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PROJECT DESCRIPTION

Recent work at Sandia National Laboratories, Imperial College, and the U.K. utility PowerGen, has identified an important mechanism believed to have a large influence on unburned carbon levels from pulverized coal-fired boilers. That mechanism is char carbon crystalline rearrangements on subsecond times scales at temperatures of 1800 - 2500 K, which lead to char deactivation in the flame zones of furnaces. The so-called thermal annealing of carbons is a well known phenomenon, but its key role in carbon burnout has only recently been appreciated, and there is a lack of quantitative data in this time/temperature range. In addition, a new fundamental tool has recently become available to study crystalline transformations, namely high resolution transmission electron microscopy (HRTEM) fringe imaging, which provides a wealth of information on the nature and degree of crystallinity in carbon materials such as coal chars.

Motivated by these new developments, this University Coal Research project has been initiated with the following two goals:

• to determine transient, high-temperature, thermal deactivation kinetics as a function of parent coal and temperature history.
• to characterize the effect of this thermal treatment on carbon crystalline structure through high-resolution transmission electron microscopy and specialized, quantitative image analysis.

Work is currently underway on the following three tasks:

Task 1 Experimental technique development.

The goal of this task is to develop and demonstrate an apparatus and procedure for measuring transient, high-temperature, thermal deactivation of coal chars. While peak gas temperatures in boilers are often in the range 1800 - 2000 K, peak particle temperatures can be much higher due to high rates of heat release at the particle surface due to exothermic carbon oxidation. The prototype transient heat treatment apparatus is based on an inert-gas purged graphite-rod sample holder that is subjected to rapid Joule heating to temperatures approaching 3000 °C. For the measurement of temperature histories an optical diagnostic is being developed that offers sufficient spatial resolution to distinguish the sample temperature from the substrate temperature. The optical diagnostic is based on a CID camera, a high-power lens, and movable mirrors to projecting multiple, filtered images onto a single chip. Oxidation kinetics are measured on the heat treated samples by a nonisothermal TGA technique.

Task 2 Thermal deactivation kinetics.

The goal of this task is to quantify thermal char deactivation as a function of temperature history and parent coal, with an emphasis on inert environments at temperatures and times found in combustion systems. The results are to be cast in the form of deactivation kinetics useful for incorporation in combustion models.
Task 3 Crystal structure characterization

Crystal structure characterization provides important insight into the mechanisms of thermal char deactivation, and the degree of crystalline transformations has shown a strong correlation with reactivity changes in recent combustion studies [Davis et al., 1992, Beeley et al., 1996]. This task seeks to improve our understanding of char carbon crystalline transformations under combustion conditions by analyzing a large set of HRTEM fringe images for a series of flame-generated chars whose reactivities have been previously reported [Hurt et al., 1995, Beeley et al., 1996]. As a first step, a new technique is being developed for the quantitative analysis of fringe images, extending previous work to allow measurement of a complete set of crystal structure parameters including mean layer size, mean stacking height, interlayer spacing, layer curvature, amorphous fraction, and degree of anisotropy. The resulting database will revealing, at a very fundamental level, the basic differences in char crystal structure due to parent coal rank and to temperature history in the range of interest to combustion systems.

PROGRESS THIS PERIOD

During this period we completed the project task on the characterization of crystal structures in flame formed chars by high resolution TEM and digital analysis. The work was presented at the Carbon Conference and at the American Chemical Society Meeting during the summer of 1998. This work is described in detail in a manuscript, to be submitted for archival publication, which is included as the main body of this report.

Also this term, a large dataset was obtained using the now-functional transient heat treatment apparatus. Kinetics of thermal deactivation were studied for four coal chars ranging in rank from anthracite to lignite, at temperatures from 1100 °C to 2400 °C and for residence times from 2 seconds to 2 minutes. This dataset contains a wealth of new information on the thermal deactivation propensities of different fuels. The analysis of this data is underway. It is clear that the extent of deactivation varies greatly among precursors exposed to the same thermal histories. There is a significant rank trend (the lower rank materials generally show higher extents of deactivation under the same conditions) but also individual variations from the trend (the anthracite deactivates more readily than the low volatile bituminous coal). We are hoping to understand these trends by examination of (1) changes in the organic matrix and carbon nanostructure, and (2) changes in catalytic activity. Preliminary work using HRTEM fringe imaging appears to be useful for explaining the anomalous anthracite behavior. This work will be reported on in detail when it is complete — at the end of the next period.

The project is reaching a successful conclusion. Work will also begin next period on the final report, due to DOE/FETC in the summer of 1999 (following the one-year no-cost extension).
A METHODOLOGY FOR ANALYSIS OF 002 LATTICE FRINGE IMAGES AND ITS APPLICATION TO COMBUSTION-DERIVED CARBONS

INTRODUCTION

Carbon nanostructure, the local spatial arrangement and orientation of graphene layers, affects many important properties of carbon materials, including mechanical strength and modulus [1,2], coefficient of thermal expansion [2], electrical properties [3] and their directional dependencies; pore size distribution [4,5]; and reactivity of cokes to oxidizing gases [5]. Several techniques provide information on carbon nanostructure, including X-ray diffraction [6-8], magnetoresistance [9], and high resolution TEM [10,4,11,12,13], allowing the identification of ordered regions by dark field techniques, and direct visualization of graphene layers in 002 lattice fringe imaging mode (002 LF). Lattice fringe imaging has been widely applied to fibers [14], soot and carbon black [13,15], pyrolytic carbons [16], polymeric carbons [12], and coal chars [14, 17-20], yielding important structural information and insight into bulk material properties.

Most of the results from TEM studies have been qualitative or semi-quantitative. Exceptions to this are the determination of mean interlayer spacing from the electron diffractogram, dark field studies [5], which can yield size distributions of molecular orientation domains, and several recent attempts to applied digital image analysis to 002 lattice fringe images [19,22,23]. Extraction of quantitative information from 002 LF images is challenging due to contrast variations, twisting and overlapping of the aromatic layers, and amorphous interference [4]. More work is needed before reliable techniques are available to extract all the information embedded in lattice fringe images.

Numerous studies have contributed to our understanding of the changes in carbon nanostructure during heat treatment [11,24-27], and gasification [28,19]. Relatively little is known, however, about the evolution of carbon nanostructure in solid fuel combustion for several reasons. First, there have been few direct studies on the materials of interest undergoing combustion or heat treatment under combustion-like conditions [19,20]. Secondly, the regime of interest in pulverized fuel combustion (rapid carbonization at heating rates ~ 10^5 K/s, residence times from 10 msec - 4 sec, temperatures from 1500 - 2100 K) differ greatly from the conditions used in the synthesis of most other carbon materials, and thus the behaviors and trends cannot be inferred from the large body of existing literature.

The range of practical solid fuels includes organic substances that become very fluid during carbonization and produce optically anisotropic cokes (e.g. high-rank bituminous coals) as well as highly crosslinked materials that undergo solid-state carbonization to produce isotropic chars (biomass and low-rank coals) with short range crystalline order. At the high temperatures typical of pulverized fuel combustion, the graphene layers in chars may undergo dynamic changes [19,29], and these changes may be reflected in decreases in surface area, and/or decreases in char reactivity. The nanostructures of solid fuel chars are thus highly variable dependent on precursor and processing conditions, and quantitative TEM characterization may provide useful insight into the behavior of fuels and the combustion process itself.
The objectives of the present study therefore are: (1) to develop an improved technique for quantitative analysis of 002 LF images of carbon, (2) to define new quantitative indices for describing orientational order in groups of graphene layers, and (3) to apply the technique to combustion-derived carbons for a better understanding of the mechanisms of nanostructure formation and evolution in flames. Special emphasis is given to the analysis of a set of coal and biomass-derived chars of widely varying properties and reactivities generated during high temperature pulverized fuel combustion under controlled conditions.

**EXPERIMENTAL**

An important objective of this paper is to characterize the nanostructures of combustion-derived chars from a wide range of solid fuels. Quantitative digital analysis was applied to HRTEM 002 LF images taken from earlier studies in which chars were generated by partial combustion in a well-characterized, high-temperature, entrained flow reactor from Illinois #6 coal [19] and from two biomass samples, switchgrass and southern pine [30]. To complete the set of solid fuel types, additional experiments were performed in this study under the same conditions to generate a series of partially combusted chars from Pocahantas #3 low-volatile bituminous coal, Pittsburgh #8 high-volatile bituminous coal, and Beulah lignite. Properties of the parent fuels are summarized in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analysis of parent fuel, %daf</th>
<th>---</th>
<th>---</th>
<th>---</th>
<th>---</th>
<th>Volatile matter*</th>
<th>Combustion O₂, mol-%</th>
<th>Char conversions for residence times of:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>O</td>
<td>N</td>
<td>S</td>
<td>47</td>
<td>72</td>
<td>95</td>
</tr>
<tr>
<td>Pocahontas #3</td>
<td>89.2</td>
<td>4.4</td>
<td>4.9</td>
<td>1.0</td>
<td>0.6</td>
<td>17.0</td>
<td>20</td>
<td>--** 0</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>82.9</td>
<td>5.4</td>
<td>8.7</td>
<td>1.7</td>
<td>1.2</td>
<td>39.9</td>
<td>12</td>
<td>--** 0</td>
</tr>
<tr>
<td>Illinois #6</td>
<td>75.0</td>
<td>4.8</td>
<td>13.4</td>
<td>1.5</td>
<td>5.4</td>
<td>44.7</td>
<td>12</td>
<td>--** 0</td>
</tr>
<tr>
<td>Beulah lignite</td>
<td>64.4</td>
<td>4.6</td>
<td>27.9</td>
<td>1.0</td>
<td>2.1</td>
<td>46.6</td>
<td>12</td>
<td>--** 0</td>
</tr>
<tr>
<td>Southern Pine</td>
<td>***</td>
<td>20-25</td>
<td>6 or 12</td>
<td>0</td>
<td>53 73 86 95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Switchgrass</td>
<td>***</td>
<td>20-25</td>
<td>12</td>
<td>0</td>
<td>48 76 91 94</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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* ASTM standard volatile matter
** raw coals
*** raw material for biomass combustion experiments were chars, prepyrolyzed at 625 °C

The chars were generated as described previously [19]. Briefly, a honeycomb flat-flame burner holds a H₂ / O₂ / N₂ flame that produces hot, vitiated air into which single coal or biomass particles (75 - 125 µm in diameter) are fed carried by a small nitrogen flow. The reactor is equipped with a rapid-quench, He-injection, water-cooled, sampling probe for removal of partially reacted char particles at known residence times up to 120 msec. 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. A residence time of 47 msec corresponds, approximately, to the completion of devolatilization, the disappearance of the visible volatile flame, and the onset of heterogeneous oxygen attack on the young char.

The char samples were ground, dispersed in methyl alcohol ultrasonically, placed on a holey carbon grid, and examined in a Phillips Model CM30 microscope (spherical aberration coefficient of 2.0 mm) operating at 300 kV. Samples were first 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) in fringe imaging mode, and representative fields of view selected and reproduced for discussion. An additional Beulah lignite char was prepared by rapid heating (2 \times 10^3 \text{ K/s}) in helium to 2400 K followed by a 4 second hold time at peak temperature in a graphite resistance heater. This sample was examined in a JEOL 2010 microscope operating at 200 kV at Brown University. Example images are shown in Figs. 1 and 2. A fringe image of ethylene soot (Fig. 3) was supplied courtesy of Prof. A. Sarofim and L. Rainey at MIT. The image processing was carried out with a combination of the commercial image analysis package SEMPERTM (Synoptics Ltd., Cambridge, UK) developed for microscopy applications, as well as custom C++ code segments (see following section).

**IMAGE PROCESSING**

A major challenge for the quantitative treatment of TEM fringe images is the conversion of the complex photographic print into a set of distinct, identifiable fringes that can be analyzed by traditional object-oriented image analysis algorithms. The section below outlines a new preprocessing procedure, which, while not unique or free from subjectivity, is a useful general procedure that yields reproducible fringe populations that reveal the essential differences between samples. The processing procedure involves the separate steps of digitization, Fourier transform filtering, binary image conversion, skeletonization, post-processing, and quantitative analysis of structure.

**Digitization and spatial filtering**

Selected image regions were digitized with a 600 dpi scanner and stored as 512 by 512 (pixels), 8-bit grayscale images (see Figs. 1 - 3). Figure 4 illustrates the image processing sequence. The digitized raw image is first converted to the frequency domain by a fast Fourier transform, then filtered through a frequency window centered on the typical spatial frequency for graphitic carbons 1/3.0 \sim 1/4.5 \text{ Å}^{-1}. After reverse transformation, the crystalline image features are accentuated and perfected, while features in the image with different spatial frequencies (including noise) are weakened.
Figure 1. Raw and processed 002 LF fringe image of high-rank, low-volatile bituminous coal char (Pocahontas) sampled from an entrained flow reactor in the early stages of combustion. Residence time: 47 msec; particle temperature: ~ 1700 K. Sample shows mesophase long-range orientational order. (Smallest fringe shown is 5 Å in length).
Figure 2. Raw and processed 002 LF fringe image of lignite char generated by heat treatment at 2400 K in helium for four seconds. Sample shows primary short-range orientational order in the form of 5 - 10 nm domains along with low-grade statistical long-range orientational order among the domains.
Figure 3. Raw and processed 002 LF fringe image of ethylene soot provided courtesy of Adel Sarofim and Lenore Rainey at MIT. Sample shows characteristic concentric order.
Figure 4. Illustration of digital processing sequence. (a) raw image (Switchgrass, 47 msec residence time), (b) binary image following filtering and threshold selection, (c) final processed image after skeletonization, reconnection, and dissolution of compound fringes.

**Binary image conversion**

In this critical step, the filtered image is transformed into a two-phase image by setting a threshold brightness value for the phase boundary. Single phase regions that are completely surrounded by the opposite phase (and hence isolated from other regions of the same phase) are identified as objects, or particles. These particles can be most clearly seen by converting the two-phase images to binary format, in which the dark phase is assigned a brightness of zero (black) and the lighter phase a brightness of 1 (white).

Generally, as the threshold brightness is increased above zero, the total number of pixels assigned to the dark phase increases and the number of (dark) fringes increases as well. After a point, further increases in threshold brightness cause fringes to merge and overlap, as the total amount of dark phase increases. Obviously, as the threshold is increased toward 255 (the maximum brightness in an 8-bit image) the area fraction of the dark phase approaches one and there is only one, very large "fringe". This thought experiment clearly illustrates that the number of fringes must pass through a maximum as threshold brightness is varied. Unfortunately, there is no single value of the threshold that results in proper identification of all fringes. At any threshold value, close examination of the image reveals fringes that have merged with neighbors to produce aggregate geometries, examples of which are structures resembling the letter "Y", or the letter "H" (see Figure 4b). For this local region of the image, the threshold has been set too high and merging of distinct neighboring fringes has occurred. In the same image, however, one finds series of short linear segments lying along a common axis but separated by small distances. This
structure is symptomatic of a threshold brightness that is set too low for local conditions†. Extracted binary fringe image using the threshold value at the maximum number of fringes is shown in Figure 4b.

Some researchers have identified fringes by setting the brightness threshold at the value giving the maximum number of identified fringes [22]. The approach taken in this paper is to keep the single threshold value for preliminary identification, but to supplement it with processing algorithms that identify and separate the aggregate structures, or identify and reconnect the disconnected segment structures (see next section).

**Skeletonization and post-processing**

The binary image is further processed by progressively eroding the periphery of each fringe until it is one-pixel in width — a "skeleton" of the original fringe††. The resulting skeleton is a useful simple representation of the fringe, containing both topological and dimensional information. The topological values include the number of end points and the number of nodes where branches meet. The metric values are the mean length of branches and the angles of the branches.

The skeletonized fringes are then subjected to a post-processing algorithm comprising:
(1) separation of the aggregate structures, (2) reconnection of the disconnected segment structures, and (3) removal of small fringes. First, each fringe is automatically inspected until a pixel is found with three neighbors, indicating a junction in a compound fringe. Angles are calculated between each of the three line segments leading to the junction, and the two line segments that are most nearly 180° apart are joined to form a single fringe. Each fringe is considered once more to identify possible disconnected segment structures. The neighborhood of a fringe end is searched for other fringe ends lying within 10 pixels and having a similar orientation (+/- 30°) to the original fringe. If such a fringe is found, the two structures are jointed. This portion of the algorithm does not have a large effect on most images.

† This phenomenon can be explained as follows. There are always small variations in brightness (gray scale) within a single fringe in the raw image. As the threshold value is increased, the darkest portions of the fringe are first to appear, and take the form of disconnected islands. As threshold value increases, the islands grow and merge to form an image of the original fringe. If the threshold value is too low, the individual elongated islands are identified as fringes, but will appear with the characteristic structure of linear segments lying along a common axis. While some of these structures may correspond to real crystalline features (short graphene layer segments associated end-to-end separated by defects) most are believed to arise during digital processing as described.

†† Two types of pixel connectivity are commonly distinguished, 4-connectivity, in which pixels are defined to be connected to their horizontal and vertical neighbors but not to their diagonal neighbors, and 8-connectivity, in which diagonal neighbors are also included. The thinning transformation applies a 3 by 3 neighborhood mapping table to each pixel, which selects and erodes neighboring pixels while maintaining a continuous structure around the chosen pixel. After multiple passes, the final result is an 8-connected skeleton of the original fringe.
Finally, fringes with length below 1.5 nm are removed from the fringe population. This last step separates the clearly recognizable fringes from smaller objects that lack sufficient structure to distinguish them clearly from noise or noncrystalline features in the image. In some sense, the user is free to choose this cutoff, and in doing so adopts a working definition of disordered carbon—in this case all material not found in recognizable fringes above 1.5 nm in length. The 1.5 nm cutoff was chosen for inclusion in the final algorithm by a calibration procedure involving samples whose mean crystallite size had been previously determined by X-ray diffraction line broadening [19]. HRTEM images of these samples were processed and mean fringe lengths sizes determined for various values of the minimum fringe size cutoff. The best cutoff value gave a reasonable match between the mean fringe length and \( La \) value from the two different techniques. The entire image is edited in this manner to produce simple binary images (see examples in Figs. 1 - 4) which are used in the quantitative analysis of structure. Note that fringes between 0.5 and 1.5 nm are included in the graphical image presentations, but are not used in the calculation of statistics.

**QUANTITATIVE ANALYSIS OF STRUCTURE**

Having reduced the complex fringe image to a set of distinct fringes, it is now possible to define and compute quantitative order indices based on readily-available object oriented image analysis functions. Fringes can be classified according to their size (length), planarity, and spatial arrangement. The description according to size and planarity is a straightforward application of image analysis as described in the following paragraph. The description of spatial order, and orientational order in particular, requires more discussion and is dealt with separately.

*Fringe length, tortuosity, and apparent crystalline fraction*

Fringe length is calculated by an automated procedure that counts the number of pixels along a fringe and computes the length using a calibrated pixel size. This calculation includes a correction factor for diagonally-oriented fringe segments in which the effective pixel size is larger by a factor of \((2^{1/2})\). Mean fringe length is obtained using an averaging technique consistent with X-ray diffraction theory: \( \frac{\sum L_i^2}{\sum L_i} \) [8]. Tortuosity represents the degree of curvature (non-planarity) in the fringe [23]. A simple tortuosity parameter can be defined by dividing the fringe length by the diagonal length of a box enclosing the individual fringe. Tortuosity is unity for straight lines and greater than unity for curved structures. The amount of ordered material varies greatly among fringe images and is quantified here as \( \frac{\sum L_i}{(\sum L_i)_{\text{max}}} \), where \( \sum L_i \) is the sum of all recognized layers larger than the acceptance threshold, and \( (\sum L_i)_{\text{max}} \) is the same value for a theoretical graphitic structure that fills the image field at 3.35 Å spacing. The image regions that do not contain recognizable layers may contain either porosity, amorphous material, or ordered domains with orientations that do not fulfill the Bragg conditions, it is therefore not possible to associate this parameter with a true crystalline fraction, and \( \frac{\sum L_i}{(\sum L_i)_{\text{max}}} \) is therefore referred to as an "apparent crystalline fraction".
Orientational order

Figure 5 depicts simple order modes for disk-like molecules in three dimensions and their rod-like projections in two dimensions. Nematic order, a term used to describe liquid crystalline phases, refers to alignment along a unique unit vector describing the preferential orientation of the entire field, that vector being referred to as the director. Note in Fig. 5 that the director and orientational unit vectors are defined parallel to the long axis of rods (or two-dimensional projections of discs), but perpendicular to the basal planes of disks in three dimensions by convention. Order around a point or pole in two dimensions can be concentric or radial. In three dimensions concentric order can be spherical (as in carbon blacks) or cylindrical (as in some carbon fibers). Radial order in three dimensions can also be spherical (though it is not typical of carbon structures) or concentric, as found in some carbon fibers. Many carbon fibers exhibit axial order, or mixed modes with axial order in the core and concentric order in an outer skin [11]. Equatorial stacking such as found in Brooks-Taylor mesospheres is not treated as a separate category, but as a nematic phase perturbed to curvature by interfacial tension. Because the relevant length scales for BT mesospheres are long (on the order of micrometers), the curvature is gradual and the underlying microscopic order is for most purposes best regarded as nematic†.

Equations 1 through 7 give definitions of quantitative order parameters for the various modes shown in Fig. 5. The parameters are defined to be one in the case of perfect order and zero for complete disorder (randomly aligned layers). The two dimensional parameters are most useful for the analysis of single HRTEM fringe images, while the three dimensional analogs are primarily useful in computer simulations or in reconstructions of actual structures inferred from TEM image sequences obtained upon sample rotation.

Three dimensional order parameters

The lowest orientational order mode for disk-like objects is axial orientation (see Fig. 5) in which the unit vectors all lie in a common plane, and are thus perpendicular to a unique directional vector. This type of order is seen many carbon fibers, where the preferential axial alignment induced by elongation during fiber spinning and stretching and the extent of axial alignment correlates strongly with the Youngs modulus along the fiber axis [11]. In this simple mode, there is no preferred

† An alternative scheme has been described by Oberlin [4], in which carbon nanostructures are classified as spherical and cylindrical, with nematic order treated as a special case of spherical order in which the radius of curvature is very large. Also, Inagaki [32] considers two types of spherical order, concentric (as in carbon blacks) and equatorial (as in Brooks-Taylor mesospheres) and discusses their formation mechanisms in terms of edge vs. basal plane energies.
Figure 5. Simple orientational order modes among disk-like objects in three dimensions and their two dimensional projections.
orientation of the planes when viewing along the axis. An axial order parameter in three dimensions can be defined as:

$$S_{3A} = 1 - 3 \left\langle \cos^2(\theta_i) \right\rangle = 1 - 3 \left\langle (\vec{a} \cdot \vec{u}_i)^2 \right\rangle$$  \hfill (1)

where $\theta_i$ is the angle between the axis of particle $i$ (the $i^{th}$ directional unit vector, $\vec{u}_i$) and the axis of symmetry, $\vec{a}$, and the brackets denote an average (see vector definitions in Fig. 5). The second term is an equivalent form in vector notation. This order parameter is one for perfect axial order and zero for a phase with completely random alignments. A high value indicates simple axial order or, alternatively, nematic order (a higher order degree). An additional order parameter is required to distinguish the two. The nematic order parameter, often used to describe liquid crystalline phases [31], is defined by:

$$S_{3N} = \frac{3}{2} \left\langle \cos^2(\theta_i) \right\rangle \cdot \frac{1}{2} = \frac{3}{2} \left\langle (\vec{d} \cdot \vec{u}_i)^2 \right\rangle \cdot \frac{1}{2}$$  \hfill (2)

where $\theta_i$ is the angle between the axis of particle $i$, ($\vec{u}_i$), and the mean orientation (the director, $\vec{d}$). For large $N$, the nematic order parameter is zero when the molecular axis are randomly distributed, and one in a system where the axis of each layer is perfectly aligned with the director. Note that perfect simple axial order yields $S_{3A} = 1$ and $S_{3N} = 1/4$.

A polar order parameter in three dimensions, $S_{3P}$, can be defined for both spherical and cylindrical symmetry as:

$$S_{3P} = \frac{3}{2} \left\langle \cos^2(\theta_i) \right\rangle \cdot \frac{1}{2} = \frac{3}{2} \left\langle (\vec{r}_i \cdot \vec{u}_i)^2 \right\rangle \cdot \frac{1}{2}$$  \hfill (3)

For spherical symmetry, $\theta_i$ is the angle between the orientational unit vector $\vec{u}_i$ and the positional unit vector, $\vec{r}_i$, that points from the origin or "pole" to the midpoint of disk $i$. (see Fig. 5). This order parameter is +1 for spherical concentric and zero for disorder (limits are for large $N$).

For cylindrical symmetry $\vec{r}_i$ is interpreted as the position unit vector pointing from the midpoint of disk $i$ to the closest point on the cylinder axis. This order parameter is +1 for cylindricalconcentric order, and -1/2 for cylindrical radial order (or for simple nematic if the director is the cylindrical axis). To distinguish cylindrical radial order from simple nematic order, one requires the following additional order parameter:

$$S_{3CR} = \frac{3}{2} \left\langle (\vec{v}_i \cdot \vec{u}_i)^2 \right\rangle \cdot \frac{1}{2}; \text{ where } \vec{v}_i \equiv \vec{r}_i \times \vec{a}_i$$  \hfill (4)

where a new vector, $v_i$, is defined as the unit vector perpendicular both to the symmetry axis vector, $\vec{a}_i$, and to the positional vector, $\vec{r}_i$. This parameter distinguishes cylindrical radial order (where unit directional vectors are perpendicular to the axis) from simple nematic order (where the unit vectors are parallel to the axis), being +1 for perfect cylindrical radial order and -1 for simple nematic order.
Two dimensional order parameters

The situation in two dimensions is less complex, requiring only two order parameters: nematic and polar. Special attention is paid here to the quantitative calculation of these parameters, as they find active use in the analysis of fringe images. A two dimensional version of the nematic order parameter is defined as:

\[ S_{2N} = 2 \langle \cos^2(\theta_i) \rangle - 1 = 2 \langle \overrightarrow{d} \cdot \overrightarrow{u}_i \rangle^2 - 1 \]  

(5)

This parameter is one for perfect order and, when \( N \) is large, it is zero for a disordered phase with completely random orientations. In the general case the director cannot be found by a simple averaging procedure, but is the eigenvector corresponding to the largest eigenvalue from solution of:

\[ Q \overrightarrow{d} = \lambda \overrightarrow{d} \]  

(6)

where \( d \) is the director and \( Q \) is the ordering tensor [33]:

\[ Q \equiv \frac{1}{N} \sum \begin{bmatrix} x_{ix_i} - 1/2 & x_{iiy_i} \\ y_{ix_i} & y_{iiy_i} - 1/2 \end{bmatrix} \]  

(7)

where \( x_i \) and \( y_i \) are then endpoints of the directional unit vectors for object \( i \). Many carbon materials, particularly non-graphitizing ones, exhibit short range orientational order, but no long range order. It is desirable to be able to calculate the extent of this order as a function of length scale, which is related to the determination of sizes for individual crystallites or molecular orientation domains. A length-dependent nematic order parameter can be determined by selecting a series of circular image regions each of a fixed radius, computing the order parameter within each circle, averaging the results, and reporting a mean order parameter, \( S(r) \), as a function of the chosen radius.

We have found that the simple nematic order parameter in equation 5 is inadequate for disordered samples at small length scales, where the number of fringes present is often small (< 10). For small \( N \), even randomly distributed layers with completely uncorrelated orientations yield order parameters systematically greater than zero. This effect arises when the director is calculated from the small set of fringes themselves, but disappears if the director is known \textit{a priori}. Figure 6 shows a stochastic calculation of the expected value of the conventional nematic order parameter for random lines as a function of sample size \( N \). For small \( N \) the expected value is much greater than the desired value of zero. An analytical solution to this problem was derived for \( N = 2 \) yielding \( S_{2N} = 2 / \pi \), in close agreement with the numerical solution in Fig. 6. In the practical analysis of 002 LF images, the director is indeed determined from the fringe population, so a modified definition or the order parameter is needed for length-dependent calculations. The modified two-dimensional nematic order parameter is:

\[ S_{m2N} = \frac{[S_{2N} - F(N)]}{[1 - F(N)]} \]  

(8)
where \( F(N) \) is the function in Figure 6. The expected value of this parameter vanishes where no order is found and is one for a perfect alignment.

![Graph showing nematic order parameter](image)

**Figure 6.** Nematic order parameter in two dimensions for sets of \( N \) randomly oriented lines as computed by stochastic simulation. Analytical solution for \( N = 2 \) is \( S_{2N} = 2/\pi \). The function shown is used to define a corrected nematic order parameter for small sample sets that has an expected value of zero for random orientations.

**Polar order parameter**

In a similar way, we define the a two-dimensional polar order parameter for fringes with either concentric or radial symmetry:

\[
S_{2P} = 1 - 2 \left( \cos^2(\Theta_i) \right) = 1 - 2 \left( \vec{r}_i \cdot \vec{u}_i \right)^2
\]

where \( \vec{u}_i \) is the direction unit vector, and \( \vec{r}_i \) the position vector relative to the pole, which in two dimensions is a point. A pole is always chosen prior to calculating \( S_{2P} \), so there is no need to correct the polar order parameter for statistical bias as was done for the nematic parameter. This order parameter has a value of unity for concentric symmetry, -1 for radial symmetry, and 0 for lines with random orientation. Use of this parameter requires specification of the origin or pole. By rastering a fixed aperture of radius \( r_c \), across the image and computing \( S_{2P} \) at each position, an
appropriate pole is found at the maximum value for concentric order or the minimum value for radial order.

APPLICATIONS

Figure 3 presents a raw and processed fringe image of ethylene soot exhibiting characteristic concentric nanostructure. Figures 7 shows polar order parameters, \( S_{2P} \), computed for the entire image using various trial poles (\( x,y \) ordered pairs) in the image plane. The maximum \( S_{2P} \) corresponds to the apparent nucleus of the concentric structure — the optimum pole. Positive values indicate concentric rather than radial order. Figure 8 shows length-dependent polar order parameters, \( S_{2P} (L) \), vs length scale, \( L \), of the region of interest. The degree of concentric order is seen to increase from near zero in the vicinity of the pole to about 0.7 at the particle periphery. Such amorphous core regions have been attributed to electron imaging limitations [4] and to increasing strain in the concentric structure associated with high curvature near the pole.

Figure 7. Application of polar order parameter to the ethylene soot fringe image in Fig. 3. Two dimensional map of \( S_{2P} \) yields the optimal pole — the apparent nucleus of the concentric structure.
Figure 8. Calculation of length dependent polar order parameter at the optimum pole from Figure 7. Positive values indicate concentric order (rather than radial order) and the extent of order increases with distance from the nucleus.

Combustion-derived solid fuel chars

The remainder of this article is devoted to the nanostructural characterization of flame-derived coal and biomass chars. Example previous fringe images are shown in Fig. 9 (early stages of combustion) and Fig. 10 (later stages of combustion). Figure 11 shows four image regions from a single sample to illustrate the degree of variability in these structures and their derived properties. Figures 12, 13, 14, and 15 give the quantitative results for mean fringe length, tortuosity, apparent crystalline fraction, and nematic order parameter, respectively.
Figure 9. Example carbon nanostructures observed in young combustion-generated chars. Residence time: 47 msec; Particle temperatures: 1700 - 1900 K. Circle with embedded line gives the director for the entire field shown.

Figure 9 clearly shows the variability in structures among the young chars prepared under identical conditions from five parent solid fuels. The two biomass chars and the high-volatile coal chars are quite disordered at this stage in combustion. The amount of recognizably crystalline material is limited, typical fringe lengths are less than 3 nm, many fringes are tortuous, and most fringes appear as singlets or in stacks of two or three. These structures are similar to those observed in slow heating experiments for nongraphitizing carbons, including sacharose[3], and low-rank coals [5]. The lignite shows more order, with stacking heights from 2 - 6 fringes and mean layer lengths between 3 and 3.4 nm. The high-rank coal, Pocahontas, exhibits a very different structure with larger mean fringe sizes (3.6 - 3.8 nm) and a high degree of long-range orientational order.
Figure 10. Example carbon nanostructures observed in combustion-generated chars from later times. Residence time: 117 msec (or 95 msec as marked with *); particle temperatures: 1700 - 1900 K.

In addition to these differences between char types, there are modest changes in the nanostructures as a function of combustion conditions. Illinois shows the largest changes: a significant increase in layer length, decrease in tortuosity, and increase in apparent crystalline fraction during combustion. Pittsburgh shows an increase in layer diameter and apparent crystalline fraction. Pocahontas shows a large increase in layer diameter and crystalline fraction from the raw coal to the chars, but little change during char combustion. The long-range orientational order is established early and does not alter appreciably during combustion. The other samples (lignite and biomass chars) show little changes in nanostructural parameters during combustion.
Figure 11. Set of four images from Beulah lignite char (residence time: 72 msec), demonstrating the degree of variability in fringe images within a single sample.
Figure 12. Summary of results for combustion-derived chars: mean fringe length vs. combustion residence time. Note: zero residence time represents the raw solid fuel. Image-to-image standard deviations are 1 - 3 Å, so the changes between range 47 and 117 msec are not statistically significant for some precursors.
Figure 13. Summary of results for combustion-derived chars: mean tortuosity vs. combustion residence time. Note: zero residence time represents the raw solid fuel.
Figure 14. Summary of results for combustion-derived chars: apparent crystalline fraction vs. combustion residence time. Apparent crystalline fraction is the fraction of the image area covered by recognizable ordered material and is calculated as \( \frac{\sum L_i}{(\sum L_i)_{\text{max}}} \) where \((\sum L_i)_{\text{max}}\) is computed for an ideal graphitic structure.

Overall, it may be said that the major features of char carbon nanostructure are established early in the flame. Only modest changes occur during the bulk of char combustion, and these changes are only observed for the high-volatile bituminous coals. A possible rationalization for these results is as follows. Pocahontas forms highly anisotropic structures early, during the fluid stage of pyrolysis, and this eliminates the possibility for subsequent rearrangements of a substantial nature that could be easily observed by 002 LF imaging. The late-residence time Pocahontas sample still shows a "meandering" [23] rather than graphitic structure, in which the fringe orientation varies about the director. Apparently the elimination of defects and coalescence of graphene layers which occurs above about 1700 K [25] does not occur significantly under these conditions (100 msec, 1800 K). The remaining coals solidify in a disordered state at the end of primary pyrolysis and have the potential to rearrange locally to more ordered states over the course of combustion. The two coals with the highest fluidity during pyrolysis and the least degree of crosslinking (Pittsburgh and Illinois) do undergo some further rearrangements. The biomass and lignite chars on the other hand are highly crosslinked and maintain their disordered states during combustion. This is particularly true of the biomass chars, which exhibit the least nanostructural order of all samples (and thus the most driving force for crystallization) yet show no tendency to develop order during combustion.

The relatively well developed short-range order in the lignite samples is an interesting feature which is not understood. Perhaps the abundant well-dispersed mineral matter which is unique to
this sample, and which is responsible for the well-documented catalysis of the oxidation reaction at lower temperatures [34], is also active in catalytic graphitization events. In some locations, regions of circular crystallinity were observed in the vicinity of dark patches, reminiscent of partial carbon shell formation in the presence of inorganic impurities in some carbons [4]. Another contributing factor is the high reactivity of the lignite chars, which under combustion conditions leads to elevation of the particle temperature above the surrounding gas phase, and results in slightly higher peak particle temperatures for the lignite chars, which are estimated at the upper end of the previously quoted range, 1700 - 1900 K.

Figure 15. Summary of results for combustion-derived chars: modified, length-dependent nematic order parameters, $S_{2mN}(r)$, for chars from six solid fuels. (72 msec for coal chars, 95 msec for biomass chars).
Figure 15 shows length-dependent nematic order parameters for four coal chars and two biomass-derived char sampled from high-temperature combustion environments. The chars are seen to vary greatly in the degree and length scale of orientational order. The switchgrass char shows a high degree of order at short length scales (below about 30 Å), but only a slight ordering tendency ($S < 0.25$) at longer length scales. This behavior is typical of samples consisting of distinct crystallites or molecular orientation domains oriented nearly at random, and the length at which the order parameter decreases sharply can be used as a 002 LF-based definition of a molecular orientation domain. The same general behavior is observed for the lignite and high-volatile bituminous chars, although the long-range order parameters are higher (0.5 - 0.6). The Pocahontas char is distinctly different, having a high order parameter ($S_{m2N} > 0.9$) that is maintained at all length scales accessible to this technique (up to 300 Å). The high degree of order and long length scale indicates that the order in Pocahontas was established in the fluid phase through the formation of the liquid crystalline intermediate, carbonaceous mesophase.

Especially noteworthy in this data set is the significant long range order in all samples. Even after correction for the apparent order in random lines, each of the samples studied retains a statistically significant non-zero order parameter up to the maximum length scale studied (300 Å). Modified order parameters in the 0.5 - 0.6 range reflect a particularly significant alignment tendency for the three lower rank coals. The next section seeks to answer this question by comparing the long-range order parameters to theoretical predictions from the Maier-Saupe mean field theory for liquid crystals.

**Mechanisms of orientational order development in coal chars**

To better understand the mechanisms leading to long-range orientational order, it will prove useful to compare the two-dimensional order parameters to those predicted by the Maier-Saupe mean field theory for nematic liquid crystalline phases. This comparison is made difficult by the fact that fringe images are two-dimensional projections of three dimensional structures. In this section we derive the relation between the two and three dimensional order parameters needed to make this comparison.

Maier-Saupe mean field theory describes liquid crystal formation in terms of an anisotropic attractive potential of the form:

$$U(\cos \theta) = -v (1/2)(3\cos^2 \theta - 1) S_{3N}$$

where $U$ is the energy, $v$ is a constant, and $S_{3N}$ is given by equation 2 [31]. The potential is designed to be zero for all molecules in the isotropic phase ($S_{3N} = 0$) and, for ordered phases ($S_{3N} > 0$), to vary from $+v/2$ to $-v$ as a given molecule rotates from perpendicular to parallel with the director. The parameter $v$ thus represents the strength of the potential. The mean field approach ignores specific pair interactions, and uses relations from classical statistical mechanics to derive the orientational distribution function and then the order parameter from Eq. 8.
Figure 17 plots the predicted order parameter, \( S_{3N} \), vs. \( kT/\nu \), showing a first order phase transition from the saturated liquid crystal phase at \( S_{3N} = 0.42 \) to the disordered liquid at \( S_{3N} = 0 \). This relation holds approximately for many liquid crystal systems and has also been shown to apply approximately to mixtures [35]. Nematic phases are predicted to have order parameters of 0.42 or greater, the values increasing as the degree of subcooling increases. We therefore expect solid structures formed through liquid crystal intermediates to have order parameters of 0.42 or greater, a useful test for evaluating possible mechanisms of formation.

The orientational frequency distribution in the Maier-Saupe solution is given by:

\[
\rho_{3D}(\cos \theta_{3D}) = \frac{exp \left[ S_{3N} \left( \frac{3}{2} \cos^2(\theta_{3D}) - \frac{1}{2} \right) \right]}{\int_0^1 exp \left[ S_{3N} \left( \frac{3}{2} \cos^2(\theta_{3D}) - \frac{1}{2} \right) \right] d\cos(\theta_{3D})}
\]

It is this distribution which must be projected into two dimensions to compute the apparent, or two-dimensional, order parameter in a lattice fringe image. The appropriate mapping is derived in the following paragraphs.

Consider the 002 LF imaging of an anisotropic solid lattice formed by glassy solidification of a liquid crystalline phase, in which the sample tilt has been adjusted to give the maximum apparent order. The liquid crystalline director then lies in the plane perpendicular to the electron beam axis. The geometry is shown in Fig. 16, where the electron beam travels along the z axis, and the x-axis is chosen for the director. Since our primary application of interest involves discotic phases, an example discotic molecule is shown along with its orientational unit vector, OA. The angle BOA represents the deviation from the director, the angle \( \theta \) in equations 1 - 3. The distribution is uniform in the angle, \( \phi = CBA \). Line segment AC is the perpendicular to the xy plane, and the two dimensional angle seen in a lattice fringe image is therefore BOC.
Figure 16. Derivation of two-dimensional nematic order parameters from three dimensional discotic mesophase structures.

\[
\theta_{3D} = \text{BOA} = \text{BOD} \\
azimuthal \text{ angle, } \phi = \text{CBA} \\
\theta_{2D} = \text{BOC}
\]

Figure 17. Predictions of Maier-Saupe mean field theory of liquid crystalline phases. Original results for three dimensional structures shown [35] as well as results for two-dimensional projections of three dimensional discotic phases as a function of Bragg tolerance in 002 LF.
Only the layers that approximately fulfill the Bragg conditions are imaged in 002 LF, and this effect must be accounted for in the calculation of order parameters. Oberlin [4] gives the 002 Bragg condition as about $5 \cdot 10^{-3}$ rad, which is essentially zero for the purposes of this analysis. The tolerance on the Bragg angle is given by $\pm \frac{d_{002}}{2L_a}$ rad, which is about $\pm 10^0$ for 1 nm layers and a typical interlayer spacing [4]. If the Bragg tolerance is $\pm \alpha$, only those fringes are imaged whose directors form an angle with the xy-plane of $\alpha$ or less. On Fig. 16 that $\alpha$ is angle AOC. The Bragg tolerance must be considered here, as it effects the apparent order in two dimensions. One can readily see that all fringes oriented along the director ($\theta = 0$, $\alpha = 0$) are imaged, while only a small fraction of the fringes at $\theta = \pi/2$ will have a values less than $10^0$ and thus fulfill the Bragg condition within an acceptable tolerance.

Equation 10 gives the distribution of two-dimensional angles corresponding to the Maier-Saupe orientational frequency distribution, $\rho_{3D}(\cos \theta_{3D})$. Integration is performed only through those azimuthal angles, $\phi$, that lie within the Bragg tolerance, and the relation between the angle $\alpha$, on which the Bragg condition is based, and the azimuthal angle, $\phi$, is given by Eq. 11.

$$\rho_{2D}(\cos \theta_{2D}) = \int_0^{\phi_{\text{max}}} \rho_{3D}(\cos \theta_{3D}) d\phi \quad / \quad \int_0^1 \rho_{2D}(\cos \theta_{2D}) d(\cos \theta)$$

(10)

where:

$$\tan(\theta_{3D}) = \tan(\theta_{2D}) / \cos \phi$$

(11)

Equations 9 - 11 were integrated for $\rho_{2D}(\cos \theta_{2D})$, from which the two dimensional order parameter was computed as $\langle 2 \cos^2 \theta - 1 \rangle$. The results are shown on Fig. 17 as a function of the Bragg angle tolerance, $\pm \alpha$. For realistic values of $\alpha$, the apparent order parameter in two dimensions is much higher than the order parameter in three dimensions. This is due to two effects, the more important being the fact that all of the layers oriented along the director are seen by 002 LF, while at two-dimensional angles near $\pi/2$, a large fraction of the azimuthal distribution lies far enough off the x-y plane to violate the Bragg criterion. The second effect is the reduction in $\theta_{2D}$ at constant $\theta_{3D}$ when the layer is rotated out of plane by $\phi$.

The results in Fig. 17 can be used to interpret the long-range order (10 - 200 nm) observed in the combustion-derived coal chars. For a typical Bragg tolerance of $10^0$, Fig. 17 predicts that liquid crystal derived phases should have order parameters of 0.85 or higher. (The presence of partial columnar order, or the action of secondary rearrangements in the semi-coke stage should, if present, increase the extent of order observed in the fringe image.) We therefore conclude that the Pocahontas char structure is quite consistent with a liquid crystal formation mechanism, but that the lower rank char structures are not. The long-range order parameters in the latter case (0.2 - 0.6) are too low to have originated from a classical liquid crystal transition.
Based on the analysis above, we can classify the orientational order in these samples into two categories: mesophasic and statistical. Mesophasic order (Fig. 1) is the direct result of liquid crystal formation in the fluid phase followed by molecular weight growth and solidification in the ordered state to produce a structure with long range $S_{2N}$ values greater than about 0.8. Statistical order (Fig. 2), which has also been inferred from dark field TEM studies [5], is characterized by lower order parameters (here below 0.2 - 0.6) and must therefore arise by another mechanism. One possible mechanism is the retention of anisotropy inherent in organic precursors from natural sources. Plant matter is often intrinsically anisotropic due to anisometric cellular structures, and high rank coals generally exhibit bedding plane anisotropy due to the lithostatic pressure during coalification. This latter mechanism is the likely explanation for the statistical order observed in anthracitic coals [5,21]. For coals of lower rank than anthracite, however, NMR [36] and optical studies [37] have shown only a slight degree of preferential alignment of the aromatic clusters. Further, optical bireflectance measurements indicate little or no anisotropy for coals with carbon contents less than about 85%, daf. Even for low-volatile bituminous coals like Pocahontas (88% C, daf), the initial anisotropy is often lost in the early phases of carbonization (around 400 °C) and then reestablished [37], presumably by liquid crystal formation, as pyrolysis proceeds. A different mechanism is most likely responsible for the statistical long-range order seen in all these samples.

A likely mechanism for the statistical long-range order is strain-induced alignment. Elongational flow in two-phase mixtures has been observed to induce alignment if the solid phase is composed of anisometric objects. Examples of this phenomenon are the alignment of floating logs at constrictions in rivers, the alignment of needle coke during extrusion [38], disk-like pitch components during melt-phase spinning or hot stretching of some carbon fibers [11,39]. Elongational strain may occur in softening coals through flow processes induced the evolution of volatile material and the growth and coalescence of bubbles. A pronounced example of this is the local ordering in the stretched regions adjacent to trapped gas bubbles [40]. Local anisotropic stress also occurs in the carbonization of nonsoftening coals in the form of wall stretching due to local pressure upon volatile release, or in the form of dimensional changes (shrinkage) occurring in the latter phases of mass release. Carbonization shrinkage occurring in semicokes (after initial solidification) is often observed to produce fissing in the final coke product. It is likely that the strain-induced statistical (nonmesophasic) alignment observed in this study, if pronounced enough, can lead to graphitizable regions in otherwise nongraphitizing carbons.

CONCLUSIONS

1. An automated digital technique has been developed that yields semi-quantitative statistics on fringe length and tortuosity, as well as new quantitative parameters describing the mode, degree, and length scale of orientational order. The absolute values of the mean layer length and tortuosity depend on parameters within the digital algorithm, and are therefore not free from subjectivity. The algorithm does yield useful relative indices. The orientational order indices are less sensitive to the choice of digital algorithm parameters and thus have more absolute significance.

2. Five order parameters have been defined for quantitative description of simple order modes in disk-like objects in two and three dimensions. For analysis of single 002 LF images, only two
order parameters are needed: one nematic and one polar, to represent mesophase order, cylindrical radial order, and cylindrical concentric order. The order parameters have been corrected for small sample size, allowing values to be determined as a function of length scale - a key feature for characterizing the long and short range order found in carbon materials.

3. During high temperature combustion of solid fuels, the major features of char nanostructure are established very early (τ < 50 msec). The young Pocahontas char exhibits long range orientational order, while the remaining materials show predominately short range orientational order. Subsequent combustion (50 msec < τ < 120 msec, T = 1700 - 1900 K) is accompanied by modest increases in layer length, increases in apparent crystalline fraction, and decreases in tortuosity for the high volatile bituminous coal chars. Chars from lower rank coals, as well as the biomass chars, show very little nanostructural rearrangement during the char combustion stage. Chars from the high-rank, low-volatile bituminous coal establish long-range, meandering orientational order early that is unchanged by subsequent combustion.

4. A noteworthy observation is the presence of two distinct length scales for orientational order in all but the highest rank solid fuel chars. At short length scales (< 30 Å) a high degree of orientational order is observed reflecting the presence of more-or-less distinct crystallites, or small molecular orientation domains. At larger length scale (> 30 Å), a lesser but significant orientational order is still present, indicating that the domains themselves have statistical preference for orientational order. Analysis of this statistical long-range order using Maier-Saupe theory indicates that it cannot arise by a liquid crystal mechanism. Long-range orientational order in carbons can thus be classified as "mesophase" (structures with $S_{m2N} > 0.8$) arising from liquid crystal mechanisms in the fluid phase of pyrolysis, and statistical ($S_{m2N}$ typically < 0.8), related to anisotropy in the precursor or to elongational strain during carbonization.
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NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$\hat{a}$</td>
<td>unit vector for symmetry axis</td>
</tr>
<tr>
<td>$\hat{d}$</td>
<td>director, mean orientational unit vector in liquid crystal phase</td>
</tr>
<tr>
<td>$F(N)$</td>
<td>order parameter for $N$ randomly oriented objects (used as a correction factor for the small sample order parameter, $S(N)$, or $S(L)$)</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzman's constant</td>
</tr>
<tr>
<td>$L$</td>
<td>fringe length, layer length, or length scale of orientational order (length)</td>
</tr>
<tr>
<td>$N$</td>
<td>number of fringes</td>
</tr>
<tr>
<td>$Q$</td>
<td>order tensor used in the determination of $\hat{d}$</td>
</tr>
<tr>
<td>$\hat{r}_i$</td>
<td>unit positional vector for object $i$</td>
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<tr>
<td>$S$</td>
<td>order parameter</td>
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<td>$S(L)$</td>
<td>length-dependent order parameter</td>
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<td>order parameter for sample of $N$ objects</td>
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<td>$S_{2N}$</td>
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<td>polar order parameter in three dimensions</td>
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<td>$S_{3CR}$</td>
<td>cylindrical radial order parameter in three dimensions</td>
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<td>$\tau$</td>
<td>combustion residence time</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$\hat{u}_i$</td>
<td>orientational unit vector for object $i$</td>
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<tr>
<td>$U$</td>
<td>orientational energy</td>
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<tr>
<td>$\vec{v}_i$</td>
<td>vector used in the definition of the cylindrical radial order parameter</td>
</tr>
<tr>
<td>$x_i, y_i$</td>
<td>cartesian endpoints of directional unit vector</td>
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Greek symbols

<table>
<thead>
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<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$\theta_i$</td>
<td>angle between directional unit vector for object $i$ and the director or symmetry axis</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>eigenvalue in the equation determining $\hat{d}$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>constant in Maier-Saupe mean field potential</td>
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<tr>
<td>$\phi$</td>
<td>azimuthal angle in the derivation of the 2D Maier-Saupe projection</td>
</tr>
<tr>
<td>$\rho$</td>
<td>number density of disc-like objects or fringes</td>
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REFERENCES