DOE/MC/27226 -- 5025
Distribution Category UC-109

Development of Biological Coal Gasification (MicGAS Process)

Quarterly Report
January - March 1995

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

April 1995

Work Performed Under Contract No.: DE-AC21-90MC27226

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
ARCTECH, Inc.
14100 Park Meadow Drive
Chantilly, Virginia 22021

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DLc

1. CONTRACT OBJECTIVE: For the DOE contract # DE AC-21-90MC 27226 MOD A006, the following tasks were performed. The project Status is within the Work Plan and according to the schedule.

2. TECHNICAL APPROACH CHANGES: No changes.

3. CONTRACT:

Task 1. NEPA Compliance and Update Test Plan - Completed.

Task 2. Enhance Methane Production - Completed.

Task 3. Effect of substrate on the microbes - Completed.

Task 4. Biomethanation of TxL in bioreactors - Completed.

Subtask 4. Two stage bioreactors.

Another experiment with dual bioreactors (BR) was started to confirm the results obtained from the previous experiment. Six upflow bioreactors (BR) were organized in three sets of two as described before (18th Quarterly Report). Each BR had a total volume of 1250 mL and working volume of 800 mL. All BRs contained 800 mL (final volume) of 0.2% SNTM-CM. Reactors #1, #3, and #5 (ABR) were inoculated with Mic-1 consortium (as 10% inoculum). In addition, TxL pretreated with citrate and methanol, was loaded at 5% and 10% (w/v) in BRs #3 and #5, respectively. Reactors #2, #4 and #6 (MBR) were inoculated with methanogens. All BRs were incubated at 30°C. Samples for total gas, gas composition, VFAs, and pH were taken depending on gas production (usually every 3 days). After 7 days of operation the medium in all BRs was changed - BRs #2, #4, and #6 received the medium from BRs #1, #3 and #5, respectively. After BRs #1, #3 and #5 were emptied, a fresh medium (0.2% SNTM-CM) was added to these BRs. Then the process continued.

After 21 days of operation the amount of CH₄ gas produced from both ABR and MBR in each set was totaled and compared for best production. The amount of CH₄ produced in the first set of BRs (BR #1 with no TxL and BR #2) was subtracted from the amount of CH₄ produced in the second and third sets. Maximum net cumulative CH₄ production (10,860 cc) was obtained in the second set of BRs - ABR #3 containing 5% pretreated TxL and MBR #4 (Figure 1). The net cumulative CH₄ production in the third set (9,230 cc) was almost the same as in the second set of BRs. The CH₄ production in both ABR #3 and #5 was similar, however the amount of CH₄ produced in MBR #6 was lower compared to MBR #4 and MBR #2, which resulted in the lower net CH₄ production in the third set. This could be due to the increased amount of inhibitory compounds released in the medium during bioconversion of 10% TxL by Mic-1 despite the fact that TxL was pretreated.

Figure 1.

CUMULATIVE CH_4 AND VFA PRODUCTION DURING BIOMETHANATION OF 10% TxL IN DUAL BIOREACTORS WITH 0.2% SNTM-CM

The VFA samples from were analyzed. There was no significant difference in VFA concentrations from bioreactors containing either 5% or 10% TxL. Maximum acetate was observed between day 3 and day 4 (Figures 2 and 3). This may be due to the metabolism of the primary coal degraders from Mic-1 consortium which first degrade/attack TxL, then convert it into VFAs (eg. acetate) that are released in the medium. This acetate was then converted into CH₄ by the methanogens after several days. The fact, that VFAs concentrations and CH₄ production were similar in both bioreactors supports our observations that Mic-1 was successfully adapted to higher solids loading.

Task 5. Characterization of solid residues

Subtask 5.3. Characterization of residual coal. Coal samples from the experiment in upflow bioreactors were characterized for mineral content. For this purpose, the samples were washed 3 times with distilled H₂O and dried. The analysis of these samples is shown in Table 1.

Table 1. Inorganic element analysis of untreated and biologically treated TxL from upflow bioreactors (BR) containing 0.2% SNTM-CM.							
Sample	Major and trace elements, % of whole dry coal					Ash, %	Moisture, %
	Ca	Fe	Mg	Ni, µg/g	Zn, µg/g		
Untreated TxL	0.90	2.35	0.23	93.90	5.17	17.3	4.5
BR with 5% TxL	0.94	2.10	0.28	82.00	14.30	19.5	2.6
BR with 10% TxL	0.93	2.16	0.26	86.60	11.10	19.3	2.7

The data from inorganic analysis showed a slight increase in Ca, Mg, and Zn content. This is possibly due to the fact that these elements were present in the medium in the form of metal salts and during the experiment these salts were utilized by the microorganisms (Mic-1) and the metals left as a residue on the coal surface. On the other hand, the decrease in Fe and Ni content could be explained by the fact that these elements are important part of the prosthetic group in microbial enzymes and possibly were utilized by Mic-1 consortium to synthesize these enzymes. Also, the ash content increased by almost 2% which indicates that the carbon from TxL was converted into CH₄.

Figure 2.

Net Methane Production During Biomethanation of 5% and 10% TxL in Dual Bioreactors Containing 0.2% SNTM-CM and Mic-1 Consortium or Methanogens

● CH₄ from second set dual BRs with 5% TxL ▽ CH₄ from third set dual BRs with 10% TxL
CH₄ from control set dual BRs deducted

Figure 3.

CUMULATIVE CH_4 AND VFA PRODUCTION DURING BIOMETHANATION OF 10% TxL IN DUAL BIOREACTORS WITH 0.2% SNTM-CM

Subtask 5.5. Evaluation of solid residue for humic acids. The samples from bioreactor experiment were analyzed for humic acid (HA) content following a procedure developed at ARCTECH. The coal sample (1 g) was treated with 10 mL of 1N KOH to solubilize TxL and extract the HA. The samples were left for 16 hours and after that the supernatant (containing HA) was separated from the residual TxL. The pH of the supernatant was adjusted to < 2 with 1 N HCl to precipitate the HA. After that the sample was diluted with distilled H₂O to approximately 35 mL, centrifuged at 3500 rpm for 20 minutes, washed with distilled H₂O and centrifuged again. After the second centrifugation, the pellet containing HA was washed twice with distilled H₂O and dried at 105°C until constant weight. The HA content was calculated using the following equation:

$$HA (\%) = \frac{W_{HA1} - W_{HA0}}{W_s} \times 100$$

where: W_{HA1} is the weight (in grams) of centrifuge tube containing the dried HA, W_{HA0} is the weight of the centrifuge tube alone, and W_s is the weight of the sample. The data from HA analysis are presented in Table 2.

Table 2. Humic acid analysis of untreated and biologically (Mic-1) treated TxL				
Sample	Humic acid, %	Increase in HA content, %	Standard deviation, s	RSD, %
Untreated TxL	5.1	100	0.0025	4.967
Bioreactor 5% TxL	8.4	165	0.0040	4.762
Bioreactor 10% TxL	8.1	159	0.0031	3.787

The HA content increase significantly (up to 165%) after biological treatment of TxL in bioreactors containing either 5% or 10% solids loading. The results indicate that the residual coal from "MicGAS process" can be successfully used as a feedstock for HA production.

4. OPEN ITEMS: Draft for the final project report

5. SUMMARY STATUS AND SUMMARY FORECAST: Revised to reflect changes according to Modification # A011.