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EXPERIMENTAL PROGRAM FOR THE DEVELOPMENT OF PEAT GASIFICATION

Interim Report No. 3

COILED TUBE REACTOR EXPERIMENTS

Submitted by

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SUMMARY

This interim report presents the results of peat hydrogasification tests conducted in a dilute-phase, short-residence time (a few seconds) coiled-tube reactor. The work was conducted by the Institute of Gas Technology for the Minnesota Gas Company, as part of ERDA Contract No. EX-76-C-01-2469, "Experimental Program for the Development of Peat Gasification." The overall objectives of this program are to obtain engineering data and develop a model for peat gasification, to select the gasification process most suitable for peat, and to determine the economics of such a process.

A total of 28 tests were conducted to determine the effects of temperature (850° to 1500°F) and hydrogen partial pressure (0 to 1000 psia) on the product distribution and yields obtained during peat hydrogasification.

In general, the results show that many features of peat hydrogasification are qualitatively similar to those of lignite and higher rank coals. However, the quantitative and kinetic characteristics of peat gasification are quite unique. Therefore, the process concept most advantageous for converting peat to SNG is different from those which are most suitable for gasifying coals.

The tests show that the carbon converted directly to hydrocarbon gases in a short-residence-time hydrogasifier is up to four times as high for peat as for lignite. Therefore, a single hydrogasification stage will be adequate for converting peat to SNG. Peat hydrogasification tests also show that a high yield of hydrocarbon gases is obtained at relatively low hydrogen partial pressures. Another unique feature of peat hydrogasification is that temperature is very effective in controlling relative yields of gas and oil. The data obtained have been quantitatively analyzed and a peat-gasification model has been developed. Based on the laboratory test results, a preferred configuration for gasifying peat has been selected and named a PEATGAS reactor. It incorporates a dilute-phase, cocurrent, short-residence time hydrogasifier and a fluidized-bed, nonslagging, char gasifier with oxygen.

Currently, process development unit (PDU) tests are under way as per the schedule of the present program. The objective of this part of the program is essentially to determine the effects of initial scale-up from laboratory to PDU-scale.

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INTRODUCTION

Peat can be considered a geologically young coal because it is material that has only begun to turn into coal. According to the most recent estimates,* U. S. peat reserves in the lower 48 states total about 56 billion tons (air dried) with a total heating value of 680 X 10^{15} Btu. In addition, there are about 60 billion tons in Alaska (outside of the perma-frost regions) and about 1 billion tons in Hawaii. As indicated in Figure 1, these reserves are more than the recoverable energy reserves in natural gas, crude oil, lignite, or oil shale. Thus, the energy available from peat is significant and peat should be considered as an important potential energy source.

Minnesota has the largest single peat reserves, totalling about 16 billion tons or 193 X 10^{15} Btu. This represents a significant energy reserve for this area. The Minnesota Gas Company, concerned about its long-term reserves of natural gas, sponsored a study[†] at IGT to evaluate converting Minnesota peat to substitute natural gas (SNG). Because of limited design information and funds, only the use of the HYGAS® Process to make SNG was studied. The results of that study, obtained by extrapolating coal-conversion technology to peat processing, indicate that converting peat to SNG is technically feasible and economically attractive.

To develop and achieve commercialization of any peat conversion process, the process concepts should be verified by obtaining design data from direct experimentation. Based on these data, the technology and economics of the process should be reassessed.

Therefore, the Minnesota Gas Company proposed a 24-month cost sharing program to the U. S. Energy Research and Development Administration (ERDA)[‡] for experimental work to develop the necessary engineering data for peat gasification. On July 1, 1976, ERDA Contract No. E(49-18)-2469

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[*] Conservation Needs Inventory, U.S. Soil Conservation Service, Dept. of Agriculture, 1967.

[†] This study, completed in August 1975, has been submitted to ERDA by Minnesota Gas Co. as Supplementary Report No. FE-2469-8 of the present project.

[‡] Now the Department of Energy (DOE).

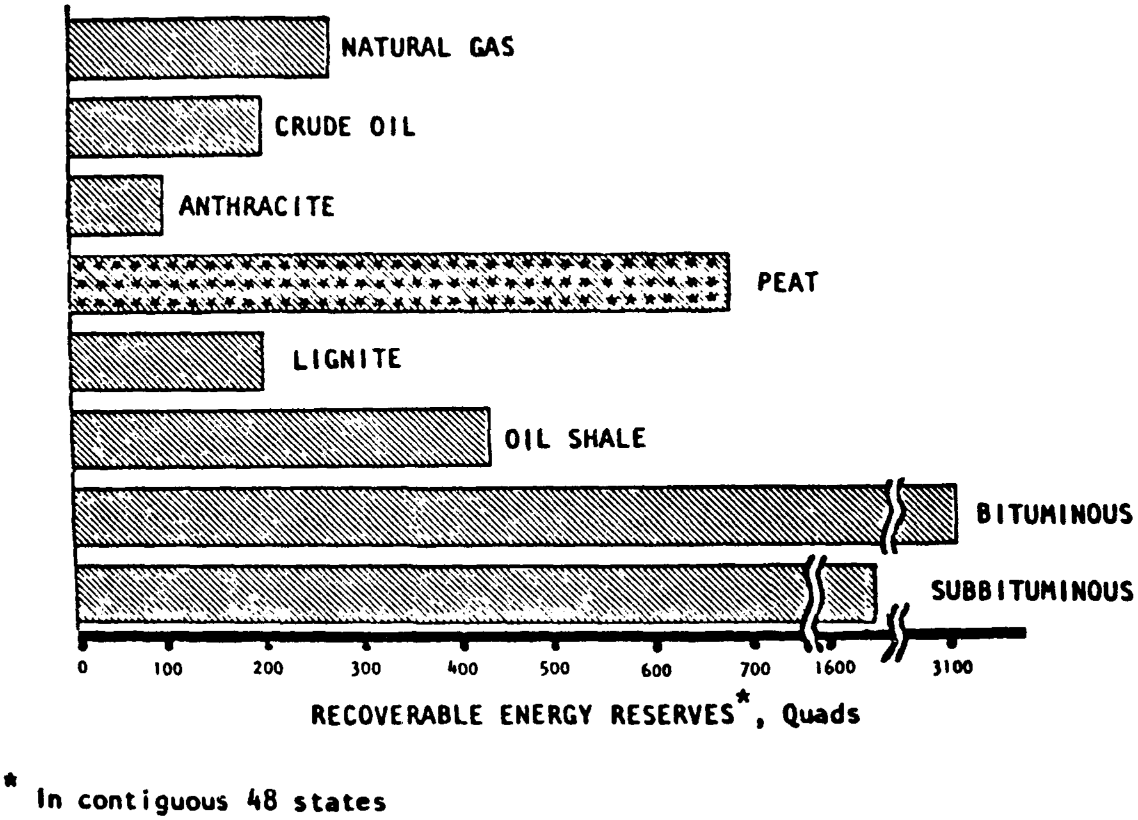


Figure 1. RECOVERABLE FOSSIL FUEL RESERVES IN THE U.S. (CONTIGUOUS 48 STATES)

was awarded for this purpose. IGT, a subcontractor to the Minnesota Gas Co., is conducting the experimental study. Based on the engineering data from this program, a peat gasification model will be developed and the coal gasification process most suitable for converting peat to SNG will be selected. After selecting the process, a technical and economic evaluation of that process will be conducted. The existing coal gasification technology will be used as much as possible.

Table 1 shows the eight major tasks of this program and their objectives. The program schedule for the individual tasks is shown in Figure 2.

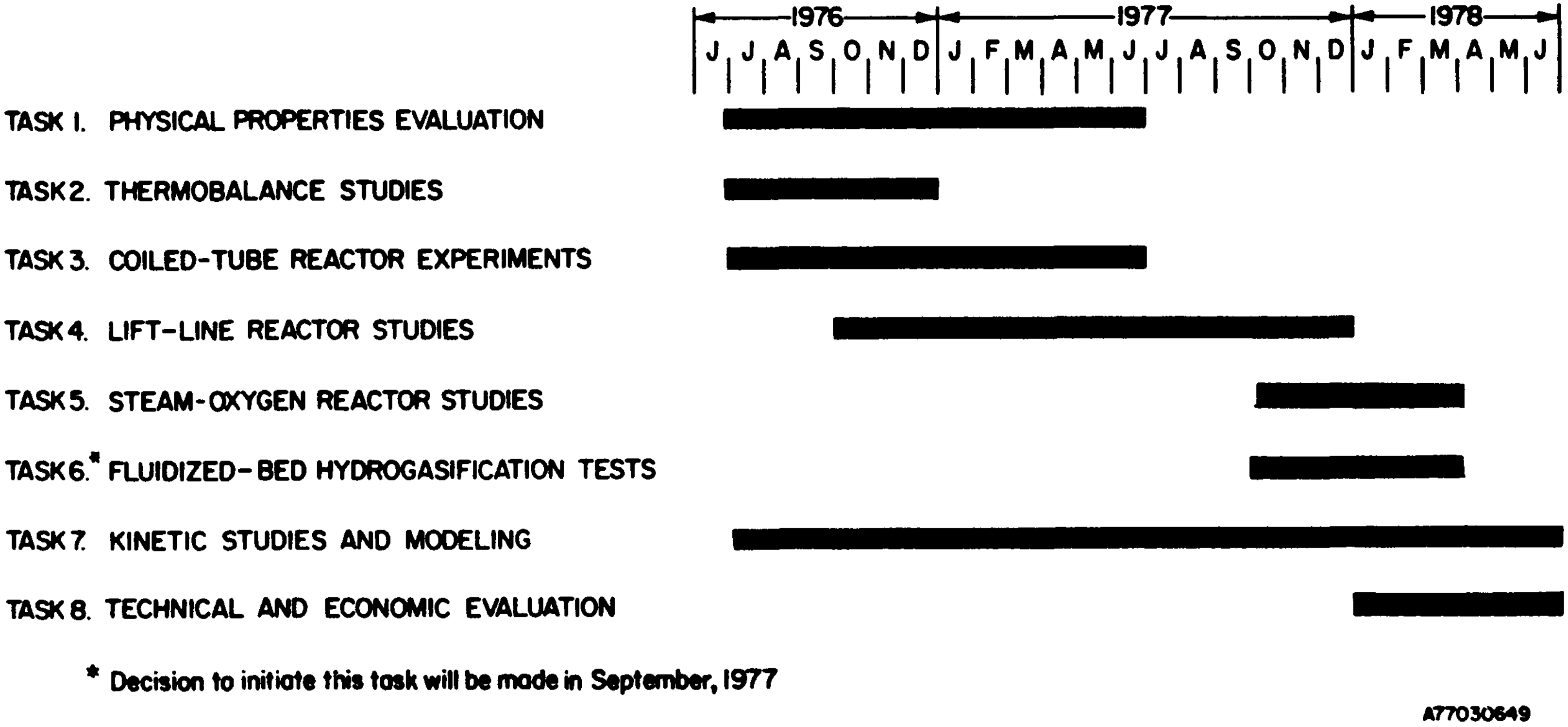
The first three tasks relate to laboratory-scale tests. The objective of the next three tasks is to conduct PDU scale tests to determine the effect of initial scale-up. The last two tasks relate to evaluating the laboratory and PDU scale data and to economic analyses of a preferred process to produce substitute natural gas (SNG) from peat.

Task 2 (Thermobalance Studies) was completed earlier and the results were reported in Interim Report No. 2 (ERDA Report Fe-2469-10). The results from Task 1 (Physical Properties Evaluation) are being reported in a separate Interim Report No. 4 (ERDA Report No. FE-2469-19).

This interim report presents the results of the tests conducted under Task 3, Coiled-Tube Reactor Experiments. The analyses of the data from tests carried out as a part of Task 7 on Kinetic Studies and Modeling are also included. Based on the data obtained in this program, a preferred process for converting peat to SNG has been recommended.

Table 1. MAJOR TASKS AND OBJECTIVES OF THE PEAT GASIFICATION PROGRAM

TASK NO.	TITLE	OBJECTIVE
1	Physical Properties Evaluation	Determine the grinding, flow, pelletization, slurring, and fluidization characteristics of peat.
2	Thermobalance Studies	Determine the gasification kinetics of peat char.
3	Coiled-Tube Reactor Experiments	Determine the hydrogasification kinetics of peat.
4	Lift-Line Reactor Studies	Conduct peat hydrogasification tests in PDU.
5	Steam-Oxygen Reactor Studies	Conduct peat char gasification tests in PDU.
6	Fluidized-Bed Hydrogasification Experiments	Conduct PDU tests for hydrogasification of peat char.
7	Kinetic Studies and Modeling	Analyze the data obtained from various experimental tasks in the program and develop a kinetic model for peat gasification.
8	Technical and Economic Evaluation	Evaluate the overall technical and economic viability of the peat gasification process.



* Decision to initiate this task will be made in September, 1977

Figure 2. PEAT GASIFICATION PROGRAM SCHEDULE

ACHIEVEMENT OF PROJECT OBJECTIVES

The overall objective of the program is to develop a process for conversion of peat to SNG and to evaluate its process economics.

All of the objectives of the laboratory scale tests (Task I, Task 2, and Task 3) have been achieved.

On the basis of the engineering data obtained from the laboratory tests, a gasifier configuration has been selected to optimize methane production.

Peat hydrogasification PDU tests (Task 4) and peat char gasification PDU tests (Task 5) are in progress. The objective of these tests is to firm up the peat gasification process yields and thus facilitate evaluation of its process economics.

EXPERIMENTAL APPARATUS AND PROCEDURE

A schematic diagram of the coiled-tube reactor apparatus is shown in Figure 3. The main component of the experimental system is a helical-coiled transport reactor formed from a 1/16-inch-ID tube. This type of equipment arrangement has been successfully used previously[3] for determining the hydrogasification characteristics of lignite. General information describing the reactor coil is given in Table 2.

The diameter of the coil is about 1 foot, with a total tube length of 200 feet and a vertical reactor height of about 2-1/2 feet. With this design, gas flow rates of 15 to 50 SCF/hr and solids flow rates of 10 to 50 g/hr are possible. The relative gas-solids flow rates used in individual tests were such that solids/gas volume ratios are less than 0.02. The solids particles used in this system were relatively uniform in size, ranging in diameter from 74 to 90 microns. Such small particles flow essentially at gas velocities, and calculated temperature differences between the gas and solids and between the reactor-tube wall and the flowing gas-solids stream are negligible.

The reactor tube itself serves as the heating element, and electrodes are attached directly at various points along the length of the helical coil. Nine independent heating zones are thereby incorporated into the system to provide flexibility in establishing desired temperature profiles.

In a typical experimental test, the following operational procedures were used:

Initially, the system was brought to a desired pressure, and a preliminary temperature profile was established in the reactor coil by adjusting the controls for the nine heating zones. When feed-gas flow was established at a desired rate, the flow from the solids feed hopper was initiated. Solids were screw-fed into a mixing zone where they combined with the feed gas, and the resulting mixture then flowed through the reactor coil. The temperature in the mixing zone was maintained at the temperature at the entrance of the coil — usually about 600°F. This temperature was sufficiently high to inhibit steam condensation at the highest pressures used in this study, but low enough to inhibit any significant reaction with peat.

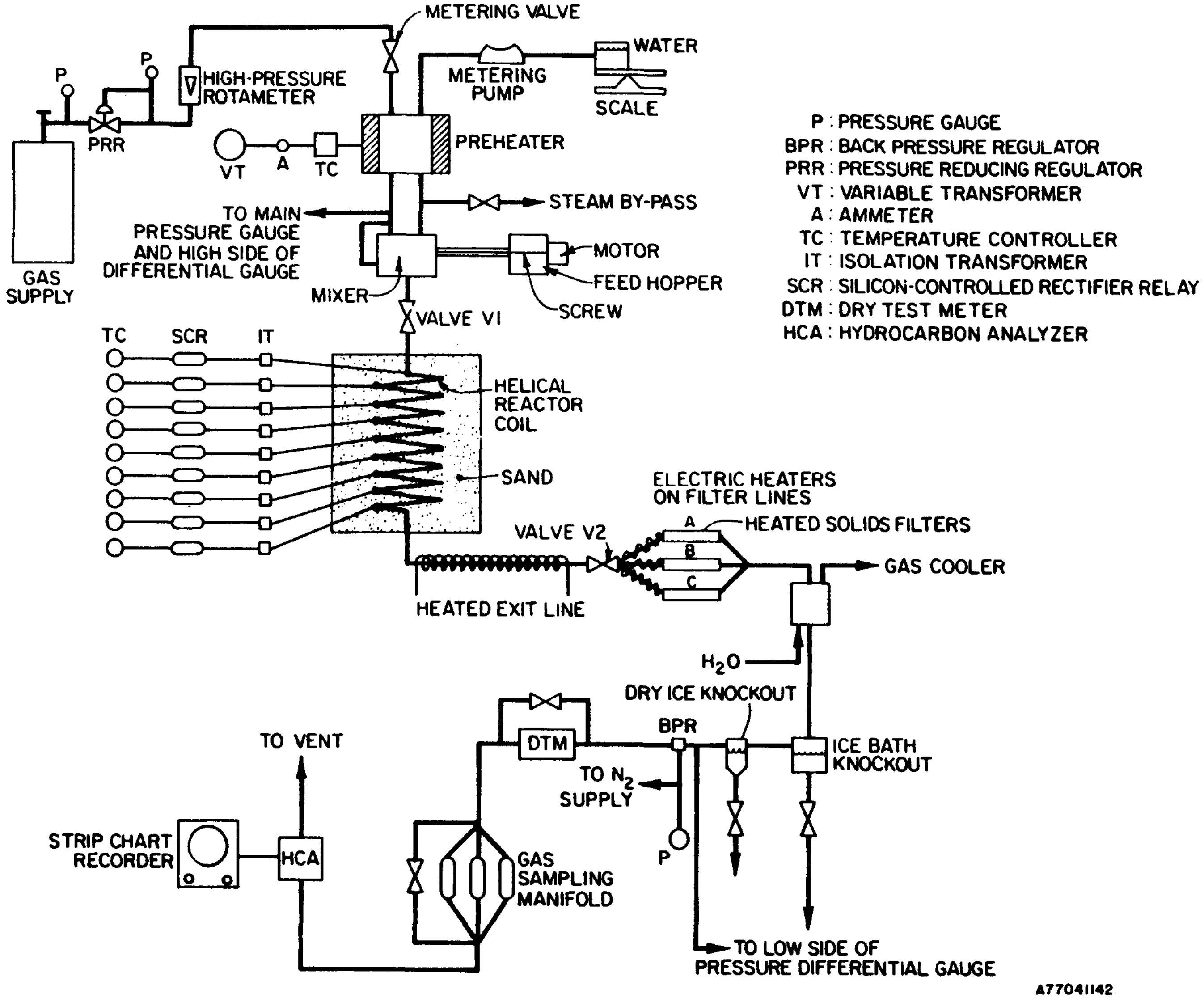


Figure 3. SCHEMATIC FLOW DIAGRAM FOR THE COILED-TUBE REACTOR SYSTEM

Table 2. REACTOR-COIL SPECIFICATIONS

Total Tube Length	200 ft
Tube ID	1/16 in.
Tube OD	1/8 in.
Tube Material	316 stainless steel, seamless
No. of Individually Controlled Heating Zones	9
Tube Length Per Zone	22.2 ft
Helix Dimensions	1-ft diameter X 2-1/2 ft high
Electrical Resistance per 22.2-ft Tube Section	1 ohm
Transformer Output	
Zones 1-6	35 volts, 35 A
Zones 7-9	40 volts, 40 A
Maximum Power Requirement for Transformers (total)	12 kW
Maximum Operating Temperature	1600°F
Maximum Design Pressure	1000 psi
Temperature Controller Type	Weathermeasure, TRA-1, Triac-Triggered SCR gate

After establishing the gas and solids flows, the final desired temperature profile was established in the reactor tube. In the various tests conducted, the temperature either increased along the coil in the direction of gas-solids flow or was maintained constant. The temperature-gradient along the coil was linear and was generally about 100°F/s. In isothermal tests, gas-solids residence time was between 4 and 8 seconds.

The hot gas-solids mixture exiting from the bottom of the reactor coil passed through an initial quench system that rapidly reduced its temperature to approximately 600°F to inhibit further reaction. At this point in the system, a lower temperature was avoided in order to prevent steam from condensing on the solids. The partially cooled mixture then proceeded through one of the three solids filters, which retained the solids but permitted gas flow. The gas continued through a condenser that removed water and oils, and then passed through a gas-sampling panel which was used intermittently to obtain gas samples for mass spectrographic analysis.

The data of primary interest in a given test correspond to steady-state operation. Since a certain amount of time is required to achieve such operation, arrangements were incorporated to permit separate collection of solid residues during unsteady and steady-state operations. The product solids could be collected in any of the three solids filters, depending on the position of a multiple-exit hot valve (valve V2 in Figure 3). During unsteady-state operation, when the desired gas and solids flows and the temperature profile in the reactor coil were being established, the product gas and solids flowed directly through solids filter A. When steady-state conditions were established, the product gas and solids were directed through solids filter B, which then accumulated a solids residue for analysis. Before the end of some tests, a direct determination of the solids inventory in the reactor coil was made to estimate the average solids residence times. This was accomplished by simultaneously closing valve V1 at the top of the coil, stopping the screw feeder, and diverting the product gas and solids flow through solids filter C. Valve V1 is a hot valve fitted with a solids filter that stops solids flow but permits gas flow when in a closed position. After these simultaneous operations, the solids inventory in the reactor coil was accumulated in solids filter C. Average solids residence times computed from chemical analyses and weight measurements of these solids generally corresponded very closely to calculated gas residence times, indicating negligible gas-solids slippage in the reactor coil.

DATA ANALYSIS PROCEDURE

The experimental system used in this study is an integral one in the sense that the gas, liquid, and solids conversion, as determined by analyses of the reactor-coil exit streams, are the result of chemical interactions occurring along the length of the coil under systematically varying environmental conditions. With this type of system, proper kinetic characterization requires knowing definitions of the conversions and local environmental conditions along the entire length of the coil, not only at the exit. Although this information could not be obtained in a single test, a good approximation was achieved using a series of properly designed tests. The tests were designed assuming that the gas and solids are essentially in plug flow through the coil and that the slip velocity between the solids and the gas flow is negligible. Under these conditions, both gas and solids conversions could be expressed solely as a function of pressure, initial gas/solids feed ratio, temperature, and temperature-time history. Two series of tests were conducted: isothermal and constant heat-up rate. In the isothermal tests, the heat-up rate was high (>1000°F/s) while in the constant heat-up rate tests, heat-up rate was relatively lower and generally about 100°F/s. The objective of the two series of tests was to determine if heat-up rates, within the test range, have any significant effect on carbon conversion and product distribution during peat gasification. The constant heat-up rate tests were designed using the following expressions:

and

$$G_o = \frac{\pi d^2 P L \alpha}{2R(T_f^2 - T_o^2)} \qquad (1)$$

$$T = [T_o^2 + (T_f^2 - T_o^2)\, z/L]^{1/2} \qquad (2)$$

where

z = length at intermediate point along the reactor coil
L = total length of reactor coil
T_o = temperature at entrance of reactor coil
T_f = temperature at reactor-coil exit (final temperature)
T = temperature at intermediate point z along the reactor coil
G_o = feed-gas flow rate (mol/time)
R = gas constant
d = reactor-tube diameter
α = gas-solids heat-up rate
P = pressure

The solid component conversions were obtained from the ultimate analyses of the feed peat and the residue chars. The gas yields were obtained from the mass spectroscopic analysis of the dry product gas. In a later discussion of the results, the values of carbon dioxide and carbon monoxide are grouped together and referred to as carbon oxides (CO_x). Methane, ethane, and ethylene are referred to as hydrocarbon gases (HG). The group containing butane and heavier hydrocarbons is referred to as heavy hydrocarbons (HHC). The carbon in HHC is determined by subtracting the carbon contents in CO_x and HG from the total carbon converted during a test. The yield of steam was calculated by subtracting the oxygen content in CO_x from the total oxygen converted. These calculated values of steam are on the high side because some oxygen goes into the HHC component as phenols.

EXPERIMENTAL RESULTS

As stated earlier, two series of experiments were conducted; one series with a constant heat-up rate and various final maximum temperatures, and the other under isothermal conditions at various temperatures.

In the isothermal tests, the solid heat-up rate was very high (>1000°F/s), whereas in the constant heat-up rate runs the value was ~100°F/s. One of the objectives of conducting the two series of tests was to find out the effect of the heat-up rate of peat on its product distribution. A total of 28 such tests were conducted. Except for seven runs made in helium atmospheres, all the tests were conducted in hydrogen at various pressures. The tests were conducted at temperatures up to 1500°F and pressures up to 70 atm.

Tables 3 and 4 summarize the operating conditions and the results obtained in the constant heat-up rate and the isothermal test series, respectively. Typical compositions of Reed Sedge peat, which was used in this study, as well as the compositions of the other coals referred to in this report, are shown in Table 5.

The carbon, hydrogen, and oxygen conversions during peat gasification in hydrogen and helium are shown in Figure 4. For constant heat-up rate tests, temperature in this figure represents the maximum temperature attained in the reactor coil. Even though the solids remained in the heated zone for nearly the same period in both the isothermal and the constant rate heat-up tests, the residence time at the maximum reaction temperature is very short in the latter. Therefore, the effective reaction temperatures for the constant heat-up rate tests are expected to be somewhat lower than for the isothermal tests.

The results in Figure 4 show that during isothermal tests, the carbon and oxygen conversions were higher compared to those obtained in constant heat-up rate runs at the same temperature. The carbon conversion achieved at 1350°F in the case of isothermal runs could be obtained under constant heat-up rate runs only at ~1500°F. The difference between carbon conversion in hydrogen and helium at low temperatures (~1000°F) is small, but it increases at higher temperatures, indicating that hydrogasification reactions become important at temperatures above 1200°F.

Table 3. DATA SUMMARY FOR PEAT GASIFICATION TESTS CONDUCTED UNDER CONSTANT HEAT-UP MODE

Run No.	CT-22	CT-21	CT-20	CT-5	CT-2	CT-23	CT-7	CT-16	CT-27	CT-19	CT-28	CT-26	CT-25	CT-6
Conditions														
Maximum Temperature, °F	1015	1210	1303	1420	1417	1405	1417	1409	1502	1408	1115	1200	1300	1409
Total Pressure, atm	36.3	36.3	37.4	20.7	38.0	36.7	71.0	67.9	37.4	38.3	39.4	39.1	37.9	38.7
Hydrogen Partial Pressure, atm	36.3	36.3	37.4	20.7	38.0	36.7	71.0	67.9	37.4	3.8	0[6]	0[6]	0[6]	0[6]
Heat-Up Rate, °F/s	96	136	140	178	164	193	106	110	187	161	81	93	104	117
Residence Time,[1] s	4.3	4.5	5.0	4.6	5.0	4.2	7.7	7.3	4.8	5.0	6.4	6.4	6.7	6.9
Results														
Solid Component Conversion (g/g maf feed component)														
Carbon	0.454	0.538	0.605	0.590	0.651	0.663	0.720	0.702	0.679	0.522	0.463	0.490	0.504	0.500
Hydrogen	0.672	0.750	0.804	0.828	0.860	0.858	0.881	0.865	0.883	0.815	0.720	0.777	0.796	0.802
Oxygen	0.770	0.872	0.922	0.948	0.950	0.943	0.965	0.960	0.962	0.909	0.800	0.839	0.889	0.890
Nitrogen	0.525	0.656	0.733	0.785	0.847	0.841	0.884	0.877	0.871	0.685	0.549	0.568	0.593	0.612
Sulfur	0.438	0.448	0.372	0.302	0.307	0.310	0.270	0.290	0.298	0.266	0.474	0.368	0.299	0.342
Gas and Liquid Yield (g mole/g atom feed carbon)														
Carbon Monoxide[2]	0.043	0.084	0.085	0.138	0.151	0.142	0.121	0.120	0.168	0.138	0.061	0.074	0.086	0.095
Carbon Dioxide[2]	0.067	0.063	0.037	0.025	0.007	0.020	0.011	0.000	0.000	0.045	0.076	0.062	0.091	0.075
Hydrocarbon Gases	0.039	0.154	0.180	0.248	0.298	0.382	0.354	0.389	0.390	0.190	0.042	0.064	0.089	0.092
Heavy Hydrocarbons[4]	0.305	0.237	0.303	0.179	0.195	0.119	0.234	0.193	0.121	0.149	0.284	0.290	0.247	0.238
Steam[5]	0.178	0.193	0.266	0.239	0.272	0.249	0.303	0.315	0.275	0.185	0.151	0.179	0.136	0.152
Hydrogen	--	--	--	--	--	--	--	--	--	--	0.020	0.045	0.067	0.095

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[1] Residence time = (temp. at outlet - temp at inlet)/(heat-up rate).

[2] Component determined by mass spectroscopic analysis of the dry product gas.

[3] Hydrocarbon Gases = carbon (mole) content in methane, ethane, and ethylene.

[4] Heavy hydrocarbons = total carbon conversion - carbon in CO and CO_2 - carbon in hydrocarbon gases

[5] Steam = total oxygen conversion - oxygen in CO and CO_2.

[6] Denotes runs in helium.

Table 4. SUMMARY DATA ON PEAT GASIFICATION RUNS CONDUCTED UNDER ISOTHERMAL MODE

Run No.	CT-12	CT-9	CT-11	CT-13	CT-18	CT-24	CT-14	CT-17
Conditions								
Maximum Temperature, °F	855	1003	1205	1350	1350	1000	1205	1350
Total Pressure, atm	41.6	39.1	38.3	38.4	38.9	39.1	39.1	38.9
Hydrogen Partial Pressure, atm	41.6	39.1	38.3	38.4	3.9	0[5]	0[5]	0[5]
Residence Time, s	5.0	4.5	4.3	4.2	4.4	5.3	5.3	4.6
Results								
Solid Component Conversion (g/g maf feed component)								
Carbon	0.411	0.510	0.659	0.694	0.597	0.487	0.544	0.554
Hydrogen	0.613	0.740	0.837	0.891	0.848	0.734	0.809	0.845
Oxygen	0.728	0.808	0.939	0.949	0.942	0.804	0.882	0.895
Nitrogen	0.456	0.613	0.816	0.878	0.780	0.572	0.654	0.686
Sulfur	0.511	0.515	0.232	0.226	0.257	0.487	0.251	0.307
Gas and Liquid Yield (g mole/g atom feed carbon)								
Carbon Monoxide[1]	0.027	0.045	0.094	0.147	0.171	0.082	0.114	0.123
Carbon Dioxide[1]	0.049	0.045	0.018	0.018	0.014	0.086	0.077	0.094
Hydrocarbon Gases[3]	0.010	0.051	0.181	0.390	0.187	0.044	0.090	0.115
Heavy Hydrocarbons[3]	0.325	0.369	0.366	0.139	0.225	0.275	0.262	0.222
Steam[4]	0.208	0.234	0.300	0.255	0.225	0.107	0.138	0.109
Hydrogen	--	--	--	--	--	0.034	0.090	0.141

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[1] Component determined by mass spectroscopic analysis of dry product gas.

[2] Carbon content (mole) in methane, ethane and ethylene .

[3] Heavy Hydrocarbon = Total carbon conversion - carbon in CO and CO_2 - carbon in hydrocarbon gases.

[4] Steam = Total oxygen conversion-oxygen in CO and CO_2 .

[5] Denotes runs in helium.

Table 5. PROXIMATE AND ULTIMATE ANALYSES OF PEAT AND COAL SAMPLES

Sample	Proximate Analysis (wt % as received)				Ultimate Analysis (wt % dry ash free basis)				
	Moisture	Volatile Matter	Ash	Fixed Carbon	C	H	S	N	O (by difference)
Reed Sedge Peat	3.2	61.2	9.4	26.2	56.8	5.6	0.3	2.7	34.6
Montana Lignite	7.2	34.2	9.7	48.9	71.8	3.7	0.6	1.1	22.8
Bituminous Coal (HVA)	1.0	36.2	8.5	54.3	81.8	5.6	1.5	1.4	9.7

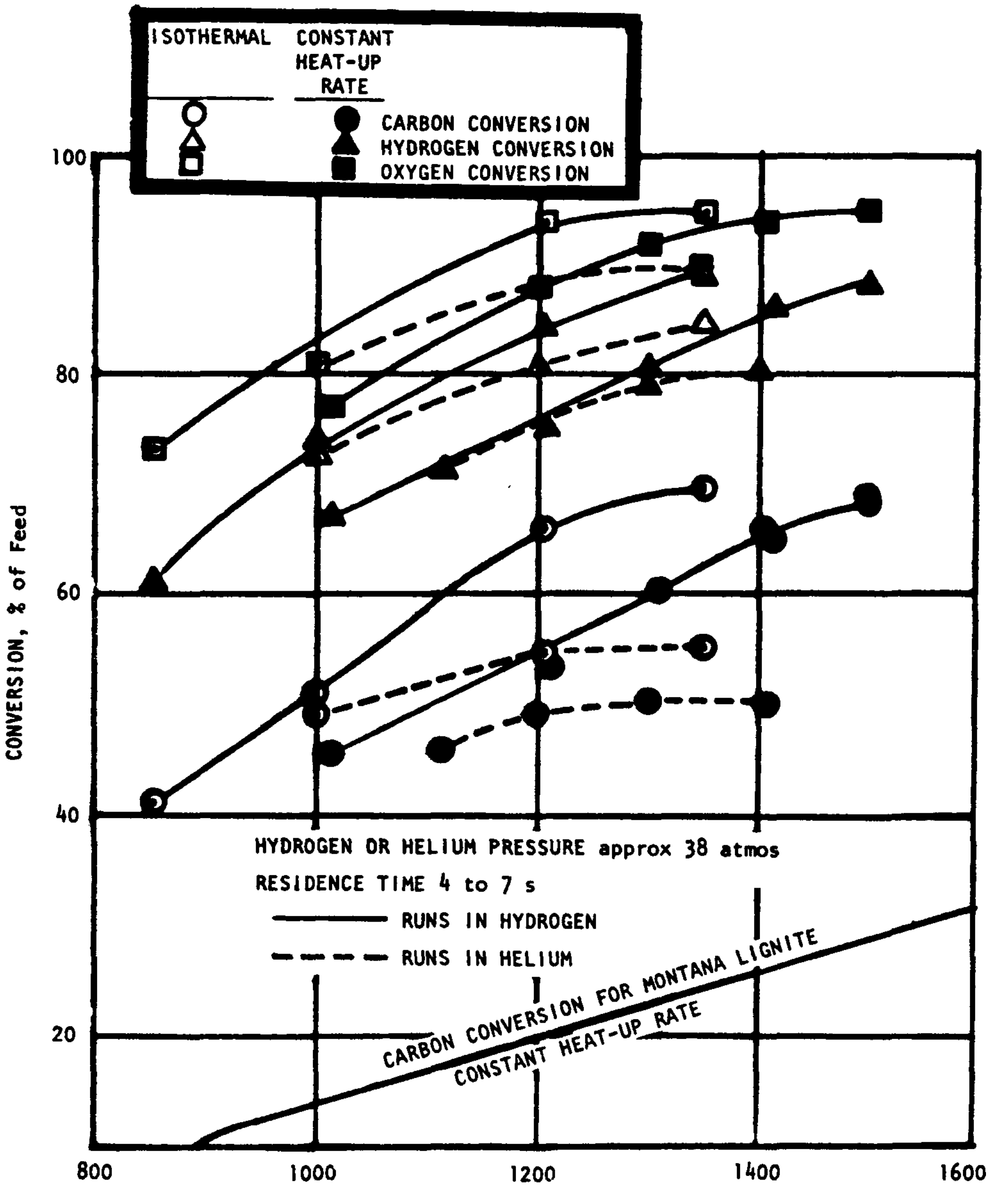

Figure 4. EFFECT OF TEMPERATURE ON CARBON, HYDROGEN, AND OXYGEN CONVERSIONS

Figure 4 also shows the carbon conversion curve for Montana lignite determined in previous tests. The carbon conversion for lignite at equivalent temperatures is much less than for peat and does not reach its limiting value in the temperature range investigated.

The yields of hydrocarbon gases (methane+ethane+ethylene) obtained during gasification of peat in hydrogen and helium are shown in Figure 5. Similar data for gasification of Montana lignite in hydrogen are also included for comparison. The carbon in hydrocarbon gases (HG) obtained during peat gasification in helium reaches a maximum value of about 10% of the feed carbon. This can be considered the maximum yield of HG that can be produced from peat by pyrolysis alone. The fractions of the feed carbon converted to HG either in helium or hydrogen are about equal at about 1000°F. However, at higher temperatures, a hydrogen atmosphere improves the yield of HG markedly. Comparison of HG yields from peat and lignite show that peat is a better raw material than lignite for direct hydrogasification to light hydrocarbon gases.

Figure 5 also shows that HG yield curves for peat under isothermal and constant heat-up rate runs are very similar in shape. The only difference is that the curves for the constant heat-up rate runs are shifted to the right (higher temperature). These results indicate that heat-up rate by itself (within the range tested) does not effect the results of peat gasification.

The effective temperature during the constant heat-up rate tests corresponds to the isothermal tests conducted at about 150°F lower than the maximum temperature during the constant heat-up rate tests.

Figure 6 shows the oxygen conversion and the yield of carbon oxides during constant heat-up rate tests. At lower temperatures, the relative amount of carbon dioxide is greater than the carbon monoxide. Production of carbon dioxide remains constant at temperatures up to 1200°F and then falls sharply at higher temperatures. At 1500°F, carbon dioxide practically disappears. Conversely, the yield of carbon monoxide increases with temperature. A portion of the total CO produced is probably the result of the following gas-phase reverse-shift reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O$$

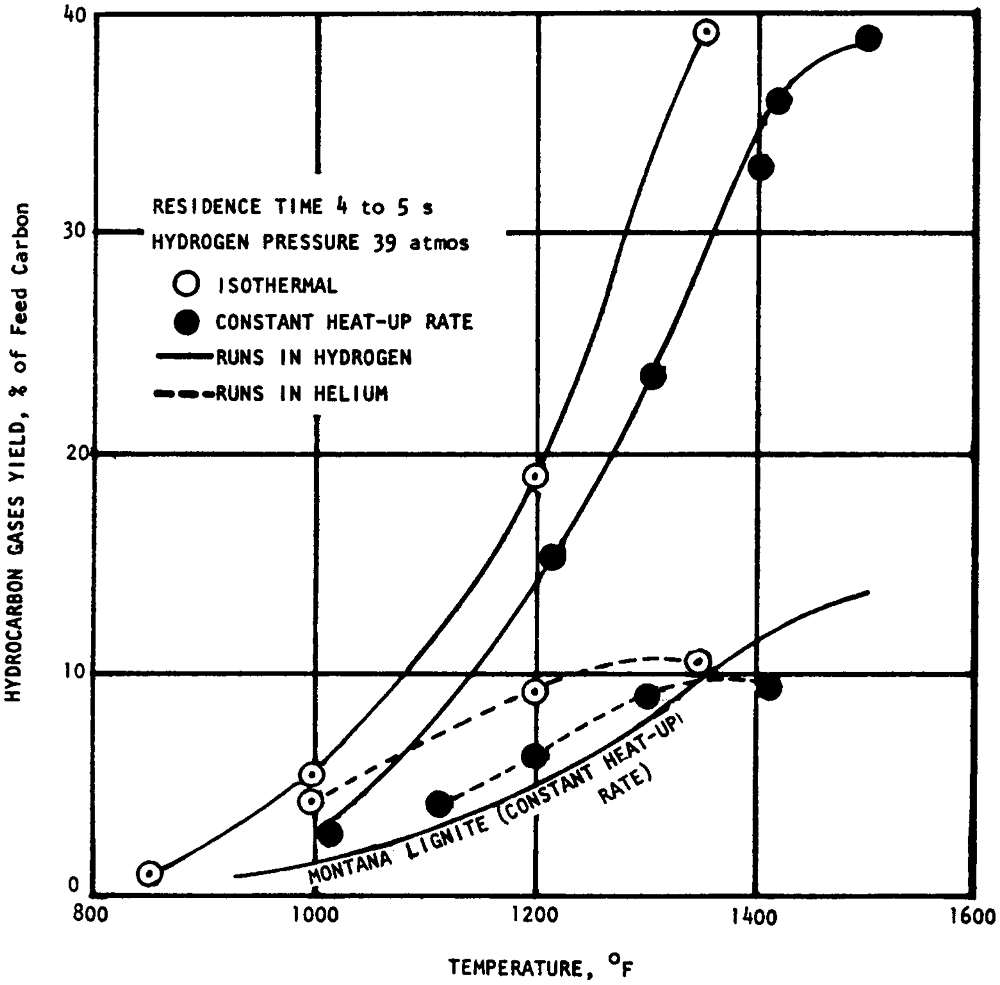

Figure 5. EFFECT OF TEMPERATURE ON YIELDS OF HYDROCARBON GASES DURING PEAT GASIFICATION

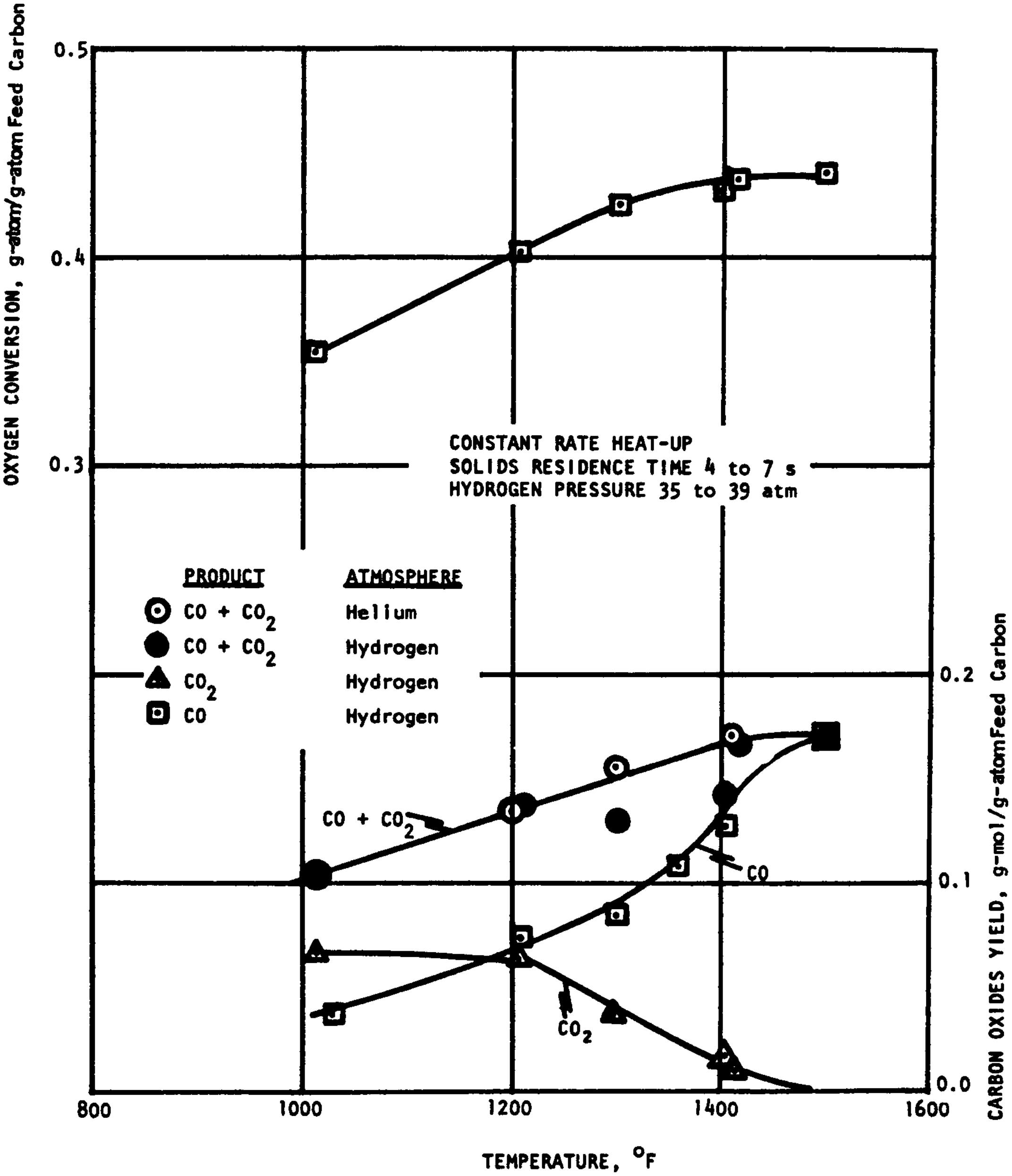

Figure 6. EFFECT OF TEMPERATURE ON OXYGEN CONVERSION AND YIELD OF CARBON OXIDES DURING PEAT GASIFICATION

Therefore, only the total carbon content $CO+CO_2$, (or CO_x) in the product gas can be considered to be related to the gasification characteristics of peat. The yield of CO_x in a hydrogen atmosphere shows slight scatter (two data points). Neglecting these two experimental points, a smooth curve was drawn for the production of CO_x. It is interesting that these data points for the CO_x yield in helium fall on the same curve. This match shows that carbon oxides production is related to the chemical structure of peat and to the reaction temperature, and is independent of the gaseous atmosphere during devolatilization. The CO_x yield curve in Figure 6 has been used for developing a quantitative correlation of the data reported in a later section.

Figure 7 shows the effect of temperature on product yields obtained during peat hydrogasification. The production of CO_x increases with temperature and attains a limiting value of 0.17 at 1400°F. The yield of heavy hydrocarbons (C_3 and oils) increases with temperature up to about 1100°F and then starts decreasing with temperature. It attains a limiting value of ~0.14 at about 1350°F. At low temperatures (~850°F), production of hydrocarbon gases (CH_4, C_2H_6, and C_2H_4), is low and the increase in hydrocarbon gas (HG) yield with increasing temperature (up to 1200°F) is nearly equal to the incremental change in total carbon conversion. At temperatures above 1200°F, the incremental change in total carbon conversion is small and the increase in HG production occurs due to hydrogenation of the HHC component.

The effect of hydrogen partial pressure on the product distribution during peat gasification at 1400°F is shown in Figure 8. The zero hydrogen partial pressure corresponds to the test conducted in a helium atmosphere. The CO_x component remains constant at all pressures. Initially, there is a rapid decrease in the yield of HHC, with an increase in hydrogen partial pressure up to 20 atmospheres. This results in an equivalent increase in HG yields. At higher hydrogen pressures, the yield of HHC remains constant and the increase in HG yields equals the incremental increase in total carbon conversion resulting from the increase in methane formed by the rapid-rate methane formation, as discussed in the next section of this report.

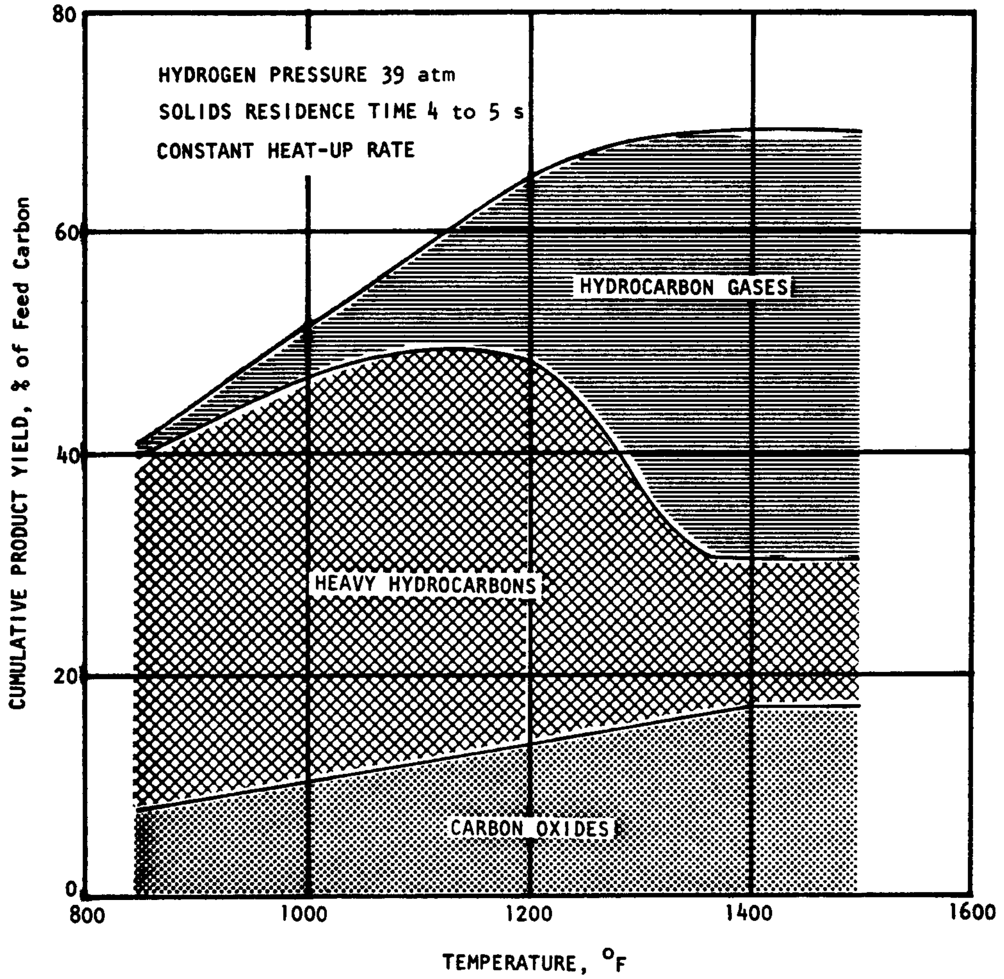

Figure 7. EFFECT OF TEMPERATURE ON PRODUCT YIELDS OBTAINED DURING PEAT GASIFICATION

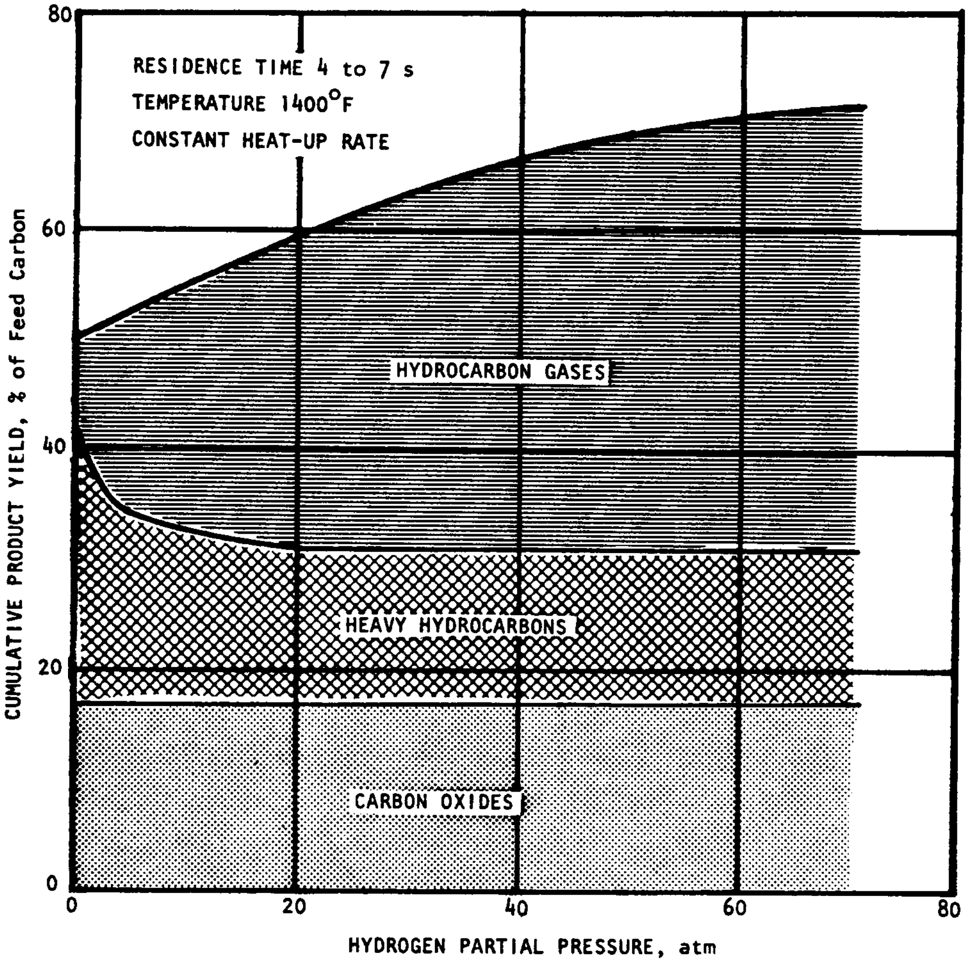

Figure 8. EFFECT OF HYDROGEN PARTIAL PRESSURE ON PRODUCT YIELDS OBTAINED DURING PEAT GASIFICATION

Figure 9 shows the effect of temperature on the yields of HHC obtained during isothermal and constant heat-up rate tests. It shows that in a hydrogen atmosphere at temperatures up to 1200°F, the yields of HHC are slightly higher during isothermal tests than during constant heat-up tests.

During isothermal tests, increasing the temperature from 850° to 1200°F increases the HHC yield only from 32 to 37 percent of the feed carbon. A further increase in temperature from 1200° to 1350°F sharply decreases the HHC yield to about 14 percent of the feed carbon. During constant heat-up runs, increasing the temperature from 1000° to 1200°F decreases the HHC yields only from about 30 to 27 percent of the feed carbon. A further increase in temperature rapidly decreases the HHC yield to about 14 percent of the feed carbon. The tests conducted in helium show that the effect of temperature on HHC yield is much less compared to those tests conducted in a hydrogen atmosphere discussed above. Increasing the temperature from 1000° to 1400°F decreases HHC yields from 28 to 24 percent of the feed carbon.

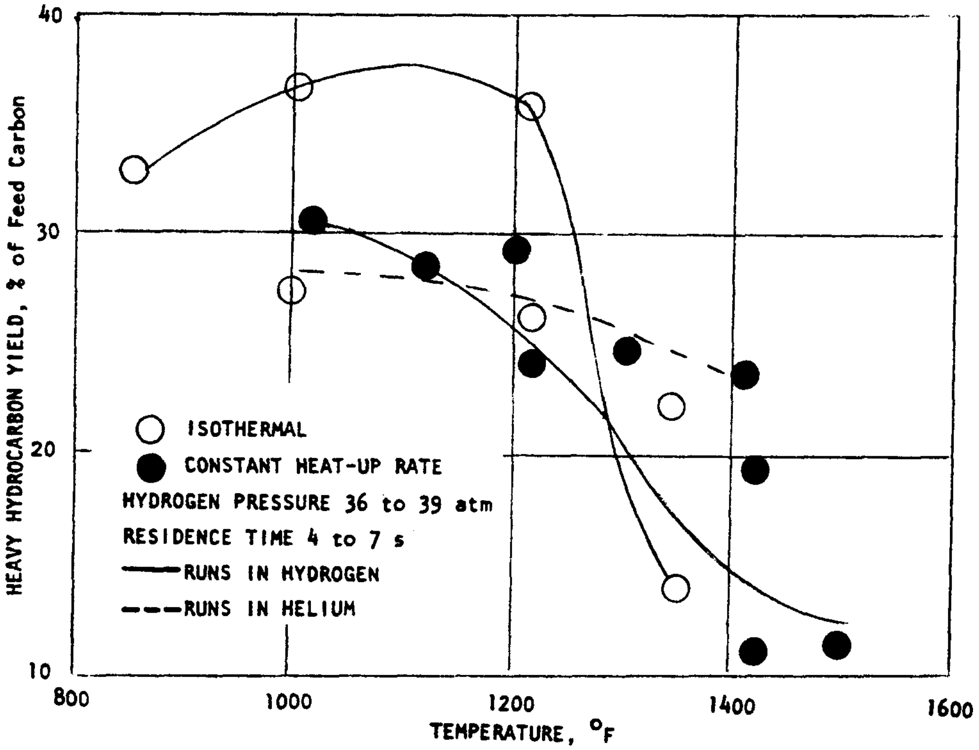

Figure 9. EFFECT OF TEMPERATURE ON HEAVY HYDROCARBON YIELDS OBTAINED DURING PEAT GASIFICATION

PEAT GASIFICATION KINETIC MODEL

A detailed model to describe overall reaction stoichiometry during primary devolatilization and rapid-rate methane formation with peat is shown in Figure 10. Reaction I refers to the primary devolatilization step and involves some gaseous hydrogen that interacts with the peat to alter somewhat the distribution of oxygenated species compared to what occurs in an inert atmosphere. In Reaction I, $CH_{0.74}$ refers to semi-char, $CH_{0.86}O_{0.07}$ refers to that portion of HHC which cannot be easily hydrogenated to HG, and $CH_{1.02}$ refers to that portion of HHC that can be hydrogenated to HG above 1400°F at relatively modest hydrogen partial pressures. Reaction II, corresponding to conversion of semi-char to a reactive intermediate with associated hydrogen evolution, is followed either by conversion of the reactive intermediate to char by Reaction IV, or reaction of the active intermediate with gaseous hydrogen to form HG by Reaction III (rapid-rate methane formation). In Reaction II, f is the fraction of semi-char that has converted to the reactive intermediate at any time, and is about equal to unity at 1400°F and above, after a few seconds. Reactions III and IV are considered to occur instantaneously after formation of the reactive intermediate.

Reaction V refers to secondary hydrogenation of HHC to form HG, with "z" being the fraction converted. "z" is also estimated as being unity above about 1400°F, at gas residence times greater than two seconds.

Primary and Secondary Devolatilization (Reaction I and II)

The devolatilization (pyrolysis) stage refers to a thermally activated decomposition process leading to the evolution of primary volatiles and the formation of semi-char. In this stage, the oxygen in peat is converted primarily to CO, CO_2, and H_2O, accompanied by the formation of some methane and ethane (hydrocarbon gases) and a substantial amount of condensible oils (HHC).

The CO_x yield reaches a limiting value at about 1200°F and oxygen conversion is also essentially complete at this temperature. This

I. Primary Devolatilization

$$\underset{\text{Peat}}{C_{1.000}H_{1.225}O_{0.440}} \xrightarrow{0.060H_2} \underset{\text{Oxygen Containing Gases}}{[0.11\ CO + 0.06\ CO_2 + 0.20\ H_2O]}$$

$$+ \underset{\text{Hydrocarbon Gases (HG)}}{[0.040\ CH_4 + 0.030\ C_2H_6]}$$

$$+ \underset{\text{Heavy Hydrocarbons (HHC)}}{[0.140CH_{0.86}O_{0.07} + 0.170\ CH_{1.02}]}$$

$$+ \underset{\text{Semi-char}}{[0.42\ CH_{0.74}]}$$

II. Secondary Devolatilization

$$\underset{\text{Semi-char}}{0.42\ f.\ CH_{0.74}} \longrightarrow \underset{\text{Active Intermediate}}{0.42\ f.\ CH_{0.36}^{*}} + 0.08\ f.\ H_2$$

III. Rapid-Rate Methane Formation

$$\underset{\text{Active Intermediate}}{0.42f.\ CH_{0.36}^{*}} \xrightarrow{0.64mfH_2} 0.21\ mf\ CH_4 + 0.10\ mf\ C_2H_6$$

IV. Char Formation

$$\underset{\text{Active Intermediate}}{0.42\ f.\ CH_{0.36}^{*}} \longrightarrow \underset{\text{Char}}{0.42\ f\ (1-m)CH_{0.36}}$$

V. Secondary Hydrogenation of HHC

$$0.170\ z\ CH_{1.02} \xrightarrow{0.21\ z\ H_2} 0.09\,zCH_4 + 0.040\,zC_2H_6$$

Figure 10. STOICHIOMETRY FOR INITIAL GASIFICATION STAGE OF PEAT IN HYDROGEN CONTAINING ATMOSPHERE

indicates that for peat, the pure pyrolytic reactions are essentially complete at about 1200°F. This conclusion is reinforced by the fact that the maximum amount of pyrolytic hydrocarbon gas (HG), obtained during pyrolysis in a helium atmosphere, is also obtained at about 1200°F. This is about 100°F lower than that required for complete primary devolatilization of lignites at short residence times and about 200° to 300°F lower than that for bituminous coals.

Rapid-Rate Methanation and Char Formation (Reactions III and IV)

Although the relative rates of Reactions III and IV are considered independent of temperature, the fraction of reactive intermediate forming methane and ethane, "m", is dependent on hydrogen partial pressure according to the relationship –

$$m = \frac{k_{III}P_{H_2}}{k_{IV} \quad k_{III}P_{H_2}} \tag{3}$$

Reactions III and IV occur essentially consecutive to primary devolatilization. In Figure 4, the increase in total carbon conversion with an increase in temperature above 1200°F can be attributed solely to increases in the gasification of the carbon in the semi-char with gaseous hydrogen to form HG. With peat, this reaction stage is completed at 1350°F at a solid residence time of 5 seconds.

From the experimental results, the value of HG (Y_{RR}) due to rapid-rate methanation can be computed using the following equation:

$$Y_{RR} = X_C - (HHC)_o - Y_{Pyr} - C_{CO_x} \tag{4}$$

where –

Y_{RR} = value of carbon in 'methane plus' due to rapid rate methane formation

X_C = total carbon conversion, g atom carbon/ g atom feed carbon

$(HHC)_o$ = carbon content in HHC at ~1200°F; (0.31 for isothermal runs and 0.26 for constant heat-up runs)

Y_{Pyr} = methane plus due to complete pyrolysis (0.1 g atom/g atom feed carbon)

C_{CO_x} = carbon content in CO_x obtained from Figure 5.

Also the fraction of the peat carbon converted solely due to the primary devolatilization reaction, λ, can be evaluated using the following expression:

$$\lambda = (HHC)_o + Y_{P_{yr}} + C_{CO_x} \qquad (5)$$

Therefore, the amount of carbon in semi-char before any subsequent gasification is equal to (1 − λ). Results obtained with peat have been analyzed with a model developed previously at IGT based on gasification of lignites, subbituminous coals, and bituminous coals.[1,2,3] The correlation derived to describe total HG yields due to rapid rate-methane formation with peat is:

$$Y_{RR} = (1-\lambda)\ \frac{bP_{H_2}}{1 + bP_{H_2}} \qquad (6)$$

Rearrangement yields —

$$\frac{Y_{RR}}{(1-\lambda)} = M = \frac{bP_{H_2}}{1 + bP_{H_2}} \qquad (6a)$$

where —

b = kinetic parameter

P_{H_2} = hydrogen partial pressure, atm

Comparison of the above equation with equation 3 indicates that

$$b = k_{III}/k_{IV} \qquad (7)$$

"M" has been calculated from experimental results and has been plotted against hydrogen pressure, as shown in Figure 11. The experimental points fall very close to the curve drawn by taking a value of 0.0092 for the kinetic parameter "b".

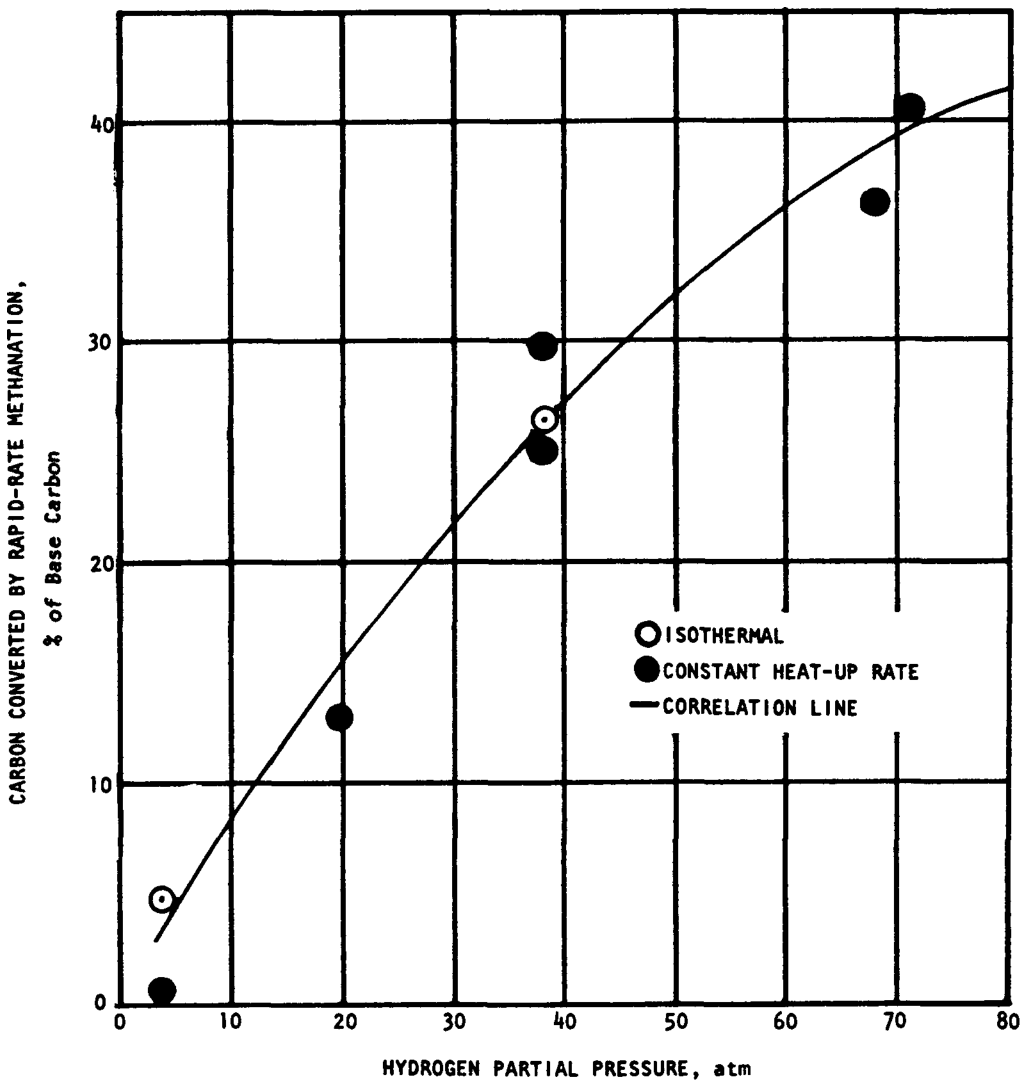

Figure 11. EFFECT OF HYDROGEN PRESSURE ON CARBON CONVERTED BY RAPID-RATE METHANATION

The value of b obtained for peat is very close to a corresponding value of $b = 0.0083$ atm $^{-1}$ derived in previous studies at IGT to describe results obtained with lignites and other coals. (The incremental yields of HG that can be achieved with peat, based on the above correlation, are shown in Figure 11 as a function of P_{H_2}). At low hydrogen partial pressures (of the order of a few atmospheres) HG yields from rapid-rate methane formation reactions with peat are relatively small compared to possible HG yields from pyrolysis and secondary hydrogenation reactions.

Secondary Hydrogenation of HHC (Reaction V).

Reaction V refers to secondary hydrogenation of HHC to HG, with "z" being the fraction converted. It will be shown later that for peat reacting in a hydrogen (~4 atm) medium, the value of "z" tends to be unity above 1400°F, at gas residence times greater than two seconds.

The yield of heavy hydrocarbons (C_3 and oils) in a hydrogen medium, shown in Figure 9, is relatively constant from 1000° to ~1200°F, drops sharply from 1200° to 1350°F, and approaches a lower limiting value above 1350°F. In a helium atmosphere no change in the yield of heavy hydrocarbons (HHC) is observed at temperatures up to 1400°F. The decrease in HHC yield at temperatures above 1200°F, in a hydrogen atmosphere, results in corresponding increases in HG yield. Although the total HG yield includes that due to direct peat pyrolytic reactions and rapid rate methane formation (as will be discussed later) a substantial portion of HG yield at temperatures above 1200°F, in the presence of hydrogen, can be attributed to the hydrogenation of HHC.

As shown in Figure 9, the maximum yield of HHC [referred to as $(HHC)_0$] is equivalent to 35 mole % of the feed carbon for isothermal tests and 31 % for the constant heat-up rate tests. The lower limiting yield of HHC at the highest temperature used in this study is 14 mole % of the feed carbon. This residual HHC is probably composed almost solely of relatively refractory oils that would require much more severe experimental conditions for hydrogenation to HG. Table 6 shows analyses of oils recovered after peat gasification tests. The major components in the recovered condensible oils are phenol and naphthalene. The results show that increasing gasification temperature decreases phenols and increases naphthalene concentrations in the oil. This is an expected result because phenols tend to convert to polycyclic aromatics rather than to benzene, even in a hydrogen atmosphere. Only about one-half or less of the HHC produced was directly recovered in experimental tests due to the relatively small size of the experimental equipment. It is possible, however, that at temperatures above 1300°F in a hydrogen atmosphere, the bulk of unrecovered HHC contained very light oils such as benzene.

Assuming the conversion of HHC to HG is a single, first order reaction, the data can be mathematically described by the following equation:

$$\text{HHC} \xrightarrow{K} \text{HG} \qquad (8)$$

and

$$K = 1.45 \times 10^{42}\, P_{H_2}^{1/2} \exp(-100{,}000/T) \qquad (8a)$$

where –

K = decomposition rate constant, s^{-1}

P_{H_2} = hydrogen partial pressure, atm

T = temperature, °K

Based on this equation, 99% conversion of HHC to HG would result at 1400°F at a residence time of about 2 seconds and a hydrogen partial pressure of 3 atm.

Table 7 compares estimated yields of oxygenated species and organic species after primary devolatilization of peat, lignite, and other coals. It shows that a unique feature of peat is that the carbon evolved during devolatilization is about 2.5 times that evolved during devolatilization of lignite and other coals.

Therefore, conditions that affect product distributions obtained during primary devolatilization are of much greater importance in gasification of peat than in gasification of higher rank fuels.

The primary distribution of major oxygenated species in Table 7 can be reasonably correlated with the oxygen/carbon ratios in the raw fuels. This

Table 6. OIL ANALYSES FROM PEAT GASIFICATION TESTS

Gasification Conditions			
Maximum Temperature, °F	1200	1410	1410
Hydrogen Pressure, atm.	40	40	0 (He only)
Total Oil Recovered, g-atm carbon/g-atm feed carbon	0.048	0.035	0.028
Oil Composition, g-atm carbon/total g-atm carbon in oil			
Single Ring Aromatic Hydrocarbon (benzene, indan, indene)	0.060	0.048	0.272
Two Ring Aromatic Hydrocarbons (primarily napthalene)	0.176	0.481	0.312
Three Ring Aromatic Hydrocarbons (phenenthrene, anthracene)	0.041	0.089	0.071
Four Ring Aromatic Hydrocarbons (pyrene, crysene)	0.027	0.058	0.009
Five Ring Aromatic Hydrocarbons (benzopyrene, binapthyl)	0.004	0.003	0.006
Oxygen-containing Aromatics (primarily phenal)	0.659	0.244	0.262
Nitrogen-containing Aromatics (pyridene, indole)	0.033	0.077	0.068
TOTAL	1.000	1.000	1.000

Table 7. ESTIMATED YIELDS AFTER PRIMARY DEVOLATILIZATION OF PEAT AND OTHER VARIOUS COALS

Material	Peat	Lignite	Subbit. C Coal	hv Cb Coal
Feed Composition, g-atm/g-atom feed carbon				
Carbon	1.000	1.000	1.000	1.000
Hydrogen	1.225	0.755	0.738	0.808
Oxygen	0.440	0.260	0.183	0.080
Primary Devolatilization Yield,				
Oxygenated Species, g-mol/g-atom feed carbon				
CO	0.11	0.05	0.03	0.01
CO_2	0.06	0.03	0.02	--
H_2O	0.20	0.14	0.11	0.07
Gasified Hydrocarbons, g-atom carbon/g-atom feed carbon				
HG*	0.10	0.03	0.05	0.06
HG**	0.27	0.05	0.08	0.10
HHC*	0.31	0.11	0.11	0.16
HHC**	0.14	0.09	0.08	0.12
Total Carbon Gasified, C_v g/atom/g-atom feed carbon	0.58	0.22	0.21	0.23

* Yields due solely to pyrolysis reactions.
** Yields after maximum hydrogenation of HHC to form HG.

distribution, however, can change through secondary water-gas shift reactions. Because of the initial high-oxygen content in peat, substantial amounts of oxygenated species are formed during devolatilization, which, in an integrated process, would require greater energy input to compensate for the generally endothermic decomposition reactions involved. Of greater significance, from a process point of view, is the substantial amounts of HG that can be formed from peat, particularly from secondary hydrogenation. As is shown in Figure 10, as much as 27% of the feed carbon can be converted to HG during this reaction stage, and this yield would represent the major contribution to the HG formed in any process. Although 10% conversion of the feed carbon in peat would occur at above 1200°F due simply to pyrolysis reactions, independent of hydrogen partial pressure, the fraction of the remaining 17% of the carbon in the HHC species group that could be converted to HG depends on hydrogen partial pressure, temperature, and residence time.

The correlation developed for peat has already been shown in Equations (8) and (8a). This conversion would also very probably depend on the mode of gas-solids contact. IGT believes that dilute, solid-phase contacting can best maximize potential HG yields, because this mode of contacting would inhibit cracking of HHC species to form carbon, a process promoted by the high solid carbon concentrations that would occur in fixed or fluidized beds.

GASIFIER CONFIGURATION SELECTION

Table 7 shows a comparison of the estimated yields of hydrocarbon gases (C_1, and C_2) and heavy hydrocarbons (C_3 and oils) obtained by devolatilization of peat, lignite, and bituminous coal before and after maximum hydrogenation of the heavy hydrocarbons (HHC). It shows the unique feature of peat — namely, that up to 55% of the HHC produced during pyrolysis can be hydrogenated to hydrocarbon gases (HG). Therefore, the yield of HG could vary from 10% to 27% of the feed carbon, depending upon the operating conditions during hydrogasification. For comparison, the HG yield for lignite and bituminous coal could vary only from 6% to 10% of the feed carbon, respectively. Therefore, a proper selection of operating conditions is more important for peat gasification than for coal gasification.

Figure 12 is a schematic diagram of the optimum reactor configuration for gasifying peat. The reactor consists of two sections — a hydrogasification zone where most of the methane is produced and a steam-oxygen gasification zone where the hydrogen-rich synthesis gas necessary for hydrogasification is produced. Only two zones are needed because the kinetics of peat gasification are so rapid as compared with coal. Thus, no intermediate hydrogasification zone is necessary to enhance direct methane production.

The optimum pressure for methane production is in the range of 200 to 500 psig. Lower pressures promote oil and decrease methane yield. Higher pressures, as pointed out earlier, do not increase methane production significantly, but they do lead to costly equipment. The optimum temperature range for methane production is between 1400° and 1600°F. Lower temperatures reduce methane and increase oil yield, whereas higher temperatures promote cracking to form coke and reduce both oil and methane yields. Cocurrent dilute-phase gas-solids contacting is very favorable in the hydrogasification zone. Countercurrent contact would lead to increased production of tars and phenols, and a dense-phase carbon bed would cause cracking of oils to coke.

The optimum temperature for the steam-oxygen-char gasification zone

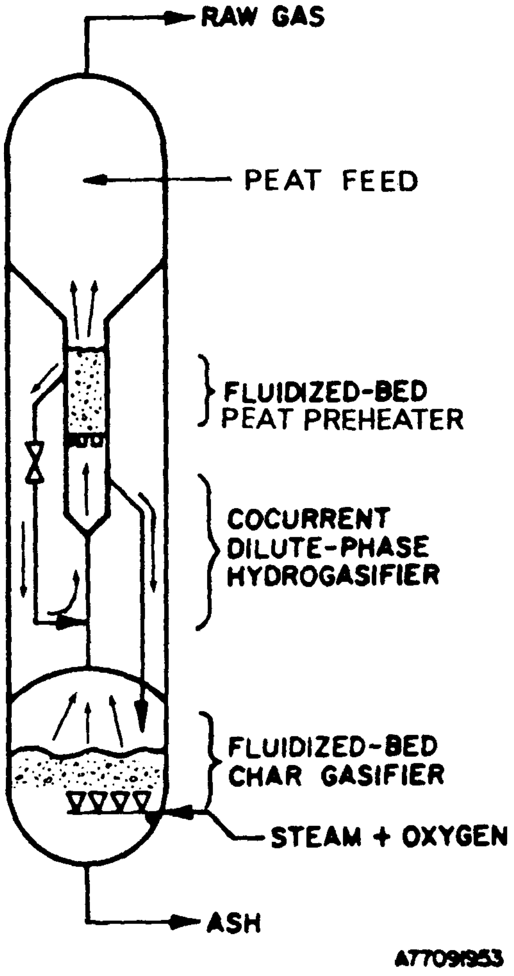

Figure 12. PREFERRED CONFIGURATION FOR A PEAT GASIFICATION REACTOR

is between 1850° and 1950°F. Lower temperatures increase the steam required, because the hydrogasification section requires a certain amount of heat and more steam is required to carry this heat if the char gasifier is operated at lower temperature. Higher temperatures cause cracking of oil in the hydrogasification section. Within the limitation of 1850° to 1950°F, only nonslagging fluidized-bed operation is possible. Slagging gasifiers for making synthesis gas require temperatures in excess of 2600°F.

Peat could be fed in the form of slurry (in by-product light oil) into a fluidized-bed slurry dryer, to be dried and heated by the product gases coming from the hydrogasifier. Peat could also be fed using a lockhopper system. In either case, the peat would be picked up by synthesis gas generated in the fluidized-bed char gasifier and entrained into a vertical cocurrent dilute-phase hydrogasifier with a residence time of a few seconds. The char from the hydrogasifier would overflow into the char gasifier. Steam and oxygen would be fed to this fluidized-bed gasifier. The only solids discharge from this section of the gasifier would be essentially ash. This reactor configuration is called a PEATGAS Reactor (PGR).

CONCLUSIONS

The results of peat hydrogasification tests show that peat is not only more reactive than other coals, but it also has a several-times-higher tendency to form hydrocarbon gases. The results also show that, compared to other coals, high methane yields can be obtained during peat gasification at relatively low hydrogen partial pressures. Another feature of peat gasification is that the proportions of gas and oil yields can be varied significantly by controlling hydrogasification temperature. Evaluation of the peat gasification results indicate that a preferred configuration for a peat gasifier should incorporate a short residence time. cocurrent, dilute-phase hydrogasifier operating at 200 to 500 psig and about 1400° to 1600°F, and a fluidized-bed, steam-oxygen char gasifier operating at 1850° to 1950°F. On an overall basis, the results show that peat is an exceptionally good material for SNG production.

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