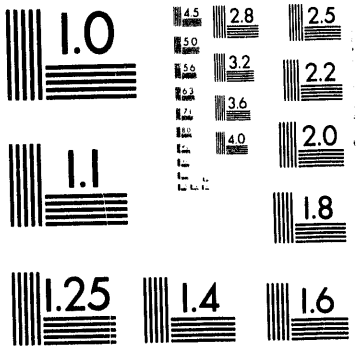
1.0
1.1
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DOE/MC/27226-3594

DEVELOPMENT OF BIOLOGICAL COAL GASIFICATION (MicGAS PROCESS)

13th Quarterly Report

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

Submitted to:

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DISCLAIMER

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. An experiment was conducted to study the mechanism of lowering the pH during biomethanation of Texas lignite (TxL) at higher solids loadings. TxL was treated with different solutions in order to modify the initial pH of TxL. Four samples of TxL (each of 20 g pulverized coal) were rinsed with tap water, 0.1 M $NaHCO_3$ (pH 8.40), 0.1 M $NaHCO_3$ + 0.1 M Na_2CO_3 (pH 10.23), and 0.1 M Na_2CO_3 (pH 11.04) solutions. The TxL samples were treated for 1 minute to 16 hours with these solutions. The pH of the reaction mixture changed for each particular case (Table 1). There was slight change in the color when TxL was treated with tap water. In all TxL samples, however, significant changes were observed in the color of the solution as well as in the washed residual TxL after drying at 104°C.

The experiment was conducted in 60-mL vials containing 40 mL 0.1% SNTM + 10% residual TxL. Mic-1 consortium was used as 10% inoculum. No significant difference in methane production between control and experimental vials was observed during 28 days of cultivation. The initial level of acetic acid in the liquid from all experimental vials decreased to 5-20 ppm after 7-14 days. The concentration of propionic acid increased during the first seven days, but decreased thereafter to 7-14 ppm. After 7 days from the beginning of the experiment, protein concentration decreased in all experimental vials. It seems that pretreatment of TxL with solutions at different pH did not affect the process.

Another experiment to investigate the lowering of pH in the reaction mixture containing higher than 1% solids loadings was started. In this experiment (using 60-mL vials), the control vials contained 40 mL 0.2% SNTM inoculated with 10% Mic-1 consortium and the experimental vials contained the same medium + 10% TxL. The initial pH of the medium in both control and experimental vials was adjusted with 1 N HCl or 1 N NaOH to the following pH 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 sampled for total gas production, gas composition, COD, protein, and VFA's analysis, as well as changes in pH. Preliminary observations show that the initial pH of the medium did not significantly influence the methane production. At higher solids

loadings (10% TxL and higher), even though the pH of the medium was corrected to 8.5 or 9.0, within an hour after the start of the experiment, the pH of the reaction mixture decreased. This is interpreted as the effect of TxL addition. This experiment is still in progress.

Table 1. Effect of different solutions on the pH of the TxL slurry during treatment of 20% Texas lignite *

Time (min)	Tap water + 20% TxL 1	0.1 M $NaHCO_3$ + 20% TxL 2	0.1 M $NaHCO_3$ + 0.1 M Na_2CO_3 + 20% TxL 3	0.1M Na_2CO_3 + 20% TxL 4
0	7.96	8.40	10.23	11.04
1	3.90	5.70	6.90	7.35
15	3.90	5.28	6.84	7.40
30	3.90	5.21	7.15	7.65
45	3.90	5.13	7.20	7.77
60	3.80	5.10	7.30	7.80
960	3.80	4.92	7.30	8.20
Observations	Slight change in the color of solution. After drying - no change in the color of TxL	Color changed; partial solubilization (yellow). After drying seems more "black"	"Foam" formation; solubilization; dense solution with dark brown color. After drying "black" TxL	"Foam" formation; "dense" solution with black color. After drying looks like charcoal

* - Experiment was carried out in 300-mL flasks containing 100 ml of respective solution and 20% TxL (w/v). The flasks were incubated on a rotary shaker (150 rpm) at room temperature.

As another avenue to enhance the biomethanation of TxL, an experiment was started to evaluate the isolates obtained from Mic-1 and Mic-4 consortia (Strains termed 1 through 7, Topical Report,

June 1993, Table-14, Pg. 57). For this experiment, selected isolates (M1-5, M4-4, M4-5, M4-8) described in the above referenced report were used based on the capability of these isolates to convert coal carbon into acetate, propionate, and butyrate. This capability was assessed as the levels of the above acids in the cell-free culture broths from these isolates. The isolates were mixed according to Table 2 and designated as follows:

D	KS14RM5K8	1458
G	KS04RM4K4	0444
H	KS54RM4K8	5448
I	KS15RM4K8	1548
J	KS04RM5K8	0458
K	KS05RM5K8	0558

Table 2. Experimental Design for the Evaluation of Isolates Mixtures

Combination	Isolates*			
	M1-5	M4-4	M4-5	M4-8
D		√	√	
G	√	√	√	√
H	√	√	√	
I	√	√		√
J		√	√	√
K	√		√	√

* Empty boxes designate that the isolates were not used

The combinations D through K did not contain any methanogens. The criterion used for mixing was to combine the isolates capable of converting propionate and butyrate to acetate. From the data obtained on COD, cellular protein and VFA's, the most promising combination was found to be combination D (KS14RM5K8 -1458). This conclusion was based on the highest accumulation of acetate in the cell-free culture broth from this consortium. After 28 days of static cultivation at 37°C, all vials were inoculated with 10% mixture of known methanogens to evaluate the capabilities of this consortium for biomethanation of TxL. This experiment is still in progress.

Subtask 2.2 Addition of Co-Substrates. No experimental work was planned for this period.

Subtask 2.3 Low cost nutrient Amendment. Anaerobic sewage sludge (SS) samples, collected from Commercial Wastewater Treatment Plant were solubilized with NaOH. Four solutions were prepared (0.5 N, 1 N, 2 N, and 4 N) and used for this study. To 5 mL of resuspended SS were added 5 mL of each of NaOH solutions and the experimental sets were run in triplicate. Five mL of bovine serum albumin (BSA, 2 mg/mL) were used as a control. A standard BCA assay was used to determine the protein concentration in the solubilized anaerobic sludge. The highest protein concentration was obtained in the experimental set where SS was solubilized with 1 N NaOH (Table 3). From the results obtained, further experiments will be conducted to compare Sheftone T, Hoffman's dried blood and SS solubilized with 1 N NaOH.

Table 3. Protein concentration in sewage sludge solubilized with different NaOH solutions

Sample	Protein Concentration (μg/mL)			
	0.5 N NaOH	1 N NaOH	2 N NaOH	4 N NaOH
BSA	685	935	345	200
Sewage sludge	866	1255	715	761

Conclusions:

- Treatment of TxL with different pH solutions did not influence the biomethanation process.
- The decrease in methane production at higher solids loadings still needs further investigations.
- Anaerobic conditions containing deoxygenated N_2:CO_2 provide better biomethanation of TxL.
- The most promising combination between the isolates from Mic-1 and Mic-4 was found to be combination D (KS14RM5K8 -1458).

- The KS14RM5K8 shows the highest accumulation of acetate in the cell-free culture broth from this consortium.

Planned Future Work:

- Investigate the effect of co-substrates and some chelators on biomethanation of TxL.
- Further investigate the effect of methanol as an additional hydrogen donor for enhancement of biogasification of TxL.

DATE
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