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MACROSCOPIC SAMPLE EFFECTS ON THE PYROLYSIS OF BITUMINOUS AND SUBBITUMINOUS COALS AT UNDERGROUND COAL GASIFICATION HEATING RATES*

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DISCLAIMER

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ABSTRACT

Two-dimensional pyrolysis behavior of 14- to 16-cm instrumented blocks of bituminous and subbituminous coals is being examined at the Oak Ridge National Laboratory, (ORNL), primarily in support of in situ coal gasification process development. The objective of the program is to develop a firm data base from which computerized models may be developed. For this reason, results described below have been obtained at conditions expected to occur underground. Experiments utilizing maximum reactor temperatures of 500 to 1000°C achieved over periods of 4 to 60 hr have produced data correlating tar and gas production rates and composition with maximum temperature and heating rate. Chars produced by some experiments have exhibited marked pyrophoricity, which has not been observed previously by other researchers. Furthermore, thermal profiles within the blocks during pyrolysis indicate clearly that volatilization of water is the heat transfer rate-limiting mechanism. Gas production from as-received specimens is observed to be significantly greater than that measured during the pyrolysis of powdered coal at similar heating rates. Diffusion of steam from a shrinking core of wet coal is postulated to account for this phenomenon.

INTRODUCTION

It has been estimated that only 6 or 7% of all U.S. coal reserves may be considered recoverable by conventional strip mining or deep-mining techniques. The approximately 2.8 trillion tons remaining comprise deposits that are either too thin or too deep to be obtained by such methods.[1,2] The energy contained by many of these deposits, however, may be largely recovered by in situ gasification processes which are currently being developed.

In situ gasification of coal entails injection of oxygen or air with or without steam into a coal seam whose permeability has been enhanced previously be explosives, high-pressure liquid injection, or some other means. The presence of injected oxygen permits ignition of the coal and subsequent maintenance of a combustion front which moves through the coal bed. The heat from combustion facilitates pyrolysis reactions, steam-carbon reaction, and other gasification reactions ahead of the moving combustion front. The gases that are produced may be piped to the surface for subsequent use.

The specific objective of the ORNL program supporting in situ or underground coal gasification (UCG) development is the generation of data describing the pyrolysis of large coal blocks under conditions which can be expected to occur underground. Clearly, a large amount of pyrolysis data has been obtained in the past, but most of that work was done using powdered samples, high heating rates, and pressure at or very near atmospheric. Recent field test results, however, indicate that heating rates may be as low as a few degrees per minute. The coal will be fractured, but not powdered, and pressures are significantly higher than atmospheric. As Dr. R. D. Gunn pointed out at last year's symposium,[3] the accuracy of computer codes developed to help interpret field test results rests upon the accuracy of the fundamental data base it uses for calculational purposes. As shown in the results presented below, two-dimensional effects are definitely significant in the determination of gas yields from pyrolysis of macroscopic samples at low heating rates.

TWO-DIMENSIONAL PYROLYSIS STUDIES - WESTERN SUBBITUMINOUS COAL

Two-dimensional effects during the pyrolysis of 16-cm right, circular cylinders of Wyodak subbituminous coal have been observed as functions of maximum pyrolysis temperature and heating rate. The apparatus used for these experiments, as well as details of block preparation, instrumentation, and product analysis,

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have been described elsewhere;[4] briefly, however, the experimental procedure consists of placing a test specimen in the reactor, establishing a stable cover gas flow, and heating the reactor at one of two heating rates chosen for these studies (3.0 or 0.3 C°/min). (Reactor temperature is referenced to a thermocouple at the surface of the coal block.) The temperature is permitted to increase to a specified maximum (500 to 1000°C), where it is held constant until thermocouples within the coal block have reached T_{max} and gas evolution has ceased. Most experiments have utilized as-received blocks (without prior drying or excessive contact with air) and an argon cover gas at atmospheric pressure.

Thermal profiles within the block, observed during pyrolysis, have been reported previously.[4] These earlier results indicated clearly that the core of the block did not exceed a temperature of ~100°C until the moisture had been evaporated. This phenomenon, rate-limited by heat transfer to the core, results in significant two-dimensional effects when macroscopic samples of coal are pyrolyzed.

Results obtained to date provide some qualitative information about two-dimensional pyrolysis. Figure 1, for example, shows the product distribution as a function of maximum pyrolysis temperature. As one would expect, the gas yield increases with temperature at the expense of char (primarily) and liquid hydrocarbons. Heating rate, within the range examined, seems to have only a small effect on this distribution. Some data taken by the Lawrence Livermore Laboratory (LLL) using this particular coal have been included in Fig. 1 for comparative purposes.[5-7]

Gas production data are summarized in Figs. 2-7. As shown in Fig. 2, three distinct regions of gas production are observed: loss of adsorbed or loosely bound volatiles, the so-called primary pyrolysis stage,[8] and a secondary stage. Staged gas production such as that snown in Fig. 2 was seen only in those experiments in which the lower heating rate was employed. The amount of gas produced during the secondary stage is significantly greater than that predicted from conventional data obtained from powdered coal and is thought to be the result of extensive tar and steam interactions with the char bank near the block surface. This is brought into focus by Fig. 3, which shows the total gas production per kilogram of coal as a function of pyrolysis temperature and of heating rate. Determinations made by LLL using traditional powder pyrolysis techniques are again included for comparison.[5-7] Figures 4 through 6 show the evolution of individual gas constituents--CH_4, C_2, C_3, CO_2, CO, and H_2--as a function of block temperature at a heating rate of 0.3C°/min.

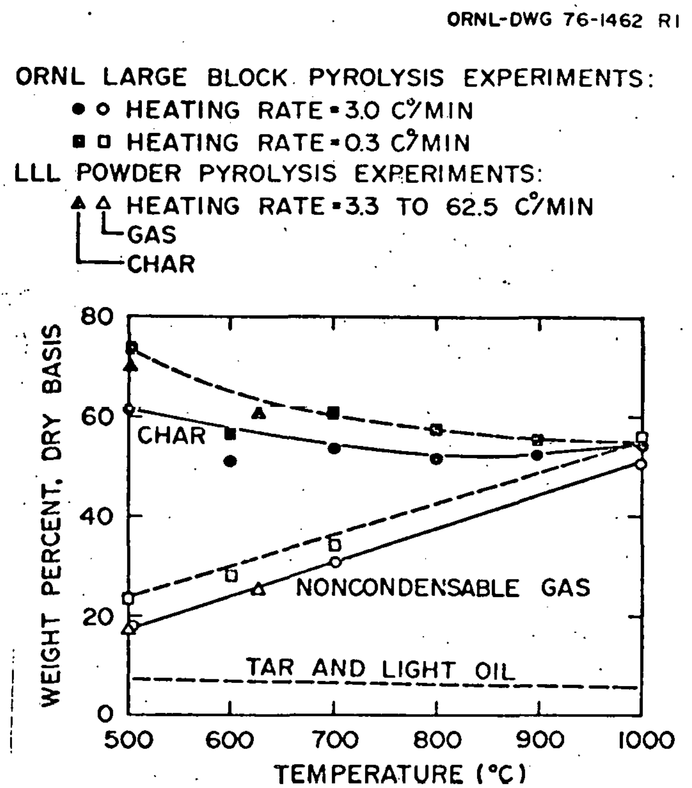

Fig. 1. Product distribution as a function of heating rate and maximum pyrolysis temperature.

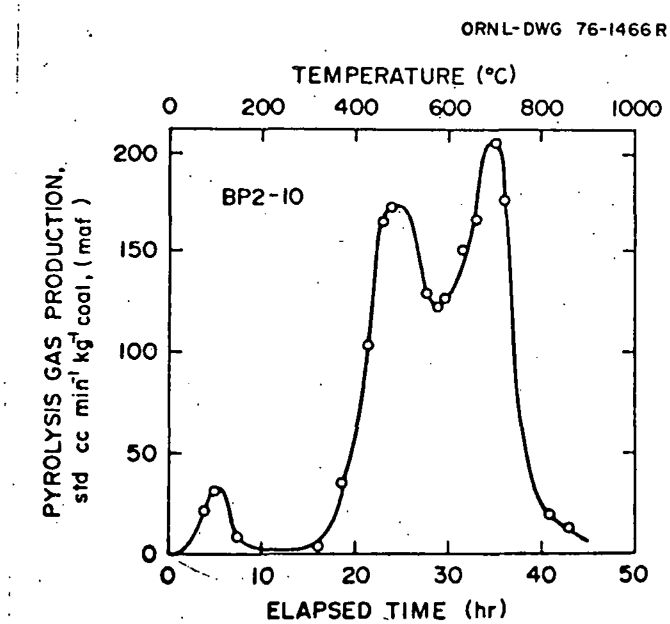

Fig. 2. Total gas production for two-dimensional pyrolysis experiments at 0.3 C°/min heating rate.

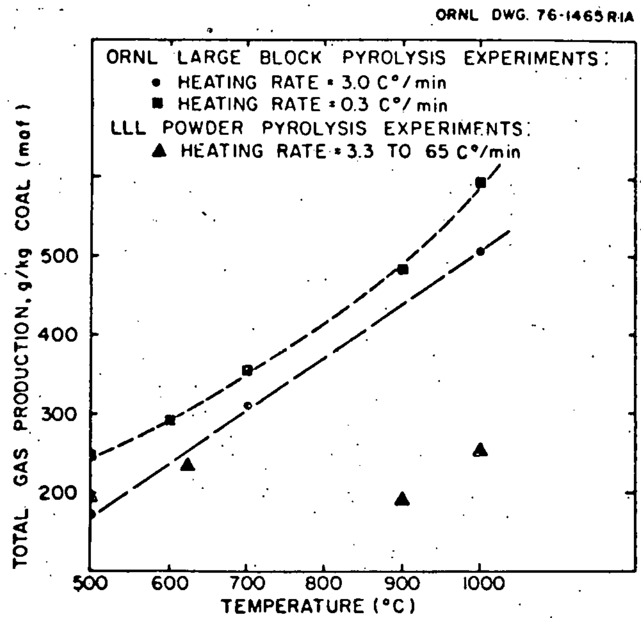

Fig. 3. Total gas production as a function of maximum pyrolysis temperature and heating rate.

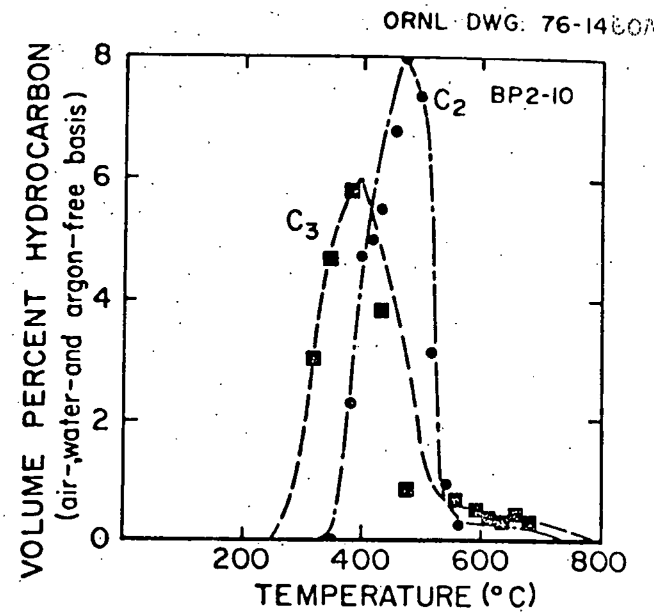

Fig. 5. Light hydrocarbon content of pyrolysis gas as a function of block surface temperature (heating rate = 0.3 C°/min).

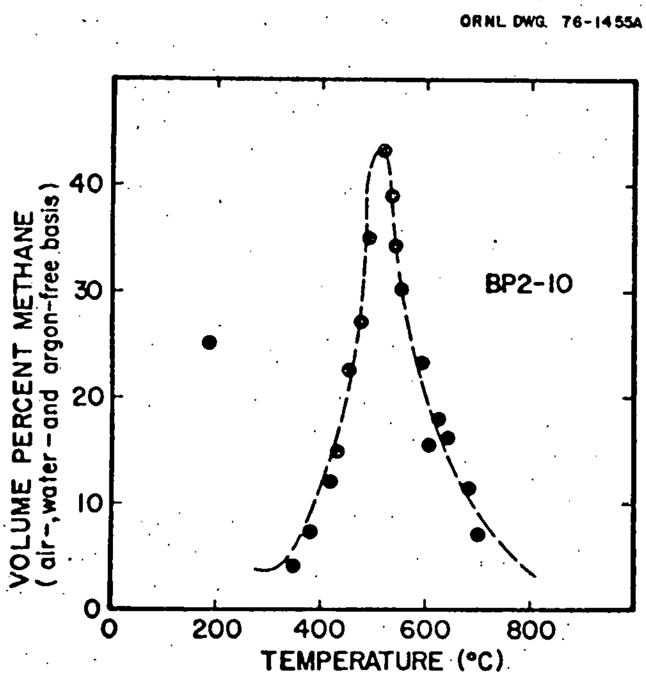

Fig. 4. Methane content of pyrolysis gas as a function of block surface temperature (heating rate = 0.3 C°/min).

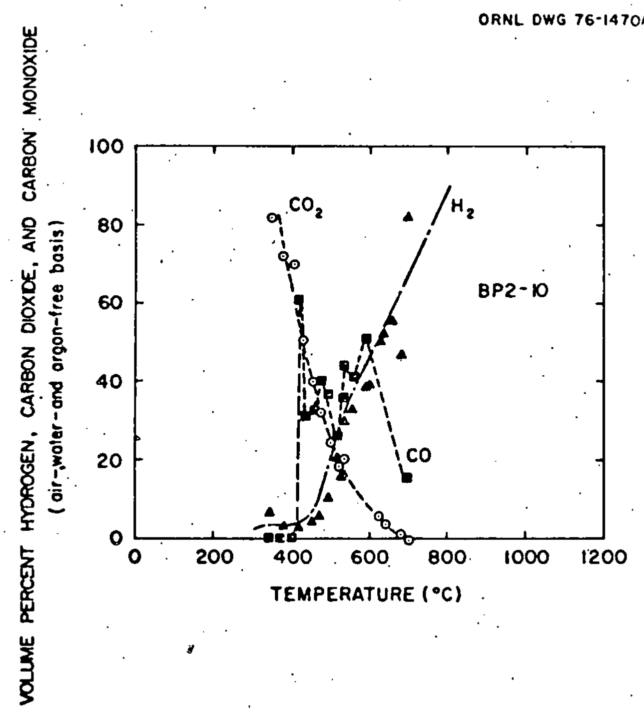

Fig. 6. Hydrogen, carbon monoxide, and carbon dioxide contents of pyrolysis gas as a function of block surface temperature (heating rate = 0.3 C°/min).

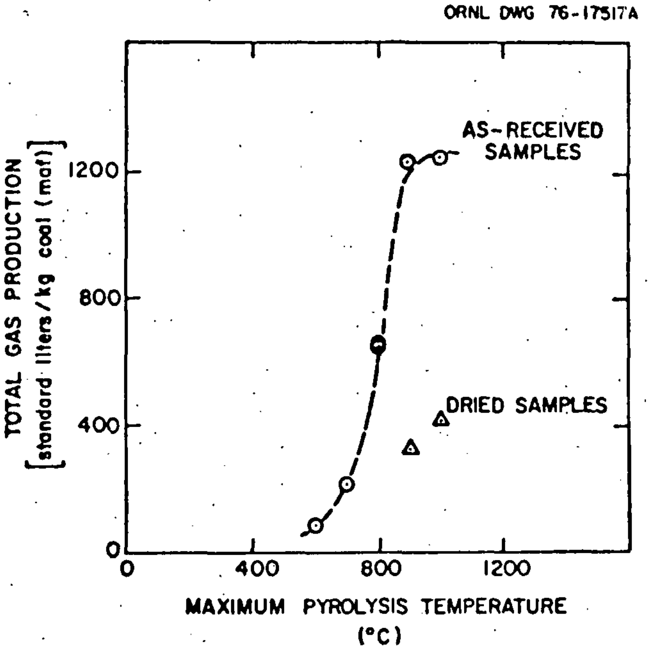

Fig. 7. Two-dimensional pyrolysis of wet and dried subbituminous coals.

Table 1. Two-dimensional and moisture content effects on the overall composition of gases produced by pyrolysis of western subbituminous coals[a]

Component gas	Dry powder[b]	Mole Percent 2-D, wet[c]	2-D, dry[d]
H_2	40.8	50.9	48.7
CO	15.0	27.0	19.6
CH_4	22.0	9.6	16.2
$C_2 - C_6$	3.6	1.6	2.8
CO_2	18.6	10.9	12.6

[a]All samples taken from Wyoming's Roland-Smith coal seam (moisture content ∿ 30%). Ultimate and proximate analyses are given in ORNL/TM-5291, p. 561 (September 1976).

[b]Reported by J. H. Campbell, UCRL-52035 (March 1976).

[c]ORNL experiment BP2-15; heating rate, 3 C°/min to maximum temperature of 900°C.

[d]ORNL experiment BP2-19; dried under vacuum at 125°C prior to pyrolysis at 3 C°/min to 1000°C.

By following changes in composition of the pyrolysis gas with time for a typical experiment, one observes that the evolution of methane and light hydrocarbons is substantial during the primary pyrolysis state but diminishes rapidly as the temperature increases beyond 600°C. Production of carbon monoxide and hydrogen (insignificant below 400°C) increases rapidly to account for nearly 90% of the total gas produced in later stages of pyrolysis. Further tests utilizing dried coal blocks have shown (Fig. 7) that gas production from as-received blocks is higher, by a factor of two to three, than that observed from dewatered coal. These data further support our contention that enhanced gas production is a result of extensive steam-char reactions which take place as steam generated at the core of the block diffuses through a high-temperature char bank at the block surface. Table 1 shows the overall composition of pyrolysis gas produced by the two types of experiments.

EASTERN BITUMINOUS COAL

More recent experiments have examined the behavior of an eastern bituminous coal under the same conditions as those described above. The coal used in these tests, obtained from the Morgantown Energy Research Center (MERC), was taken from the Pittsburgh seam near Pricetown, West Virginia, where MERC is to conduct field tests of their in situ gasification process. Proximate and ultimate analyses for the coal are given in Table 2.

Results of the pyrolysis tests to be described are significantly different from those observed during studies of western subbituminous coal. The coal was machined into 14-cm right circular cylinders, as before, and then drilled to accept 1.2-mm thermocouples for internal temperature measurement. Table 3 summarizes the test conditions for bituminous coal experiments performed thus far. The ranges of both maximum temperature and heating rate are the same as those utilized for subbituminous coals, although fewer data have been taken for this type of coal.

The chars produced in every experiment described by Table 3 exhibited characteristics significantly different from those of chars produced by the pyrolysis of western coal (described in ref. 4). These chars, which have a higher density and a much greater crushing strength, are not pyrophoric to any degree. Char reactivity tests (to be performed at Argonne National Laboratory) are expected to show the materials to be far less active chemically. In addition to the data shown in Table 3, it was observed that the density of the char passes through a maximum as one traverses the block from the center to the surface; conversely, the porosity passes through a minimum. Workers with coke oven experience report[9] that this is the result of tar cracking and subsequent carbon deposition, which take place as tars evolved near the center of the block encounter the hot char bank in their outward diffusion path. This effect was not observed with western coal because the porosity of

Table 2. Proximate and ultimate analyses for Pittsburgh Seam Coal used in two-dimensional pyrolysis studies (wt %)

	Analysis Identification				
	BP2-WVA-1	BP2-WVA-2	BP2-WVA-4	MERC hole No. 1[a]	MERC hole No. 2[a]
Proximate analysis					
Moisture	1.14	0.68	0.59	0.98	1.04
Volatile matter	34.4	37.3	34.1	42.23	40.00
Ash	6.46	6.92	6.43	10.09	8.90
Ultimate analysis (maf)					
Carbon	83.73	84.92	84.23	81.6	81.8
Hydrogen	5.32	5.95	5.78	5.54	6.06
Nitrogen	1.55	1.71	1.65	1.34	1.46
Sulfur	3.80	2.69	4.29	4.61	4.58
Oxygen (by difference)	5.61	4.73	4.05	5.87	6.10

[a]Data obtained from core samples taken at the Pricetown UCG field test site. Values shown represent a range of determinations (i.e., 10.09% ash is an average of determinations ranging from 3 to 40%). See Chemical and Mineralogical Characterization of Core Samples from Underground Coal Gasification Sites in Wyoming and West Virginia, Report No. MERC/RI-75/2 (December 1975).

the char was much greater and the product oils were lighter. A summary of char characteristics from some representative tests is given in Table 4. Note that, as expected, the hydrogen content of the char decreases as the maximum pyrolysis temperature rises. These data also support the observation that increases in char density at radial positions about halfway from the center to the surface of the residual block are caused by tar cracking and subsequent carbon deposition. Samples from BP2-24, for example, show increased carbon content at r/R = 0.5.

Table 3. Two-dimensional pyrolysis experiments utilizing an eastern bituminous coal (Pittsburgh seam)

Pyrolysis test no.	Heating rate (C°/min)	Maximum temperature (°C)
BP2-23[a]	0.3	1000
BP2-24	3.0	1000
BP2-25	3.0	800
BP2-26[a]	0.3	1000
BP2-27[b]	3.0	600

[a]Considerable fluctuation in gas production observed and severe temperature cycling.

[b]Gas analysis data not complete.

During each experiment, the fluid nature of this coal, upon reaching the softening point, could be inferred from the sound of gases bubbling within the reactor and from observed fluctuations in the gas production rate. Figure 8 is typical of this behavior for the low-heating-rate experiments. Also, the residual char block produced by each test showed many effects of swelling and fluid behavior during pyrolysis, such as interior bubble voids and smooth, glasslike surfaces.

Figures 9 through 11 provide details of component gas production for some of the tests described by Table 3. Note that nearly all C_2-C_3 hydrocarbons are evolved when the surface temperature of the block lies between 300 and 500°C. As observed with the western coal, CO and H_2 are produced in large quantities only at higher temperatures. At the lower heating rate, CH_4 appears to be produced by two different mechanisms, peak production taking place when the surface temperature lies within the ranges 100 to 300°C and 400 to 600°C. This behavior is not observed at the higher heating rate due to the increased volume of gas production per unit time. Table 5 gives the observed total gas production for all tests, normalized to a unit weight of maf sample. Results for western coals are also presented for comparison.

Table 4. Characteristics of chars produced by two-dimensional pyrolysis of Pittsburgh seam coal

Sample number	Maximum pyrolysis temperature (°C)	Heating rate (C°/min)	Radial position ($^r/R$)[a]	Component weight percent[b] Moisture	Ash	Carbon	Hydrogen	Nitrogen	Sulfur	Heating value[c] (Btu/lb)
BP2-24F	1000	3.0	1	0.43	8.06	95.95	0.66	1.43	2.02	14,192
BP2-24G	1000	3.0	0.5	<.01	7.47	97.47	0.53	1.31	1.62	13,698
BP2-24H	1000	3.0	0	0.33	8.73	96.82	0.85	1.43	1.96	14,254
BP2-25B	800	3.0	0.5	0.52	7.84	94.62	1.11	1.71	3.39	14,418
BP2-27C	600	3.0	0	0.65	9.25	90.88	2.85	2.06	1.96	15,987
BP2-23C	1000	0.3	0.5	0.15	4.63	96.37	0.63	1.64	1.35	14,207
BP2-26D	1000	0.3	1	0.14	9.95	97.44	0.68	1.07	1.77	13,967

[a]Char samples were taken from three areas of the cylindrical block: at the axis of symmetry ($^r/_R$ = 0), at the surface ($^r/_R$ = 1), and between these extremes ($^r/_R$ = 0.5).

[b]All values are maf except those shown for moisture and ash.

[c]Values shown are maf. Multiply by 2.326 to obtain kJ/kg.

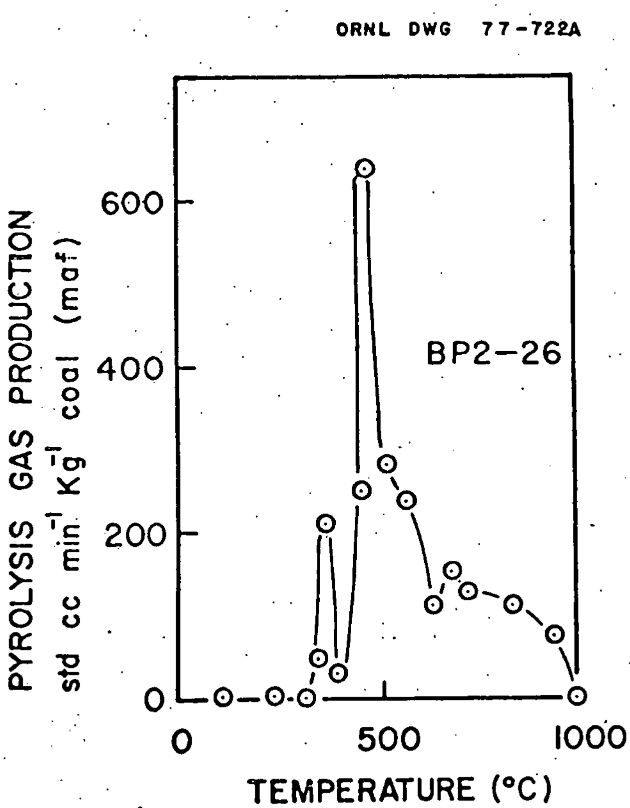

Fig. 8. Fluctuating gas production at 0.3 C°/min heating rate using Pittsburgh coal.

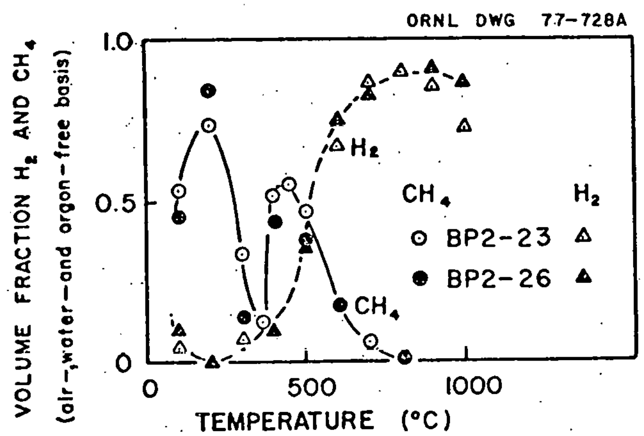

Fig. 9. Hydrogen and methane content of pyrolysis gas as a function of block surface temperature (heating rate = 0.3 C°/min).

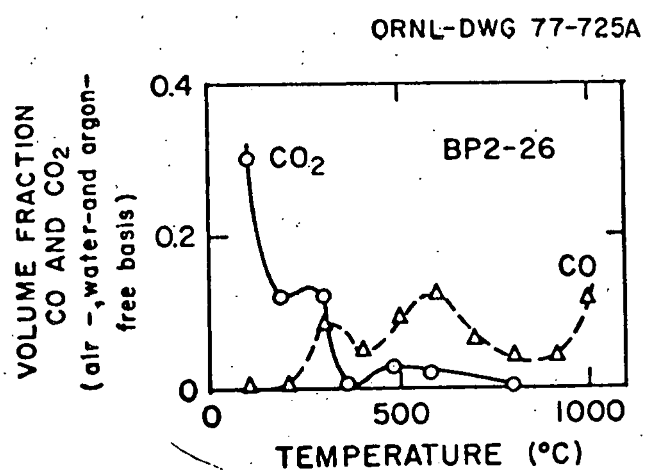

Fig. 10. Carbon monoxide and carbon dioxide content of pyrolysis gas as a function of block surface temperature (heating rate = 0.3 C°/min).

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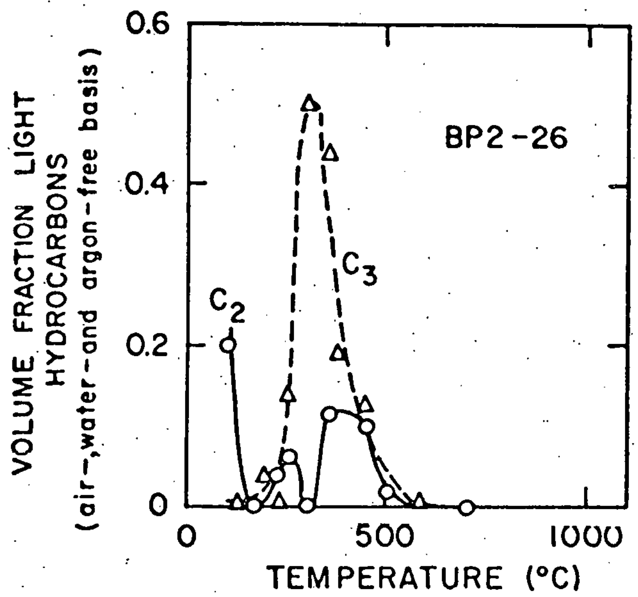

Fig. 11. Light hydrocarbon content of pyrolysis gas as a function of block surface temperature (heating rate = 0.3 C°/min).

Table 5. Total gas production for bituminous coal pyrolysis tests and selected subbituminous tests

Test description	Maximum temperature (°C)	Total gas production (g/kg coal)[a]
For 3.0°C/min heating rate		
BP2-24	1000	215
BP2-25	800	193
BP2-27	600	150
BP2-17[b]	1000	486
BP2-19[b] (dried)	1000	296
BP2-20[b]	600	242
For 0.3°C/min heating rate		
BP2-23	1000	183
BP2-26	1000	162
BP2-16[b]	1000	249

[a]Gas production for each test is normalized to the maf weight of the coal specimen pyrolyzed.

[b]Tests using western subbituminous coal (Roland-Smith seams) having an as-received moisture content of about 27 wt %.

DISCUSSION

Although the results of pyrolysis experiments utilizing eastern coals are incomplete, several points of similarity and difference between the two coal types being studied are already obvious:

(1) Produced chars possess significantly different characteristics; western coals yield a more friable, reactive residue.

(2) Two-dimensional gas production during pyrolysis of the wetter subbituminous coal is significantly greater, although the overall mechanisms for the production of specific components appear to be similar.

These observations and the results described above clearly suggest that UCG process applications to eastern coal fields will require special attention to porosity losses through swelling, low char reactivity, and reduced gas production from pyrolysis.

Future experiments at ORNL will be directed at determination of the effects of pressure on the results obtained thus far using an atmospheric-pressure system. Such effects are presently unknown and may greatly influence the accuracy of present-generation diagnostic codes.

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