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PYROLYSIS OF BITUMINOUS COAL BLOCKS

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PYROLYSIS OF BITUMINOUS COAL BLOCKS*

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ABSTRACT

Internal heat and mass transfer resistances were observed to affect the pyrolysis of bituminous coal blocks in experiments at Oak Ridge National Laboratory (ORNL). Pyrolysis, the reaction step which occurs after drying and before gasification, is conventionally studied by the rapid heating of powdered samples so that internal resistances can be minimized. Because monolithic coal rather than powdered coal is reacted in underground coal gasification (UCG), the measurement of differences between powder and block pyrolysis is particularly important to the successful, broadly applicable modeling and development of UCG.

In a block pyrolysis reactor at ORNL, 0.15-m (6-in.) -diam cylinders of bituminous coal were heated at 0.3, 3, or 14 C°/min; in inert gas (Ar) and in H_2; and to maximum pyrolysis temperatures of 600-1000°C. In the tests performed at higher heating rates, a significant reduction in swelling of the coal was observed which can be correlated with the steep temperature gradients caused by heat transfer resistances. Also, at higher heating rates, pyrolysis gas evolution was increased as oil and char yields decreased. Such behavior is evidence of secondary cracking reactions caused by a combination of the steep temperature gradients and mass transfer resistances.

Introduction

This paper reports and examines data from the pyrolysis of large blocks of Pittsburgh seam bituminous coal at different heating rates, different maximum temperatures, and in inert and reducing atmospheres; all experiments were conducted at atmospheric pressure. Before beginning any discussion of the thermal behavior, swelling, and products yields from these experiments, it is important to understand the purpose and application of the research.

Pyrolysis of large coal blocks has been studied at ORNL since 1975, in support of the Department of Energy program for development of in situ coal conversion. A recent series of experiments was conducted to extend this study of the effects of transport phenomena to an Eastern bituminous coal. Such work directly supports the field and modeling program of Morgantown Energy Research Center (MERC).

ORNL experiments have studied pyrolysis as a separate step in the conversion of coal. Although most pyrolysis data describe product yields from small samples of powdered coal, accurate modeling of underground coal gasification (UCG) requires data which describe bulk effects on pyrolysis. Results have included the description of swelling behavior, correlation of pyrolysis yield structures, measurement of thermal properties, and study of drying mechanisms.

To understand the applications of block pyrolysis research, it is useful to analyze the different modes of in situ gasification. UCG processes may be classified physically as permeation-flow, stream-flow, or jet-flow methods.[1,2] In permeation-flow (percolation) methods, bulk gas flow permeates the coal seam to feed a broad, moving combustion front or flame front (see Fig. 1). Such flow

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describes the idealized gasification step of Linked Vertical Well (LVW) technology or the Longwall Generator concept. In contrast are the stream-flow methods, where the direction of bulk gas flow is at right angles to the directions of flame front movement and of the local reactant and product flows (Fig. 2); these methods have been proposed for use in DOE field tests. Jet-flow methods which blast air at a burning reaction front are similar to stream-flow in that bulk gas flow feeds, but does not pass through, the flame front.

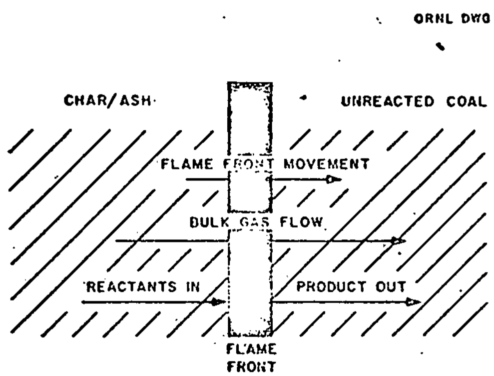

Figure 1. Flows in permeation-flow UCG

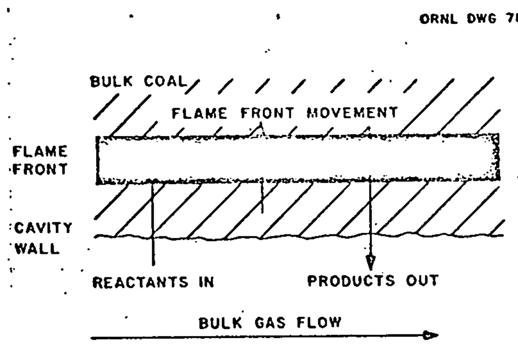

Figure 2. Flows in stream-flow UCG

Realistically, the field processes combine stream flow, permeation flow, and other phenomena. In LVW, permeation flow clearly describes reverse combustion linkage, but permeation flow and stream flow apparently both occur as the linkage channel grows during forward gasification; Schwartz and Eddy's UCG model uses this approach.[3] In an experiment where a directionally drilled hole is used for linkage, some permeation flow will occur, at least in the char boundary of the cavity. In addition to these simple flow schemes, coal blocks can fall into the reaction zone from the roof. Also, Douglas has described laboratory gasification experiments in which burning blocks of bituminous coal became isolated behind the flame front as old permeation paths were plugged by tars and new paths were forced open.[4]

Block pyrolysis experiments simulate these phenomena by heating the surfaces of cylindrical coal blocks. In situ pyrolysis of chunks from roof collapse, bypassing, or rubblizing is directly simulated; however, good simulation of stream-flow pyrolysis is also useful. As in stream-flow methods, a thermal wave moves into the coal at right angles to the bulk gas flow. Pyrolysis gases, vapors, and steam are forced to diffuse out of the coal block through a hot surface region, just as they must at the reaction face in steam-flow methods.

Correlation of data from coal block pyrolysis can thus describe important UCG phenomena both qualitatively and quantitatively.

Apparatus and Procedure

Using the apparatus shown in Fig. 3, the surface temperature of coal blocks can be increased at a uniform rate, internal block temperatures can be measured, and pyrolysis products—char, aqueous and organic liquids, and gases—may be collected or monitored. Details of the apparatus design are described elsewhere.[5]

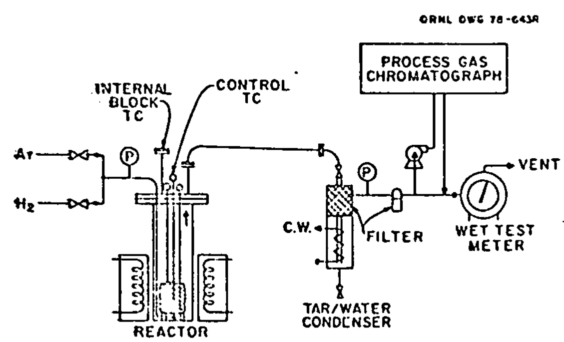

Figure 3. Coal block pyrolysis experiment

Large pieces of coal, which have been protected from drying and exposure to air, are machined into right circular cylinders sized to 0.15-m diameters and heights of 0.15 to 0.2 m (analysis in Table I).

Gas yields are monitored during the experiment, while yields of char and condensibles are measured later. From the base flow rate of purge gas, the flow rate of noncondensible off-gases, and gas compositions from off-line analysis or (in recent experiments) a process gas chromatograph, yield of principal gases can be determined. Cooled char blocks are raised out of the reactor, photographed, weighed, and sampled. Condensate is separated into an aqueous phase, which is analyzed for total organic carbon, and a tar/oil phase, which is analyzed for water content by azeotropic distillation with benzene.

Thermal Behavior and Swelling Properties

Heat transfer resistances were observed to have pronounced effects on the temperature profiles within blocks of bituminous coal, and as a result, on the amount of swelling. Because monolithic coal is a poor conductor of heat, steep temperature gradients can be present at moderate heating rates.

Temperature profiles for subbituminous and bituminous coal blocks may be compared, as in Fig. 4, where temperature is plotted as a function of dimensionless radius r/r_o. In both cases, blocks of the same size were heated at 3 C°/min in purges of inert gas. From experiment BP1-4 (subbituminous coal), a temperature profile at surface temperature 825°C shows a shrinking core of wet coal. The rate of drying was limited by conductive heat transfer, producing a steep gradient.[5,6]

TABLE I

Analysis of Pittsburgh seam coal

Identification	Coal for ORNL block pyrolysis	Coal for Pricetown UCG tests[a]
Source	CONOCO mines, Monongalia County, West Virginia (5 samples)	Core drilling (2 holes, 37 samples), Wetzel County, West Virginia
Moisture, wt %	0.80	1.00
Ash, % moisture-free	5.80	9.5[b]
Volatile matter, % moisture- and ash-free (maf)	39.7	45.4
Ultimate analysis, % maf		
Carbon	84.2	81.7
Hydrogen	5.90	5.8
Nitrogen	1.60	1.4
Sulfur	3.23	4.6
Oxygen (by difference)	5.1	6.0
Heating value, Btu/lb maf	14,540	14,680

[a]Source: P. A. Estep-Barnes and J. J. Kovach, Chemical and Mineralogical Characterization of Core Samples from Underground Coal Gasification Sites in Wyoming and West Virginia, MERC/RI-75/2 (December 1975).

[b]Average includes carbonaceous shale stringer in the seam cross section.

Because natural moisture content was much less for bituminous coal in BP2-32 (0.80% vs. 30.0%), profiles around the center of the block are like the concave-shaped profiles which would result from conduction into an infinite cylinder. However, gradients were observed to decrease near the surface, possibly because of high-temperature, exothermic pyrolysis reactions or because of endothermic pyrolysis reactions occurring in the primary pyrolysis stage (typically 350-600°C).[7]

Since these phenomena result from heat transfer and heat of reaction effects, the temperature profiles depend on surface heating rate of the block. Internal block temperatures were nearly uniform when the block was heated at a rate of 0.3 C°/min. Typically, the difference between surface and center temperatures in 0.3-C°/min experiments was 20°C or less. In contrast, at 14 C°/min the temperature profiles were steeper than at 3 C°/min.

By observation, different heating rates also produced different degrees of swelling during pyrolysis, opposite behavior from that in powder pyrolysis. When char blocks were removed from the reactor and sampled, the shape, size, external texture, and internal textures changed depending on heating rate.

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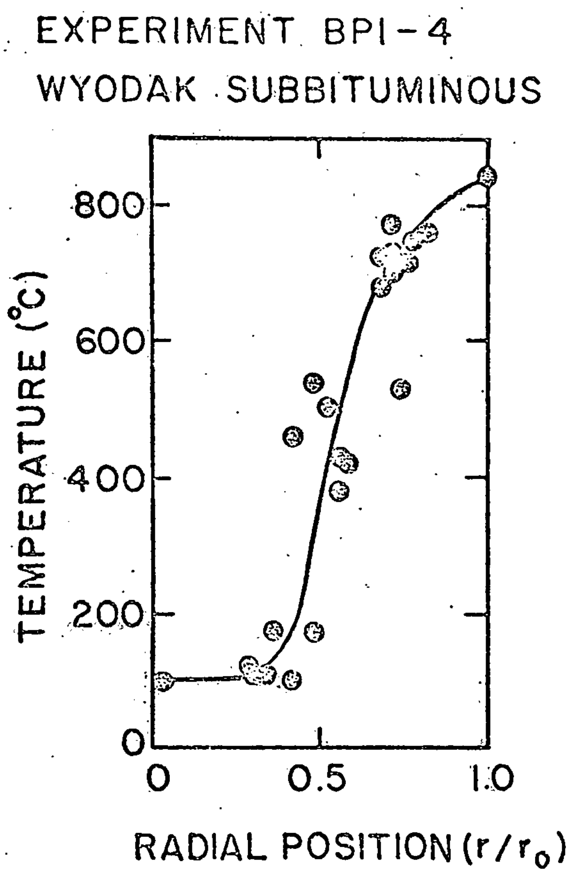

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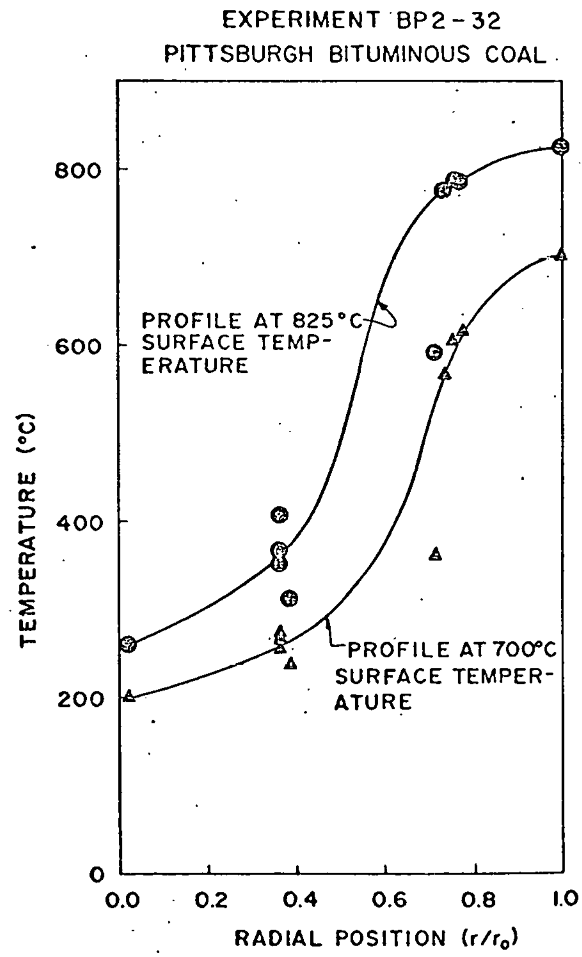
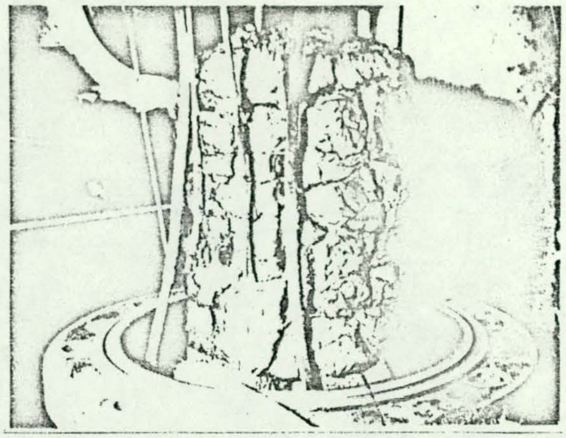


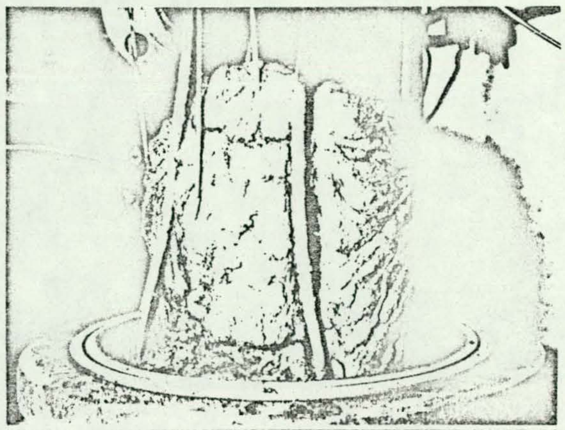
Figure 4. Temperature profiles in coal blocks heated at 3 C°/min, (a) subbituminous coal and (b) bituminous coal. Block radius r_o = 3 in. (0.076 m).

In experiments at 0.3 C°/min, the 0.15-m-diam blocks usually swelled outward to fill the cross section of the 0.3-m-diam (8-in.) reactor (33^{+}% expansion) and swelled axially (vertically) as much as 45%. The chars were hard and brittle, and large hollows were frequently found at the center. Figure 5 shows the char block from experiment BP2-39, produced by heating a 0.149-m-diam, 0.225-m-high coal block at 0.3 C°/min. The block had swelled against the reactor wall giving a porous, glossy appearance to its surface. Around the sides of the cylinder, a thick rim swelled upward 100 mm, while the center of the top sagged 50 mm. The combined effects produced a 0.2-m-diam, 0.33-m-high char block with a crater in the top.

Less swelling was observed in experiments at 3 C°/min, and the surface of all these blocks melted in layers resembling lava. Figure 6 shows this lavalike char on the block from experiment BP2-37. Because of swelling, the height increased from 0.184 m to 0.22 m (20%) and the diameter increased from 0.151 m to 0.193 m (28%). In addition, internal textures in these blocks varied with radial position. The lavalike char at the surface was porous and brittle, but deeper into the block a harder, cohesive coke was found. Near the center, char was crumbly around the hollow cores. Comparing those Ar-purged experiments having a maximum temperature of 1000°C, the cylindrical hollows were smaller in blocks prepared at 3 C°/min (about 9 cm^3) than in those at 0.3 C°/min (about 30 cm^3).

In a single experiment at 14 C°/min, a glazed, slightly enlarged block of char was produced (Figure 7). Block height increased from 0.197 m to 0.222 m (11%) and diameter from 0.154 m to 0.171 m (13%). Around the block center, bubbles were found within a 16 mm radius, and a grainy char radiated from them out to the surface.





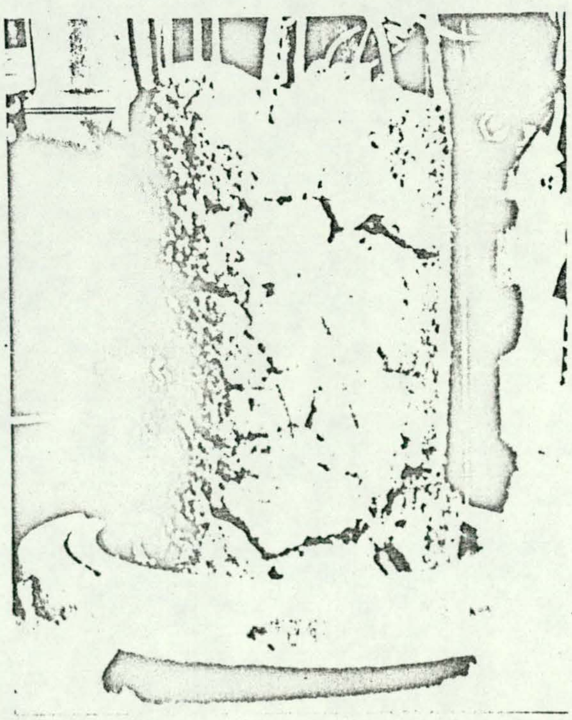


Figure 5. (Top) Char block after experiment BP2-39 (0.3 C°/min to 925°C in H_2)

Figure 6. (Center) Char block after experiment BP2-37 (3 C°/min to 880°C in H_2)

Figure 7. (Bottom) Char block after experiment BP2-38 (14 C°/min to 890°C in H_2)

These differences in swelling behavior at different heating rates may be related to the steepness of temperature profiles by the nature of coal plasticity. Ignoring other effects, plasticity or fluidity is commonly described as a simple function of temperature.[7,8] When temperature is increased to some temperature θ_s, the solid structure of caking coals will begin to soften and can be plastically deformed. Fluidity will increase to a maximum as temperature continues to rise, and at temperature θ_r the coal (as char or semi-coke) will resolidify. Because gas is formed at the same temperatures by pyrolysis reactions, bubbles can make foam in the plastic coal as convective mass transfer is restricted, thus swelling the coal. Data in the literature (Table II) describe these temperatures of fluidity for Pittsburgh seam coal.

At 0.3 C°/min, when internal temperatures are nearly uniform, the entire block is fluid for a long time, and extensive melting and swelling can occur. An extreme example was the fluidity in experiment BP2-43 (pyrolysis in H_2 at 0.3 C°/min to 1030°C), in which nearly all of the block melted and flowed into the bottom of the reactor.

However, at higher heating rates (steeper temperature profiles), only a narrow band of coal is within the range of fluidity temperatures. This band in Fig. 4b, produced by a 3-C°/min surface heating rate, was 8 mm wide when surface temperature had reached 700°C and 11 mm wide at 825°C. Thus, the outside layer melted first and flowed as a layer on the solid coal core. As the experiment progressed, the surface resolidified, but the narrow band of plastic coal continued to

TABLE II

Experimental measurements of fluidity in Pittsburgh seam coal
(overall heating rate = 4.8 C°/min)

Coal source	% Volatile matter (dry, mineral-matter-free)	Range of fluidity (°C)	Range of high fluidity[a] (°C)	Maximum fluidity[b] (°C)
Warden Mine[c]	38.1	341-449[d]	412-446[a]	428
Bruceton Mine[c]	40.1	336-435[d]	415-438[a]	426
Monongalia County, West Virginia[e]	41.5	--	--	--
Wetzel County, West Virginia[f]	45.2	343-(400+)	--	--

[a]Average from Gieseler and Davis plastometers.

[b]Average from Agde-Damm dilatometer, Gieseler plastometer, and Davis plastometer.

[c]Source: R. E. Brewer and J. E. Triff, Ind. Eng. Chem. (Analytical Edition), Vol. 11, No. 5, May 1939, p. 242.

[d]By Gieseler plastometer.

[e]Coal for ORNL block pyrolysis experiments.

[f]Source: H. D. Shoemaker et al., Directional Viscoelastic Properties of the Pittsburgh Coal at Elevated Temperatures in Compression and Shear, MERC/RI-76/5 (August 1976).

move in toward the block center with the moving temperature gradient. The reduction in swelling may be caused by (1) easier exit of pyrolysis gases through a porous, solid surface than from the plastic coal, and (2) by the mechanical constraint of a hard, semi-coke surface. At 14 C°/min the band of coal within range of fluidity was even smaller, and the surface could only glaze before it resolidified; the amount of swelling was likewise reduced.

No effects of H_2 and kinetics on swelling were observed. Although swelling can increase in H_2,[9] no difference was observed at 1 atm between chars produced in H_2 or in inert gas. Studies of plasticity with an Audibert-Arnu dilatometer[8] showed that θ_s changes little with heating rate, but that some change occurs in θ_r. For example, θ_r approached θ_s at low heating rate, but θ_r was 437°C at 1 C°/min, 462°C at 4 C°/min, and 482°C at 20 C°/min. This kinetic effect of a slightly broadened range of fluidity was not detectable in these experiments because of the stronger effect of temperature gradients.

Restriction of swelling to a plastic zone can be expected during UCG field tests in bituminous coal. Martin simulated reverse combustion linkage in large blocks at METC and observed a similar zone.[9] Sectioning of the coal block revealed a 6-mm-wide "phase change zone" of glossy, bubbly char and a 50-mm-wide band of semi-coke at the edge of the reacted area of coal. In studies of pyrolysis in coke ovens by X-ray techniques, these zones have also been observed within the waves of heat moving from the walls toward the center of the oven.[8] Similar thermal behavior and swelling are likely in situ.

Yield Structures from Block Pyrolysis

Heat and mass transfer resistances can also exert a major effect on yields and products from pyrolysis of bituminous coal blocks. Effects of maximum block temperature and of H_2 purge gas were also observed. Table III summarizes yields of oil and tars, of char, of water, and of gases from the matrix of experiments; values are normalized by the moisture- and ash-free weight of the original coal block. Table IV lists yields of the individual gases.

Effects of Heat and Mass Transfer Resistances--Pyrolysis reactions in powdered bituminous coal can be classified into primary devolatilization and secondary degasification.[7] During primary devolatilization (~ 350-600°C), evolution of C_2^+ hydrocarbon gases, oils and tars, and many heteroatom compounds takes place. Above ~ 600°C, CH_4 and H_2 are evolved as the principal products of secondary degasification.

Heat and mass transfer resistances primarily affect the products of primary devolatilization in bituminous coal. In experiments at higher heating rates (steeper temperature gradients), volatile products of pyrolysis must diffuse from the reaction site through a much hotter char surface. Secondary cracking or pyrolysis of the volatile products can result.

Trends in yields are generally consistent with this description. Yields of oils and tars (the reactants for secondary cracking reactions) decreased with increasing heating rate for a given maximum block temperature and sweep gas, while yields of water and gases (including the products from cracking oils and tars) increased. In particular, yields of CH_4 and C_2's increased with heating rate both in Ar and in H_2, and in H_2 the char, H_2, and CO yields likewise increased with heating rate. Comparing yields in Ar at 3 C°/min to those at 0.3 C°/min, less char was produced while H_2 and CO yields remained unchanged.

Oil characteristics are further evidence in support of this qualitative description. Detailed analysis of oils and tars from experiments using 0.3, 3, and 14 C°/min (reaching 900°C, sweeping with H_2) showed decreased H/C atomic ratios as the heating rate increased. From 0.3-C°/min block pyrolysis to the 14-C°/min experiment, H/C ratios dropped from 1.26 to 0.92 to 0.89. By comparison, the ratio for naphthalene is 0.8; the bituminous coal block, 0.88; benzene, 1.0; butadiene, 1.5; n-decane, 2.2; and methane, 4.0. Production of more condensed structures in hydrocarbons, as observed here, is characteristic of cracking.

Also, ethylene yields increased significantly with block heating rate while ethane stayed nearly constant. The average ethane yield was 8.58 std liter/kg maf coal over 14 data points, with a sample standard deviation of 1.52. Apparently ethane was evolved almost solely from coal pyrolysis reactions occurring below 600°C. Little or no direct cracking to ethylene, production from hydrogenation of ethylene, or production from secondary cracking of liquids seems to have occurred. However, yield of ethylene, a major product obtained from the cracking of hycrocarbons, accounts for the significant increase when the heating rate was increased (Fig. 8). Again, these results indicate that as volatile products encounter mass transfer resistance while escaping the coal block, they can be cracked on the hotter surface layer of char, which is itself the result of heat transfer resistances.

Effect of Maximum Block Temperature--Yields from block pyrolysis of bituminous coal and yields from powder pyrolysis follow the same trends as the maximum reaction temperature is increased. As Table III shows, from 600 to 1000°C char yields decrease, gas yields increase, water yield does not vary significantly, and oil yields are little changed above 600°C. These trends are consistent with a transition from primary devolatilization to secondary degasification reactions at temperatures near 600°C (i.e., oils and tars are generated in primary pyrolysis).

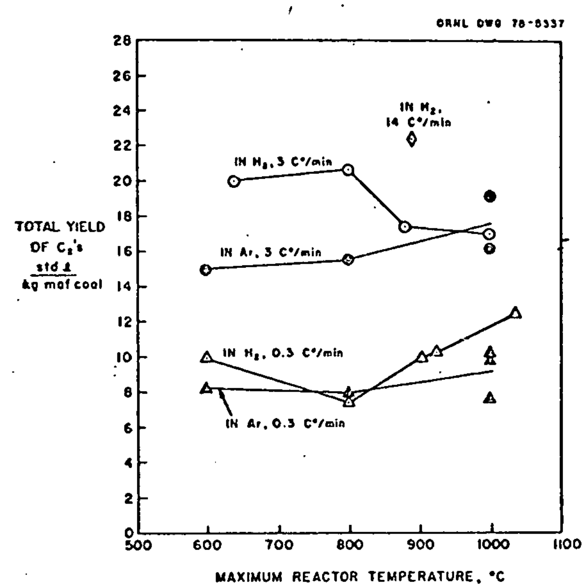


Figure 8. Total yield of C_2 hydrocarbons from block pyrolysis of bituminous coal. Ethane yield nearly constant at 8.6.

TABLE III

Yield structure for block pyrolysis experiments, Pittsburgh seam coal (g/kg maf coal)

Yield data	Reactor heating rate (C°/min)	Maximum block temperature; sweep gas: To 600°C		To 800°C		To 900°C	To 1000°C	
		In Ar	In H_2	In Ar	In H_2	In H_2	In Ar	In H_2
Oil and tar yield	0.3	158.8	126.5	126.6	121.2	144.1	133.3	123.1
	3	107.4	76.7	90.1	69.2	87.9	86.7	88.8
	14	—	—	—	—	68.5	—	—
Char yield[a]	0.3	820	735	708	723	667	724	688
	3	723	772	692	747	706	646	743
	14	—	—	—	—	703	—	—
Water yield[b]	0.3	28.3	27.9	33.8	53.3	31.1	41.5	50.5
	3	53.1	75.5	66.0	62.9	53.4	68.5	58.5
	14	—	—	—	—	62.3	—	—
Net gas yield	0.3	107.7	69.0	130.2	77.2	193.1	178.8	155.4
	3	127.8	140.8	144.4	151.0	167.2	177.1	153.4
	14	—	—	—	—	208.5	—	—

[a]Includes ash content of char.

[b]Includes natural moisture content of 8.0 g H_2O/kg maf coal.

Volatility of tars from pyrolysis is important in field development of UCG, and Table V shows yields of the different boiling fractions as maximum block temperature was increased. These experiments were conducted at 3 C°/min in H_2 sweep gas. Little variation was observed at the different cuts except that maximum boiling point decreased with maximum block temperature. Cracking of heavy ends to coke and gases may account for the latter effect.

Effects of H_2 atmosphere--Sweep gas composition would be expected to have little effect on pyrolysis reactions because product convection from the block will limit its participation; however, H_2 would be the most likely gas to cause any effect because of its high diffusivity. Hydrogen would not affect the thermal decomposition of coal but instead would react with pyrolysis products.

Possible reactions include hydrogenation of vapor-phase free radicals, hydrogasification of char, reaction with pyrolysis gases, and hydrodesulfurization. It has been proposed that tars and oils begin as free radicals in the vapor phase, which can combine with themselves to form heavier hydrocarbons or with hydrogen to form light hydrocarbons.[10] The latter reactions (hydrocracking) require high pressures. Hydrogasification reactions forming CH_4 directly are favored by high pressures but can proceed at 1 atm. Several gases produced by pyrolysis can react with H_2, including CO_2 and unsaturated hydrocarbons.

Changes in the yield structure of block pyrolysis do result from the purge of H_2 at 1 atm. Of the yields reported in Tables III and IV, only CO_2 yield seems to be unaffected when H_2 is the purge gas instead of inert gas. At both heating rates, the yields of H_2, oil

TABLE IV

Component gas yields from block pyrolysis experiments, Pittsburgh seam coal

Sweep gas	Reactor heating rate (C°/min)	Maximum temperature (°C)	Gas evolution (std. liter/kg coal maf)							
			H_2	CH_4	C_2's	C_3's	CO	CO_2	H_2S	Total[a]
Ar	0.3	600	46.2	46.7	8.12	4.30	6.75	3.42	2.54	115.8
Ar	0.3	800	125.8	55.1	7.88	3.45	16.34	3.96	2.81	213.5
Ar	0.3	1000	175.5	67.0	9.22	6.72	20.0	5.1	3.45	290.4
Ar	3	600	49.3	63.9	14.96	9.29	6.75	4.50	2.15	145.3
Ar	3	800	131.9	77.3	15.54	3.28	13.20	4.75	5.62	250.2
Ar	3	1000	164.3	92.8	17.64	4.16	20.0	5.37	1.72	305.8
H_2	0.3	600	-95.8	55.3	9.93	3.69	3.33	2.77	5.29	-15.5
H_2	0.3	800	39.3	65.6	7.35	b	9.32	2.55	0.27	124.4
H_2	0.3	900	33.3	91.7	7.12	2.55	14.6	3.35	20.14	165.5
H_2	0.3	1000	48.7	103.8	12.43	3.82	24.5	5.98	6.78	206.0
H_2	3	600	17.53	80.9	19.90	7.74	9.49	5.16	3.11	143.8
H_2	3	800	93.8	97.9	20.54	2.08	11.27	4.37	2.65	232.7
H_2	3	900	125.4	96.9	17.42	3.55	19.92	4.84	2.16	324.0
H_2	3	1000	179.2	79.6	16.98	4.30	27.2	4.61	2.41	314.3
H_2	14	900	123.0	111.4	22.34	1.53	42.9	5.44	0.54	307.2

[a]Does not include N_2, C_4's, or condensible vapors.

[b]Not detected.

TABLE V

Comparison of tar yields from block pyrolysis of Pittsburgh seam coal, compared by boiling point

Experiment:	BP2-33	BP2-35	BP2-34
Heating rate (C°/min)	3	3	3
Maximum block temperature (°C)	600	800	1000
Cumulative yield (g/kg maf coal) boiling at:			
<200°C (392°F)	15 (20%)	8 (11%)	14 (16%)
<300°C (572°F)	36 (47%)	37 (53%)	49 (55%)
<400°C (752°F)	55 (72%)	62 (90%)	79 (89%)
<500°C (932°F)	71 (93%)	69 (100%)	89 (100%)
Maximum boiling point (°C)	590	490	440

and tar, and H_2O decrease in an H_2 sweep gas, while char and H_2S yields increase. An effect of heating rate was to increase CH_4 yield and decrease CO yield in H_2 (relative to inert sweep gas) at 0.3 C°/min but to reverse the trend at 3 C°/min.

Reactions can be suggested to explain several of these yield changes. Because of slow kinetics and the longer times at reaction temperatures, hydrogasification reactions were more important at 0.3 C°/min than at 3 C°/min, thus accounting for the increased yield of CH_4 and some of the decreased H_2 yield. Hydrogen extraction of organic and pyritic sulfur (hydrodesulfurization) probably caused an increased H_2S yield. Also, cracking of oils was increased in H_2 instead of being decreased as it would have if H_2 had participated in hydrocracking reactions. The increased cracking apparently produced coke deposits that increased the net yield of char.

Conclusions and Recommendations

These data emphasize that there are important differences between the experimental results of powder pyrolysis and block pyrolysis, differences caused by the presence of internal heat and mass transfer effects in block pyrolysis research. Because similar effects are likely to occur during UCG, an understanding of them is important to the understanding and control of UCG processes.

In bituminous coal, as in subbituminous coal, the direct effect of internal heat transfer resistances is a steep temperature gradient which can form even at low heating rates (on the order of 3 C°/min). The structural swelling associated with high-volatile bituminous coal was measurably reduced in experiments having these steep gradients. Based on the temperature dependence of coal plasticity, the link between swelling behavior and temperature gradients can be explained.

Product yields from block pyrolysis of bituminous coal were affected by internal heat and mass transfer and also by temperature and the presence of an H_2 sweep gas. Temperature gradients combined with mass transfer resistance to cause secondary cracking of pyrolysis oil vapors as they diffused outward through the hot char surface region from the 350-550°C primary pyrolysis region in the interior. In comparison to temperature effects on powder yields, though, yields from block pyrolysis followed similar trends. Finally, H_2 had an effect on yields from block pyrolysis despite mass transfer resistance, increasing the amount of secondary cracking to coke and causing slow hydrogasification of the char.

Because of the value of block pyrolysis data from bituminous and subbituminous coals, ORNL has begun similar experiments with a Texas lignite and plans to conduct a series of experiments in simulated UCG product gas. Evaluation of data from earlier experiments continues and includes correlations of thermal properties and of yields. Subject to DOE approval, ORNL intends within the next year to extend this basic understanding of pyrolysis to block pyrolysis at pressure by modifying the existing system and operating it principally in the range of 50-300 psig but ultimately to 800 psig.

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