

Development of Char Structure During Pyrolysis of a hvB Bituminous Coal

Guangwei Huang and Alan W. Scaroni
The Combustion Laboratory
The Pennsylvania State University
404 Academic Activities Bldg
University Park, PA 16802

Introduction

When coal particles are heated rapidly they undergo radical changes in chemical and physical properties. The sequence of events in the pyrolysis of caking coals includes heatup of the coal particles, plasticity development in part of, or the whole coal particle, swelling, and resolidification. The occurrence and the nature of these events depend on the rank of the coal and its thermal history. The rate of evolution of gaseous products of pyrolysis is affected by mass transfer inside the pores. There has been much work published on the thermoplastic behavior of coals and the development of char structure during pyrolysis of pulverized coal (1-7). However, very little work has been published recently on the behavior of millimeter-sized coal particles, even though this size is widely used in fluidized-bed combustors. The objective of this work was to study the morphological and compositional changes in the chars produced during pyrolysis of single particles of a hvB bituminous coal using scanning electron microscopy (SEM) and elemental analysis (CHN). The mechanism for the transport of volatiles out of the pyrolyzing coal particle is also discussed.

Experimental

Pyrolysis experiments on single coal particles 1.0 to 1.5 mm in diameter were performed in an electrically heated reactor, details of which have been provided elsewhere (8,9). A hvB bituminous coal (volatile matter 48.3%, fixed carbon 47.1%, ash 4.6%) was used in this study. For each run, a coal particle was injected into the preheated reactor which was maintained at a temperature of 973 K under an atmosphere of nitrogen. The temperature gradients in the gas surrounding the particle were measured using a thermocouple array and the particle surface temperature history was obtained by extrapolation of the measured gas temperature gradients (10). Before particle injection, the gas flow was stopped so that the experiments were carried out essentially in a stagnant system.

Char particles were collected and weighed after the required residence time by quickly withdrawing them from the reaction zone into an extension of the quartz reactor and cooling them to ambient temperature using a high flow rate of nitrogen. A calculation considering the heat lost by convection and radiation from the particles estimated that cooling to below 400 °C occurred in about 0.5 s.

Results and Discussion

The elemental analyses of the coal and the chars were performed using a Leco CHN-600 Determinator and are given in Table 1. Weight Loss was calculated by averaging the weight of the chars from 10 runs conducted at the same residence time. The weight loss (ΔW) and the average rate of weight loss ($\Delta W/\Delta t$) between successive

residence times are also listed in Table 1. The rate of weight loss reached its maximum between 3.0 to 4.5 s, representing a 21% loss in weight in 1.5 s (weight loss from 15 to 36 %), and then decreased sharply. Little weight loss was observed after 6 s. The overall H/C ratio for the volatiles evolved was 1.48. The atomic H/C ratio for the volatiles released between successive residence times (H/C (VM)) was determined from a mass balance using the weight loss and ultimate analysis data. The H/C ratio for the volatiles released before 763 K was slightly greater than one, probably due to the carbon oxides released during decarboxylation. The H/C ratio for the volatiles released during the maximum rate of weight loss was one, which is almost the same as the value for the starting coal (0.94). These numbers indicate that a) the relatively weakly held volatiles such as those physically adsorbed in micropores or weakly bonded to the coal matrix are released early and possess intermediate H/C values (1 to 2); b) the major fraction of the volatiles escaping the coal particles by evaporation or diffusion during the peak devolatilization rate has the lowest H/C value, (~1); and c) the volatiles released last, produced by cracking or repolymerization reactions, have the highest H/C value (~4).

A scanning electron microscope was used to examine the changes in morphology of the coal particles at different extents of reaction. Figure 1 shows the surface of a raw coal particle. At 1000 \times magnification the surface appears smooth with some scattered mineral clusters. An obvious morphological change (Figure 2) is observed for the char after 1.5 s corresponding to about 10 % weight loss. The coal particle appears to have become partially molten and some open holes and bubbles have appeared. Further pyrolysis (Figure 3) yields a char having a molten surface with fewer bubbles than observed at shorter residence time. The fact that some bubbles adjacent to open holes have deflated instead of bursting suggests the development of internal pores which allowed the decomposed gaseous products trapped in the bubbles to escape through new tunnels into neighboring open holes. The char morphology shown in Figure 4 clearly indicates a surface structure resulting from resolidification of the fluid phase. A lower magnification of 500 \times was used for Figure 4 to show a larger region of the char surface. It is noteworthy to see a strong viscous fluid pattern for a hvB bituminous coal classified as a poor coking coal. The viscous coal melt has flown over the particle surface and sealed some open holes. The exiting gases have had to escape from a very viscous melt to create vortex-like structures (as seen in the concentric patterns in Figure 4). A similar behavior for a lignite was reported by Solomon et al (11), suggesting that the melting, bubbling, and swelling phenomena may be due to the high heating rate, which mitigates the crosslinking reactions responsible for decreasing fluidity.

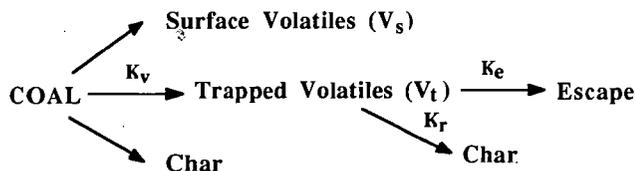
The open holes mentioned above are defined as those found on the particle surface throughout the pyrolysis (from beginning to end). An open hole is distinguished from a blowhole by its smooth rim and larger size (5~30 μm in diameter). The cause of early open holes on the coal surface may be the expansion of existing micropores or the localized acceleration of devolatilization due to catalytic pyrolysis by the dispersed mineral clusters.

In order to examine internal structural changes, a char particle collected at a residence time of 5 s at about 40% weight loss was cut in half and the electronmicrograph of its cross section is shown in Figure 5. The very porous internal structure shown in Figure 5 consists of interconnected pores formed by coalescence of bubbles of various size, with a few large pores (up to 400 μm) in the center and many smaller ones near the surface. The surface, however, is a relatively dense crust with a thickness of about 30 μm . Figure 6 shows the pore structure beneath the dense crust, revealed by peeling off the surface layer of the char, indicating a more developed structure consisting of many macro-

and meso-pores. The internal surface area provided by these pores, nevertheless, would generally be inaccessible for char gasification and/or combustion unless the reactants could pass through the dense crust.

A major morphological change in the chars during the maximum rate of evolution of volatiles can be seen from Figure 3 (residence time of 3 s and 15% weight loss) and Figure 4 (residence time of 5 s and 40% weight loss). Before the peak rate of volatiles evolution (Figures 2 and 3), the coal particle undergoes melting, bubbling, and release of volatiles through the open pores and from the external surface. Blowholes generated from bursting of bubbles were not observed before 15% weight loss. Most bubbles caused by the buildup of pressure of the gaseous products in the coal melt either flattened (Figure 3), or later burst (Figure 4) during the period of the maximum rate of volatiles evolution.

Suuberg et al (12) suggested a competitive kinetic scheme for metaplast evaporation and repolymerization. In order to explain the increased rate of evolution of volatiles with higher heating rate Niksa et al (13) classified the products of primary devolatilization into two categories, namely the light, stable volatiles from the elimination of peripheral groups and the reactive intermediates from bridge cleavage. A similar scheme with more emphasis on volatiles transfer out of coal particles is proposed below:



Here, surface volatiles (V_s) represent the easily released volatiles, generated by decomposition reactions on the external surface or on the internal surface of the open holes, leaving the particle as soon as they are formed. The resistance to volatiles liberation from the coal particle is negligible. Trapped volatiles (V_t) are those produced within the tortuous micropores or trapped in the bubbles, and are not registered as weight loss even though they are decomposed from the coal matrix. Trapped volatiles can either: (1) leave the particle by bursting the bubbles or penetrating to the particle surface or neighboring open holes, or (2) redeposit onto the solid residue (R) by repolymerization. The total yield of volatiles is given by the sum of V_s and V_t . The K_v , K_r , and K_e , represent the rate constants for the formation and repolymerization of the trapped volatiles, and the overall mass transfer coefficient for the liberation of trapped volatiles, respectively. Both the trapped volatiles formation and the repolymerization processes have been modeled as first order reactions (14). It is suggested that K_e should be proportional to an ordinary bulk diffusion coefficient, which in turn varies inversely with pressure. Therefore, the total yield of volatiles should also be pressure sensitive.

Unlike the cenospheres found with smaller particles, large caking coal particles were observed to form porous, but not hollow, char structures with dense external crusts under the experimental conditions of this study. The volatiles were formed mainly in the internal micropores (due to the larger surface area) as trapped volatiles rather than on the external surface or in open holes as surface volatiles. This implies a dependence of the total yield of volatiles on pressure and heating rate. High pressure is detrimental to high yields

because the coal melt is more viscous and less penetrable. On the other hand, a high heating rate is beneficial due to an increased internal pressure and increased fluid range of the coal melt.

Conclusions

Two kinds of holes were found on the surface of the chars produced from the hvB bituminous coal particles under the experimental conditions studied. The open holes played the predominant role during volatiles release, whereas the blowholes made a contribution to the weight loss only near the maximum rate of devolatilization. The average H/C ratio of the released volatiles was about 1.5. The volatiles released at higher conversion had H/C ratios as high as 4. Micrographs of the cross sections of the char particles indicated a well developed internal pore structure covered by a dense crust at the particle surface.

References

- 1 Solomon, P. R., Ch 4 in 'Chemistry of Coal Conversion' (Ed. R.H. Schlosberg), Plenum Press, New York, 1985
- 2 Tsai, C. Y. and Scaroni, A. W., Fuel 1987, 66, 220
- 3 Khan, M. R., Lee, C. W., and Jenkins, R. G., Fuel Processing Technol., 17, 1987, 63-71
- 4 Lowenthal, G., Wanzl, W., and Heek, K. H. V., Fuel, 1986, 65, 346
- 5 Shibaoka, M., J. Inst. Fuel 1969, 59, 42
- 6 Khan, M. R., and Jenkins, R. G., Fuel 1986, 65, 725
- 7 Gray, V. R., Fuel 1988, 67, 1298
- 8 Huang, G., Vastola, F. J., and Scaroni, A. W., Prepr. Am. Chem. Soc., Div. Fuel Chem., 1987, 32 (3), 1
- 9 Huang, G., Vastola, F. J., and Scaroni, A. W., Energy & Fuels, 1988, 2, 385
- 10 Huang, G., Vastola, F. J., and Scaroni, A.W., Prepr. Am. Chem. Soc., Div. Fuel Chem., 1988, 33 (1), 283
- 11 Solomon, P. R., Serio, M. A., Carangelo, R. M., and Markham, J. R., Fuel, 1986, 65, 182
- 12 Suuberg, E. M., Peters, W. A., and Howard, D. B., 17th Symp. (International) on Combustion, The Combustion Institute, Pittsburgh, 1979, 117
- 13 Niksa, S., Heyd, L. E., Russel, W. B., and Saville, D. A., 20th Symp. (International) on Combustion, The Combustion Institute, Pittsburgh, 1984, 1445
- 14 Anthony D. A., Howard, J. B., Hottel, H. C., and Meissner, H. P., 15th Symp. (International) on Combustion, The Combustion Institute, Pittsburgh, 1974, 1303

Table 1. Characterization of the Coal, Chars, and Volatiles

Time (s)	0	1.5	3.0	4.5	6.0	9.0
Weight Loss* (g/coal×100)	0	9.1	14.8	35.8	41.0	43.2
ΔW (g/coal×100)		9.1	5.7	21.0	5.2	2.2
$\Delta W/\Delta t$ (g/coal/s×100)		6.1	3.8	14.0	3.4	0.7
Ultimate Analysis**						
C	75.9	77.7	77.3	77.6	78.7	80.9
H	5.9	5.7	5.3	4.7	3.3	3.2
N	1.5	1.4	1.5	1.5	1.6	1.6
S+O	13.1	11.3	11.7	10.7	10.4	8.1
Ash	3.6	3.9	4.2	5.5	6.0	6.2
H/C (char)	0.94	0.88	0.82	0.73	0.51	0.48
H/C (VM)***	1.13	2.27	1.01	3.77	3.82	

* Weight loss is the average for 10 runs

** Dry basis

*** Overall H/C for released volatiles is 1.48

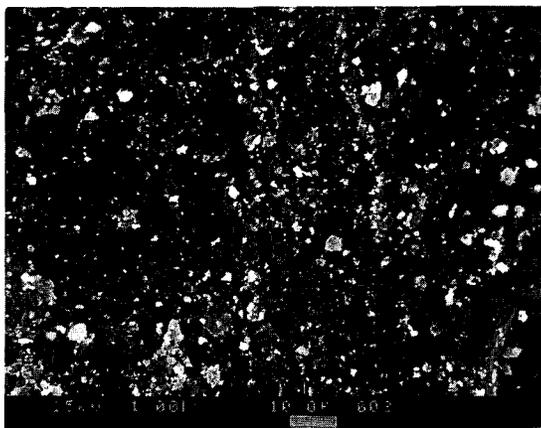


Figure 1 SEM micrograph of a PSOC 435 coal particle

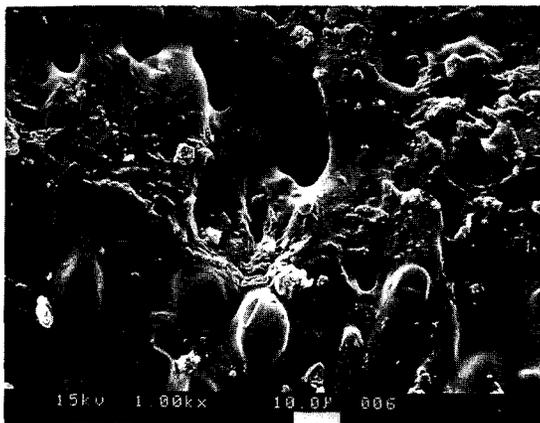


Figure 2 SEM micrograph of a char particle from pyrolysis of PSOC 435 at 973 K, 1.5 s

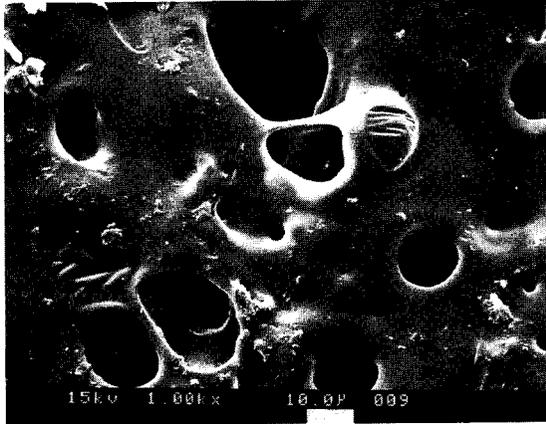


Figure 3 SEM micrograph of a char particle from pyrolysis of PSOC 435 at 973 K, 3.0 s

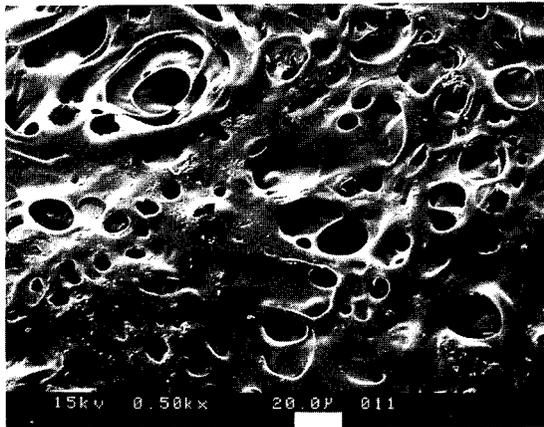


Figure 4 SEM micrograph of a char particle from pyrolysis of PSOC 435 at 973 K, 5.0 s

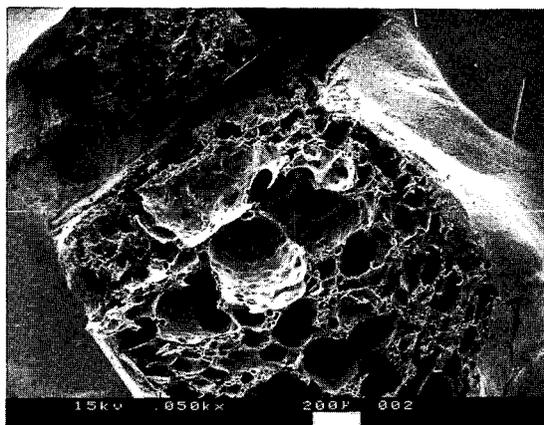


Figure 5 SEM micrograph of the cross section of a char particle from pyrolysis of PSOC 435 at 973 K, 5.0 s

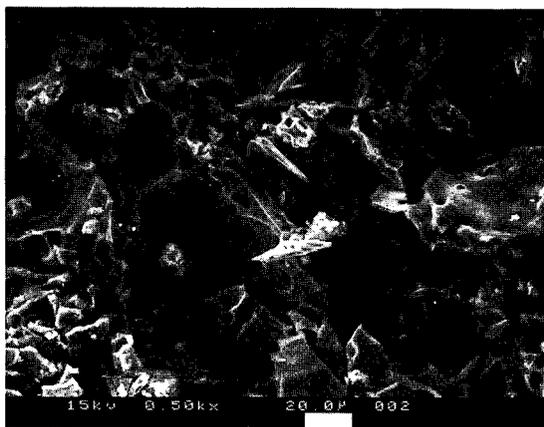


Figure 6 SEM micrograph of the pore structure beneath the particle surface of a char particle from pyrolysis of PSOC 435 at 973 K, 5.0 s