Mechanisms and kinetics of rapid, elevated pressure pyrolysis of Illinois No. 6 bituminous coal

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Mechanisms and Kinetics of Rapid, Elevated Pressure Pyrolysis of Illinois No. 6 Bituminous Coal

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An investigation was conducted of the effects of pressure on rapid pyrolysis behavior of a caking coal, using a high-pressure entrained-flow reactor (10^3–10^4 K/s heating rate) under applied pressures of 100, 309, and 530 psig of N_2, with residence times of up to 1.7 s, supplemented by collateral experiments at ambient pressure. Cracking reactions begin at an earlier stage as applied pressure increases, and the time over which cracking reactions occur decreases with increasing pressure. The tar becomes more aromatic and less substituted with increasing residence time. The product gas distribution is strongly dependent on pressure and residence time. The aromatic structures in the char become more condensed at higher applied pressures. Kinetic models for devolatilization and swelling during pyrolysis were developed, and the apparent first-order rate constants were calculated. Applied pressure influences the devolatilization rate and swelling rate differently.

Introduction

Pyrolysis is the first and most important step in virtually every coal utilization process and influences the course of any subsequent reactions such as combustion, gasification, or liquefaction. Due to the heterogeneous nature of coal and the complexity of the processes involved in pyrolysis, attempts to develop a comprehensive mathematical model for describing the kinetics of pyrolysis often meet with limited success. These difficulties have been thoroughly discussed in several excellent reviews.[1-3] However, like all chemical processes, the pyrolysis reactions are dependent on the nature of the reactant (i.e., coal) and the reaction conditions. The structure and reactivity of the resultant char are largely consequences of the pyrolysis behavior. Coal pyrolysis phenomena are strongly rank dependent because of the differences in coal structures of different ranks. Compared to bituminous coals, the lower rank coals have more oxygen functional groups, and therefore oxygenated species such as CO, CO_2, and H_2O are the principal pyrolysis products for lignites, while hydrocarbon gases and tars are the major volatile yields for bituminous coals.[4] Bituminous coal tars are more aromatic and thermally stable than those of lignites.[2] It has been postulated that the chemical properties of coal are determined by a relatively small number of functional groups common to all coals and that coals differ by their content of these functional groups.[5] When all experimental conditions are held constant except for coal type, the kinetics of evolution of individual species from decomposition of functional groups are relatively insensitive (i.e., within an order or magnitude) to coal rank.[5] This observation led to the development of the functional group (FG) model which used rank-independent kinetics to describe evolution of individual species during coal pyrolysis.[6]

A traditional approach to the kinetics of pyrolysis has been the assumption of a first-order decomposition occurring uniformly throughout the particle, so that the rate of volatile release is given by

$$dV/dt = k(V^* - V)$$

where V is the cumulative volatile yield up to reaction time t and V^* is the effective volatile content of the coal. The definition of V^* is ambiguous, and many approaches have been suggested for estimating its value.[7-9] There is also

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little agreement on pyrolysis rates; values of k vary by several orders of magnitude at a given temperature and the apparent activation energy ranges from 1 to 45 kcal/mol (ref 2). Because coal pyrolysis is not a single reaction but a wide range of overlapping decompositions, the use of a single set of parameters to describe reactions occurring over a wide range of conditions is inadequate.

Alternatively, coal pyrolysis can be considered to consist of a number of independent reactions representing the cleavage of various bonds within the coal structure. The occurrence of different reactions in different temperature intervals is a result of differences in bond strengths. The first approach in this direction was a statistical activation energy distribution curve.[10] Later refinements allowed for nonisothermal treatment of weight loss and a Gaussian activation energy distribution.[2,7] A more sophisticated approach applies a multiple reaction model to the release of single compounds or classes of compounds; a number of reactions having distributions of activation energy can be used for each stage of the evolution of a compound.[11] Rate constants for release of tar and for thermal decomposition of various functional groups depend on the nature of the bond or functional group, but appear relatively insensitive to rank.[5] The FG model, developed from this assumption, considers coal to be composed of tar-forming and non-tar-forming materials, with rate constants for formation of gaseous species dependent on functional group but independent of rank.[6] A subsequent refinement of the FG model describes the cracking of hydrocarbons released in primary pyrolysis and the equilibration of O-, H-, and C-containing species at high temperatures.[12] Recent work indicates poor performance of the FG model in predicting tar evolution rates from bituminous coals at heating rates of $0.05-10^3$ K/s (ref 13).

A more theoretical approach models the detailed elementary reactions occurring during pyrolysis.[14,15] Rates of generation of volatiles are calculated from kinetic data in the literature or from the thermochemical kinetic techniques.[16] A distributed energy chain model assumes coals to consist of three components: aromatic units linked by labile bridges to form nominally infinite chains, with peripheral groups branching from the aromatic nuclei.[17] Since the reactive species are lumped gross species rather than functional groups, detailed structural information is not required and the number of adjustable parameters in the model is minimized. Good agreements between predictions and experimental data for bituminous coal at heating rates of 10^2 and 10^3 K/s have been reported.[18]

Many of the recent previous studies on entrained-flow pyrolysis at elevated pressures have been conducted with low-rank coals.[19-22] Very little work has been reported on

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Table I. Characteristics of Illinois No. 6 Coal Used in This Study

proximate analysis	as received, wt %	dry, wt %
moisture	3.2	
ash	9.8	10.1
volatile matter	35.0	36.1
fixed carbon (by diff)	52.0	53.8

ultimate analysis	as received, wt %	dry ash free, wt %
carbon	67.2	77.2
hydrogen	4.8	5.2
nitrogen	1.3	1.5
sulfur	3.3	3.8
oxygen (by diff)		12.3

petrographic analysis	dry mineral matter free, vol %
vitrinite	88.8
liptinite	2.9
semifusinite	4.4
inertinite	3.9

caking property	
free swelling index	1.0

Figure 1. Configuration of high-pressure entrained-flow reactor.

pyrolysis of caking coals at elevated pressures in entrained-flow reactors because of the experimental difficulties caused by coal particle agglomeration. Reactions are completed in a short time in rapid pyrolysis, and the residence time of the pyrolyzing coal particles can only be estimated accurately under well-defined gas flow conditions inside the reactor. Coal cannot be pyrolyzed in a well-defined time interval when agglomeration occurs to block the gas flow in an entrained flow reactor. Agglomeration of particles might also obscure the true pyrolysis behavior of individual particles. This study was undertaken to investigate the early stages of rapid pyrolysis behavior of a bituminous coal under the rapid heating and elevated pressures relevant to gasification. This paper describes the effect of elevated applied pressure on devolatilization mechanism and kinetics. A subsequent paper will discuss the physical structure and gasification reactivity of the chars produced in the elevated pressure entrained-flow pyrolysis.

Experimental Section

Sample Selection. The coal used in this study was an Illinois No. 6 high-volatile B bituminous coal supplied by the Morgantown Energy Technology Center (METC), U.S. Department of Energy. The characteristics of the coal are summarized in Table I. The

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Table II. Reactor Operating Conditions for Pyrolysis under Elevated Pressure

pressure, psig	100	100	100	100	309	309	309	309	530
primary gas stream									
diameter, cm	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
gas velocity, cm/s	41.8	10.2	10.2	8.4	14.8	14.8	14.8	9.7	8.8
gas flow rate, mL/s at STP	253.2	61.9	61.9	50.7	253.2	253.2	253.2	166.6	253.2
secondary gas stream									
diameter, cm	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
gas velocity, cm/s	69.5	17.0	17.0	13.9	24.6	24.6	24.6	16.2	14.6
gas flow rate, mL/s at STP	1500.0	366.7	366.7	300.0	1500.0	1500.0	1500.0	987.5	1500.0
reynolds no.	938	229	229	187	939	939	939	618	940
collection position, cm	33.1	27.9	34.7	50.0	19.4	32.1	40.2	49.3	25.9
residence time, s	0.3	0.8	1.0	1.7	0.5	0.8	1.0	1.7	1.0

coal had been ground at METC and sieved to obtain a 200 × 270 mesh (64 μm mean particle size) and then stored in a closed container for shipment to this laboratory. After arrival in our laboratory, the coal sample was repackaged in 500-mL plastic bottles under a nitrogen atmosphere. The coal was dried at 100 °C under vacuum overnight before use to facilitate entrainment by the primary gas flow.

High-Pressure Entrained-Flow Pyrolysis. A detailed description of the high-pressure reactor system has been published.[23,24] The configuration of the reactor is shown in Figure 1. The reactor system is designed to feed coal dust at a preset rate into a controlled, high-temperature pressurized furnace using a carrier gas. Coal particles are supplied from a screw feeder at a uniform and continuous rate and fall vertically into the reaction tube through the semi-Venturi. The coal, entrained in its primary carrier gas, is maintained at ambient temperature until it is delivered from the tip of the injector probe. At this point the entrained coal mixes with a pre-heated secondary carrier gas stream. The coal heating rate is 10^3-10^4 K/s. The gas flow conditions used in this work are listed in Table II. The conditions were obtained from computer modeling of residence time.[25] Nitrogen gas of 99.9% purity was used as the pyrolysis medium. Experiments were performed at 1189 K with a coal feed rate of 0.2 g/min. A water-cooled collector probe rapidly quenches and collects the stream of particles. The residence time of the coal particles is adjusted by varying the distance between the tips of the injector and collector probes. Solid and gaseous products are separated at the reactor's exit and collected for analysis. Gas compositions are monitored by an infrared gas analyzer and a gas chromatograph.

Gas chromatographic analysis of the product gas was performed using a Carle Series 100 unit with hydrogen transfer tube and thermal conductivity detector interfaced with a Hewlett Packard 3380A integrator. H_2, O_2, N_2, CH_4, and CO are determined on a molecular sieve 5A 42/60 column. H_2S, CO_2, C_2H_2, C_2H_4, and C_2H_6 are separated by using two columns: 15% SF96 on Porapak P 50/80, and 75% Porapak N plus 25% Porapak QS 50/80. SO_2 and the C_3 and C_4 hydrocarbons are determined by using 20% Carbowax 1540 on Chromosorb T 40/60.

Atmospheric Pressure Entrained-Flow Pyrolysis. An entrained-flow reactor with a conceptual design similar to the high-pressure reactor was used for pyrolysis in the absence of applied pressure. The design of the atmospheric-pressure reactor is shown in Figure 2. Detailed descriptions of the system have been published elsewhere.[26,27] As in the high-pressure reactor, coal particles supplied by a screw feeder are entrained in a primary gas stream. A preheated secondary gas stream is injected isokinetically into the primary gas stream at the tip of the injector probe. The coal particles experience a heating rate of 10^3-10^4 K/s. The reaction is quenched when the gas stream and entrained particles pass through the water-cooled collector probe. Solids are collected in the cyclone, condensable liquids are deposited
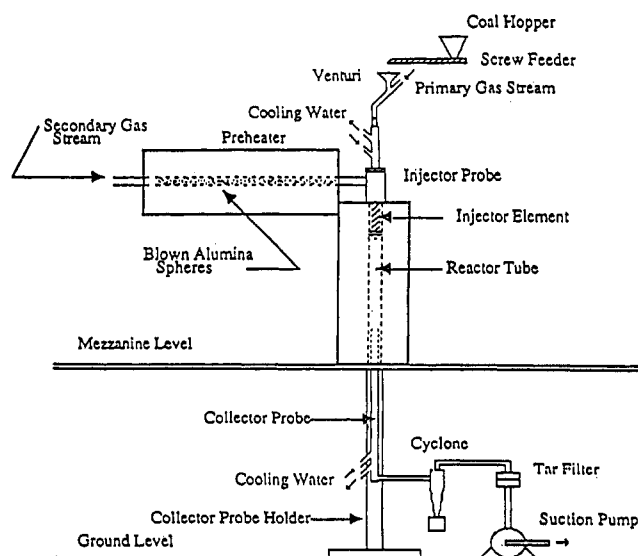
Note: Not to Scale

Figure 2. Configuration of atmospheric pressure entrained-flow reactor and ancillary equipment.

Table III. Reactor Operating Conditions for Pyrolysis at Atmospheric Pressure

temperature, K	1189
primary gas stream	
diameter, cm	0.3
gas velocity, cm/s	120.0
gas flow rate, mL/s at STP	8.5
coal feed rate, mg/s	8.3
secondary gas stream	
diameter, cm	5.1
gas velocity, cm/s	120.0
gas flow rate, mL/s at STP	609
Reynolds no.	308

on the tar filter, and gases are vented to the exhaust stack. Residence times are varied by changing the distance of the collector probe relative to the injector probe. Residence times of the particles are calculated by using a computer model of the reactor that accounts for changes in gas properties with pressure.[28] Nitrogen of 99.9% purity was used as both the primary and secondary gas streams; pyrolysis was performed at 1189 K. The experimental conditions used in this reactor are summarized in Table III.

Product Work-Up and Characterization. The solid pyrolysis products and material trapped by the filter inside the collector vessel were extracted in a conventional Soxhlet apparatus using tetrahydrofuran (THF). It was necessary to use a solvent to remove condensed "tar" from the char particles. While the selection of THF as the solvent is somewhat arbitrary, it has proved to be, in these laboratories, a useful measure of tar evolution. The THF solubility of the untreated coal was determined to be 5.58%. Extractions were performed under a nitrogen at-

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Table IV. Ultimate Analysis of Tar Produced from Pyrolysis of Illinois No. 6 Coal at 1189 K and 100, 309, and 530 psig of N₂

	100 psig				309 psig				530 psig
residence time, s	0.3	0.8	1.0	1.7	0.5	0.8	1.0	1.7	1.0
ultimate analysis, wt % dry									
carbon	80.4	77.9	81.4	84.7	80.9	82.5	81.6	84.3	81.6
hydrogen	5.7	5.6	5.4	4.8	5.6	5.3	5.3	5.1	5.3
nitrogen	1.8	1.8	2.0	2.2	1.9	2.0	2.0	1.9	2.1
sulfur	2.0	1.8	2.4	2.4	2.0	2.0	1.9	1.9	2.3
oxygen (by diff)	10.1	12.9	8.8	5.9	9.6	8.2	9.2	6.8	8.7

mosphere with solvent recycle every 2 min. Extractions were continued until the solution in the extractor appeared colorless; this always was achieved in less than 24 h. The extract was concentrated by rotary vacuum evaporation; the concentrated solution was air dried for 24 h. The residue in the extraction thimble and that recovered from the solvent were vacuum-dried at 100 °C for 16 h before weighing. The THF-solubles represent the tar produced, and the THF-insolubles represent the char. Carbon, hydrogen, and nitrogen analyses were performed with a Leco CHN-600 instrument. Sulfur was determined by using a Leco SC-132. Oxygen was calculated by difference. Fourier transform infrared (FTIR) spectroscopy of the tars was done with an Analect Instruments FX-6260 system by coadding 200 scans at a resolution of 4 cm⁻¹. Standard KBr pellets were used.

Particle Swelling. Char particle sizes and shapes were determined by optical image analysis, following methods described elsewhere.[24,29] A CUE-2 Image Analysis System designed by Olympus Corp. was used. The Feret diameter and shape factor were measured. The relevance to the present paper is that here we interpret the previously published results in light of the pyrolysis kinetics.

Results and Discussion

Tar Composition and Structure. Elemental analyses of tars are summarized in Table IV. The ash contents of all tar samples were well below 1%. In general, the carbon content of the tar increases and the hydrogen content decreases as residence time increases. Except for tars generated at 1.7 s, tars produced at higher pressures have higher C/H ratios at comparable residence times. As pyrolysis severity increases, hydrogen is preferentially removed from the tar. The higher C/H ratios of the short residence time tars generated at 309 psig compared to those generated at 100 psig indicate that mass-transfer limitations are more significant at the higher pressure, resulting in more extensive cracking reactions that reduce the hydrogen content. In addition, at high temperatures primary tar vapors can be aromatized rapidly by a variety of reactions, including dealkylation and ring condensation.[31] The higher C/H ratio of tar generated at 100 psig and 1.7 s compared to that of the tar generated at 309 psig and the same residence time is consistent with the observation that more CH_4 is produced in the lower pressure case (gas yields are discussed below). These observations suggest that more cracking reactions occur at 1.7 s at 100 psig than at 309 psig.

The oxygen content of the tars decreases with increasing residence time (Table IV). Both nitrogen and sulfur contents show very little variation with increasing residence time. The nitrogen content, which varies between 1.8 and 2.2%, is higher than the 1.5% in the unreacted coal. The higher nitrogen content in the tars suggests that fuel nitrogen is preferentially evolved in the tar. This result indicates a distinction between the present work and

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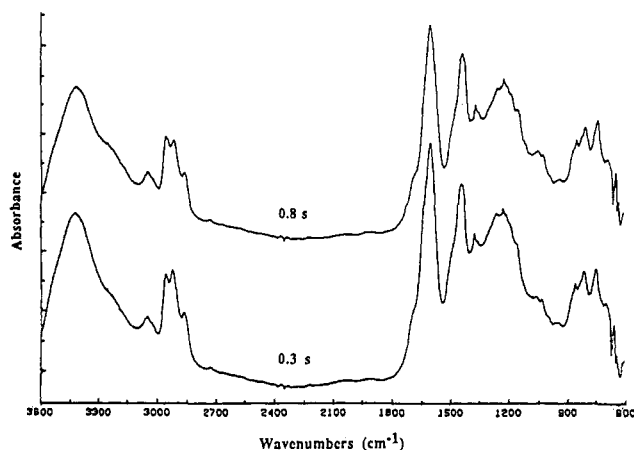
Figure 3. FTIR spectra of tars produced from pyrolysis of Illinois No. 6 coal at 1189 K, 100 psig N₂, and 0.3 and 0.8 s residence times.
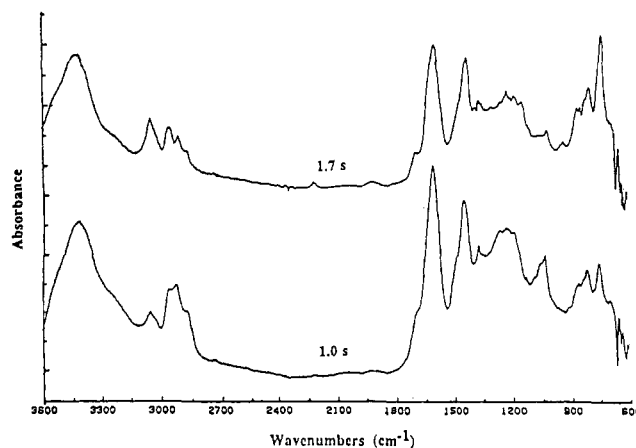
Figure 4. FTIR spectra of tars produced from pyrolysis of Illinois No. 6 coal at 1189 K, 100 psig N₂, and 1.0 and 1.7 s residence times.

earlier work on rapid pyrolysis (albeit with 20 s residence times) of an hvA bituminous coal which suggested that the tar was essentially unchanged in nitrogen content relative to the parent coal.[30] At atmospheric pressure the fraction of fuel nitrogen evolved as tar is known to be directly proportional to the fraction of coal mass evolved as tar.[29] On the other hand, the sulfur in the tar is considerably lower than that in the unreacted coal, similar to an observation with subbituminous coal,[25] but again in distinction to pyrolysis of hvA bituminous coal at 20 s residence time.[30] The latter work showed that the tar was moderately enriched in sulfur compared to the unreacted coal. Although it is convenient to distinguish qualitatively between "fast" and "slow" pyrolysis, it is also important to recognize that there can be differences in product yield and composition for, say, 2 and 20 s residence times, even though both processes are fast relative to the more traditional slow heating rate pyrolyses. The results discussed here suggest that nitrogen species may be evolved fairly rapidly, at times ≤1.7 s, while the evolution of sulfur species may be slower and only overtakes the evolution of

Table V. Calculated Ratios of Aromatic C-H Band Area to Aliphatic C-H Band Area

	100 psig				
residence time, s	0.3	0.5	0.8	1.0	1.7
$(C-H)_{Ar}/(C-H)_{Al}$	0.11		0.12	0.14	0.79
	309 psig				
$(C-H)_{Ar}/(C-H)_{Al}$		0.14	0.24	0.25	0.40
	530 psig				
$(C-H)_{Ar}/(C-H)_{Al}$				0.36	

the other tar components at residence times of ~20 s.

The FTIR spectra of tars produced at 100 psig, 0.3 and 0.8 s, are shown in Figure 3; spectra for the tars produced at 1.0 and 1.7 s are shown in Figure 4. The tar produced at 0.3 s shows strong bands in the 2800–3000-cm^{-1} region of aliphatic C–H stretching. These bands decrease significantly for the 0.8-s tar, while the bands in the 700–900-cm^{-1} region (aromatic H out-of-plane bending) become stronger. Generally the bands near 3050 cm^{-1} and 700–900 cm^{-1} become stronger with increasing residence time and the intensities of the 2800–3000-cm^{-1} bands weaken. The tar becomes significantly more aromatic with increasing residence time with concurrent loss of aliphatic structures. The peak near 750 cm^{-1}, assigned to four adjacent aromatic H bending modes, increases systematically with residence time, indicating that the aromatic structures in the tar become less substituted as residence time increases. This observation has also been reported for atmospheric pressure pyrolysis of high volatile bituminous coal.[29]

To compare the relative amounts of aromatic and aliphatic hydrogen in tar samples generated at different conditions, the ratios of areas under the aromatic C–H (3000–3100 cm^{-1}) and aliphatic C–H (2800–3000 cm^{-1}) bands were calculated. The results are shown in Table V. In general aromatic hydrogen increases with increasing residence time. Except at 1.7 s, tar generated at higher pressure has a higher aromatic H/aliphatic H area ratio at comparable residence times, indicating that the tars generated at higher pressure are more aromatic, consistent with the trend noted in the C/H ratios. The higher aromatic H/aliphatic H area ratio of the tar generated at 100 psig, 1.7 s, compared to that at 309 psig, 1.7 s, is also consistent with the higher methane yield (discussed below) at the lower pressure. At extended residence times, more secondary reactions of the tar occur at 100 psig than at 309 psig. External secondary reactions of the tar become more important as pyrolysis times increase.[3] At 1.7-s residence time, the majority of the tar escapes the char particles and secondary reactions of the tar occur outside the particles. The more aromatic structure of tar produced by external secondary reactions at lower pressure may be due to a higher concentration of tar species at the lower total pressure.

The effect of pressure on secondary reactions of volatiles depends strongly on the stage of the pyrolysis. Very rapid bond cleavage can result in a high-pressure gradient in the coal pore system, the gradient driving the diffusion of primary tar to the exterior of the coal particle.[31,32] The rate of internal transport through the pore system is inversely related to the external applied pressure.[33] During early pyrolysis, while volatiles still remain inside the coal particle, a higher external applied pressure keeps the internal concentration of volatiles high because of a higher resistance to escape. Consequently, this higher concentration will promote secondary reactions of volatiles inside

the coal particles. The extent of internal secondary reactions increases with increasing applied pressure.[3] However, when the volatiles leave the particle at a later stage of pyrolysis, a lower applied pressure increases the external concentration of volatiles and more secondary reactions occur outside the coal particle.

As discussed in detail elsewhere,[24] we have shown in this study that the evolution of gases from the Illinois No. 6 coal at these pyrolysis conditions is a complex function of residence time and applied pyrolysis pressure. The principal results are summarized as follows: The CO yield increases more rapidly as a function of residence time at 309 psig than at 100 psig. The difference between the CO yields at the two pressures also increases with residence time. There is a large difference in CO_2 yield at the two pressures at short residence time. The differences in both CO and CO_2 yields at the two pressures diminish at 1.7 s residence time. The CH_4 and C_2H_4 yields at 100 psig increase steadily from 0 ppm at 0.3 s to 600 and 200 ppm, respectively, at 1.7 s. At 309 psig the yields of the gases increase sharply as residence time increases from 0.5 to 0.8 s, but then decrease significantly at 1.0 s and remain relatively constant to 1.7 s. Increased methane yields with increased pressure were observed in pyrolysis of subbituminous coal.[20,25] Reduced ethylene yields with increased pressure have also been observed for subbituminous coals.[19,20]

Product gas distribution from the pyrolysis of Illinois No. 6 coal is a strong function of applied pressure and residence time.[24] It is important, however, to make some general comments on the chemical processes which give rise to such behavior. As hydrogen atoms are liberated by thermal bond rupture during pyrolysis, the formation of simple hydrocarbon gases becomes thermodynamically more favorable than formation of hydrogen gas as pressure increases. (Formation of gases also becomes more thermodynamically favorable, relative to formation of liquids, with increasing temperature.[34]) Formation of hydrocarbon gases reduces the total gas volume relative to formation of hydrogen. Using the formation of methane as an example, the reaction

$$C + 2H_2 \rightarrow CH_4$$
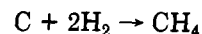
is favored by increased pressure because of the attendant reduction in volume. In the absence of an external source of hydrogen (i.e., hydropyrolysis) the amount and composition of the volatile pyrolysis products will be determined by the H/C ratio of the parent coal and the ability to make effective use of the available or transferrable hydrogen.[12,35,36] Back-reaction of evolved hydrogen with char (autohydrogenation) is more affected by residence time than by applied pressure.[37] At higher applied pressure, the residence time of hydrogen within the char pores increases, enhancing autohydrogenation. The rate of formation of methane by the char–hydrogen reaction increases with increasing H_2 partial pressure.[37]

Maxima in hydrocarbon gas yields with residence time were observed in pyrolysis of a bituminous coal at atmospheric pressure[38] and of a lignite[22] and subbituminous

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coal[25] at elevated pressures. The decrease of gas yields with increasing pressure has also been reported for subbituminous coal.[25] The complex dependence of hydrocarbon gas yields on residence time and applied pressure results from internal secondary reactions in the pyrolyzing coal and external gas-phase reactions. The external gas-phase reactions are pressure dependent and can serve as sources or sinks for the various pyrolysis products. For example, a decreased methane yield with increasing pressure can result from methane decomposition catalyzed by coal char.[39] An increased pressure increases the residence time of methane in the char pores, enhancing the surface-catalyzed methane decomposition. Methane decomposition can also occur by a free-radical mechanism in the gas phase

$$CH_4 + M \rightarrow {}^{\bullet}CH_3 + H^{\bullet} + M$$
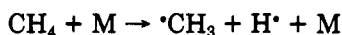
where M is some other molecule in the gas phase.[40] The collision frequency of CH_4 with M increases with increasing pressure. On the other hand, increased methane yields with increased pressure, resulting from enhanced secondary repolymerization of tar to char, have been reported in other pyrolysis studies.[41,42] Since many reactions are possible with such simple and relatively unreactive molecules as methane, pressure trends for the evolution of other volatiles are likely to be more complex and therefore more difficult to predict.

There was no measurable hydrogen in the product gas for any of the pyrolysis experiments reported in the present study. The detection limit of the chromatograph used was 300 ppm, so it cannot be said that the hydrogen yield was actually zero. The *apparent* low hydrogen yield from this coal reflects the fact that there are many pathways for the consumption of hydrogen during pyrolysis before it can be released as hydrogen gas. The way in which hydrogen is released is of critical importance to the pyrolysis behavior.[2] Pyrolysis can be viewed as a depolymerization of the coal structure occurring in parallel with thermal decomposition of the functional groups, with the products competing for the available hydrogen to become stabilized.[12,35,36,38] Thus light hydrocarbons compete with tar for the hydrogen to stabilize free radicals. The stabilized structures either evolve as volatiles or remain as part of the char, depending on the vapor pressures of the decomposing structures. In principle, the hydrogen present in medium- and low-rank coals would be sufficient to approach complete volatilization if allocated appropriately to the carbon. However, hydrogen use is always inefficient because of the preferential evolution of hydrogen as pyrolytic water and light, highly stable hydrocarbons such as methane and ethylene, depriving the remaining carbon of badly needed hydrogen. Devolatilization tends to cease when the internal donatable hydrogen has been consumed. Thermoplasticity developed during the pyrolysis of bituminous coals is also important in determining pyrolysis behavior.[2] The development of thermoplasticity is a result of internal hydrogen transfer reactions within the coal structure. The effects of applied pyrolysis pressure on char structure and thermoplasticity are discussed in a companion paper.[43]

DRIFT Spectroscopy of Char Samples. The DRIFT spectra of the unreacted coal and char samples generated
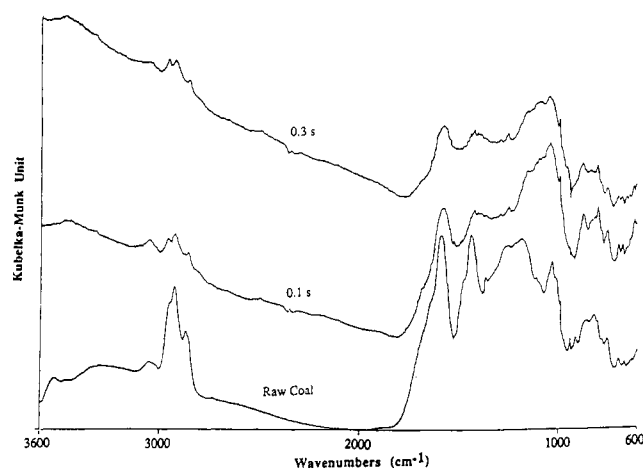
Figure 5. DRIFT spectra of unreacted coal and chars produced at 1189 K, atmospheric pressure, 0.1 and 0.3 s residence times.
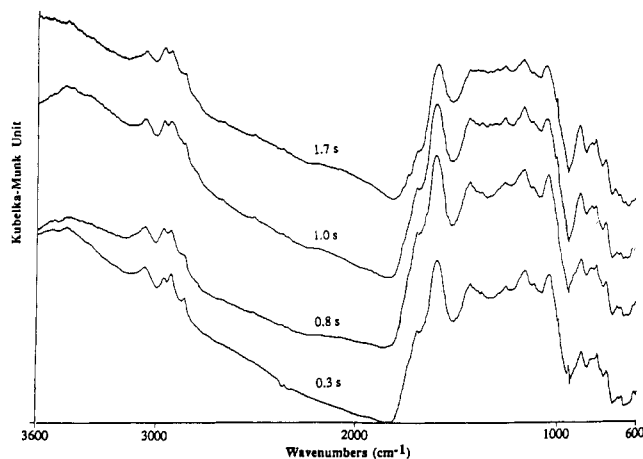
Figure 6. DRIFT spectra of chars produced at 1189 K, 100 psig, 0.3–1.7 s residence times.

at atmospheric and 100 psig pressures are presented in Figure 5 and 6, respectively. Strong absorption bands at 2800–3000 cm⁻¹ in the spectrum of the unreacted coal indicate that this coal has a relatively high aliphatic hydrogen content. This observation is corroborated by relatively weak bands near 3050 cm⁻¹ and between 700 and 900 cm⁻¹, indicative of low aromatic hydrogen content. The intensities of the 2800–3000-cm⁻¹ bands decrease significantly, and the 3100-cm⁻¹ band remains relatively unchanged for char produced at 0.1 s residence time, indicating that aliphatic hydrogens are removed preferentially to aromatic hydrogens during pyrolysis. The aromatic ring stretching peaks near 1600 and 1490 cm⁻¹ diminish substantially in the spectrum of the 0.1-s char, indicating that the aromatic structure is less substituted and more condensed in the char than in the unreacted coal. In addition, the 700–900-cm⁻¹ bands have become more intense in the char relative to the coal.

As the residence time of pyrolysis increases to 0.3 s, the intensities of all major absorption peaks decrease, and the sample exhibits a strong background absorption that increases with increasing wavenumbers. This char has the highest pyrolysis weight loss (53%) of any of the samples in the study. The increased background absorption results from a more condensed and larger aromatic ring system, which in turn is a product of extensive carbonization. The almost complete disappearance of the aromatic hydrogen stretching peak at 3100 cm⁻¹ indicates that aromatic hydrogens are removed in the later stage of pyrolysis. Other workers have observed the rapid removal of aliphatic hy-

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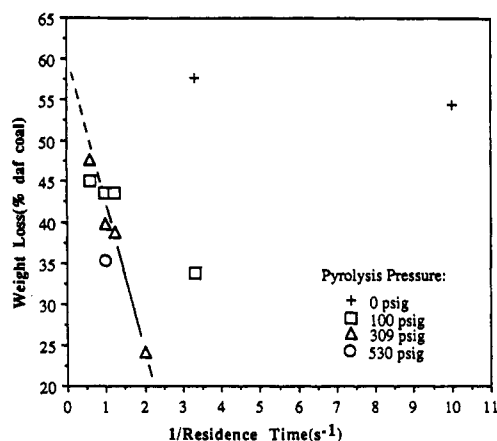(43) Lee, C. W.; Jenkins, R. G.; Schobert, H. H. *Energy Fuels*, in press.

Figure 7. Relationship between weight loss and reciprocal of residence time.

drogens followed by aromatic hydrogens at later stages of atmospheric pressure pyrolysis of bituminous coals.[37,38] NMR studies have shown that the aromaticity of char is increased relative to its parent coal.[44] Indeed, there seems to be general agreement in all pyrolysis models that the final stages of thermal decomposition are accompanied by an increasing aromatization of the char.[31]

For chars generated at 100 psig, the absorption intensities of the 1600-cm^{-1} bands decrease systematically as residence time increases. The 1490-cm^{-1} bands follow the same trends. The significant increase in intensity of the peak near 860 cm^{-1} (isolated aromatic hydrogen bending) indicates that the ring structure is more condensed at longer residence time. The decrease of aromatic hydrogen stretching peaks at 3100 cm^{-1} as residence time increases to 1.0 and 1.7 s suggests that aromatic hydrogens are removed at more severe pyrolysis conditions. Trends similar to those observed at 100 psig are observed for chars generated at higher pressures. In general, the intensities of absorption peaks for chars decrease with increasing applied pressure during pyrolysis for comparable residence times. This observation suggests that higher applied pressures lead to more condensed aromatic structures in the chars.

Pyrolysis Kinetics. The kinetics of devolatilization are determined not only by the generation of primary volatiles, but also by volatiles transport and secondary reactions within the particle. Other results from this project, published in detail elsewhere, have shown that the devolatilization behavior of Illinois No. 6 coal is pressure dependent.[24] To compare volatile release rates under different applied pressure conditions, a first-order reaction was used to model the kinetics. The value of the effective volatiles, V^*, needs to be estimated before weight loss data can be fitted into the first-order devolatilization equation. Many approaches to the estimation of V^* have been suggested.[23,45-47] The approach used in this study was to plot residual volatile values (as determined by proximate analysis of the char) as a function of the reciprocal of pyrolysis residence time. This plot is shown as Figure 7. Except for the outlier at 100 psig, 0.3 s, a good linear correlation was obtained between weight loss and reciprocal residence time. This plot allowed extrapolation of weight loss at infinite time, V^*, which was assumed to be
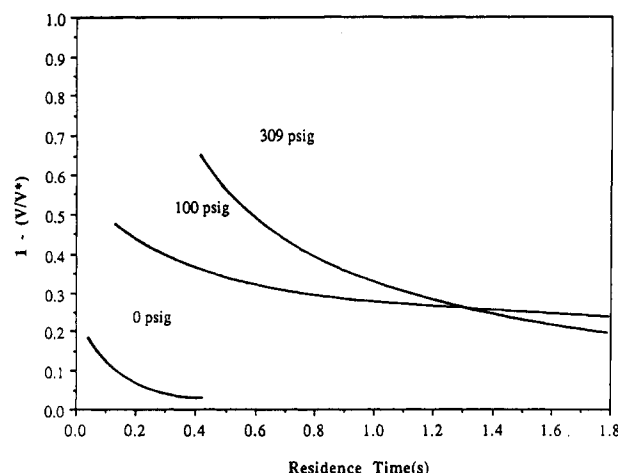
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Figure 8. Weight fraction of volatiles remaining as a function of residence time at 1189 K, N_2 atmosphere.
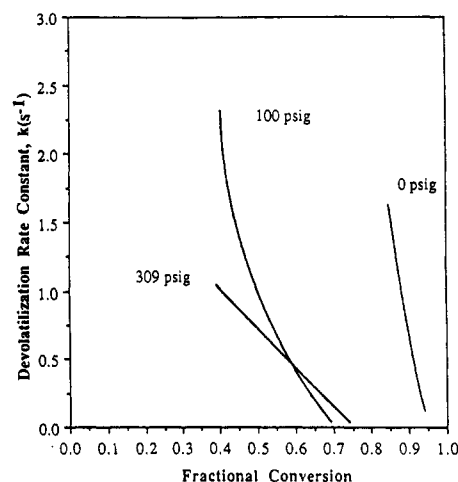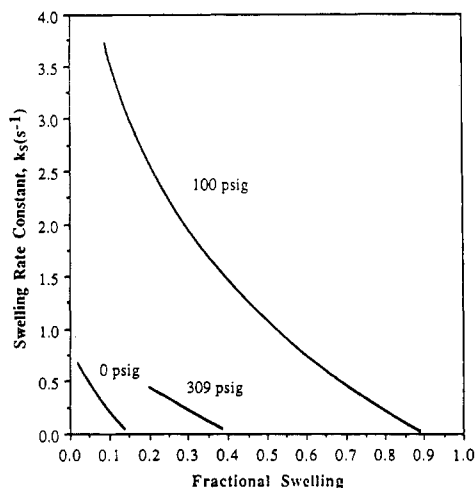

Figure 9. Effect of pressure and extent of pyrolysis on derived devolatilization rate constants for Illinois No. 6 coal at 1189 K, N_2 atmosphere.

independent of applied pressure. The weight loss data were then fitted with the first-order model

$$d(V)/dt = -k(V^* - V)$$

where (V) is defined as the fraction of volatile matter remaining at time t

$$(V) = 1 - V/V^*$$

and V is the cumulative mass of volatiles released at t. A plot of (V) as a function of residence time is shown in Figure 8. The curves were smoothed by a logarithmic curve-fitting procedure; correlation coefficients of the fitted curves are ≥0.95. The devolatilization rate constants at atmospheric, 100, and 309 psig pressures were determined by differentiating these curves. The differentiations for each pressure were only performed on the range of fractional conversions covered by actual experimental weight loss data; rate constants outside this range were not determined.

The results of the derived rate constants are shown in Figure 9. The apparent first-order rate constants are dependent not only on the extent of pyrolysis but also are pressure dependent. In general, the rate constant decreases as applied pyrolysis pressure increases. The dependence of the rate constant on the extent of pyrolysis decreases as applied pressure increases. For example, at 100 psig the rate constant decreases from 2.4 to 0.1 s^{-1} as the fractional conversion increases from 0.4 to 0.7. In a

Figure 10. Effect of pressure and extent of pyrolysis on derived swelling rate constants for Illinois No. 6 coal at 1189 K, N_2 atmosphere.

companion paper we have shown that the decrease in pyrolysis rate as pressure increases is consistent with the release of volatiles being retarded at elevated pressures, as indicated by weight loss data and as suggested by the char morphology.[24] It has been shown that the devolatilization rate constant for a high-volatile bituminous coal at 1173 K decreases from >20 to 1 s^{-1} as the fractional conversion varies from 0.9 to 0.1 (ref 40). The much smaller variation in devolatilization constant as pyrolysis pressure increases indicates that transport of volatiles out of the pyrolyzing coal particles is the predominant process determining the rate of weight loss at pressurized conditions. As pressure increases, the resistance of volatiles leaving the coal particle is enhanced, and the physical volatile transport rate becomes more important than the chemical rate of volatiles generation in determining the overall rate of pyrolysis.

To compare the pyrolysis weight loss rates with particle swelling behavior, the particle size data[24,29] were fitted with the first-order equation

$$d(S)/dt = -k_s(S* - S)$$

where (S) is defined as the fraction of swelling, based on percentage change in diameter of the particle remaining at time t, and

$$(S) = 1 - S/S*$$

where S is the cumulative swelling at time t and $S*$ represents the maximum potential swelling at $t = \infty$ for this coal pyrolyzed at 1189 K. $S*$ was determined by extrapolating a plot of swelling data generated at residence times >0.3 s as a function of reciprocal residence time. (It was assumed that $S*$ is independent of pyrolysis pressure for externally applied pressures >0 psig.) The particle swelling data were replotted as (S) vs t, fitting the data with smoothed curves, and then differentiating the fitted curves. Results are shown in Figure 10. Both pressure and the extent of swelling have significant influence on the rate of swelling. In general, swelling rate decreases as the extent of swelling increases; swelling rate increases sharply from atmospheric pressure to a maximum at 100 psig, then dropping to the lowest values as pressure increases to 309 psig.

Comparison of Figures 9 and 10 allows correlation of devolatilization and swelling rates. At atmospheric pressure, the devolatilization rate drops from 1.6 to 0 s^{-1} when the extent of pyrolysis changes from 90 to 95%, while the

swelling rate decreases from 0.75 to 0 s^{-1} and achieves only about 15% of the potential maximum swelling. At 100 psig, the decrease in devolatilization rate from 2.2 to 0 s^{-1} between 40 and 70% devolatilization is less rapid than that at atmospheric pressure, and the swelling rate decreases from 3.7 to 2.0 s^{-1}. When the extent of swelling increases from 10 to 30%, the swelling rate decreases and approaches zero as the extent of swelling reaches 90%. Both the swelling the devolatilization rates at 309 psig are lower than those at atmospheric or 100 psig pressure.

Conclusions

It is well-known that the study of the mechanisms and kinetics of coal pyrolysis is a complex area which has generated a voluminous literature over the years. The effect of pressure on pyrolysis kinetics has been of considerable recent interest in several laboratories.[33,48-51] The data presented and discussed here are one part of a study to understand the effects of pressure on the rapid pyrolysis of Illinois No. 6 coal and the effects of pressure on the structure of the resulting char. To summarize briefly, increasing pressure delays the devolatilization, lowers the volatiles yield and promotes secondary tar reactions.[24] Both the extent of coal swelling and the mechanism of volatiles transport, that is, diffusion or bubble transport, through the coal are dependent on the applied pressure.[24] The swelling behavior of the coal depends both on the development of fluidity during pyrolysis and on the resistance to swelling caused by the externally applied pressure.[24] Chars produced at 100 psig are more reactive (to air) than those produced at atmospheric pressure or pressures >100 psig.[43] The improved fluidity of the char at 100 psig relative to ambient pressure increases the number of active sites, improving reactivity, but at higher pressures increased ordering of the structure reduces the number of active sites.[43] The development of microporosity in the chars also depends on pressure.[43]

The effects of applied pressure on secondary reactions of the volatiles were residence-time dependent. When the volatiles were still inside the coal particle, more secondary reactions of the volatiles were observed as the pressure was increased from 100 to 309 psig. However, as more volatiles leave the particle as pyrolysis proceeded to longer times, more secondary reactions were observed at 100 than at 309 psig. The cracking reactions of the volatiles, tar species in particular, outside the coal particle were promoted at lower applied pressure because the concentration of volatiles increased as the applied pressure decreased. Oxygen-containing groups and aliphatic hydrogen were removed more readily from tars than was aromatic hydrogen, and more highly condensed, less substituted aromatic ring structures with higher C/H ratio were produced as pyrolysis proceeded. In general, tars generated at 309 psig are more aromatic than those produced at 100 psig, except at 1.7 s residence time, when cracking of tar outside the coal particle is favored by lower pressure.

The fact that a greater amount of CO is produced at 309 than at 100 psig, indicating that elevated applied pressure increases the severity of pyrolysis, e.g., by accelerating the release of tightly bound CO. The increase in pressure also produced higher CO_2 yields. The influence of pressure and

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residence time on CH_4 and C_2H_4 yields indicates that the cracking reactions of the volatiles (which generate more hydrocarbon gases) begin at an earlier stage during pyrolysis as pressure increases from 100 to 309 psig, consistent with both the weight loss and the tar yield decreasing more rapidly during the early stage of pyrolysis at 309 psig than at 100 psig.

The apparent first-order rate constants for devolatilization were dependent on the extent of devolatilization and on the applied pressure. The devolatilization rate decreased significantly with increasing pressure. At each pressure, rate constants decreased as pyrolysis proceeded to greater extents of devolatilization. The first-order rate constants for swelling were similarly dependent on extent of swelling and applied pressure. Swelling rates reached a maximum at 100 psig and decreased as pressure was increased further. At each applied pressure, swelling rate constants decreased as swelling proceeded. The different effects of pressure on devolatilization rate and swelling rate

provide evidence that two different mass-transfer mechanisms are operative, depending on applied pressure. At 100 psig or higher, the reduction in both devolatilization and swelling rates suggests that bubble transport was the main mass-transfer mechanism. At atmospheric pressure the devolatilization rate is higher but the swelling rate is lower than those observed at elevated pressures, indicating that a diffusional mechanism is predominant.

Viscous Sintering of Coal Ashes. 1. Relationships of Sinter Point and Sinter Strength to Particle Size and Composition

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Several tests were performed to evaluate the sintering characteristics of coal ashes prepared from four coals ranging in rank from lignite through bituminous. The ashes were prepared by standard ASTM ashing procedures and then separated into three different particle size fractions. Measurement of electrical resistance as a function of inverse absolute temperature showed that the sinter point decreased with decreasing particle size, as a result of the increased surface area to volume ratio of the ash particles. Compressive strength was studied as a function of temperature in the range 750-950 °C. For any given particle size of each coal ash, the strength of the sintered ash increased with sintering temperature. At a given sintering temperature, the strength was inversely proportional to particle size. The compressive strength test results showed qualitative agreement with the Frenkel sintering equation. X-ray diffraction of the sintered ashes showed that, as sintering temperature increased, there was a depletion of anhydrite and increase in the amount of calcium-containing aluminosilicate phases. This result suggests that chemical reactions accompanying sintering lead to the formation of relatively low-melting calcium aluminosilicates that can act as the "glue" helping to form strong sintered ash deposits.

Introduction

Deposition of ash on heat-transfer surfaces is a significant problem in the operation of coal-fired boilers. The problems have been discussed in detail in the coal combustion and ash chemistry literature.[1-5] In addition to the reduced heat transfer, ash deposits also impede gas flow and can cause physical damage to boiler internals.[2]

The overall process of ash deposition involves transformations and reactions of the inorganic components of coal in the flame; transport of ash particles to deposition surfaces; initial adhesion of the ash particles, both to the deposition surface and to each other; and finally, further

interactions among deposited ash particles to form a strong deposit. Particularly with low-rank coals, the initiation of deposition onto clean boiler surfaces begins with the formation of a so-called white layer, usually rich in sulfates.[6] The white layer is able to capture ash particles that

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