the addition of co-substrates (Table 1).

Table 1. Theoretical and actual methane production from different carbon sources used as co-substrates*			
Carbon Source	Total Carbon Available, (g)	Theoretical Production, (cc)	Actual Production, (cc)
Sheftone T (2%)	0.044	56	5
TxL (1%)	0.314	398	7
0.2% Sheftone T + 1% TxL	0.358	455	34
Methanol (0.5%)	0.074	94	53
0.2% Sheftone T + 0.5% Methanol	0.118	150	123
0.2% Sheftone T + 0.5% Methanol + 1% TxL	0.432	549	174
Citrate (10 mM)	0.036	46	6
0.2% Sheftone T + 10 mM Citrate	0.070	102	2
0.2% Sheftone T + 10 mM Citrate + 1% TxL	0.394	500	86

* - All calculations are based on 50 mL medium. Theoretical production - 100% of the carbon available is converted to CH₄.

The experiment to study the effect of additional co-substrates on biomethanation of TxL was conducted by using lactate, succinate and formate. This experiment was conducted in 125-mL vials containing 60 mL 0.2% SNTM (or NTM) and 1% TxL. Control vials contained 60 mL of 0.2% SNTM (or NTM) only. Sodium formate (CHO₂Na), L(+) lactic acid (C₃H₅O₃) and sodium succinate (C₄H₄O₄Na₂·6H₂O) were used as co-substrates in 10 mM concentration. Mic-1 consortium was used as 10% inoculum. Both control and experimental vials (in triplicate) were incubated at 37°C (static conditions). Samples for total gas, gas composition, COD, VFAs and pH analyses were taken. Preliminary observations showed that the highest CH₄ production was obtained from the vials that contained 0.2% SNTM and 1% TxL supplemented with 10 mM lactate. This experiment is still in progress and will be discussed in the next Quarterly Report.

Subtask 2.3 Low cost nutrient Amendment. No experimental work was planned for this period.

Conclusions:

- Correction of the initial pH of the medium did not significantly influence the biomethanation process.
- CH₄ production observed in the experimental vials without additional correction of initial pH of the medium was 53% higher than the CH₄ produced in the control vials.
- The COD was significantly higher in the experimental vials where the initial pH of the medium was corrected to 8.5 -9.0.
- Highest COD/CH₄ ratio was obtained in the experimental vials containing TxL with correction of pH to 9.0.
- The most promising combinations between the isolates from Mic-1 and Mic-4 were found to be combinations D and G.
- The addition of co-substrate (10 mM citrate or 0.5% methanol) enhances biomethanation of TxL.
- Mass balance calculations show, that CH₄ production is due to the biomethanation of TxL and not from the addition of co-substrates.

Planned Future Work:

- Continue to study the effect of co-substrates addition on biomethanation of TxL.
- Study the effect of co-substrate and methanol addition on biomethanation of TxL in upflow bioreactors.
- Further improvement of Mic-1 consortium by using ethylmethanesulphonate (EMS) and N'-methyl-N'-N'-nitrosoguanidine (NTG).

Figure 1. Cumulative methane production during biomethanation of 10% Texas lignite by Mic-1 consortium in 0.2% SNTM with different initial pH.

Figure 2. Change in COD concentrations during biomethanation of 10% Texas lignite by Mic-1 consortium in 0.2% SNTM with different initial pH.

Figure 3. Change in pH of the medium during biomethanation of 10% Texas lignite by Mic-1 consortium in 0.2% SNTM with different initial pH.

Figure 4. Cumulative methane production (day 35) from different combination of Mic-isolates after adding methanogens at day 28.

Figure 5. Effect of citrate, oxalate and methanol on biomethanation of 1% Texas lignite by Mic-1 consortium in 100-mL vials containing 50 mL 0.2% SNTM. Methane from controls deducted.

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