

PYROLYSIS OF LARGE COAL BLOCKS: IMPLICATIONS
OF HEAT AND MASS TRANSPORT EFFECTS FOR IN SITU GASIFICATION*

Phillip R. Westmoreland and Richard C. Forrester III

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

Gas production during pyrolysis of blocks of coal is strongly affected by heat and mass transfer resistances. Since large pieces of coal must be pyrolyzed during in situ gasification, these effects become important in modeling, production, and resource recovery. Experiments have shown that pyrolysis of subbituminous coal blocks, which are typically heated at $3.0\text{ C}^\circ/\text{min}$ at the block surface and which have the high moisture content of in situ coal, evolves substantially more gas than does pyrolysis of powders.

Coal pyrolysis reactions are fundamental in all coal conversion processes. Coal chemical structures are thermally decomposed at 250°C or higher to produce liquid vapors, noncondensable gases, and a solid char residue. This decomposition may be utilized in coking or as part of the combustion, gasification, or liquefaction processes. For example, pyrolysis, partial combustion, and steam-char reactions combine in gasification to produce a combustible gas and an ash residue. Heat and mass transfer interferences with these chemical reactions are normally minimized in conventional coal conversion by crushing and drying the coal prior to processing.

Underground coal gasification (UCG) or in situ gasification represents a modeling challenge for coal pyrolysis because of three unusual characteristics: large particle size, high water content, and low heating rates. A typical UCG process feeds oxygen or air into a coal seam, supporting a moving, high-temperature reaction front (flame front). To permit flow of air to the front and flow of product gases away from it, seam permeability is increased by explosive fracturing, by burning a high-permeability path between injection and production pipes, or by other methods. Each of these methods leaves large blocks or sections of coal intact. Also, since seams are chosen to be below the water table, in situ coal reserves for UCG may be typically 30% moisture. Finally, the gasification front in several schemes moves at about 1 m/day, cocurrent with the faster gas flow. Hot product gases thus produce a slow-moving temperature gradient ahead of the front, slowly heating the coal.

Understanding of block pyrolysis and other aspects of UCG is important in its development toward being a significant, economical energy source. The concept of UCG was first proposed in 1868 by Sir William Siemens, and full-scale UCG operations in the U.S.S.R. have continued since the 1930's; however, despite large research programs immediately after World War II, no Western nation was able to develop an economical UCG process (1). The United States began UCG development in 1971, and results to date have been both technically and economically promising. Successful development of UCG would make an estimated 750 billion tons of coal available for energy production, as compared to the 297 billion tons of coal reserves listed by the Bureau of Mines as recoverable by strip or underground mining (2). In addition to utilizing otherwise inaccessible coal, UCG could have less of an environmental impact than either underground or strip mining and could improve resource recovery and personnel safety over that of underground mining.

Because of the potential of UCG and the unavailability of adequate data for process modeling, Oak Ridge National Laboratory began research in 1974 on pyrolysis of coal blocks at low heating rates. Primary variables in this study have been

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heating rate and final temperature, and these data have been compared to data on pyrolysis of powdered coal from the same source. Data and observations from these experiments have been shared with Energy Research and Development Administration UCG process developers at Laramie (Wyoming) Energy Research Center, Lawrence Livermore (California) Laboratory, and Morgantown (West Virginia) Energy Research Center, and have been incorporated into process models as deemed appropriate.

Equipment and Procedure

Figure 1 depicts the block pyrolysis equipment schematically. In the experiment, an approximately 15-cm-diam by 15-cm cylindrical block of coal was positioned on insulating blocks in the bottom of a 60-cm deep, thin-walled reactor vessel, fabricated from 8-in. Sched 10 304L stainless steel pipe. Protection of the reactor from external oxidation at high temperatures was afforded by a commercially prepared nickel-chromium-aluminum coating (Metco No. P443-10). Heat for pyrolysis was supplied by an electrical furnace, with reactor temperature controlled by an ORNL-fabricated temperature programmer. Control thermocouples, thermocouples for internal and external block temperature measurements, an inert gas purge line, and an exhaust line heated to 250°C were connected to the reactor through a flanged top. Condensibles (water and tars) were removed from the hot reactor exhaust by direct contact with water-cooled copper coils and by a fine glass-wool demister. A sufficient number of noncondensable gas samples were collected into evacuated sample bottles to describe gas evolution as a function of time. Finally, gases were metered and vented.

For these experiments, blocks of unweathered subbituminous coal were selected at the mine face from the Roland and Smith seams (Wyodak Resources Development Corporation, Wyodak, Wyoming). To prevent drying and breakage, these blocks were bagged in plastic and cushioned for shipping. Upon receipt at ORNL, coal was placed under water for storage until and after it was machined into cylinders. All machining operations were performed under a water spray for cooling and to prevent drying. Thermocouple holes (1.6-mm diam) were drilled through the top of the coal cylinder down to a middle, common plane. Hole patterns were chosen to minimize heat conduction through radially placed thermocouples (for example, spiraling outward from the block center); 1.0-mm-diam thermocouples were used for similar reasons. Standard analyses of the coal are reported in Table 1.

Table 1. Analyses of coal taken from the Roland-Smith seams, Wyodak Resources Development Corporation, Gillette, Wyoming

Moisture, wt %	30.0	Ultimate analysis, moisture- and-ash-free wt %	
Proximate analysis, dry wt %		Carbon	73.3
Ash	5.3	Hydrogen	5.2
Volatile matter	47.0	Nitrogen	1.1
Fixed carbon	47.7	Sulfur	0.56
		Oxygen	19.8
Standard calorific content, Btu/lb moisture-and-ash-free	12,800		

The experiment was preceded by an argon purge of air from the closed system. A constant flow of argon was maintained throughout the experiment, both to establish a tie element for calculating gas flowrates and to sweep gases and vapors from the reactor. The experiment itself consisted of elevating reactor temperature at a predetermined rate to a predetermined maximum, then holding it until the reaction was complete. Meanwhile, pressure, temperature, and flowrates were monitored, liquids were condensed and collected, and gas was sampled periodically. After completion,

the reactor was cooled to ambient temperature. Because pyrophoric chars were created in most experiments, the block of char (still dimensionally stable) was carefully removed and sampled under an argon blanket. Liquids were carefully removed and weighed, and gases were analyzed by a combination of low-resolution mass spectrometry and gas chromatography.

Data and Interpretation

General effects of heat and mass transfer resistances may be observed by comparison of block and powder pyrolysis data and by comparison of block pyrolysis data at different heating rates. Three representative experiments permit these analyses:

1. powder pyrolysis at 3.33 C°/min to 950°C (3),
2. block pyrolysis at 3.0 C°/min to 950°C, and
3. block pyrolysis at 2.0 C°/min to 1000°C.

Because of minimal heat and mass transfer effects indicated in the powder data of Campbell (3), a small heating-rate difference does not hinder comparison with the resistance-hindered second experiment. A satisfactory comparison may be made between experiments 2 and 3 since the effects of slightly different final temperatures are negligible compared to the effects of the different heating rates. The unimportant difference between powder heating rate and 3.0 C°/min may be eliminated and data at the two block heating rates may be compared directly by changing the ordinate from time to τ , a pseudo-temperature (°C) defined as:

$$\tau = T_0 + \dot{T}_s \cdot t, \quad (1)$$

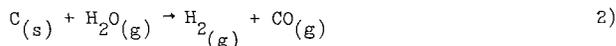
where T_0 is ambient starting temperature, \dot{T}_s is the rate of temperature increase at the block surface, and t is elapsed time. It may be observed that τ is the same as surface temperature until maximum surface temperature is reached; from that point, it continues the same proportional relationship to time.

Heat transfer in block pyrolysis is most significantly affected by water content. In Fig. 2, temperatures at the block surface (radius ÷ block radius = 1), the equivalent point ($r/R_0 = 0.707$), and the block center ($r/R_0 = 0$) are compared as functions of τ for the two block experiments. In a coal powder at these heating rates, particles are so small that the temperature is the same throughout a particle ($T = \tau$ to T_{maximum} for all r). In a large, dried block, thermal conductivity would cause some temperature profile to build during heat up. However, in a realistically wet block, generation of steam soaks up a great deal of heat, resulting in high heating rates at the center and in sharp temperature profiles. Figure 2 shows that most of the block will heat up to 100°C as steady heating continues at the surface. A wet-dry interface gradually moves inward from the surface as steam is generated, creating a shrinking core of damp coal. This effect may be seen graphically in the temperature profiles of Fig. 3. (Placement of radial thermocouples in a central plane satisfactorily describes radial temperatures without heating effects from the cylinder top or bottom. These effects were further prevented by making the cylinder height greater than or equal to cylinder diameter.) Figure 2 also shows that at a lower block heating rate, internal block temperatures do not lag surface temperature as much (i.e., temperature profiles are not as steep), but that absorption of heat by steam generation still exerts a considerable resistance.

Gas evolution, the critical parameter for in situ gasification, is substantially greater in pyrolysis of blocks than of powders from the same coal. Figure 4 shows gas evolution and gas composition for powder pyrolysis and for block pyrolysis as functions of τ , again equivalent (up to 950°C) to block surface temperature; in this case, they correspond to approximately the same heating rate and elapsed time. Gas evolution rate (Fig. 4 only) is the sum of H_2 , CO , CO_2 , CH_4 , C_2H_4 , and C_2H_6 (those compounds cited by Campbell), normalized per gram of moisture-and-ash-free

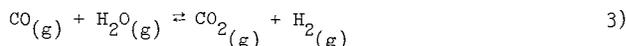
coal (maf). Similarly, mole fraction refers to a fraction of the total volume of gases listed above (Fig. 4 only - all gases included in Fig. 5).

Most of the increased gas yield may be attributed to self-gasification of char by the generated steam. Initial evolution rates and compositions from block pyrolysis lagged those of the powder pyrolysis, but strongly resembled them. Since the fraction of coal block at pyrolysis temperatures (250°C or higher) gradually increased with τ , thus lagging the powder particles that were all at uniform temperature, this behavior is consistent with the occurrence of straightforward pyrolysis reactions. Beginning at about $\tau = 700^\circ\text{C}$, gas evolution from block pyrolysis produced more gas than would have been expected from powder pyrolysis data, in particular, more H_2 and CO. A reasonable explanation is that as steam diffused outward from the shrinking, damp core through the hot, outer char layer of the block, a form of the reaction



occurred. This explanation is particularly plausible considering that the reaction equilibrium constant, K_p , is greater than 1 for temperatures higher than 670°C .

Gas component evolutions in Table 2 suggest that steam-char reactions account for only a part of the increase in gas evolution observed in block pyrolysis. Increases in total evolution of H_2 and CO are $253 \text{ cm}^3/\text{g}$ and $106 \text{ cm}^3/\text{g}$, respectively, while less marked changes occur in CO_2 ($15 \text{ cm}^3/\text{g}$ increase), CH_4 (11 cm^3 decrease), and C_2 compounds (3.9 cm^3 increase). If only steam self-gasification of carbon took place, stoichiometry dictates that the increased evolution of H_2 and CO would be the same, rather than $147 \text{ cm}^3/\text{g}$ more of H_2 than of CO. Contribution from the water-gas shift reaction



should be negligible or counterbalanced, since K_p exceeds 1 only for temperatures less than 810°C . It is reasonable to expect steam reduction of hydrocarbons ($K_p > 1$ for $T > 610^\circ\text{C}$ for CH_4), but hydrocarbon light gases are not greatly different; in any case, they could not contribute such a large amount of hydrogen. A likely explanation is that pyrolysis-generated tar and oil vapors, diffusing outward into hotter char, are themselves pyrolyzed or cracked to carbon and H_2 .

Exothermic reactions in the center of the block were observed thermally in Fig. 3 near the end of the $3.0 \text{ C}^\circ/\text{min}$ block pyrolysis experiment. Since H_2 generated by the very high-heating rates at $r/R_0 = 0$ was restricted in outward diffusion, it may have participated in highly exothermic hydrogenation reactions.

Comparison of block pyrolysis at different heating rates indicates that similar gas-evolution behavior occurred relative to powder pyrolysis. In each case (see Table 2), block pyrolysis produced more gas than powder pyrolysis, primarily because of increased H_2 and CO production. For block pyrolysis, as observed in Fig. 5, overall gas-evolution rates in the $3.0 \text{ C}^\circ/\text{min}$ experiment did not begin to increase beyond those of the $2.0 \text{ C}^\circ/\text{min}$ experiment until about at $\tau = 700^\circ\text{C}$; gas compositions in the two experiments remained quite similar. This difference reinforces the hypothesis that steam reactions in the hot outer layer produced extra H_2 and CO, since at $\tau = 700^\circ\text{C}$, approximately three-fourths of the $2.0 \text{ C}^\circ/\text{min}$ block had been dried, as compared to approximately one-half of the $3.0 \text{ C}^\circ/\text{min}$ block.

Table 2. Comparison of gas component evolution among three pyrolysis cases

	Gas evolution, cm ³ (STP)/g coal (maf)						
	H ₂	CO	CO ₂	CH ₄	C ₂ 's	C ₃ 's	C ₄ 's
Powder, 3.3 C°/min to 950°C (ref. 3)	134	48	60	71	8.5	-- ^a	-- ^a
Block, 3.0 C°/min to 950°C	387	154	75	60	12.4	6.4	1.2
Block, 2.0 C°/min to 1000°C	317	101	78	76	17.1	9.8	1.7

^aNot reported.

Conclusions and Future Plans

Dewatering of coal blocks at in situ moisture levels was shown to markedly affect pyrolysis gas production by being the rate-limiting mechanism in heat transfer, and by causing self-gasification of the block as steam diffuses from a shrinking core of damp coal through a hot, outer layer of char. Cracking of product oil vapors as they diffuse outward may also contribute to the increased combustible gas evolution of block pyrolysis compared to powder pyrolysis.

These results influence modeling and design of in situ coal gasification. Since no data are available on coal-block pyrolysis, improved understanding of heat and mass transfer effects significantly improves semitheoretical models which have depended on powder pyrolysis data. For satisfactory resource recovery, the shrinking core of unreacted coal makes it critical to limit flame-front speed. If the flame front moves too fast, only an outer layer of any large masses of coal will be gasified, leaving damp, ungasified centers behind the front.

More experimentation is planned to quantify and expand these results. Specifically, a matrix of experiments is being performed at 0.3 C°/min and at 3.0 C°/min, proceeding to maximum temperatures of 500 to 1000°C. Analyses will be made of data on oil, char, and gas yields; oil, char, and gas compositions; thermal histories; and oil and gas physical properties. Later experiments are planned to investigate the effects of pressure, reducing gas atmospheres, and other coal ranks (lignites, caking and noncaking bituminous coals). The ultimate result is a satisfactorily accurate model of pyrolysis as it affects in situ coal gasification.

Acknowledgments

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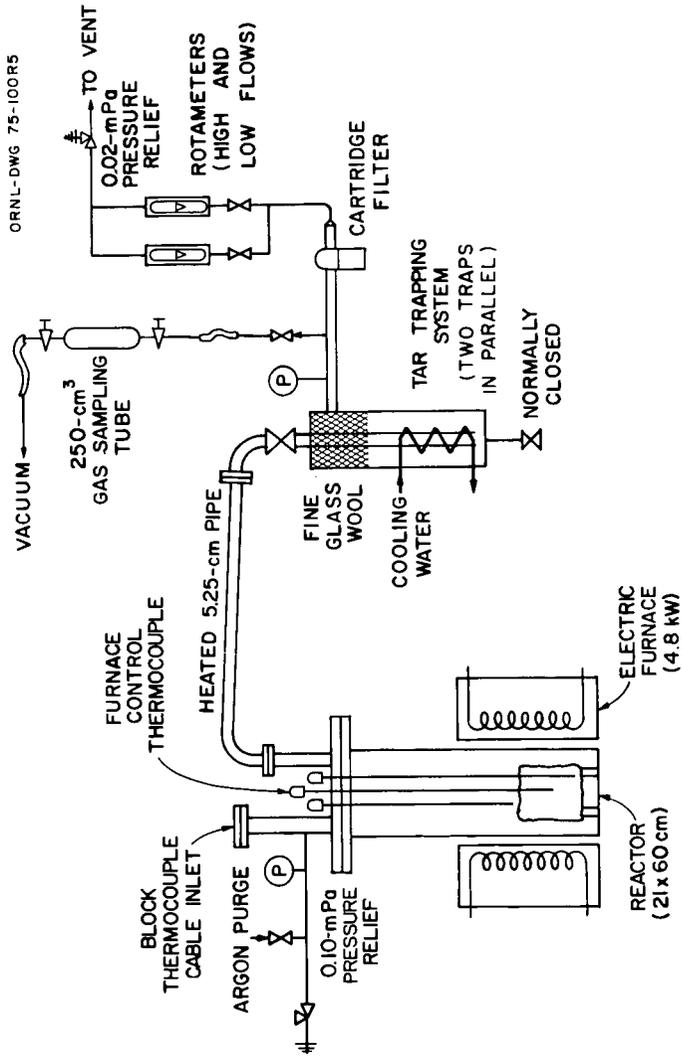


Fig. 1. Schematic diagram of block pyrolysis experiment.

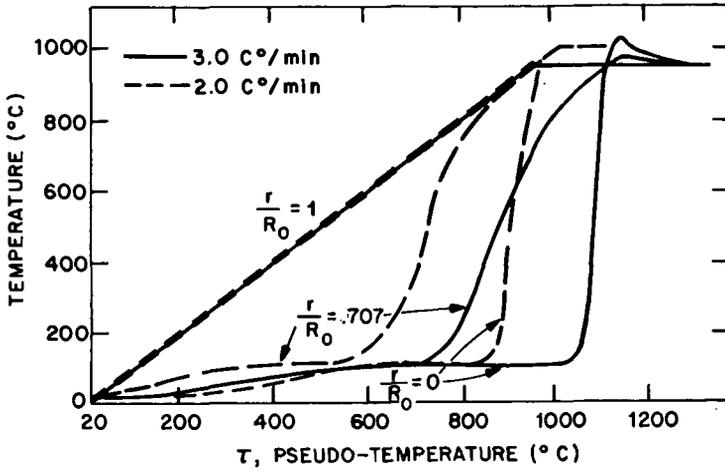


Fig. 2. Temperature changes at selected block radii in experiment BFL-4, pyrolysis at 3.0 C°/min to 950°C, and in BFL-13, pyrolysis at 2.0 C°/min to 1000°C.

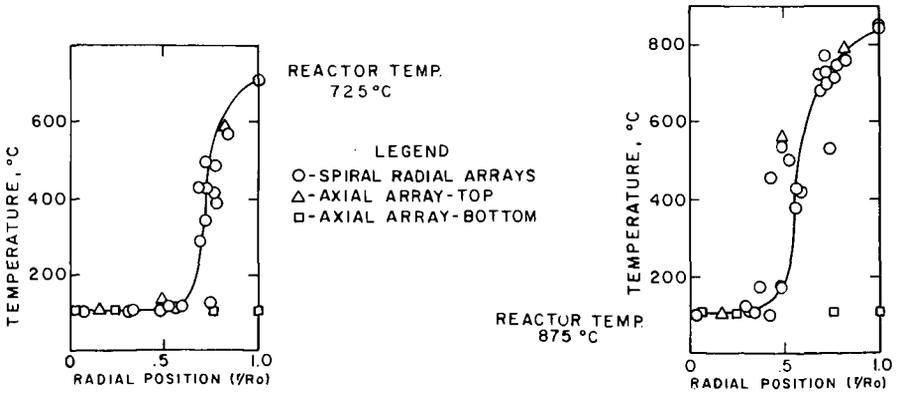


Fig. 3. Temperature profiles in experiment BFL-4, block pyrolysis at 3.0 C°/min to 950°C.

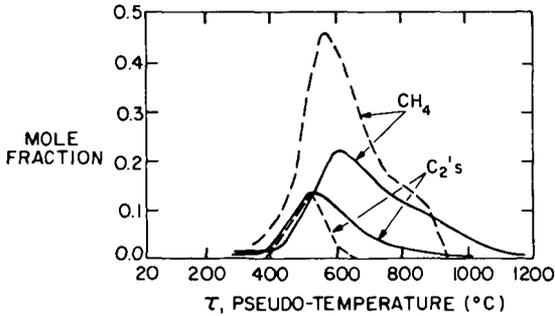
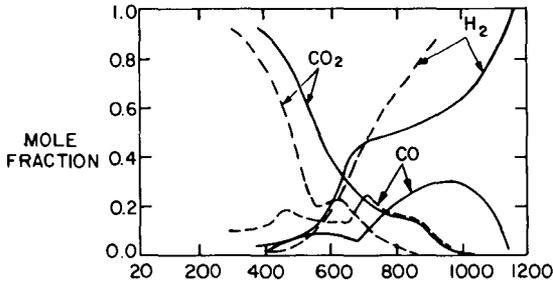
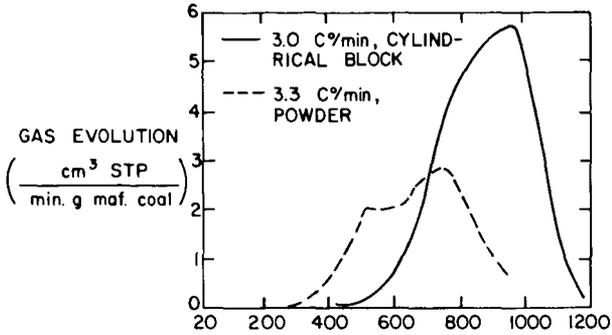


Fig. 4. Gas evolution rates and compositions in powder pyrolysis and block pyrolysis.

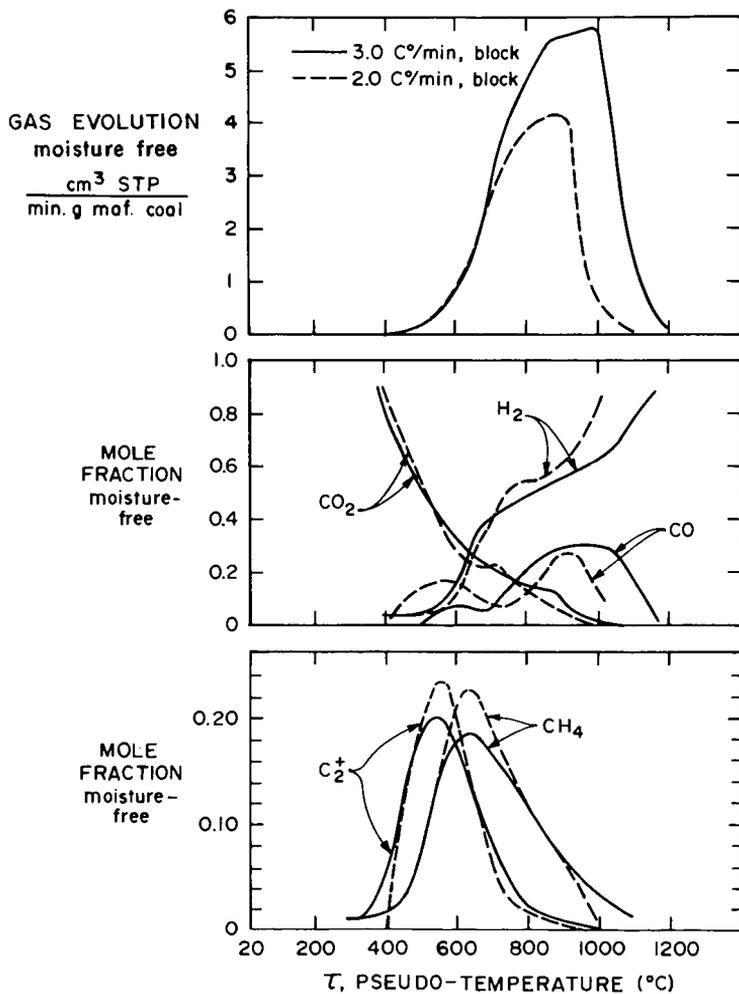


Fig. 5. Gas evolution rates and compositions in block pyrolysis at different heating rates.