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PEAT BIOGASIFICATION DEVELOPMENT PROGRAM

Quarterly Progress Report No. 4 for the Period July 1—September 30, 1980

October 15, 1980

Work Performed Under Contract No. AC01-79ET14696

Dynatech R/D Company
Dynatech Corporation
Cambridge, Massachusetts

U. S. DEPARTMENT OF ENERGY

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PEAT BIOGASIFICATION
DEVELOPMENT PROGRAM

Quarterly Progress Report No. 4
For the Period July 1 through September 30, 1980

Dynatech Project No. MGC-2
Dynatech Report No. 2065

Submitted by:

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Prepared for:

UNITED STATES DEPARTMENT OF ENERGY
Under Contract No. DE-AC01-79ET14696

October 15, 1980

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This report has been reviewed and approved for release by Dynatech R/D Company.

A handwritten signature in dark ink, appearing to read "Donald L. Wise". The signature is fluid and cursive, with the first name "Donald" being the most prominent.

Donald L. Wise, Ph.D.
Principal Investigator
Peat Program

ACKNOWLEDGEMENT

This is to acknowledge the work of others at Dynatech R/D Company who have contributed to the development of the peat biogasification program. Mr. Carl F. Ruoff has assisted in the management of laboratory experiments and data reduction. Mr. Robert G. Murphy, Mr. Bruce A. Farmer, and Mr. Phillip A. Korb have performed fermentation monitoring, GPC and HPLC analysis, and classical solvent extraction analysis, respectively. Drs. Edward Ashare and John E. Sanderson have contributed significantly in the areas of evaluation of experimental data and engineering analysis. Mr. Robert G. Kispert is contract liaison on this program.

The work described in this report was
conducted by Dynatech R/D Company
under subcontract to Minnesota Gas Company

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I. PROGRAM OBJECTIVES

The objective of the continued Peat Biogasification Development Program, September 28, 1979 through March 27, 1981, is to obtain necessary information for design and operation of a Process Development Unit (PDU). The program is divided into the following five task areas:

- Task 1: Simulate Multi-staged Reactor - the objective is to evaluate reaction conditions of temperature, pressure, degree of oxidation, degree of solubilization, and alkali concentration using Minnesota reed sedge peat. Batch model pretreatment information will be obtained prior to multi-stage design and operation.
- Task 2: Anaerobic Fermentation - the objective of this task is to confirm that peat pretreatment products are utilized by anaerobic microorganisms for methane production. Yields and gas production rates will be determined using microorganisms acclimated to peat pretreatment products.
- Task 3: Evaluation of Solid and Liquid Process Effluent Streams - the objective is to evaluate solid residue streams as a boiler fuel and assess the environmental aspect of liquid streams on peat extraction areas.
- Task 4: Predictive Process Model and Economic Analysis - the objective of this task is to continue a comprehensive engineering analysis of the entire biogasification process based on additional experimental data obtained and detailed unit operation performance. The process model will determine operating parameters and costs of plants ranging in size from 25 to 250 billion Btu/day of SNG.

Task 5: Planning for Process Development Unit - the objective of this task is to prepare a detailed proposal for specific design plans and experiments at the PDU scale.

II. SUMMARY OF PROGRESS July 1 - September 30, 1980

Task 1: Pretreatment Experiments

During this reporting period preliminary data were taken for the kinetic models necessary for a peat biogasification process. A limited number of batch experiments were conducted to obtain rate data for the solubilization kinetic model.

The analysis of the pretreatment batch tests was slowed down this quarter because the High Pressure Liquid Chromatography (HPLC) solvent system was altered. This was done because a mass balance around the HPLC with the solvent system (85% H₂O/15% acetonitrile) was incomplete. The preliminary data indicate that the new solvent system developed seems to be acceptable.

Task 2: Anaerobic Fermentation

Pretreated peat, both oxidized and unoxidized, has been fermented to fuel gas with conversions up to 20%. The fermentation experiments show that oxidation temperature has little effect on anaerobic digestion. Continuous digesters were setup to obtain rate data for the fermentation model.

Task 4: Process Model

Preliminary process models were developed for the three phases of peat biogasification, namely, solubilization, oxidation, and fermentation. Rate data for the solubilization phase were taken, but more is needed to develop the model further.

III. DETAILED QUARTERLY PROGRESS REPORT

Task 1: Pretreatment Experiments

1.1 Pretreatment Tests, Batch

In its native state peat is not chemically accessible to fermentation by anaerobic microorganisms. If such peat is treated with hot, aqueous alkali it is brought into solution. The solubilized peat then may be partially reacted with oxygen, a process which converts the relatively large molecules of the peat structure into small molecules. These smaller molecules are expected to be suited to utilization by anaerobic microorganisms and conversion through normal metabolic processes to methane. These treatment steps using alkali and oxygen are termed peat pretreatment, that is, treatment prior to fermentation.

During this quarter seventeen pretreatment batch tests were performed. Two of the batch (Table 1) tests (Runs 98, 99) were identical to Run #56, a 113°C oxidation of NaOH solubilized peat liquor. The purpose of these experiments was to obtain pretreated peat liquor identical to the peat liquor obtained in our best fermentation trials. The second identical batch was continuously extracted with trichloroethylene (TCE) and ethyl ether (Et₂O) to obtain enough material for melting point determination and identification of the products. Run #96 was a 160°C oxidation of NaOH solubilized peat. Oxygen was added in 40 psi shots every hour for four hours. In Run #97 raw peat was added to the Parr® reactor along with enough Na₂CO₃ to solubilize the organic matter in an attempt to solubilize peat at a high total solids concentration. Runs #102 and 103 were five-hour, 130°C oxidations. Liquid and gas samples were withdrawn every 10 minutes for 40 minutes and hourly thereafter. In Runs #104 and 105 a peat slurry was added to the Parr® reactor and heated to 150°C. Alkali, NaOH, or Na₂CO₃ was injected into the reactor. After 10 minutes at temperature

Table 1

Data and Results from Peat Pretreatment

Run Number	96 08125A	97 08137A	98 08138A	99 08139A	100 08141A	101 08141B	102 08142A	103 08142B	104 08148A	105 08148B
Total Run Time (min)	255	125	105	105	125	125	360	360	65	65
Time at temp (min)	230	60	60	60	60	60	300	300	10	10
<u>Run Conditions</u>										
Operating temperature (°C)	120	200	114	115	200	200	130	130	150	150
Alkali Type	None	Na ₂ CO ₃	None	None	Na ₂ CO ₃	Na ₂ CO ₃	None	None	NaOH	Na ₂ CO ₃
Alkali Added (grams)	0.0	60	0.0	0.0	13.0	13.0	0.0	0.0	8.0	13.0
Peat Added (grams)	37.4	125.3	28.1	28.1	26.0	26.0	38.0	24.3	29.4	29.4
Peat Organic matter (grams)	29.4	110.3	22.5	22.5	24.0	24.0	22.9	14.7	25.0	25.0
Peat Ash (grams)	8.0	15.0	5.6	5.6	2.0	2.0	15.1	9.6	4.4	4.4
Oxygen Added (grams)	10.9	0.0	13.4	13.4	0.0	0.0	13.6	9.4	0.0	0.0
<u>Output (Solid/Liquid)</u>										
Soluble Organic (grams)	17.8	59.3	19.0	19.8	18.5	18.5	*	*	16.2	18.2
Soluble Ash (grams)	8.2	65.2	5.8	7.2	8.5	8.5	*	*	4.8	8.8
Insoluble Organic (grams)	10.0	40.0	1.4	1.0	4.6	4.6	*	*	4.5	2.9
Insoluble Ash (grams)	0.0	0.0	0.0	0.0	3.4	3.4	*	*	2.7	1.0
<u>Output (Gas)</u>										
Oxygen	*	*	*	*	*	*	**	0.1	*	*
CO ₂ (gas)	*	*	*	*	*	*	**	2.8	*	*
CO ₂ Dissolved	*	*	*	*	*	*	**	*	*	*
H ₂ O (calculated)	*	*	*	*	*	*	**	N/A	*	*
Percent Mass Accounted For	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Percent Organics Solubilized	N/A	54	N/A	N/A	77	77	N/A	N/A	65	73

* Test not performed. ** Test not performed due to equipment failure.

the reactor was cooled down. The amount of organics solubilized was comparable to amounts solubilized in runs made at longer times. This suggested that lower temperature solubilizations must be studied to obtain meaningful rate data. The final seven runs this month were low temperature tests conducted to determine solubilization rates at different temperatures and alkali loadings to develop the solubilization model. These batch tests were conducted by adding a 3 percent T.S. slurry to the reactor, heating the reactor to the desired temperature, 25°C, 75°C or 100°C, and injecting the desired amount of alkali, 0.1, 0.3, or 1.0 gm NaOH/gm dry peat. Samples were taken at 10 and 20 minutes, and the reaction was stopped at 30 minutes. The room temperature test was reacted for seven hours with samples taken hourly. The samples taken were analyzed for total solids, volatile solids, total dissolved solids, volatile dissolved solids, and pH. From these data solubilization rates can be calculated, and the kinetic model can be developed. The preliminary analysis is discussed in Task 4, Predictive Process Model and Economic Analysis.

1.1.1 High Pressure Liquid Chromatography Analysis

Work continued this quarter to identify and classify products of peat solubilization, oxidation, and fermentation. After several HPLC's were run on pretreated peat, a mass balance around the HPLC was attempted by comparing the total absorbance of the individual HPLC peats with the total absorbance on 254 nm U.V. visible spectrophotometer. When this was completed it was apparent that the HPLC chromatographs showed only 30% of the material, the remaining material was being held up on the C₁₈ Bondapak® column. Thus, the main emphasis this quarter was placed on the development of a gradient elution scheme and mass balance calculations.

Gradient elution was deemed necessary when it was determined by solvent extraction and Thin Layer Chromatography (TLC) that both solubilized and oxidized peat liquors contained cinnamic acid/cinnamaldehyde derivative compounds. Compounds of this type do not elute off a C₁₈ column

using the present solvent system. The solvent being used, 85% H₂O/15% acetonitrile, was too polar to elute these compounds. Thus a gradient elution solvent system was designed to take advantage of the original polar solvent mix, 85% H₂O/15% acetonitrile, then become significantly less polar, 50% H₂O/50% acetonitrile to elute the cinnamate class of compounds. The solvent scheme decided upon began as a 85% H₂O/15% acetonitrile solvent mix; the acetonitrile concentration was then gradually increased until a 50% H₂O/50% acetonitrile solvent mix was obtained. Preliminary work indicates that this system elutes 100% of the material off the column. Further analysis of this system is needed. Once this system is fully developed, the concentration of peat oxidation products and reactants can be measured as a function of time. This data is necessary for the peat oxidation process model.

1.1.2 Extraction Analysis

During this quarter five continuous extractions were started; the data and results are presented in Table 2. Small amounts of material are still being extracted from each continuous set-up. Extraction #3 is not completed, but the total amount of extracted material can be estimated from the extraction data. The amount that will be extracted is approximately 100% of the organic matter, which is similar to the amount extracted from the oxidized coals (Extractions 1 and 2). Note: Extraction 4 is the same as Extraction 3, except that it is larger and more material will be collected. This result seems to suggest that all of the soluble material in the pretreated peat is of low molecular materials, because high molecular weight materials would not be extracted in the solubilization step. This result also suggests that most of the peat breakdown occurs in the solubilization step.

The analysis of the extracted fractions has consisted of Thin Layer Chromatography (TLC) and Infrared (IR) Analysis. Thin Layer Chromatography analysis has been discontinued because the results were not quantitative and the process was lengthy. Infrared analysis shows that all

Table 2

Summary Continuous Extractions

EXTRACTION NO.	IDENTIFICATION NO.	RUN CONDITIONS	VOLUME OF SLURRY EXTRACTED	ORGANIC MATTER CONCENTRATION	TOTAL AMOUNT EXTRACTED CONCENTRATION	% OF ORGANIC MATTER EXTRACTED
1	42	200°C NaOH Sol. 175°C Oxidation	100 ml	19 g/l	19g	100%
2	56	200°C NaOH Sol. 113°C Oxidation	500 ml	21 g/l	2C g+/e- 20%	100%
3	100	200°C Na ₂ CO ₃ Solubilization	100 ml	26 g/l	Not Finished With Extraction	From Rate Date 100%
4	100	200°C Na ₂ CO ₃ Solubilization	800 ml	24.8 g/l	Not Finished With Extraction	N/A
5	CONTROL RAW PEAT	Minnesota Peat	80 g	<u>0.18 gm organic</u> gm of wet peat	<u>.002 gm organic</u> gm of wet peat	1.3%

the extracted fractions contain carboxylic acid, phenol, and possibly of ketones and esters. This result suggests that the oxidation step is incomplete, as aldehydes would predominate with complete oxidation. IR analysis suggests that there is little difference between oxidized and unoxidized pretreatment runs.

Task 2: Anaerobic Fermentation

2.1 Acclimatization of Anaerobic Bacteria to Model Pretreatment Compounds

The model compound cultures are now in their third month of optimum acclimatization. The bacteria are still converting their respective aromatic substrates to fuel gas in two weeks. The percent conversion to methane has also levelled off to about a 90-95% yield. These cultures are being maintained for possible use as inocula for future fermentations. As mentioned in previous status reports, these active cultures are acclimated to four aromatic substrates: syringaldehyde, syringic acid, benzoic acid, and cinnamic acid.

Task 2.2 Fermentation of Pretreated Peat Using Various Inocula

Model Compounds Used as Inocula

The fermentations (113°-130°C oxidations) that have shown the best conversions of peat organic matter to fuel gas, approximately 20-22%, are producing methane at a slower rate than in previous months. The recently active cultures, i.e. peat oxidized at 150-165°C, are converting the pretreated peat at a rapid rate. There are two possibilities for the decreased rate of the lower temperature fermentations: the first is that the bacteria cannot digest the remaining organic material, and the second is that the cultures have been depleted of active bacteria because these fermentations were used as inocula in the other fermentation experiments.

Peat Liquid Used as Inoculum

These cultures are now three months old and have converted between 7.0 and 14.0 percent of their total organic matter to fuel gas. The absence of a lag time before methane production is due to the pooled inoculum which was taken from cultures that were actively digesting pretreated

peat liquor. These fermentations contain peat liquor oxidized at temperatures between 113°C and 180°C. Virtually all of these cultures are actively producing methane, with the 150°C culture having the highest total conversion, 14%.

A new set of fermentations using solubilized but unoxidized peat liquor was one month old at the end of September. The solubilized peat liquor substrate was kept constant, with the only variable being the inocula, which was taken from a variety of fermentations. After 30 days these cultures are converting the solubilized peat to fuel gas at the same rate as the cultures fermenting oxidized peat liquor.

At the end of September a new set of fermentations was set up in a different mode. These experiments involve the continuous digestion of peat liquor (see Figure 1), as opposed to all the previous fermentations which involve batch digestion. These continuous digesters, once they start actively producing methane, will be waste and fed with buffered peat liquor daily at 20 and 30 day hydraulic retention times. When a steady state is reached, a rate constant for the conversion to methane will be determined for that specific retention time.

Task 4: Predictive Process Model and Economic Analysis

The pretreatment of peat into fermentable products can be broken down into two phases, solubilization and oxidation. It is essential that a kinetic model be developed for design purposes.

Two approaches can be used to analyze kinetic data. One approach is to assume a mechanistic model and determine whether the model fits the experimental data. If it does not, a different mechanistic model must be assumed and the model fitting step is repeated. This approach is dependent upon finding a mechanistic model which describes the reactions that occur.

Figure 1

Schematic Diagram of Apparatus for
Continuous Digestion of Peat Liquor

A second approach to kinetic data analysis is to use an empirical model which incorporates all the processing variables and model parameters. Since the pretreatment process is a complex process resulting in many different products from a complex reactant (peat), it would be preferable to use the empirical approach for data analysis.

For the solubilization model it is assumed that the peat is solubilized by the following reaction;

where

C_p - concentration of insoluble peat
 C_B - concentration of hydroxyl ion
 C_S - concentration of soluble peat

Assuming this mechanism the following rate equation is developed:

$$\frac{dC_S}{dt} = kC_pC_B$$

Integral analysis of data obtained follows the procedure outlined below.

$$\frac{dC_S}{dt} = kC_pC_B$$

$$C_S = k \int_0^t C_p C_B dt$$

- I. Plot $C_p C_B$ vs. t (Figure 2)
- II. Measure area vs. t , i.e. $\int_0^t C_p C_B dt$
- III. Plot C_S vs. area ($\int_0^t C_p C_{OH} dt$) for each t (Figure 3)
- IV. Least squares fit gives slope which equal k

Figure 2

Graph of (Concentration of peat)(Concentration of base) versus time

Figure 3
Least squares fit of $\int_0^t C_P C_R dt$ versus peat organics solubilized to obtain rate constant K.

This procedure was followed in the data analysis for Run #106, a seven hour, room-temperature solubilization. Figure 2 is a plot of the concentration of peat (g/l) multiplied by the concentration of base (gmole/l) versus time. The area under the curve was computed and Figure 3 is a plot of the amount of peat solubilized versus the area, i.e. $\int C_p C_B dt$ for each time. Using the least squares regression method to compute the slope, a value of 33.8 l/gmole-hr is obtained with a correlation factor of 0.984. This indicates that the proposed model corresponds very well to the data analyzed, but more analysis must be performed to confirm the model.

The second modelling phase is the oxidation of solubilized peat. For this process it is assumed that the products will be a complex mixture of low molecular weight fermentable and non-fermentable (refractory) materials. An empirical kinetic model can be developed which relates product formation to reactant concentrations. Thus,

$$\frac{dC_F}{dt} = k_1 C_O^a C_S^b \quad (1)$$

$$\frac{dC_R}{dt} = k_2 C_O^c C_S^d \quad (2)$$

where C_S = soluble peat concentration
 C_O = oxygen concentration
 C_F = fermentable concentration
 C_R = refractories concentration

It should also be noted that similar relationships can also be developed which give change in reactant (peat and oxygen) concentrations as functions of the reactant concentrations. The exponents, a, b, c, and d, and the kinetic constants, k_1 and k_2 , must be determined from experimental data. It is assumed that temperature will affect only the kinetic constants and that this will be a typical Arrhenius dependency. This must also be determined from experimental data.

In order to determine all the constants in the empirical model, it is necessary to have data showing the concentration of each reactant and product as a function of time. The method of data analysis consists of plotting concentrations as a function of time and then determining the slope or rate (dC/dt) as a function of time. These values of concentrations and rates are then fitted to the empirical model by a least squares fit which will determine the exponents and rate constants.

For Equation 1, taking the natural logarithm of each side gives

$$\ln \frac{dC_F}{dt} = \ln k_1 + a \ln C_O + b \ln C_S$$

which is of the form

$$z = k_1' + a x + b y \quad (3)$$

where

$$z = \ln \frac{dC_F}{dt}$$

$$x = \ln C_O$$

$$y = \ln C_S$$

$$k_1' = \ln k_1$$

The parameters k_1' , a , and b can be determined by a least squares fit of Eq 3 to experimental data. A series of experiments with measurement of fermentable products concentration as a function of time (sufficient to give the initial slope) and the initial reactant concentrations would be used to

determine the various parameters. The parameters can also be determined by fitting the model (Eq. 3) to experimental data giving the rate and concentrations as a function of time. (The attached tables are examples of the calculated data to be used for least squares fit to determine model parameters.)

The analytical method of Levenspiel* describes the mathematical manipulations necessary to determine the rate constants and exponents. An optimization routine using a computer can also be used, but the analytic method should be simple enough.

*Levenspiel, O. 1956. A Numerical Solution to Dimensional Analysis. Ind. and Eng. Chem. 48: 324-325.

Initial Measurements Method

Exp. No.	$\ln(\text{Initial O}_2 \text{ Conc.})$	$\ln(\text{Initial Peat Conc.})$	$\ln(\text{Initial Slope of Ferm})$
1	X ₁	Y ₁	Z ₁
2	X ₂	Y ₂	Z ₂
3	X ₃	Y ₃	Z ₃
4	X ₄	Y ₄	Z ₄
5	X ₅	Y ₅	Z ₅
6	X ₆	Y ₆	Z ₆
7	X ₇	Y ₇	Z ₇
8	X ₈	Y ₈	Z ₈
9	X ₉	Y ₉	Z ₉
n	X _n	Y _n	Z _n

Complete Concentration and Rate vs. Time Method

Time (hours)	$\ln(\text{O}_2 \text{ conc})$	$\ln(\text{Peat conc})$	$\ln(\text{Ferm rate})$
1	X ₁	Y ₁	Z ₁
2	X ₂	Y ₂	Z ₂
3	X ₃	Y ₃	Z ₃
4	X ₄	Y ₄	Z ₄
5	X ₅	Y ₅	Z ₅
6	X ₆	Y ₆	Z ₆
7	X ₇	Y ₇	Z ₇
8	X ₈	Y ₈	Z ₈
9	X ₉	Y ₉	Z ₉
n	X _n	Y _n	Z _n

IV. CONCLUSIONS

The analysis of peat pretreatment products before and after fermentation were slowed down this month as a new HPLC solvent system was developed. The new solvent system appears to have corrected the problems encountered when using the old system. Use of this new system will enable us to obtain the kinetic data necessary for the oxidation phase of the process model. The solubilization phase of the process model is under development and the results of preliminary data are very encouraging.