Carbon Crystal Structure Evolution in Combustion by Quantitative Digital Analysis of HRTEM Fringe Images

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High resolution transmission electron microscope (HRTEM) fringe imaging can reveal large variations in coal char crystalline structure as a function of parent coal rank and residence time in the flame. A new digital image analysis algorithm has been developed and is being used to quantify various features of the carbon crystallinity, including fringe curvature, length, and orientational correlation.

Samples and HRTEM fringe images

Partially combusted char samples were prepared in a flame-supported, entrained-flow reactor by combustion in vitiated air streams at a nominal gas temperature of 1600 K. Char samples were collected at residence times of 47, 72, 95, and 117 msec, yielding a range of carbon conversions from 0% (at the end of devolatilization and beginning of char combustion) to a maximum value of 50 - 80%. Oxygen concentration was systematically varied from 12 to 20 mole-% to produce similar peak particle temperatures (1900 - 2000 K) and similar degrees of carbon conversion for each of the precursors. An additional sample (referred to herein as a residual carbon sample) was prepared by separating a carbon-rich extract from fly ash produced by a utility boiler. [1] The char samples were ground, placed on a holey carbon grid, and examined in a Phillips Model CM30 microscope operating at 300 kV. [2] Carbon structures were examined at moderate magnification to find wedge-shaped fragments that are optically thin at the edge. A number of such edge regions (typically ten or more) are then photographed at high magnifications (2,000,000X), and representative fields of view are selected and reproduced.
The sets of HRTEM fringe images for a series of flame-generated chars have been analyzed using newly developed algorithm.

New Algorithms for HRTEM Image Analysis

Quantitative information on the size, shape, and amount of carbon crystallites was extracted from the lattice-fringe images using a computer code (C++), the commercial code Semper™ (Synoptics), and a custom image analysis algorithms developed in the course of this work.
A six step algorithm is being used to analyze the set of HRTEM fringe images: (1) digitization of the fringe image, (2) noise reduction through numerical filtering procedures including Fourier transform, (3) identification of a fringe population based on threshold brightness criteria and skeletonization (4) post-processing through identification and separation of the aggregate structures, or identification and reconnection of the disconnected segment structures, (5) determination of fringe size and shape statistics, and (6) interpretation of the statistical results in terms of the reactivity indices, the nongraphitic amorphous index (NGI), and the edge index (EI), and the orientational order parameter.

NGI and EI are associated with two types of structures: (i) amorphous carbonaceous matter and (ii) layer edges. Both have values between one and zero. We have defined a new orientational order parameter (OOP) that is related to the 2D nematic order parameter [3, 4], but is calculated as a function of length and is designed to be valid for small sample sizes. OOP is zero for random lines and one for perfectly aligned fringes.

To have reasonable results from this technique, required variables for the process are configured by using a raw coal HRTEM image as a blank and by comparing the resulting mean crystallite

[1] Hurt, R. H. and Gibbins, J. R. *Fuel* 74:471 (1995).
[2] Davis, K. A., Hurt, R. H., Yang, N. Y. C., and Headley, T. H., *Combust. Flame* 100:31 (1995).

[3] Tsvetkov, V. *Acta Physicochim.* 16:132 (1942).
[4] Zannoni, C. in *The Molecular Dynamics of Liquid Crystals*, Kluwer Academic Publishers, 11-40 (1994).

diameter from the image analysis with previously reported x-ray diffraction (XRD) results.[2]

Figure 1 illustrates this process from the raw image to the binary filtered image to the post-processed final image used for the quantitative analysis.

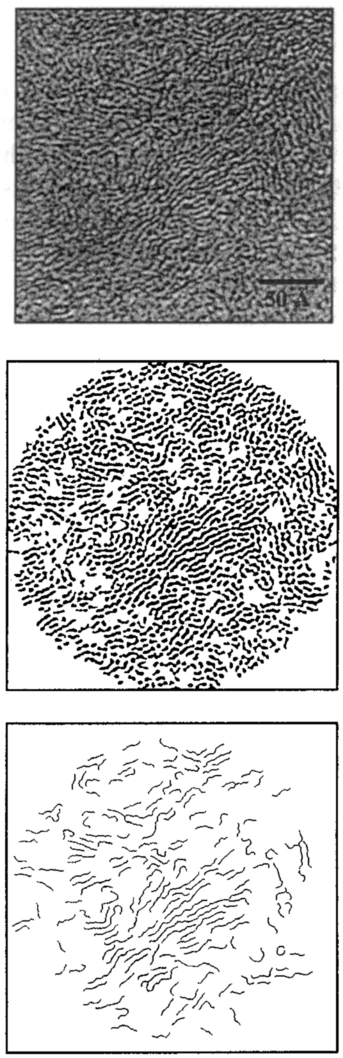

Figure 1. Image analysis sequence: raw fringe image, filtered binary image, and the final image after post-processing

Results and Discussion

Selected results are shown in Figure 2 and 3. The mean crystallite diameter (L_a) from HRTEM image analysis is shown in Figure 2. The lowest rank materials (from biofuels) show the smallest diameters among chars investigated and maintain their disorders throughout combustion. The two high-volatile bituminous coals (Illinois #6 and Pittsburgh #8) undergo increases from 47 msec to 72 msec. The high rank Pocahontas char shows a large mean diameter after only 47 msec of residence time, suggesting an ordering process in the fluid stage of carbonization.

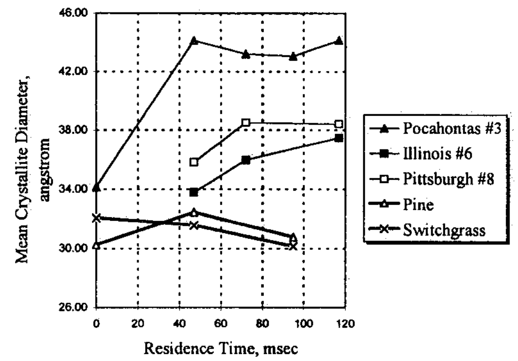

Figure 2. Mean crystallite diameter (L_a) for various char samples as a function of residence time

Figure 3 shows tortuosities determined from the HRTEM image analysis. Tortuoistiy represents the degree of curvature in the fringe. Tortuosity has a value larger than one for most cases and one for the straight line. As in Figure 2, high rank Pocahontas shows a big change from 0 msec (raw coal) to 47 msec. With one exception, the char samples show decreasing tortuosity values throughout combustion.

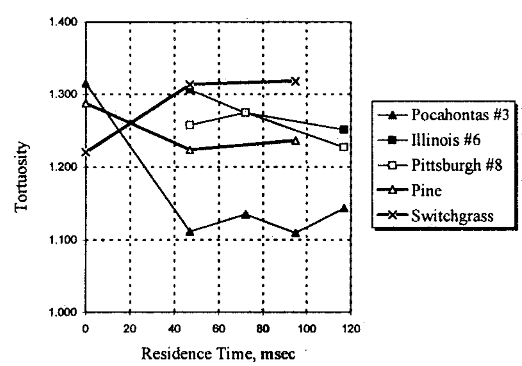

Figure 3. Tortuosity for various char samples as a function of residence time