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Soot and char molecular representations generated directly from HRTEM lattice fringe images using Fringe3D

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ABSTRACT

Char and soot are complex carbonaceous structures that are important in traditional energy generation, reactivity, biomass combustion, pollution, climate change, and human health. HRTEM lattice fringe images have significantly improved how we "see" these complex structures. Yet our attempts to use molecular modeling to explore the structure behavior relationships are hampered by the complexity and difficulty in capturing the alignment, graphene to polyaromatic "hydrocarbon" stacks, any symmetry, and more importantly the *distribution* of structural features. It is the structural detail, which often controls the behavior of soots and chars that are otherwise similar in bulk properties. As a consequence, modeling efforts are often highly simplistic or highly complex with considerable expense being utilized in obtaining structures that do not capture all these structural details. Here we attempt a new approach: Fringe3D to directly generate the lattice fringe images in molecular space from HRTEM lattice fringe images. Image analysis determines the Cartesian coordinates, fringe length, orientation, and more importantly the distributions of those parameters. A Perl script populates the model space with a centroid representing the center of each fringe. From calibration files, either a known molecule or selected number of carbon atoms in the desired catenation style, molecules are constructed for each fringe around each centroid. The molecules are pitched to match fringe orientation. In this manner the: symmetry, stacking, orientation, and structural distributions are retained along with fine-structural details. The approach is demonstrated, with a bituminous coal char and a primary diesel soot particle, to produce initially simplistic atomistic representations of the aromatic carbon structure with greater ease, and far more rapidly than existing approaches.

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1. Introduction

1.1. Structural data from HRTEM lattice fringe images

Image analysis of lattice-fringe-extracted HRTEM micrographs has made significant improvements in the evaluation of chars [1–8], and soots [9–15]. The lattice-fringe-extracted technique utilizes image processing to generate a series of lines, termed fringes, from HRTEM micrographs. With these fringes, it is much easier to visualize and determine structural transformations. But are they quantitative? Analysis of polyaromatic standards generated average fringe lengths that were in reasonable agreement with expected values, for example 0.9 nm for coronene from lattice fringe length measurements [16] vs. 0.91 nm for hydrogen nuclei to hydrogen nuclei [17]. There was however a range of fringe length, reflecting the nature of the HRTEM process. Slight curvature/tortuosity was also observed in these "flat" molecules and was more extensive in chars and soots, indicating the potential role of non-hexagonal rings. When compared with XRD data there was "good agreement" with HRTEM data for a phenol–formaldehyde resin char, specifically evaluating average layer diameter and stacking values [4]. Thus, HRTEM lattice fringe data appears reliable to gleam structural information for soots and chars. Indeed, to show agreement with HRTEM observations many carbon-rich structural models generate HRTEM simulations [13,18–22].

1.2. Soot formation, structure and molecular models

Early views on soot formation considered soot particles to arise from condensation and subsequent carbonization of high molecular weight hydrocarbons [23]. Supported by laser microprobe mass analysis and bright and dark field HRTEM, evidence was presented for such processes [24,25]. The condensation of heavy hydrocarbons was a logical consequence of aromatic ring growth along the Stein–Fahr stability roadmap [26] and was well-supported by detailed optical measurements [27]. Growth by the well-known hydrogen abstraction, acetylene addition (HACA) mechanism

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provided the chemical basis for the aromatic molecular growth [28]. Yet soot particles were observed to undergo continued mass growth well past the (primary) particle nucleation stage in most combustion systems. Two seemingly competing processes were advocated to account for soot surface growth: the HACA mechanism and PAH addition [29,30]. Both processes were well-supported with experimental evidence, albeit on rather different flame systems. Following this, models were proposed to study PAH growth in flame environments based on the detailed PAH mechanism using a Kinetic Monte Carlo (KMC) algorithm, molecular dynamics calculations [31] or a Kinetic Monte Carlo aromatic site (KMC-ARS) model [32].

Regardless of whether soot formation occurs through a direct carbonization of oily-droplets or via heterogeneous growth with different gas-phase species, the structure of the soot thereafter has largely remained unaddressed. For a considerable time, the soot particle internal structure (pre-dating the terminology "nanostructure") was considered rather generic and invariant regardless of the combustion system (or soot formation details thereafter). Therein it was logical that soot mass and particle size be the end-point of interest and modeling at that time. Yet more recent measurements have shown that soot can possess profound differences in soot nanostructure depending upon its formation chemistry and temperature history [10,33–38].

Recently a comprehensive model for soot formation and growth, named as the aromatic site counting-primary particle (ARSC-PP) model [39] has been developed based on the assumption that soot particle is formed from planar PAH molecules. Combined with computed ensembles of PAHs within model flames permits composition (in terms of the number of C and H atoms) and the size distributions of soot particles and even representative "TEM-like" images of soot particles [40].

Several important schematic representations of basic structural units and soot/carbon black exist [41–43] along with a few molecular representations. The 2D model of Akhter et al. [44] was reconstructed as a stacked energy-minimized molecule and used in pyrene and other PAH sorption simulations [45,46]. Clusters of pyrene and coronene have also been examined as soot components [13]. Kinetic Monte Carlo with molecular dynamics approach has been used to construct soot precursors [31,47], structural evolution [32,42,48], and PAH agglomeration coupling modeling across time- and length-scales [42]. The cutting edge of soot modeling is perhaps the coarse-grain approach enables 10,000 molecules (representing 2 million carbons) to be generated [49]. Unfortunately, these simulations were large-scale constructions of two (about 200 carbon atom) structures, that required super computing facilities and generated a structure without capturing the symmetry of the soot primary particle. Despite these limitations, the significant advance permits insight (across time and length-scales) into soot processes such as clustering [50] and in later work primary particles by forming a spherical model of about 15 nm [51]. However, little structural complexity is present in the current approach but will likely be included in future work. Soot models have also been used to evaluate interaction with biologic system (lipid bilayer) [52]. Thus significant advances have been made, and the significant vision of crossing time- and length-scales is present. However, the computational approaches are expensive, and capturing the symmetry and interlay spacing is challenging. What is missing is a rapid computational construction approach to capture the many structural features observed in HRTEM micrographs, their diversity, and symmetry.

1.3. Char structure and molecular models

Char structure, similarly to soot, is also dependant on the feed, combustion/gasification system and the particle time–temperature history [53]. These structural differences also impart reactivity differences and thus a range of structures and behaviors are possible [2,53–56]. Fully devolatilized chars are usually highly aromatic [57,58], have various degrees of: stacking [59], interlayer spacing [59], atomic H/C, and aromatic structures [1,58,60]. Unlike soot, the char formation process is a solid phase transformation although thermoplastic transformations often also occur and will influence both the macroscopic [61–63], the nanostructure [5,64] including char annealing [3,65]. These average structural values determined from various analytical techniques are confirmed by HRTEM lattice fringe images but with the structural *diversity* being determined rather than simply an average value. Structural differences in coals and macerals produce different particle morphologies [62,66–69] that also influence the stacking, arrangement, and alignment of the char. Thus, structural modeling of char structure is highly challenging, transient, and no char model structure has captured this structural complexity.

Only a few coal derived char structural representations exist. They range from the small simplistic representations that are easy to construct by-hand to the highly complex renditions constructed with high-powered computational approaches. Simple char models were generated from existing small-scale (one thousand to several hundred carbon atoms) coal structural models [70–74]. The more complex construction approach using hybrid reverse Monte Carlo generated stacked, disordered planes to meet pair correlation function data [75]. There they also used TEM micrographs, specifically diffraction intensity at larger angles aided by the pair correlation function data, to generate the model. The char produced (around 1300 carbon atoms) required advanced computing capabilities. However carbon modeling (for example [76–79]) and even coal modeling [20,80] are more advanced.

A new construction approach is desirable that can capture the structural details of chars and soots (their structural diversity), at scale, with ease of construction, rapidly, and at low-cost. A new computational approach is presented here (Fringe3D) that attempts to *directly* duplicate the lattice fringe micrographs to create large-scale aromatic molecular representation of a primary soot particle and a coal char.

2. Methods

2.1. HRTEM lattice fringe analyses

The methodology of the application of the HRTEM technique and image processing approach utilized to extract lattice fringes are discussed in the literature for soot [9,11,81] and char structure [3,5]. Images obtained were already image-processed to generate the lattice fringe image format. Image analyses and false-coloring fringes were performed utilizing the Image Processing Toolkit from Reindeer Graphics in conjunction with Photoshop software. The soot image was used as received, however for the char structure some cleaning was necessary. Any remaining branch points were removed such that the fringes were individual fringes (not intersecting lines). However, some of these overlapping fringes may have been real, for example a graphitic disclination, and removing them may have artificially reduced the length values determined from the images. Alternatively, separate-displaced yet adjacent fringes may appear to be a single larger fringe. Features smaller than five pixels were ignored. It is desirable to work with the originally produced lattice fringes rather than reproduction and to use high quality images. The model produced is obviously dependant on the quality of the original HRTEM micrograph, and the processing to produce the lattice fringe image. Advances in HRTEM techniques/digital cameras have improved the image quality and emerging advances have great potential to simplify the image

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