IMPROVED MOLECULAR MODEL GENERATION FOR SOOT, CHARS, AND COALS: HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY
LATTICE FRINGES REPRODUCTION WITH FRINGE3D

A Thesis in
Energy and Geo-Environmental Engineering

by

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ABSTRACT

Large-scale molecular models for carbon-rich structures are beneficial for advanced simulations and scientific progression. However, the generation of such structures is challenging and expensive, have considerable creator bias and often unrealistic simplifications are necessary. An improved and more desirable approach for carbon-rich structures should ease the construction process, enable large-scale model creation (>20,000 atoms) with reduced bias, improve accuracy, diversity capture, and greater utility. For this project models for carbonaceous materials were constructed by integrating HRTEM lattice fringe image analyses with computational techniques. The models constructed were the aromatic moieties of a diesel-soot “primary particle”, a coal gasification char, and an extensive model of the economically important Powder River basin, Wyodak-Anderson subbituminous coal, which included heteroatom, aliphatic carbons, and water forms.

Image analyses obtained from published HRTEM lattice fringe images were utilized to directly duplicate aromatic structural features such as fringe lengths (aromatic layer dimensions), fringes separation distance (interlayer spacing), the number of fringes per stack (stacking distribution), and fringe orientation. Basically, the Fringe3D process creates three dimensional (3D) aromatic structural features directly from HRTEM lattice fringe micrographs and populated the appropriate aromatic structures in 3D molecular space. The resulting slice aromatic models are an improved molecular representation as it captures the microstructure and more importantly the distributions of structural features.

This approach was used to construct a diesel soot “primary particle” model with a realistic diameter and periodicity and gasification char with variation in stacking and orientations. Also,
an extensive model of the economically important Powder River basin Wyodak-Anderson
subbituminous coal was created, including heteroatom, aliphatic carbons, and water. The soot
model was produced due the fact that only small-scale models with limited utility were available
in the literature. A 60,000 atom aromatic carbons model was generated as a base structure. This
model could assist to explain reactivity/microstructure relationships for fuel and generation-
condition specific soot “primary particle” structures, in addition to benefits for
soot/environment/health issues. The gasification char model contains about 800 molecules based
on graphene-like structure with various stacking extents and orientations. Such a large-scale
model could aid in the process of exploring structure reactivity relationships, which are
important in energy applications and offers a new cheaper and faster construction approach that
are an improvement in comparison to current methods used such as Reverse Monte Carlo or
manual manipulations. Modification to the base structure such as oxygen functionality, cross-
links, and aliphatic components could be added to this method.

Notwithstanding the economic importance to power generation in the U.S. and potential for coal-
to-liquids production, few models of subbituminous coals exists. Around 40% of domestic coal
production comes from the Powder River basin in Wyoming. Coal, especially low-rank coal,
was a more extreme test of the model construction approach and it required some refinements to
progress from aromatic carbons layers model to 3D representation including an extensive
molecular weight distribution, heteroatom functionalities, aliphatic components, and water
forms. The model created has ~25,000 atoms and was constructed utilizing a variety of published
data, specifically nuclear magnetic resonance (NMR), fast neutron activation analysis, laser
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CHAPTER 1: INTRODUCTION

Overview

If the challenges of construction, increased model scale (necessary for many behavioral aspects), and model accuracy could be overcome, the molecular models of carbonaceous matter have the potential to be useful for computational modeling and simulation. For the purpose of this research, carbonaceous materials of interest include: soot, char, and a low-rank coal. This technique also has broad applicability in several other areas. Many analytical methods yield average structural parameters, yet the distribution is often important but overlooked. The microstructure and microstructure diversity can been captured by HRTEM lattice fringe imagery. Indeed the recreation of HRTEM images is a common approach to demonstrate structural compliance from model structures\textsuperscript{1-3}. Here an innovative new approach to perform the reverse (directly generate a structural representation from a HRTEM lattice fringe image) was attempted. This approach has great potential for the capturing of aromatic structural diversity (nanostructures features) and improving the accuracy of the model.

This microstructural diversity has yet to be adequately incorporated into structural representations. Characteristics of carbonaceous materials such as distribution of aromatic molecular sizes (fringe lengths), interlayer spacing ($d_{002}$), number of aromatic molecules per stacks and degree of orientation were extracted from high-resolution transmission electron microscopy image analyses. Most of the computer-aided construction methodology had been utilized to generate expensive and complex molecular simulations for small-scale ($<3,000$ atoms) aromatic structural features. This attempt to correlate carbonaceous materials associated structure with behaviors observed by analytical techniques. However, these methodologies have
limited ability to link average properties and aromatic molecular structure diversity. Access to advance models is often limited to those with considerable construction expertise and requires a significant allocation of time and resources. With today’s computer capacity and sophisticated molecular simulations program, there is an opportunity to create a rapid construction protocol capable of generating large 3D molecular diversity models for all forms of carbonaceous matter observed from HRTEM lattice fringe images analyses. The project creates a construction method, producing large-scale 3D aromatic structural diversity for carbonaceous materials directly generated from high-resolution transmission electron microscopy lattice fringe images.

For carbon rich materials model, existing approaches such as reverse Monte Carlos and hybrid-reverse Monte Carlos are limited to small-range of intermolecular interactions. These models describe the final configurations based on pair distribution function. Diffraction patterns techniques provide experimental data that can be related to modeling microstructure molecular description of the aromatic structural features. For carbon rich materials complex computer simulations are used to generate 3D aromatic structural configuration that resembled average experimental data. These simulation methods enable detail molecular information describing the diversity between realistic physical properties of carbonaceous matter measurements and possible model configurations. Here, modeling lattice fringe micrographs of the aromatic molecular features (e.g. stacking distribution) of primary soot particle, a gasification char, and a low-rank coal are examined. Chapter 2 presents the 3D aromatic slice model for a diesel soot “primary particle” and gasification coal char generated with the Fringe3D construction methodology. In Chapter 3 structural features for a low-rank coal specifically, Wyodak-Anderson subbituminous coal model was generated. A slice model was constructed and scripts generated to allow the population of oxygen functionality (hydroxyl, carboxylic, carbonyl, open
and closed ethers) as well as nitrogen and sulfur functionality. Scripts also populated aliphatic side chains with specific lengths and cross-links being created by-hand to meet statistical approaches for molecular weight distribution capture. The model was evaluated for their agreement with analytical data via a variety of scripts (NMR parameters, molecular weight distribution, extractability), and simulations.

**Objectives**

The main objective was to create a simple semi-automated process for production of large-scale models directly from HRTEM lattice fringe images. Three different carbon-rich entities were selected to demonstrate the utility of this approach across disciplines. With increasing complexity: a soot “primary particle”, a gasification char, and subbituminous coal were selected with goals of model generation utilizing the Fringe3D approach.

- Capturing diversity of aromatic molecules directly from HRTEM lattice fringe images.
  - Fringe lengths.
  - Fringe stacking (average number of aromatic molecules in stack).
  - Interlayer-spacing.
  - Spatial orientation (angle of declination, and rotation).

Soot particles are highly complex and often their microstructure will be dependent on the fuel chemistry and combustion/pyrolysis conditions. They are the simpler of the structures considered here because of the high aromaticity and general periodicity in forming a spherical particle. Char aromatic structural features are considered to be more challenging due to aromatic layers’ diversity (e.g., stacking and orientations) which influence reactivity. In both cases bulk properties can be similar but behavioral differences are significant. Hence capturing microstructural features is required. For both soot and char structures slice models were generated from hexagonal geometry dimensions, e.g. polycyclic aromatic hydrocarbons.
Coal, specifically a low-rank coal was more challenging due to the lower aromaticity, greater diversity, more random orientation, greater heteroatom contributions, and extractability. Part of the objectives was the creation of a scripting approach to utilize the base aromatic structure created by Fringe3D and populate appropriate aliphatic and heteroatom components to meet known coal chemistry and allow large-scale model construction. The manipulation of slice model to 3D structure was also evaluated.

**References**


CHAPTER 2: CAPTURING AROMATIC STRUCTURAL FEATURES FOR MOLECULAR REPRESENTATIONS OF SOOT, & CHAR

Abstract
Computational models are commonly utilized in many fields to simulate processes and predict outcomes. Soot contributes to health, environmental, and energy utilization issues such as diesel vehicle emissions. Char is important in energy generation (combustion and gasification), pollution control and biomass co-firing. However one of the barriers preventing progression with molecular simulation of carbon-rich materials is the difficulty and expense of large-scale model generation. For example, many chars and soot have generally similar bulk composition but can differ extensively in reactivity that has been linked to its microstructure. For this project, 3D molecular aromatic slice models of diesel soot and a gasification char were generated directly from HRTEM lattice fringe images via a new approach (Fringe3D.) Utilizing image analysis data, centroids are created in the modeling environment at the appropriate locations based on relative fringe center of mass positions. The centroid is then populated with the appropriate carbon atoms based on fringe length and is pitched to the correct fringe moment angle. In this manner the distributions of fringe length, stacking, and orientations are captured, duplicated and microstructural properties retained. The approach enables more accurate graphene sheets model generation, increases the ease of generation, reduces creator bias, and generates very large-scale models (many 1,000’s of atoms) with minimal computational expense. Here the largest primary soot particle slice model, with a diameter of ~360Å, and mean aromatic molecular size of 11Å was directly generated from diesel soot lattice fringe micrograph. Approximately, 460 aromatic molecules represent the microstructural features: length, stacking (periodicity) and alignment.
simultaneously. Such a structure can be used as a base to study soot properties and behavioral simulations. Similarly, for a gasification char model, the aromatic structural features were reproduced from a HRTEM lattice fringe image. This char model contains 800 aromatic molecules (25,000 aromatic carbons.) Integration of Fringe3D to model generation enables the capturing of aromatic structural moieties. Furthermore this method simplifies models construction without the need of extensive computer processing or expertise.

**Introduction**

Impact of computer modeling/simulations in the areas of soot and char has been hampered by our ability to generate accurate, large-scale representations. Primary soot particles, are complex, but may be considered the simpler of the two generation models because of the greater periodicity and highly aromatic nature. Char aromatic structural moieties is relatively more complex, since it is less uniform and the char precursors aromatic sites, stacking, and orientation will influence char porosity, and reactivity among others. For both entities, the fine structure depends upon the precursor and generating conditions yet may have similar bulk parameters. There is consensus on the importance of aromatic composition and spatial arrangements relative to carbonaceous matter structure-behavior relationships\(^1\)\(^-\)\(^2\). Typically X-ray diffraction (XRD) and diffraction pattern techniques are used to examine aromatic components in carbonaceous matter\(^3\)-\(^5\). Quantitative data on aromatic size, and spatial orientation features has been extracted from soot\(^6\), and char\(^7\) utilizing high-resolution transmission electron microscopy (HRTEM) lattice fringe images coupled with image analyses. The advantage of HRTEM over XRD techniques is direct observation and distribution of data via lattice fringe image analysis. Such advances in HRTEM images algorithm analysis enable structural features such as *distribution* of aromatic molecular size, orientation, stacking, and interlayer spacing to be recorded\(^6\)-\(^8\).
average aromatic layers size and interlayer spacing for carbon rich materials are observed by XRD technique \(^5, 9-12\). Here, the construction of soot primary particles, chars, and coals directly generated from HRTEM image analyses that enable large-scale models to be easily generated. Thus, can a new approach, directly capturing structural features be created to enable scientific progression in this field utilizing simulation approaches?

**Structure and modeling of soot**

Primary soot particles are spherical and often exist in agglomerates\(^13\). A primary soot particle can have a molecular mass range \(\sim 10^2\)-\(10^4\) amu with a mean diameters between 5-30nm, and may contain \(>100,000\) carbon atoms\(^14, 15\). For soot formation, generally the polyaromatic gas/solid phase material undergoes functional group elimination, ring condensation and ring fusion accompanied by dehydrogenation and “particle” growth, as well as regional alignment of the aromatic carbon layers to yield a certain degree of periodicity\(^6, 16\). These aromatic molecules are formed from highly complexes reaction pathways and have been extensively studied within the combustion sector\(^16-18\). Yet molecular modeling of soot is generally highly simplistic and of limited scale. **Figure 1(a)** shows a sketch of the soot particles represented by inner core disorder (low aromaticity) and a more crystallite (graphene-like structure) in the outer shell was observed by transmission electron microscopy\(^13\). This primary soot particle is initially composed by inner core (d\(\sim 10\)nm), which consist of fine particles of diameter range 3-4nm\(^13\). The outer shell, evaluated as planar aromatic layers of 1nm thick and 3.5nm wide, resembling long-range graphitic-crystalline long-range order\(^13\). Structures are commonly oriented perpendicular to the radius of the primary soot particles\(^13\). In **Figure 1(b)** schematic carbon black spherical shape rendering fringes as straight aromatic layers was interpreted from HRTEM lattice fringe image\(^19\).
However, lattice fringe micrographs image processing also describe soot primary particles of spheroidal shape composed by fringe with wavy-line shapes are shown in Figure 1(c). In Figure 1(d) show spherical shapes with a certain amount of curvature incorporated by curved molecules, interpreted from HRTEM lattice image fringe analyses.

Figure 1. (a) Schematic of soot particle segments. (b) Spheroidal shape particles were observed from carbon blacks (soot primary particles) HRTEM micrograph. (c) HRTEM lattice fringe and skelotonized micrograph analyses of soot primary particles. (d) Spherical shapes for soot primary particle represented by using 2D model compounds with different degree of curvatures.

It is fair to say that molecular models have not yet captured the scale and periodicity due to challenges in soot model construction. Soot chemical structural parameters has been evaluated with various fuels, combustion devices, and analytical approaches: Fourier transform infrared spectroscopy (FTIR), NMR, X-ray photoelectron spectroscopy (XPS), HRTEM, and electron energy loss spectroscopy (EELS). Extensive experimental data were used to generate a relatively simplistic small scale structural model for hexane-derived soot shown in Figure 2(a).
The model has a general formula of $\text{C}_{489}\text{H}_{160}\text{O}_{34}$ (~683 total atoms) representing the aromatic, aliphatic, cross-linking, and functional groups compositions\textsuperscript{20}. The 3D molecular representation of the hexane soot was constructed by Kubicki\textsuperscript{26, 27}. \textbf{Figure 2(b)}. Here, stable molecular configuration was obtained by energy minimizations and molecular dynamics methods\textsuperscript{26}. Representation of stacking configuration between pyrene and soot aromatic layers was created after molecular dynamics simulations. This layering in \textbf{Figure 2(b)} resembles the soot primary particle aromatic layers configuration observed by HRTEM micrographs\textsuperscript{14, 22, 27}. Further insight between different types of polycyclic aromatic hydrocarbons and hexane soot structural reactivity characteristics using computer simulations such as energy minimizations, and molecular mechanics has been proposed\textsuperscript{27, 28}.

\textbf{Figure 2}. (a) Hexane-derived soot model. (b) 3D Molecular representation of the aromatic components and associated stacking model after molecular dynamic simulation. Sources: (a) Akhter et al.\textsuperscript{20} and (b) Kubicki\textsuperscript{28}.

Recently, an internal molecular representation of soot, utilizing polycyclic aromatic hydrocarbons (PAHs) model compounds as soot precursors with simulation methods was developed by Kubicki\textsuperscript{29}. Utilizing coronene and pyrene cluster of 50 molecules (1,800 total
atoms) undergoes energetic configuration that resembles experimental data\textsuperscript{29}. However, no current soot model construction methodologies are capable to generate realistic atomistic scale concentric particle diameter of (\textasciitilde15-30nm), without the use of complex simulation methods and simplistic structural assumptions. Such scale size allows the addition of quantitative data to be incorporated as small polyaromatic hydrocarbons to larger graphene. To enhance construction of soot aromatic layers and molecular structural features there is a need to capture the structural details that are relative to their source of fuels chemical structure and combustion device\textsuperscript{14, 23, 24, 30, 31}.

**Structure and modeling of chars**

Chars are commonly investigated for pulverized coal combustion or gasification. Char microstructure-reactivity depends on multiple factors such as precursor structure, atmosphere, temperature, heating rate, residence time, and others\textsuperscript{32-36}. The transition from different coal-ranks to char has been studied by X-ray diffraction\textsuperscript{7, 37}, HRTEM\textsuperscript{38, 39}, and NMR analysis\textsuperscript{40}.

Molecular mechanics was used to determine steric molecular conformations, geometric optimization for a variety of coals to char structural transition molecular models have been constructed from coal models simulating pyrolysis\textsuperscript{41-43}. Figures 3(a), and 3(b) shows coal-to-char structural models transitions generated from hand-constructions coal models directly manipulated from multiples analytical techniques and different pyrolysis conditions. In Figure 3(a), the relationship between transition of bituminous vitrinite coal-char structural model configurations and morphology changes under thermal decomposition was constructed\textsuperscript{44, 45}. The Pittsburgh #8 coal-char structural model production is based by devolatilization under wire-mesh reactor conditions as shown in Figure 3(b)\textsuperscript{43}. The total amount of atoms for each coal-chars model was < 2,000 atoms. However, close agreement between average coal to chars structural
behavior (e.g. energy configurations) and experimental data were related to different temperature profile stages. With computational advances atomistic scale modeling such as Reverse Monte Carlo (RMC) was used to generate a 3D industrial char model primarily from pair-distribution function techniques\(^{47}\).

**Figure 3.** (a) Lewiston-Stockton vitrinite coal to char molecular modeling under drop-tube pyrolysis conditions was constructed by Mathews et al. (b) Pittsburgh #8 coal-char molecular structure characterization in a wire-mesh reactor was generated by Jones et al. Sources: (a) Mathews et al.\(^{44, 45}\), and (b) Jones et al.\(^{43}\)

Such an approach allows construction of char microstructure models to be constructed to represents experimental diffraction data\(^{47}\). However, char 3D microstructure generated via this approach is limited to dense regions characteristics of aromatic carbons in graphite-like layers with interlayer spacing between (3.4-3.8Å) located within the respective periodic cell dimensions\(^{47}\). A total of 1,296 atoms are used by RMC simulation of char model\(^{47}\). Simulations of this form tend to be computationally expensive usually requiring supercomputing access running for days or in larger simulations weeks to months.
Thus existing char models, similarly to soot models, are often limited in comparison to the complexities of char structural reactivity and physical properties among others factors. Their construction is also hampered often by scale and a general lack of ability to generate structures capturing features of interest. However, HRTEM lattice fringe images have aided in our understanding of char morphology\textsuperscript{3, 38, 39}.

**Insights from HRTEM lattice fringe images**

Micrograph and lattice images for carbon rich materials selected samples are shown in **Figure 4**. Numerical information for asphaltene\textsuperscript{48}, low-rank coals\textsuperscript{38, 49}, soot\textsuperscript{22, 50}, and chars\textsuperscript{38, 51} correspond to aromatic structural features such as size distribution, stacking, interlayer spacing and degree of orientation. Here, soot (specifically a primary particle), coal gasification char and a low-rank coal were considered. The digital image subjected to computational algorithm provides quantitative information. Information that is fundamental to develop large-scale 3D carbon rich materials model directly from HRTEM lattice fringe images.

![HRTEM lattice fringe images](image_url)

**Figure 4.** HRTEM lattice fringe image and digitalize lattice fringe image after filtration techniques for asphaltene, low-rank coals, soot, and char. Sources: (asphaltene) Sharma et al.\textsuperscript{48}, (low-rank coals) Sharma et al.\textsuperscript{11}, (soot) Palotas et al.\textsuperscript{14}, (char) Sharma et al.\textsuperscript{51}.
Confidence in HRTEM lattice fringe image analyses, is high, due to supportive information and applications to studies of microtexture analysis of char\textsuperscript{38, 39, 51}, activated carbons\textsuperscript{52}, soot formation\textsuperscript{14, 24}, asphaltenes\textsuperscript{48}, carbon black\textsuperscript{3, 53}, coals and coal-derivates\textsuperscript{11, 54-57}. Furthermore close agreement between XRD aromatic structural values, and HRTEM lattice fringe image analyses have been observed\textsuperscript{3}. There are some limitations to HRTEM images analyses. However, the micrographs generated from interactions between incident beam and aromatic layers are observed as dark lines\textsuperscript{1}. Commonly referred to as fringe, that captures aromatic molecular structures as seen edge-on\textsuperscript{58}. Aromatic structures not aligned perpendicular to the incident beam are not projected in the lattice fringe micrograph object plane\textsuperscript{59}. Contrary to the absence of lattice fringe observed, extreme curved and long fringes results in the overlap between two or more aromatic layer structures in close proximity can be projected as a single lattice fringe\textsuperscript{60}. In addition these lattice fringe images are subjected to digital filter methods and threshold values that can significantly affect the output image data\textsuperscript{38}.

**Model generation**

Image analysis can quantitatively determine the absolute positions of the centroid of every lattice fringe in 2D space. Also captured are the fringe length, structural arrangements, and interlayer spacing among others. Essentially, the HRTEM lattice fringe image is a two dimensional x-y “graph”. The image data for all the fringes was formatted in Protein Data base (pdb) file format via simple file text format manipulation, a Perl script named Fringe3D was created to populate molecular structures at each fringe centroid. This slice model typically contains >600 or so fringes, thus it was desirable to automate the construction process. The amount of polyaromatic carbons per fringe lengths is related to aromatic structural parameters observed from NMR analyses.
The absence of the third dimension in HRTEM micrographs object plane is viewed edge-on and depths lengths of the lattice fringe are not observed. The aromatic carbons layers, hexagonal-like structures, were related to graphene edges. Equations were used to determine average aromatic carbon layers per fringe lengths, determined by Mathews et al. \textsuperscript{42, 56, 61}. Figure 5(a) and Figure 5(b) shows the number of average aromatic carbons generated from a parallelogram catenation assumption.

<table>
<thead>
<tr>
<th>Fringe lengths (Å)</th>
<th>Cmax</th>
<th>Cmin</th>
<th>Cave</th>
<th>Cmodel</th>
</tr>
</thead>
<tbody>
<tr>
<td>~7.7</td>
<td>15.61</td>
<td>14.24</td>
<td>14.93</td>
<td>14</td>
</tr>
<tr>
<td>~10</td>
<td>24.97</td>
<td>22.28</td>
<td>23.63</td>
<td>24</td>
</tr>
<tr>
<td>~11.5</td>
<td>29.63</td>
<td>26.23</td>
<td>27.93</td>
<td>22</td>
</tr>
</tbody>
</table>

Figure 5. Comparison between fringe lengths to number of aromatic carbons lengths-mass relationship (Cave), and model compound number of aromatic carbons (Cmodel) from the molecule maximum lengths, false-colored by red dots to aid scale.

Centers of mass, determined by image analysis, of fringes are placed in 3D space as shown in Figure 6(a). Thus, the Fringe3D script places a centroid marker molecule then populates the appropriate structural composition at the appropriate 3D centroid x, y, z coordinates. It is desirable to generate molecules that represent a range of sizes and shapes in accordance with known carbon chemistry. A named molecule or a specified number of carbon atoms from a calibration file, with specific catenation, are utilized to populate molecules into their respective centroid positions. Automated methods are required to populate hundreds of molecules, simultaneously capturing diverse experimental data. Here calibration molecules with circular,
parallelogram and other catenation approaches were created. The first six atoms comprising the central benzene ring are shown in Figure 6(b). This image shows a circular catenation growth from C6 to C54 aromatic molecules with the fringe lengths representation of the aromatic molecules viewed edge-on. These structures are then pitched to capture the appropriate momentum angle of the fringe, thus periodicity, stacking and fringe length/size are captured and duplicated in 3D space.

An innovative construction process converting quantitative data from HRTEM lattice fringe images is described in Appendix A.

Figure 6. (a) Diesel soot HRTEM lattice fringe image after filtration technique, colors sphere represent the fringe centroid. (b) Calibration file for circular growth from C6 to C54, the central benzene ring false-colored (grey), and the centroid (green). The arrows represent fringe lengths distance scale of the molecules viewed edge-on. Source: HRTEM fringe image published by Palotas et al.14.
Results and discussion

Lattice fringe image analyses provide the groundwork to create large-scale 3D molecular model of soot from different fuel chemistry and combustion device. In Figure 7(a) and 7(b), a raw HRTEM image of diesel soot primary particle was subjected to image digital analyses producing skeletonized image published by Palotas et al.\textsuperscript{14} is depicted. In Figure 7(c) a lattice fringe image false colored by fringe length was used to aid viewing. Also, shown are the (xy) graphs’ fringe center of mass (blue dots) generated from lattice fringe lengths Figure 7(d). Agreement between model average fringe length of 12Å, and the experimental average fringe length of 12.47Å was observed\textsuperscript{14}.

\textbf{Figure 7.} (a) Diesel soot HRTEM, (b) lattice fringe image analyses, (c) lattice fringe false colored by lengths, and (d) Centroid locations in xy-coordinates.
Source: HRTEM image published by Palotas et al\textsuperscript{14}.

\textbf{Figure 8} shows the fringe lengths range. Facilitating the distribution of an aromatic molecular mass range the distribution of fringe lengths produced a distribution of different sized graphene molecules.
Figure 8. Lattice fringe lengths range distribution for diesel soot model.

Model compounds used to populate soot centroids (lattice fringe center of mass) are shown in Figure 9. The molecules centroid is artificially-colored (red) and hydrogen atoms are not included, these model compounds are made of aromatic layer with the appropriate number of carbons being reproduced to relate length to molecular size.

Figure 9. Examples of model compound used to represent total aromatic carbons related to fringe lengths (Å), molecules rotated edge-on view aids on differentiate between coordinate dimensions.
The distribution of interlayer spacing was defined as the nearest separation distance between adjacent fringes center of mass. Sixty percent of the fringes are stacked within a separation distance ranging of (3.1 - 5.1Å) via image analyses. That is within the relative range observed from experimental values\textsuperscript{22, 23, 62}. Distribution of stacking fringes separation distance is shown in \textbf{Figure 10(a)}. Fringes with separation distance below or above of the stipulated stacking range were classified as single aromatic molecules \textasciitilde40\% of total fringe. The distribution of two, three, and four fringes in a stack is shown in \textbf{Figure 10(b)}.

![Figure 10](image)

\textbf{Figure 10.} (a) Distribution of fringes separation distance within a range. (b) Percentage of fringe per stack formations.

The generated soot model consisted of 578 aromatic molecules, with a diameter particle \textasciitilde190Å and is in good agreement within experimental data\textsuperscript{6, 23, 31}. Agreement between soot model aromatic carbon \textasciitilde50,000 and literature value \textasciitilde10\textsuperscript{5}-10\textsuperscript{6} total aromatic carbons per primary particle were observed\textsuperscript{63}. It is noteworthy to mention that soot model resemble a cross-sectional area (i.e., slice) of the primary particle. These are shown in \textbf{Figure 11}, enlargement view provide proper visual scale of aromatic carbons layer (polycyclic aromatic hydrocarbon compounds).
Further insight into the molecular mass range from aromatic molecules to soot particles microstructural properties is important for health/environmental topics\textsuperscript{64}. In Figure 12, molecular weight distributions ranging from (156-1,649 Da) with an average molecular weight of 958 Da was observed in reasonable agreement with soot experimental laser desorption ionization mass spectroscopy data\textsuperscript{64}.

\textbf{Figure 11.} False-colored HRTEM lattice fringe structure and corresponding mirror image soot “slice” model generation from diesel soot primary particle.

It is relatively easy to include C5- and C7-member rings in the calibrations files, producing curved fringes relative to HRTEM lattice fringe image. However, this was not attempted as more
work is necessary in enhancing the image analysis algorithmic processes and evaluating reasonable curvature and extent for specific soot microstructure formation.

![Aromatic molecular weight distributions ranging (150-1,649 Da) for soot model, the inset molecular weight range (1,650-5,200 Da) were extracted from soot model. HRTEM lattice fringe image of soot primary particle color by fringe lengths then color layers were extracted from low molecular mass (short fringe lengths) to high molecules mass (long fringe lengths).](image1)

**Figure 12.** Aromatic molecular weight distributions ranging (150-1,649 Da) for soot model, the inset molecular weight range (1,650-5,200 Da) were extracted from soot model. HRTEM lattice fringe image of soot primary particle color by fringe lengths then color layers were extracted from low molecular mass (short fringe lengths) to high molecules mass (long fringe lengths).

**Char model construction and evaluation**

A HRTEM image of Pocahontas #3 (POC) char is shown in Figure 13(a) was used to generate the char “slice” model. Skelotonized image show lattice fringe as dark lines in Figure 13(b).

These skelotonized filter image of POC represent quantitative aromatic structural features such as distribution of fringe lengths, number of fringe per stack, and interlayer spacing. Such statistical values were used by Sharma et al.\textsuperscript{51} to quantify reactivity, conversion and structural
transformation characteristics of aromatic moieties between raw char and 1% O₂-He mixture at gasification temperature of 600°C for 60% and 90% conversion, dry ash free basis⁵¹. Changes in aromatic moieties between raw char and yields conversion percentage was recorded by HRTEM lattice fringe image processing analyses⁴⁹,⁶⁵. Small differences between char raw average fringe lengths of 1 nm were compared to the slight longer values at higher conversions 1.1nm (60%) and 1.2nm (90%) conversion⁵¹. However, more significant differences in average stacking height was determined with increasing conversion: 3.4Å (60%) and 4.5Å (90%) was obtained by HRTEM⁵¹. Good agreement between the char-derived HRTEM and XRD data was reported⁴⁹. HRTEM lattice fringe image analyses gives important information about char formation and transitions during conversion processes. No current model generation approach utilizes these parameters for construction goals.

In Figure 13(a), aromatic structural features from char HRTEM are converted to numerical values after imaging analyses seen in Figure 13(b). False-colored fringes (by length) are used to aid viewing shown in Figure 13(c). These lattice fringe image analyses are based on (x,y) Cartesian coordinates enable Fringe3D to generate a 3D “slice” char model from lattice fringe image analyses capturing experimental data such as interlayer spacing, separation distance between lattice fringe from the center of mass. The models capture the diversity of aromatic molecules and enable automated molecular growth integrated into HRTEM lattice fringe image by Fringe3D.
Figure 13. (a) Char HRTEM raw image. (b) Char lattice fringe image analyses. (c) Char lattice fringe color by lengths. (d) Char centroid (xy-coordinates).
Source of micrograph, and lattice fringe image: Sharma et al.\textsuperscript{51}.

Figure 14. The model compounds related to lattice fringe length in 3D char “slice” model directly from char HRTEM lattice fringe image. Some, 800 aromatic molecules are generated with >20,000 total atoms.
In Figure 15 shows molecular weight distribution range for char model. The dominant peaks range from 150-250 Da. The molecular mass is generated from fringe length-mass relationship. Thus the length of lattice fringe could be affected by image processing threshold values parameters, thus misleading molecular mass maybe produced.

![Figure 15](image)

**Figure 15.** Char model aromatic compounds molecular weight distribution.

Small difference between average fringe length model of 9Å and experimental average fringe length of 10Å was observed (literature data being based on multiple micrographs.) In Figure 16, distribution of interlayer spacing defined as the nearest separation distance between adjacent fringe center of mass determinate by image analyses. Char reactivity is complex and depends on many factors of which carbon structural features are an important one. **Figure 16** demonstrates a variety of structural diversity has been captured.
Figure 16. Char model interlayer distance distribution within a range.

Conclusions

Large-scale molecular representation of carbonaceous matter such as soot, and coal chars will aid health, environmental issues, and energy processes. The barrier preventing inexpensive, large-scale construction with an improved suitability has been broken with the creation of a new approach for aromatic moiety hexagonal like-structures (e.g. graphene sheets) model generation (Fringe3D). This script duplicates the microstructural features of aromatic components directly from the image analysis of HRTEM. In this manner the distributions of fringe length, stacking, and orientations are captured, duplicated and microstructural properties retained. This approach enables detailed computational large-scale model generation based on quantitative data. Since the automated process reduces creator bias, multiple large-scale models with minimal computational expense can be produced. This approach was used to generate a large-scale aromatic diesel primary soot particle (>60,000 atoms) and a coal gasification char slice (>25,800 atoms) models.
References


CHAPTER 3: MOLECULAR REPRESENTATION OF WYODAK-ANDERSON SUBBITUMINOUS COAL

Abstract

To optimize coal conversion processes, large-scale coal models capturing mass diversity, chemical, and physical structural features are desirable. Despite the economic importance of subbituminous coal, Wyoming alone producing around 40% of the total US coal production, only a few early (1980-90’s) small-scale molecular representation exits. However, they do not capture many structural features and their utility in advanced simulations is limited. A new approach was created directly capturing coals aromatic carbons layer from HRTEM lattice fringe images enabling large-scale model generation. This approach will reduce construction expense, improve extensibility, significantly reduce personal bias, and enable scientific progression through a wide variety of coal simulations. Here the slice model generated was manipulated with scripts to add heteroatom functionality, aliphatic, and oxygen functional groups in agreement with analytical data as nuclear magnetic resonance, fast neutron activation analysis, wet chemistry etc). Innovative statistical analysis automatically assign cross-linking location throughout the entire model was performed to agree with the molecular weight distribution from laser desorption ionization spectroscopy, and capture average lattice parameters values from NMR data. Fragment manipulation generated the first large-scale 3D Wyodak-Anderson subbituminous coals model that incorporated bulk and bound water forms. Model was in good agreement with a variety of analytical data for Powder River basin coals.
Introduction

The Wyodak-Anderson coal zone of the Powder River basin (PRB) is located in Wyoming and Montana. It is one of the most important coal regions in United States. In 2008 total U.S. coal production was 1,171 million short tons. In the same year production from PRB coal zones accounted for 44% of the total U.S. production\(^1\). Wyoming is the leading state for coal production\(^2\). The PRB coal has one of the lowest sulfur content (0.3-1.0 S wt % as-received) in the national coal reserve\(^3\)-\(^5\). The Wyodak-Anderson coal zone is the largest subbituminous coalfield in the United States with an average coalbed thickness of 120 ft\(^3\). Here “Wyodak-Anderson coal”, denote the Argonne Premium Coal Sample (APS), that has been well studied. Penn State Coal Sample Bank (PSOC) coals from the same region but from different seams have also been evaluated. Figure 3-1 shows various seam names within PRB coal zones.

![Figure 3-1](image.png)

**Figure 3-1.** Stratigraphic relationship between Wyodak-Anderson subbituminous coal zone, and coal beds associated. Sources: Ellis et al. and Triplehorn et al.\(^6\), \(^7\).

The Wyodak-Anderson subbituminous coal is one of the 8 APS samples. It was sampled from a 6-in. core sample through the entire seam in Campbell, Wyoming\(^8\). It is a high moisture coal typically containing 20-30% moisture by mass\(^9\). The moisture content forms can be split between bound (non-freezable) and bulk (freezable) water via differential scanning calorimetry\(^10\). The
freezable water content for Wyodak-Anderson subbituminous coal is 34%, and 66% being non-freezable water with 39g of water per 100g of dry coal\textsuperscript{11}.

Subbituminous coals molecular representations capable in simulating structure-behavior relationship for coal conversion processes would be beneficial. However, in the United States no studies have generated large-scale subbituminous coal molecular models. Generating meaningful large-scale coals molecular representations requires a continuum structure based on distribution of aromatic, aliphatic, heteroatom, inorganic-organic components, and water forms. Advances in HRTEM lattice fringe images algorithms enable digital image processing. Fringe length planes are related to aromatic carbon layers (e.g. hexagonal-like structure, graphene). Confidence, for HRTEM lattice fringe image analyses and XRD values for subbituminous coals were observed\textsuperscript{12, 13}. Typically, the average fringe lengths of 7Å for subbituminous coals was calculated from HRTEM\textsuperscript{14}, closely agree with low-rank coals average aromatic carbon layers diameter range from 7Å to 8Å XRD data reported by Hirsch et al\textsuperscript{15}. The aromatic carbon layer structural configuration was referred to geometrical hexagonal-shape, e.g. polyaromatic hydrocarbons to graphene structures\textsuperscript{25}. Such aromatic layers can be gathered, with others layers in stack formations give periodical structures of graphite crystallite\textsuperscript{16}. These is the building blocks for all carbonaceous matter normally named basic structural units\textsuperscript{17, 18}.

**Coal Structure Data**

Subbituminous coals are rich in oxygen. Table 3-1 presents the ultimate analyses for some of the PRB coal samples. The data are presented in descending C wt%. The H/C values range from a low of 0.787 to 0.926. Both atomic H/C and O/C ratios were used as coal parameters that depict the transformation and chemical variation.
Table 3-1. Ultimate analysis for Wyodak-Anderson subbituminous coals and low-rank coals selected from the Powder River basin.

<table>
<thead>
<tr>
<th>Samples</th>
<th>State</th>
<th>C%</th>
<th>H%</th>
<th>S% a</th>
<th>O% b</th>
<th>N%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decs 38 (subB)</td>
<td>MT</td>
<td>77.0</td>
<td>5.35</td>
<td>0.46</td>
<td>16.48</td>
<td>1.04</td>
</tr>
<tr>
<td>Dietz (subB)</td>
<td>MT</td>
<td>76.5</td>
<td>5.27</td>
<td>0.50</td>
<td>17.22</td>
<td>0.95</td>
</tr>
<tr>
<td>WY (subC)</td>
<td>PSOC 1488</td>
<td>MT</td>
<td>75.4</td>
<td>4.95</td>
<td>0.47</td>
<td>18.48</td>
</tr>
<tr>
<td>School (subC)</td>
<td>PSOC 99</td>
<td>WY</td>
<td>72.9</td>
<td>5.20</td>
<td>0.72</td>
<td>21.63</td>
</tr>
<tr>
<td>Smith (subB)</td>
<td>PSOC 1400</td>
<td>WY</td>
<td>72.7</td>
<td>5.19</td>
<td>0.67</td>
<td>20.78</td>
</tr>
</tbody>
</table>

dmmf = analysis on a dry, mineral matter-free basis; "dry = analysis on a moisture-free basis; "Oxygen% (by differences); PSOC = data provided by the Penn State Official Coal Data Basis. *APS, is the Argonne data from Argonne Premium Coal Sample Program.
Sources: Vorres^8.

The empirical formula, normalized to 1,000 carbon atoms, for different PRB selected samples are given in Table 3-2. They are presented in order of descending hydrogen content. There is variability in composition as expected.

Table 3-2. Empirical formula for Powder River basin selected samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>State</th>
<th>Empirical Formula a</th>
</tr>
</thead>
<tbody>
<tr>
<td>WY (subC)</td>
<td>APS*</td>
<td>C_{1000}H_{850}N_{13}S_{2}O_{188}</td>
</tr>
<tr>
<td>Smith (subB)</td>
<td>PSOC 1400</td>
<td>Wyoming</td>
</tr>
<tr>
<td>School (subC)</td>
<td>PSOC 99</td>
<td>Wyoming</td>
</tr>
<tr>
<td>Decs 38 (subB)</td>
<td>PSOC 1488</td>
<td>Montana</td>
</tr>
<tr>
<td>Dietz (subB)</td>
<td>PSOC 1400</td>
<td>Montana</td>
</tr>
</tbody>
</table>

^a Empirical formula based on 1,000 carbon atoms per ‘formula weight’ as dry, mineral-matter free basis. *APS = Argonne Premium Coal Sample Program. Sources: Smith et al.^8

Proximate analyses for selected coals are shown in Table 3-3 along with the maceral group composition and vitrinite mean-maximum reflectance. Maceral composition influences coal behavior during conversion processes^3, 19. The dominant maceral group/type in Wyodak-Anderson coal zones has been classified as huminite/vitrinite^20. Interaction between micro-organism (bacteria and fungi) in lignin, cellulose, and tannin is thought to be the precursors of the huminite/vitrinite macerals^21. Liptinite is likely produced from microorganism consuming...
fatty acids and lipids\textsuperscript{22-24}. The maceral composition for high-rank coals in the United States are dominated by (75-80\%) vitrinite macerals\textsuperscript{25, 26}. Low contributions of liptinite with higher contributions of inertinite are observed in these coals. Low-rank coal (lignite and subbituminous) maceral have a larger degree of structural variation than those in high rank-coals\textsuperscript{26,27}.

**Table 3-3.** Proximate analysis, maceral composition, and mean-maximum vitrinite reflectance for Wyodak-Anderson subbituminous coals, and Powder River basin selected samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Moist\textsuperscript{a}</th>
<th>VM% (db)</th>
<th>Ash yield</th>
<th>Vit %\textsuperscript{c}</th>
<th>Int %\textsuperscript{d}</th>
<th>Lipt %\textsuperscript{e}</th>
<th>R\textsubscript{o} %\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>WY (subC)</td>
<td>APS*</td>
<td>28.09</td>
<td>44.73</td>
<td>12.61</td>
<td>89</td>
<td>10.3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Dietz (subB)</td>
<td>PSOC 1488</td>
<td>24.68</td>
<td>41.85</td>
<td>6.37</td>
<td>87.7</td>
<td>7</td>
<td>5.3</td>
</tr>
<tr>
<td>Smith (subB)</td>
<td>PSOC 1400</td>
<td>20.96</td>
<td>46.32</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>School (subC)</td>
<td>PSOC 99</td>
<td>24.12</td>
<td>52.57</td>
<td>24.04</td>
<td>81.8</td>
<td>10.4</td>
<td>7.8</td>
</tr>
<tr>
<td>Decs 38 (subB)</td>
<td></td>
<td>22.07</td>
<td>44.34</td>
<td>4.8</td>
<td>85.5</td>
<td>11.7</td>
<td>2.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Moist = moisture content (as received %); \textsuperscript{b} Ro\% = reflectance (vitrinite), mean-max in oil; dry = analysis on a moisture-free basis; \textsuperscript{c} Vitrinite, volume \% mineral free. \textsuperscript{d} Inertinite, volume \% mineral free. \textsuperscript{e} Liptinite, volume \% mineral free. PSOC = data provided by the Penn State Official Coal Data Base. *APS, the Argonne data from Argonne Premium Coal Sample Program.
Sources: Smith and Smoot\textsuperscript{3}.

The structural parameters of PRB selected samples were determined by cross-polarization/magic angle spinning, CPMAS with dipolar dephasing, solid state $^{13}$C NMR\textsuperscript{28-30}. The fractional compositions of carbon atoms hybridizations are provided for selected coal samples in **Table 3-4**. Both of these coals are similar in structure. From **Table 3-4**, the aromaticity ($f\alpha'$) for the APS coal was 55\%, after carbonyl correction, with a very similar value for PSOC-1488.
Table 3-4. Average aromatic carbon structural parameters for Powder River basin samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>f\textsubscript{a}</th>
<th>f\textsubscript{a}'</th>
<th>f\textsubscript{a}\text{\textsuperscript{C}}</th>
<th>f\textsubscript{a}\text{\textsuperscript{H}}</th>
<th>f\textsubscript{a}\text{\textsuperscript{N}}</th>
<th>f\textsubscript{a}\text{\textsuperscript{P}}</th>
<th>f\textsubscript{a}\text{\textsuperscript{B}}</th>
<th>f\textsubscript{al}</th>
<th>f\textsubscript{al}\text{\textsuperscript{H}}</th>
<th>f\textsubscript{al}\text{\textsuperscript{N}}</th>
<th>f\textsubscript{al}\text{\textsuperscript{B}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>WY (subC)</td>
<td>*APS</td>
<td>0.63</td>
<td>0.55</td>
<td>0.08</td>
<td>0.17</td>
<td>0.38</td>
<td>0.08</td>
<td>0.14</td>
<td>0.16</td>
<td>0.37</td>
<td>0.27</td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dietz (subB)</td>
<td>PSOC 1488</td>
<td>0.64</td>
<td>0.56</td>
<td>0.08</td>
<td>0.19</td>
<td>0.37</td>
<td>0.09</td>
<td>0.15</td>
<td>0.13</td>
<td>0.36</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Fraction of sp\textsuperscript{2}-hybridized (aromatic) carbon (error estimated)*: f\textsubscript{a} = total aromatic carbon (±0.03); f\textsubscript{a}' = total aromatic carbon in an aromatic ring (±0.04); f\textsubscript{a}\text{\textsuperscript{C}} = carbonyl, d > 165 ppm (±0.02); f\textsubscript{a}\text{\textsuperscript{H}} = protonated and aromatic (±0.03); f\textsubscript{a}\text{\textsuperscript{N}} = non-protonated and aromatic; f\textsubscript{a}\text{\textsuperscript{P}} = phenolic or phenolic ether, d = 150 – 165 ppm (±0.03); f\textsubscript{a}\text{\textsuperscript{B}} = aromatic bridgehead (±0.04). Fractions of sp\textsuperscript{3}-hybridized (aliphatic) carbon (error estimate): f\textsubscript{al} = total aliphatic carbon (±0.02); f\textsubscript{al}\text{\textsuperscript{H}} = CH, CH\textsubscript{2} or non-protonated (±0.02); f\textsubscript{al}\text{\textsuperscript{O}} = CH\textsubscript{3} (±0.02); f\textsubscript{al}\text{\textsuperscript{b}} = bonded to oxygen, d = 50–90 ppm (±0.02). *APS, the Argonne data from Argonne Premium Coal Sample Program. Sources: Solum et al. and Orendt et al. \textsuperscript{30, 31}.

Additional NMR derived data are presented in Table 3-5. The mole fraction of peripheral aromatic carbons per cluster (x\textsubscript{b}) was obtained by, (x\textsubscript{b} = 1-x\textsubscript{p}= 0.710). This value represents the aromatic H/C atomic ratio of Wyodak-Anderson coal, calculated from NMR structural parameters assuming linear catenation\textsuperscript{30}. Based on these data there are an average of 14 aromatic carbons per cluster or about 3 aromatic rings (e.g. phenanthrene). For WY, the average molecular weight of 408 amu was determined including the bridge mass per cluster attachments\textsuperscript{30}. A lower average molecular weight of 310 amu for Dietz subbituminous coal was reported by NMR parameters\textsuperscript{30}. Significant variation between WY and Dietz molecular weight per cluster are obtained from aromatic mole fraction structural features, Table 3-5.

Table 3-5. Aromatic cluster parameter for Powder River basin selected samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>x\textsubscript{b}</th>
<th>AC/CL</th>
<th>σ+1</th>
<th>P\textsubscript{o}</th>
<th>BL</th>
<th>M\textsubscript{d}</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>WY (subC)</td>
<td>*APS</td>
<td>0.29</td>
<td>14</td>
<td>5.6</td>
<td>0.55</td>
<td>3.1</td>
<td>42</td>
</tr>
<tr>
<td>Dietz (subB)</td>
<td>PSOC 1488</td>
<td>0.23</td>
<td>11</td>
<td>4.7</td>
<td>0.54</td>
<td>2.5</td>
<td>37</td>
</tr>
</tbody>
</table>

x\textsubscript{b} = mole fraction of bridgehead carbons; AC/CL = average number of aromatic carbons per cluster; σ+1 = number of attachments per cluster of the coordination number; P\textsubscript{o} = mole fraction of intact bridges; BL = number of bridges and loops on a cluster; MW = total molecular weight of a cluster, M\textsubscript{d} = bridge mass per attachment on a cluster. *APS, the Argonne data from Argonne Premium Coal Sample Program. Sources: Solum et al. and Orendt et al. \textsuperscript{30, 31}.
For low-rank coals a wide range of oxygen functionalities has been studied\textsuperscript{32}. Oxygen functionality is important as these interactions influence the structural properties of subbituminous coals in coal-liquids\textsuperscript{33}, and pyrolysis conversion technologies\textsuperscript{34}. Furthermore, some inorganic elements are commonly associated with these oxygen functionalities in low-rank coals\textsuperscript{35}. The analyses of oxygen functional groups, for Wyodak-Anderson subbituminous coal, are well studied by different analytical approaches. Among them are Fourier transform-infrared (FTIR)\textsuperscript{36, 37}, fast neutron activation analysis (FNAA)\textsuperscript{38}, and ion exchangeable techniques\textsuperscript{33} among others. In Table 3-6 fraction distributions of the oxygen functionality for Wyodak-Anderson coal was calculated by FNAA\textsuperscript{39}. For WY coal, based on total organic oxygen 14 wt\%, more than 50\% is present as hydroxyl forms, 23\% carboxylic groups, 5\% carbonyl, and 18\% ether were reported\textsuperscript{72}.

### Table 3-6. Oxygen functional groups distribution for Wyodak-Anderson subbituminous coal by fast neutron activation analysis (dry wt\%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total organic O wt%</th>
<th>O wt% as COOH</th>
<th>O wt% as OH</th>
<th>O wt% as C=O</th>
<th>O wt% as ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>WY APS</td>
<td>14.31</td>
<td>3.33</td>
<td>7.68</td>
<td>0.74</td>
<td>2.56</td>
</tr>
</tbody>
</table>

APS, the Argonne data from Argonne Premium Coal Sample Program.  
Source: Jung et al.\textsuperscript{38}

The hydroxyl forms or phenolic groups [Ar-OH] in subbituminous coals were found to be >45\% of the total oxygen by acetylation methods\textsuperscript{40, 41}. Yarzab et al. reported variation of phenolic content with coalification, where subbituminous coals varied from 34 to 46 OH\% of the total oxygen in dry, mineral matter free basis\textsuperscript{42}. For Belle Ayr subbituminous coal were obtaining 47\% phenolic oxygen of the total oxygen by acetylating in pyridine at 90°C\textsuperscript{32, 41}. The silylation method replace the hydrogen, in phenolic groups, with silicon label compound
trimethylchlorosilane in pyridine solvent give similar results. Determination of carboxylic acid [Ar-COOH] for subbituminous coals were obtained via exchange of barium Ba(ac) acid-treatment. Kashimura et al. determined the carboxylic composition for Wyodak-Anderson coal, ~20% of the total oxygen. For Belle Ayr subbituminous coal 36% carboxylic acid of the total oxygen was determined by ion exchange using calcium acetate. Nuclear determination gave 23% carboxylic acid of the total organic oxygen for Wyodak-Anderson subbituminous coal determined by FNAA.

The reaction between carbonyl groups [Ar-C=O] and hydroxylamine (OHNH₂) produces oxime (R₂-C=NOH), H₂O, and HCl. Difference between oxime derivates and oxime decomposed by sulfuric acid provide the content of [Ar-C=O] to be approximated. For Belle Ayr subbituminous coal was found to be 8% [Ar-C=O] of the total oxygen. Some 5% carbonyl groups of the total organic oxygen for Wyodak-Anderson subbituminous coals were determined from FNAA. Analysis of open ethers (Ar-O-Ar or Ar-O-C₆H₄) corresponding to the amount of ether cleavage in subbituminous coals were determined by Zeisel method, refluxing coal in hydrogen iodide at 130°C, with SiCl₄-NaI. The Zeisel method gave 7% ether groups of the total oxygen in Belle Ayr subbituminous coal.

For WY, and Dietz subbituminous coal observation of subtle changes in aliphatic carbons bonded to oxygen (f₀) was observed by C-NMR structural parameters, Figure 3-2. For Dietz coal decrease of f₀ can be related to the reduction bridge mass between clusters (per attachments) compared to WY coal. However, no changes on WY and Dietz coal were observed from fractional aromatic carbon bonded to phenolic/phenolic ether (fₚ) and aromatic carbon fraction of carbonyl (f₃).
Determinations of close-ether, referred as nonreactive oxygen, were determined by difference between total oxygen and total functionalities (Ar-OH + Ar-C=O + Ar-COOH + Ar-O-Ar). The presence of close ethers were reported by Flash pyrolysis gas chromatography mass spectrometry (flash-Py-GCMS) producing pyran compounds that can be derived from dibenzofuran as intact molecule in subbituminous coalified wood macromolecular\textsuperscript{46}.

\textbf{Figure 3-2.} Structural distribution of C-O forms in Wyodak-Anderson subbituminous coal (APS\textsuperscript{*}) and Dietz subbituminous coal (PSOC 1488). $f_a^C =$ aromatic carbon atoms bonded to carbonyl; $f_a^P =$ aromatic carbon atoms bonded to phenolic/phenolic ether; $f_a^O =$ aliphatic carbon atoms bonded to oxygen. Source: Solum et al.\textsuperscript{30}, and Smith and Smoot\textsuperscript{3}.

In summary the distribution forms of oxygen functionality for WY coal and PRB selected samples are: >50% Ar-OH, carboxylic range from 20-25% Ar-COOH, carbonyl range from 5-8% Ar-C=O, and ethers ~19% Ar-O-X of the total oxygen. The distribution as well as the spatial arrangements of organic-inorganic interactions, e.g. $-\text{COO-M}^+$, $-\text{COO-M}^{2+}$OH, $-(\text{COO})_2\text{M}^{2+}$, where M is an alkali (Na\textsuperscript{+}, K\textsuperscript{+}) or alkaline (Ca\textsuperscript{42}, Mg\textsuperscript{42}) earth metal, influences coal-to-liquids\textsuperscript{47, 48}, and pyrolysis conversion processes. Some, 62% Na and 4% Ca from Wyodak-Anderson coal was removed by H\textsubscript{2}O. The organic-Na interactions are in the forms of $-\text{COOM}^+$, and the
organic-Ca interactions types are in the forms of –COO⁻ Ca⁺² OH⁻, -(COO)₂ Ca⁺². NH₄Ac removed some 33% of the Na and 34% of the Ca. An increase in Wyodak-Anderson coal direct liquefaction conversion yields from 69 to 76% was observed with the removal of NH₄ ion-exchangeable cation⁴⁷. Evidence of higher yields in dematerialized Wyodak-Anderson subbituminous coal was recorded with crude methylnaphthalene oil⁴⁵.

WY Subbituminous coals and PRB selected coal samples contain high level of water within their structures, the as-received moisture values range from 28 to 21%³. For WY coal there is 27% moisture as-received and 18.5 wt% oxygen by differences, dmmf. There are, as a simplification, four forms of water within coal: superficial free water (freezeable), capillary condensed water (non-freezable), sorbet water associated with polar group and cations, and water released by chemical decomposition of organic or inorganic matter⁴⁹-⁵¹. Characteristics of water in Wyodak-Anderson subbituminous coal were calculated by low-temperature heat capacity analysis¹¹, and NMR techniques¹⁰. For WY coal, two forms of water, with different heat-capacity values are observed as non-freezable and freezeable water¹⁰,¹¹. Approximately, 39 g of H₂O per 100 g of dry WY coal loading 40% is bulk, and 60% it is probable bound water to the coal-oxygen via hydrogen bonding¹¹,⁵².

Total sulfur has contributions from both the inorganic sulfur (e.g. pyrite, and mineral sulfates), and the organic sulfur. Typically total sulfur for subbituminous western basins coals range from 0.3-2 wt%⁵³. For WY coal, the elemental analysis of total and organic sulfur (% dry basis) of 1.21%, and 1.15% was observed. The organic sulfur, made more than 80% of the total sulfur forms, important structural characteristics of organically bound sulfur were quantified by two different X-ray techniques. Unique, distribution values for species (nitrogen, and sulfur) in coals
were obtained by the K-edge X-ray absorption near-edge structure spectroscopy (XANES)\textsuperscript{54}, and the X-ray photoelectron spectroscopy (XPS) respectively\textsuperscript{55}. For Wyodak-Anderson coal, 63\% of the organic sulfur was thiophenic and the remainder 37\% was bound to aliphatic\textsuperscript{56}. Interpretations of the X-ray spectra data requires species model compounds capable to describe sulfur compounds binding energy. Thus, for WY coal a good agreement between organically attached sulfur compounds like (dibenzyl sulfide, 2,5-dimethylthiophene and diphenyl sulfur) and experimental data was observed\textsuperscript{56}. It appears that sulfur content affects liquefaction yields. Generally high-rank coals with unusually high total sulfur content 6-10 wt\% (also often in high organic sulfur) gave higher yields than low-rank coals with total sulfur range 0.3-2 wt\%, a reversal of expected trends\textsuperscript{57}. Analyses of the yields and products from different coal ranks provided insight into the role of thiophenic compounds and these higher conversion yields\textsuperscript{40,41}.

The amount of total nitrogen in WY, and PRB subbituminous coal samples range from 1-2\%\textsuperscript{58}. Determination of nitrogen functional groups and composition were calculated from XPS spectrogram high, middle and low energy peaks\textsuperscript{59,60}. For WY coal, nitrogen functionality and distribution mole percentage of 16\% quaternary, 56\% pyrrolic, and 23\% pyridinic were observed\textsuperscript{60}.

Coals macromolecular networks are often based on a two-part system; the mobile-phase, and the immobile-phase components\textsuperscript{61,62}. The mobile-phase components with low molecular weight are easily liberated by mild thermal treatment or by strong basic solvents such as pyridine solvents\textsuperscript{63}. It is assume that pyridine extracts were impounded to the immobile-phase macromolecular structure by secondary interactions (hydrogen bonding and dipole-dipole interactions)\textsuperscript{64}. Thus, each solvent interaction provides unique information on coals molecular components.
distribution. For WY coal, 7.4 wt% pyridine yield moist and ash free basis was observed. The aromatic pyridine fractionation yields were analyzed by capillary column gas chromatography coupled with mass spectrometry. Some of the aromatic compounds detected by GC/MS resemble the average aromatic cluster size of Wyodak-Anderson coal obtained from \(^{13}\text{C}\) NMR structural parameters such as aromatic carbon per cluster was 14. The mean of 460 Da and the average molecular weight of 1,480 Da for WY coal were determined from size exclusion chromatography (SEC). Hayatsu et al. used SEC technique to separate coal molecular mass compounds existence in the yield of pyridine extracted (% dmmf) from soluble fraction of THF. This fraction of pyridine extracts contains a broad range of molecular mass. Thus, better representation of continuum structure as coal molecules non-covalent bonded to coal macromolecular networks is observed from these pyridine extracts.

Considerable amount of oxygen functional groups (phenolic –OH, and carboxylic –COOH) were found through different THF-fractions (alkali-soluble) in moisture and ash-free values basis. WY raw atomic H/C ratio of 0.83 was exposed to reagent potassium-crown ether producing THF-fraction of 7.38 wt% solubility contents an atomic H/C ratio of 1.37 was observed. These extractions retrieve hydrocarbon materials, bonded to oxygen functional groups, via cleavage or non-covalent interactions. Some, 68% yields for WY subbituminous coals were obtained by THF alkali-soluble extractions under potassium-crown ether.

The matrix-assisted laser desorption ionization (MALDI) mass spectrometry was used to estimate the molecular mass distribution of the coal samples. This technique has a mass capacity spectrum range of 270,000 Da, with two different resolution modes. The linear mass resolution mode is at 400 Da provided high sensitivity for low molecular mass compounds. The reflector
mode has a higher mass range. The MALDI mass spectra for Wyodak-Anderson coal was observed by linear mode at two different laser power levels. In Figure 3-3a MALDI mass spectra for Wyodak coal showing a broad molecular mass range in 400-1,400 Da\textsuperscript{67}. The intense peak is 410 Da at laser power level 11\textsuperscript{67}. Higher power MALDI-MS spectra for WY coal with molecular fragments >20,000 Da is shown, Figure 3-3b.

![Figure 3-3. (a)MALDI mass spectra of Wyodak-Anderson subbituminous coal at laser power level 6. (b) MALDI mass spectra for high molecular mass of Wyodak-Anderson coal at laser power level 26. Source: Herold et al.\textsuperscript{67}](image)

The average data relating aromatic stacking, and aromatic ring size in coals were determined by XRD analyses\textsuperscript{16}. Since, the presence of aromatic molecules in subbituminous coal was confirmed by XRD analyses and observed by TEM techniques. High-resolution transmission electron microscopy (HRTEM) was used to describe distribution of coals aromatic structural parameters such as, interlayer spacing (d-spacing), aromatic molecular sizes, and number of aromatic molecules per stack\textsuperscript{13,68}. These values reflect contributions to the surface area across the pore size range. Small-angle X-ray scattering (SAXS) has also been used to determine size, shape, and orientation of pores\textsuperscript{69-71}. Advanced HRTEM image algorithm analysis provide unique information in coal ranks aromatic structural diversity based on lattice fringes images\textsuperscript{72-74}. Some HRTEM image analysis for Argonne Premium sample such as; Beulah-Zap, Illinois #6, Upper
Freeport, and Pocahontas coals had been studied\textsuperscript{75,14, 76}. Unfortunately, no HRTEM images for Wyodak-Anderson subbituminous coal, or any PRB coal have been generated. While many others coal properties change with coalification, unvarying average fringe lengths of \~7Å occurs between coals with a carbon content range (~73 wt% to ~80 wt% dmmf) were observed by HRTEM lattice fringe images\textsuperscript{14, 75}. For WY coal, the expectations are that the lattice fringe images quantitative data should be equivalent to Beulah-Zap lignite coal. The aromatic molecular weight distribution for Wyodak-Anderson subbituminous coal was calculated from Beulah-Zap lignite HRTEM lattice fringe images analysis, published by Sharma et al\textsuperscript{75}. **Figure 3-4a and 3-4c** shows Beulah-Zap and Illinois #6 HRTEM lattice fringe images\textsuperscript{75}. There lattice fringe image analysis is shown in **Figure 3-4b and 3-4d**, respectively, each fringe is an edge view of planar aromatic molecules that are quantified by image analyses in fringes length, interlayer spacing, stacks, and orientation\textsuperscript{73, 75, 77}.

**Figure 3-4.** (a) HRTEM image for Beulah-Zap lignite coal. (b) Beulah-Zap lattice fringe image after filtration technique. (c) HRTEM image for Illinois #6 coal. (d) Illinois #6 lattice fringe image after filtration technique. Source: Sharma et al.\textsuperscript{75}
Assumption on fringe length range from 3.6 to 4.75Å were considered to be naphthalene, has been proposed\textsuperscript{14, 72}. Agreement between high aromaticity molecules and increasing fringe length were observed by char formation between XRD and HRTEM techniques. Different HRTEM model compounds, for example coronene, reproduced appropriate average fringe length of \textasciitilde 9Å, yet a distribution of fringe lengths were observed from coronene HRTEM lattice image, when a single length of 9Å was expected\textsuperscript{78, 79}. Although, HRTEM provided direct observation of fringe sizes and spatial orientations, some fringes in coal cannot be considered legitimate. In particular for subbituminous coals, <60% fraction of aromatic carbon, the lack of well define aromatic plane are expected for subbituminous coals HRTEM lattice fringe image\textsuperscript{80}. It is also possible for fringes to overlap to cause artificially long fringes, not supported by NMR or other experimental observations.

The helium density for Wyodak-Anderson is 1.45 g/cm\textsuperscript{3} and 1.46 g/cm\textsuperscript{3} for the Dietz coal on a dmmf basis\textsuperscript{81}. Coal physical properties such as: surface area, pore volume, and pore size distribution (macropores, mesopores, and micropores systems) are constituted by coal chemical structural parameters such as aromatic cluster, and oxygen functional groups spatial arrangements among others\textsuperscript{70}. The surface area as measured by gas adsorption is shown in Table 3-7. These coals have similar surface areas: 206 and 218 m\textsuperscript{2}/g of CO\textsubscript{2} surface area by the Dubinin and Radushkevich method\textsuperscript{9} and from 3 to 5 m\textsuperscript{2}/g of N\textsubscript{2} derived surface area by BET equation method\textsuperscript{9}.
Table 3-7. Surface Area for Wyodak-Anderson subbituminous coal and Powder River basin selected sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>CO₂</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>WY (subC)</td>
<td>APS*</td>
<td>206</td>
<td>5.0</td>
</tr>
<tr>
<td>Dietz (subB)</td>
<td>PSOC 1488</td>
<td>218</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*APS, the Argonne data from Argonne Premium Coal Sample Program (daf basis).
(Source: Smith and Smoot³).

Subbituminous Coal Molecular Modeling Overview

In coal science, higher-rank coal structural model representations are most common. Given the importance of subbituminous coal and the significant amount of analytical data is available, it is surprising that only a few structural models were constructed⁸²-⁸⁵. The construction of the Shinn’s⁸⁶ subbituminous models was made from direct liquefaction yield and products compositions analyses in a similar manner to his more renowned bituminous model⁸². Figure 3-5(a) shows Shinn’s subbituminous model, the “general” formula of C₆₆₁ H₅₆₁ O₇₄ N₄ S₆, and a molecular weight of 9,935 Da⁸⁶. The application to studies of coal conversion processes based on Shinn’s subbituminous structure model was limited. However, Shinn’s bituminous model⁸² is one of the most cited in coal science. The Taiheiyo subbituminous structural model in Figure 3-5(b) shows a small continuum of structures. The “general” formula of C₅₂₂ H₅₂₉ O₇₅ N₇ S₁ and the molecular weight of 8,127 Da for Taiheiyo subbituminous coal model⁸⁷. Both models lack significant structural parameters such as reasonable diversity range of molecular mass, interlayer spacing, stack distribution, and orientations of aromatic molecules that are required for improved simulation methods. Also, neither of the subbituminous coal structures facilitates the integration of water forms and inorganic-organic interactions as part of the structural range. Although, cations and water has been included in small-scale low-rank coal⁸⁸-⁹⁰, and water in high-rank coal models⁹¹.
The structural units model of subbituminous coal coalified wood samples are based on NMR structure parameters and known lignin chemistry\(^9\). Figure 3-6(a) and 3-6(b) show a modified model showing coalification changes. Hatcher’s models were developed to understand specific chemical reactions through coalification stages based on lignin-guaiacyl structural unit as a main precursor of vitrinite types\(^9\). Oxygen loss was determined for lignite to subbituminous coalified wood samples with the structure transformation being from cathecol compounds to phenols or alky-phenols\(^{46}\). Therefore, one possible description as increase in aromatic parameters (ring condensation and attachment reduction) was due to the loss of oxygen functional groups\(^{46,94}\).
Figure 3-6. (a) Coalified wood basis on lignin structural unit to model subbituminous coal rank ($C_{89}H_{80}O_{14}$). (b) Structural model for subbituminous coalified wood modified ($C_{87}H_{78}O_{14}$). The (R) indicate cross-link sites to other (R) letters. Sites R3 and R4 are cross-links to the coal macromolecules. Sources: Hatcher et al.46,93

In summary, relatively small-scale model exist for subbituminous coal that were constructed by-hand. An approach that would allow large-scale model construction within reasonable expenditure of time and cost, with improved accuracy, would be beneficial to explore the science of subbituminous coals.

Model Construction & Evaluation

The HRTEM lattice fringe micrographs were provided by Sharma et al75. The scale bar was used to calibrate the images. Data for fringes length, momentum angle, Cartesian coordinates center point, and nearest-neighbor distances between center points were determined from image analysis techniques. A Perl script was written to create a 2D slice model directly from lattice fringe images (Fringe3D). Figure 3-7 shows the sequence from raw HRTEM images to 3D molecular representations. The contribution of Fringe3D was converting large amount of quantitative and average numerical values from two-dimensional coordinates into three-dimensional space in a few second. From the image analysis the center of mass of each fringe was determined and converted into a centroid in three-dimensional space. Atoms are populated
around this centroid from either a named molecule or catenation files. These files were generated within modeling software, assigned a centroid and sent to the 0, 0, 0 location. The molecule was flipped 90° so it resided flat in the z-plane. Thus, the centroid placement from the image analysis of the molecule could be created at that location. Basically, every atom in a given plane or space was assigned a vector from the origin (unit point mass) or centroid. Thus, the 3D aromatic molecules reproduced HRTEM image data (e.g. fringe angle of momentum), and others parameters were converted to 3D space. For catenation files a similar process was performed with the additional step of renumbering the carbon atoms such that any number of carbon atoms could be selected and the resultant structure would grow ring-by-ring with the addition of between 3-4 carbon atoms (depending on location of ring). Thus, the stacking, slight orientation, and fringe lengths are directly captured, including the diversity of those structural features. To increase the “organic” nature of the representation generated molecules could also be rotated around their centroid, like a wheel rotating around its hub, so a diversity of orientations could be included.
Figure 3-7. Integrated Fringe3D and sequence of events generate three-dimensional models from HRTEM lattice fringe image.

For subbituminous coals, when there is a continuum of fringe lengths observed, extreme fringe lengths (for example assuming > 50 aromatic carbons per clusters) are not supported by other analytical methods. Others analytical techniques show that aromatic molecules have an average composition of 3 fused aromatic rings. Artificially long fringe lengths and filter image threshold values, overlapping aromatic molecules, and disclamations among others can produce curvature. The HRTEM 002 lattice fringe image is made from electron interactions (diffractions) with separation distance (d-space) between two or more parallel aromatic molecules, characteristics of Bragg’s conditions. Therefore, it is possible for two or more fringes can be merged into one large fringe. These fringes will generate large amount of aromatic carbons significantly increasing the
aromatic structural parameters such as fraction of bridgehead carbons affecting the entire molecular mass distribution. Misleading hydrogen distributions among the structural fragments could be obtained. Heteroatom and scattered electrons not fulfilling Bragg’s diffraction conditions are in part responsible for discontinuity in fringe lengths, assumed aromatic layers, thus not visible on HRTEM micrograph.

A rational approach was systematically implemented to reject unreasonable regions containing longer fringe lengths. Aromatic parameters for the generated aromatic WY model, directly generated from HRTEM lattice fringe, the fraction of bridgehead carbons $f_a^B$ of 0.39 far exceeding the amount of low-rank coals reported by $^{13}$C-NMR for Beulah-Zap lignite and Wyodak-Anderson subbituminous coals, range in 0.09 and 0.16, respectively$^{30}$. Since, the model overestimates $f_a^B$, resulting in mole fraction of bridgehead carbons ($x_b$) of 0.34, thus aromatic $H/C$ ratio is 0.61 for WY model. Agreement between $x_b$ WY aromatic model and experimental $13$C-NMR mole fraction for WY coal is required for WY coal model to maintain consistency structural information with others analytical methods. The outer edge of the micrograph had a region with longer fringe lengths sample$^{18, 95, 96}$. This region is shown within the red box of Figure 3-8(a). The red boxes (50Å lengths and 176Å heights) were divided in five slices each 10Å length, indicated by roman numbers in Figure 3-8(a). The roman numbers identify rejected fringes with cutoff lengths from (I) 10Å to (V) 50Å into the micrograph.
Figure 3-8. (a) Color map of HRTEM lattice fringe image, and selection of fringes areas (roman numbers). Adaptation of color map was made to original HRTEM images published by Sharma et al. (b) Average mole fraction of bridgehead carbons corresponding to the selection of fringes areas deleted, (roman numbers).

Figure 3-8(b) show average mole fraction of bridgehead carbons ($x_b$) is observed by increasing cutoff edge-lengths. Fringe length data and average aromatic carbon data are shown in Table 3-8. The model fraction of aromatic bridgehead carbons is significantly reduced by rejecting fringe from outer areas of the HRTEM image. A cutoff of 30Å was required to achieve good agreement with the rest of the micrograph and improved agreement between WY HRTEM mole fraction of bridgehead carbons and experimental NMR data. Approximately, 51 fringes were rejected from the original lattice image of 606 fringes due to “edge effects” of the zone not representing the interior of the micrograph. The extracted fringes, aromatic 0.34 H/C atomic ratio, reveals a highly aromatic condensed structure were extracted from the original images.
Table 3-8. Amount of aromatic molecules extracted from original lattice fringe image per cutoff edge-lengths (roman numbers).

<table>
<thead>
<tr>
<th>Cutoff-length (Å)</th>
<th>Fringes extracted</th>
<th>Aromatic H/C ratio extracted</th>
<th>Average extracted fringe lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (no cut)</td>
<td>0</td>
<td>0.66</td>
<td>7.5</td>
</tr>
<tr>
<td>10 (I)</td>
<td>8</td>
<td>0.30</td>
<td>15</td>
</tr>
<tr>
<td>20 (II)</td>
<td>22</td>
<td>0.35</td>
<td>13</td>
</tr>
<tr>
<td>30 (III)</td>
<td>21</td>
<td>0.38</td>
<td>11</td>
</tr>
<tr>
<td>40 (IV)</td>
<td>27</td>
<td>0.45</td>
<td>10</td>
</tr>
<tr>
<td>50 (V)</td>
<td>43</td>
<td>0.30</td>
<td>11</td>
</tr>
</tbody>
</table>

Statistical analysis of lattice fringe images shows consistent average fringe length values of 0.7nm for coal with a carbon contents between (74-82wt%) was reported by Sharma et al. For WY model, the average fringe length of 0.76nm was determined from digital image statistical analyses. Close agreement between different experimental and model digital image statistical techniques was observed from the same HRTEM lattice fringe images. A cutoff lengths range for fringes >15Å and <1.8Å were introduced. These types of fringe morphology are “not” expected based on evidence from others analytical techniques. For WY model, ~27% of the fringes in HRTEM lattice fringe image were removed. However the possibility if their existences are related to coalification stages within inertinite maceral composition is not discarded. Thus, following additional image processing lattice fringe image data such as momentum, and fringe length distributions were utilized in model construction. Aromatic moiety data agreed with experimental expectations prior to construction.

Figure 3-9 shows the sequence for model construction. Fringe3D was used to develop and model aromatic structural features of WY coal according to HRTEM lattice fringe images, $^{13}$C NMR structural parameters, and elemental analysis. The formation of 3D aromatic “Slice” model for WY coal was obtained from Fringe3D. Due to the large-scale model this approach can
generate a new approach for heteroatom inclusion was created using Perl scripts within the molecular modeling program.

**Figure 3-9.** Information flow model construction.

**Figure 3-10,** shows the approach used for the addition of aliphatic, oxygen functional groups, and heteroatom functionality. Due to the model scale it was desirable to create an automated process for the population of heteroatom and aliphatic components to the aromatic core structure. See Appendix B for actual script.
Cross-linking was performed using manual approach based on a statistical evaluation of fringe connectivity to yield an appropriate (match) molecular weight distribution. Water incorporation was achieved via two approaches: inclusion of bounce-water through heated ice block addition and sorption simulation run to add bulk-water. Four sections of roughly cubic shape was separated and populated within the model prior to 3D atomistic construction. Following 3D model generation but prior to minimizations (larger-scale simulation box) sorption module was used to add 500 water molecules in energy minima configurations (mostly hydrogen bound to oxygen functionality). An excess of water was added to accommodate expected association with the bulk-water present.

Model evaluation was performed with a variety programming Perl scripts and simulations. Scripts that evaluated the $^{13}$C-NMR parameters, molecular weight distribution, hydrogen bonding count, and solubility calculations had been created in previous work$^{97}$. Slight additions
to the force field parameters were added to accommodate subbituminous coal functionality. Briefly, the Perl scripts interrogated the force field assignments for calculations of chemical environment for NMR parameter determination for comparisons with Solum et al.\textsuperscript{30}. Similarly, solubility was calculated, according to summation approach, by Painter et al.\textsuperscript{98}. Molecular weight for each molecule was determined from its atomistic composition.

**Results and discussion**

The agreement between a variety of chemical and physical evaluations for Powder River coal samples (specifically WY and Dietz subbituminous coals) was model was determined. In summary, for WY coal, the average molecular weight range was observed by $^{13}$C-NMR, and LDMS between 400-480amu. The average amount of aromatic carbon per cluster was 14. On average the aromatic molecule consisting of 3 aromatic rings and 4 bridgehead carbons were similar to phenanthrene ($C_{14}H_{10}$). Macerals are mostly humite/vitrinite (89%) with little contributions (<1%) from liptinite. The sulfur content was 63% thiophenic and the nitrogen form 60% pyrrolic. Pyridine extractable material in Wyodak-Anderson coal was 7.4 wt% (39% being aromatics such as naphthalene like compounds of less than 4 aromatic rings). Some 39 g of H$_2$O per 100 g of dry coal of which 66% is bound water was reported. Major cations are sodium and calcium.

For WY coals, phenolic >50% of the total oxygen was observed. Carboxylic acids range 18-23% was determined from ion-exchange and FNAA techniques for WY coals. The composition of 5% carbonyl groups, and 18% open ethers of the total oxygen for WY coals were determined from FNAA technique. The close ethers were reported as the differences between total oxygen and total oxygen functionalities, suggested 1% of the total oxygen. Trace (less than 1%) or non methoxy were found in Wyodak-Anderson subbituminous coals\textsuperscript{99}. Good agreement between
average atomic 0.84 H/C ratio and WY model 0.85 H/C ratio was observed, additional H/C ratio, and “general” formula for different coals samples are provided on Table 3-9.

Table 3-9. General formula for Powder River Basin selected samples and Wyodak-Anderson subbituminous coals model.

<table>
<thead>
<tr>
<th>Samples</th>
<th>State</th>
<th>Empirical Formula a</th>
<th>Atomic H/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>WY (subC)</td>
<td>Wyoming</td>
<td>C_{1000}H_{850}N_{13}S_{2}O_{180}</td>
<td>0.85</td>
</tr>
<tr>
<td>Dietz (subB)</td>
<td>Decs 38</td>
<td>C_{1000}H_{830}N_{11}S_{2}O_{150}</td>
<td>0.83</td>
</tr>
<tr>
<td>Dietz (subB)</td>
<td>PSOC 1488</td>
<td>C_{1000}H_{820}N_{11}S_{3}O_{169}</td>
<td>0.82</td>
</tr>
<tr>
<td>WY Model</td>
<td></td>
<td>C_{1000}H_{850}N_{13}S_{2}O_{188}</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table 3-9: General formula for Powder River Basin selected samples and Wyodak-Anderson subbituminous coals model.

*Empirical formula based on 1000 carbon atoms per “formula weight” as dry, mineral-matter free basis.
*APS is the Wyodak-Anderson coal, (PSOC) Argonne data from Argonne Premium Coal Sample Program.

A Wyodak-Anderson subbituminous coal model was created and evaluated. The model total amount of carbon was 11,040. The general formula of C_{11,038}H_{9,357}N_{138}S_{26}O_{2,063} was obtained for WY model. Aromatic parameters of 57% of total aromatic carbon were obtained. This fraction of aromatic carbon is a good representation of the NMR 55% of total aromatic carbon for subbituminous coals reported in literature\(^{30}\). The aliphatic carbons represent 37% of the model total carbon. Agreement between WY model and experimental data was observed. The average molecular mass for Wyodak subbituminous coal was obtained from different analytical techniques such as HRTEM, \(^{13}\)C-NMR, LDMS, and GC/MS analysis pyridine extract. Approximately 272 associated molecules, with average fraction of aromaticity of 63% of total carbon were calculated from HRTEM lattice fringe. Similar values are observed by NMR average aromatic structural parameters. Comparison between the NMR average structural parameters for WY model and experimental selected samples are provided in Table 3-10\(^{30}\). The fraction of aromatic carbons protonated and non-protonated for WY model are represented.

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by 64% aromatic (~6,954 sp\(^2\)-carbon) and 37% aliphatic (~4,082 sp\(^3\)-carbon) of the total amount of carbon. For Wyodak-Anderson subbituminous coals, corrected fraction of aromaticity \(f_a\)' of 0.58 is equivalent to 6,349 carbons\(^{30}\). This fraction is divided in protonated (\(f_a^H\)), and non-protonated aromatic carbons (\(f_a^N\) \(^{30}\)), more fraction values are illustrated in **Table 3-10**. The fraction of protonated carbons of ~0.18 for WY model was generated by ~1,088 (Ar-H).

**Table 3-10.** Carbon structural parameter distribution of Powder River basin selected samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>(f_a)</th>
<th>(f_a')</th>
<th>(f_a^C)</th>
<th>(f_a^H)</th>
<th>(f_a^N)</th>
<th>(f_a^P)</th>
<th>(f_a^S)</th>
<th>(f_a^B)</th>
<th>(f_a^H)</th>
<th>(f_a^N)</th>
<th>(f_a^O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WY (subC)</td>
<td>0.63</td>
<td>0.55</td>
<td>0.08</td>
<td>0.17</td>
<td>0.38</td>
<td>0.08</td>
<td>0.14</td>
<td>0.16</td>
<td>0.37</td>
<td>0.27</td>
<td>0.10</td>
</tr>
<tr>
<td>Dietz (subB)</td>
<td>0.64</td>
<td>0.56</td>
<td>0.08</td>
<td>0.19</td>
<td>0.37</td>
<td>0.09</td>
<td>0.15</td>
<td>0.13</td>
<td>0.36</td>
<td>0.25</td>
<td>0.11</td>
</tr>
<tr>
<td>WY Model</td>
<td>0.64</td>
<td>0.58</td>
<td>0.06</td>
<td>0.18</td>
<td>0.40</td>
<td>0.10</td>
<td>0.13</td>
<td>0.17</td>
<td>0.35</td>
<td>0.27</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Fraction of sp\(^2\)-hybridized (aromatic) carbon (error estimated): \(f_a\) = total aromatic carbon (±0.03); \(f_a^C\) = total aromatic carbon in an aromatic ring (±0.04); \(f_a^H\) = carbonyl, d > 165 ppm (±0.02); \(f_a^N\) = protonated and aromatic (±0.03); \(f_a^P\) = non-protonated and aromatic; \(f_a^S\) = phenolic or phenolic ether, d = 150 – 165 ppm (±0.03); \(f_a^B\) = aliphatic aromatic, 135 – 150 ppm; \(f_a^H\) = aromatic bridgehead (±0.04). Fractions of sp\(^3\)-hybridized (aliphatic) carbon (error estimate): \(f_a^O\) = bonded to oxygen, d = 50–90 ppm (±0.02). Sources: Solum et al\(^{30,31}\) and Smith and Smoot\(^{31}\).

Comparisons between experimental and model distributions of oxygen functional groups percentage are in **Table 3-11**. The model amount of total oxygen has slightly higher oxygen content compared to experimental data on similar dry-mineral-matter free basis. Approximately, 58% of WY model total oxygen is formed by hydroxyl functional groups exceeding experimental values of 53% hydroxyl on similar coals. Slightly lower content of carbonyl group in WY model compared to experimental data are illustrated in **Table 3-11**.
Table 3-11. Evaluation of oxygen functional groups distribution for Wyodak-Anderson subbituminous coals model were obtained from Wyodak-Anderson experimental data.

<table>
<thead>
<tr>
<th>Oxygen functionality</th>
<th>Total Oxygen</th>
<th>COOH</th>
<th>OH</th>
<th>C=O</th>
<th>Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental</strong></td>
<td>2,003 (100%)*</td>
<td>461 (23%)</td>
<td>1,061 (53%)</td>
<td>100 (5%)</td>
<td>381 (19%)</td>
</tr>
<tr>
<td><strong>Model Data</strong></td>
<td>2,083 (100%)</td>
<td>426 (21%)</td>
<td>1,213 (58%)</td>
<td>42 (2%)</td>
<td>402 (19%)</td>
</tr>
</tbody>
</table>

*Total oxygen for WY coal experimental data was calculated from elemental oxygen (18.03 wt% dmmf, basis), and normalize to 11,038 carbon.

Distribution of organic sulfur for WY subbituminous coal was determined from X-ray photoelectron spectroscopy (XPS) techniques. The total amount of sulfur was 26, and the distribution percentages are observed in Table 3-12. Determinations of nitrogen functionalities such as pyrrolic, pyridinic, and quaternary for WY coal were observed by X-ray angle near edge spectroscopy (XANES).

Table 3-12. Experimental and model evaluation for Wyodak-Anderson subbituminous coals heteroatom composition percentage.

<table>
<thead>
<tr>
<th></th>
<th>Pyridine</th>
<th>Pyrrolic</th>
<th>Quaternary</th>
<th>Thiophenic</th>
<th>Aliphatic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental</strong></td>
<td>63%</td>
<td>29%</td>
<td>8%</td>
<td>63%</td>
<td>37%</td>
</tr>
<tr>
<td><strong>Wyodak Model</strong></td>
<td>62%</td>
<td>25%</td>
<td>12%</td>
<td>68%</td>
<td>32%</td>
</tr>
</tbody>
</table>

Sources: Kelemen et al\(^{60}\).

The matrix-assisted laser desorption ionization (MALDI) mass spectrometry was used to estimate the molecular mass distribution of the Argonne Premium Coals selected sample. Close agreement was observed from WY model dominant peak of 386 m/z, and literature value of 410 m/z as dominant molecular mass. Furthermore, significant similarity between WY subbituminous coal model and literature values for distribution of continuum molecular mass and spectrometer shape curved model and literature mass-to-charge ratio are observed, see Figure 3-11(a), and Figure 3-11(b).
Figure 3-11. (a) Mass distribution for Wyodak coal showing a broad range 97-1,828 g/mol. (b) matrix-assisted laser desorption mass spectra for Wyodak-Anderson subbituminous coals showing a broad range in 400-5,000.

Recently, coal model were used to determine the percentage of extractable molecules$^9$. In Table 3-13 extractable mass from two different pure solvents at cutoff range (±0.5) was provided by Painter et al. solubility equation$^9$. This values are not expected to represent specific structure-behavior extractable matters, since others factors such as transportation and diffusion are omitted. WY coal extractable mass using pyridine cutoff 0.5 gave good agreement between WY model extractable molecular mass of 9wt% and WY coal experimental 7wt% soluble fraction in pyridine was observed$^{62}$. 
Table 3-13. Wyodak-Anderson subbituminous coals model solvent solubility parameters of pyridine and NMP with different cutoff variations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Cutoff</th>
<th>Amount of extractable molecules</th>
<th>Average aromaticity extractable ($f_a$)</th>
<th>Molecules extractable %</th>
<th>Molecular mass extractable %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wyodak Model</td>
<td>Pyridine</td>
<td>0.5</td>
<td>31</td>
<td>0.48</td>
<td>9%</td>
<td>9%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>66</td>
<td>0.49</td>
<td>24%</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>113</td>
<td>0.53</td>
<td>42%</td>
<td>44%</td>
</tr>
<tr>
<td>Wyodak Model</td>
<td>NMP</td>
<td>0.5</td>
<td>79</td>
<td>0.56</td>
<td>29%</td>
<td>33%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>131</td>
<td>0.56</td>
<td>48%</td>
<td>55%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>173</td>
<td>0.56</td>
<td>64%</td>
<td>72%</td>
</tr>
</tbody>
</table>

In Figure 3-12, WY model extractable molecules in pure pyridine solvent are shown in blue color. The molecular weight distribution of extractable mass with pyridine solubility cutoff (0.5) is shown in Figure 3-12.

Figure 3-12. Wyodak coal, pyridine solubility parameters cutoff 0.5, the extractable molecular mass (blue) false colored to aid view. Hydrogen atoms are not shown for clarity, and oxygen atoms (red).
Significant similarity were found between the model dominant peak molecular weight range in 387-481 g/mol, seen in Figure 3-13, and the experimental molecular weight of 460 g/mol\textsuperscript{62}. For WY coal of \textasciitilde7wt% (dmmf) pyridine yields was observed from capillary column gas chromatography coupled with mass spectrometry\textsuperscript{62}.

**Figure 3-13.** Wyodak-Anderson subbituminous model extractable mass distribution in pyridine solubility parameters cutoff (0.5).

The molecular extractable representstions, false colored to aid view, for pyridine solubility parameters cutoff range from 0.5 to 1.5 are shown in **Figure 3-14.** The pyridine cutoff (1.0) extractable materials have a slightly similar fraction of aromaticity of 0.47 compared to cutoff (0.5) value. The amount of 66 extractable molecules for pyridine cutoff (1.0) are shown in **Figure 3-14** (green false color).
**Figure 3-14.** Wyodak coal, pyridine solubility parametr cutoff for different cutoff range (blue, 0.5, green 1.0, and red 1.5).

The amount of moisture 26 wt% (ash-free basis) for Wyodak-Anderson coal was obtained from literature\textsuperscript{11}. Some, 700 water molecules were based on total model molecular weight basis. Typically, coals water forms are classified in bulk-water, and bound-water. For WY subbituminous coal 0.39g of water per 1g of dry coal\textsuperscript{11}. Some, 30% of the water are found as bound-water within WY coal microporosity structures. The other 70% of the water are omitted from WY model, since bulk-water is found at macropores scale (e.g. cleats), non-macropores area were generated. Approximately, 500 water molecules represent bulk-water were included, within the WY model exterior, using package simulation sorption software in Materials Studio 5v. The sorption method provides Metropolis Monte Carlo location task to determine global minimum energy sites for 500 water molecules at 300K. These automated processes allow molecules interactions between sorbate-sorbate, and sorbate-sorbents structures were observed. **Figure 3-15(a)** show loading configurations of 500 bulk-water molecules, were predominantly located in the exterior of the coal model. Location of the water molecules are based on the number of accepted interactions to translation/rotation. This construction/destruction ratio used by sorbate location task interaction between bulk-water and oxygen functional groups adsorption sites of the coal was observed. The bound-water, ~200 molecules within WY coal model are
contained by 4 bucket of ~50 water molecules are shown in Figure 3-15(b). Each bucket of bound-waters was manually placed from ice water structure configuration.

Figure 3-15. (a) View of the dominant loading location of 500 bulk-water molecules for Wyodak-Anderson subbituminous coal. (b) View of the Wyodak-Anderson subbituminous coal model loading bound-water molecules, enlarged spheres to aid visualization. Carbon atoms (green) and oxygen water (red) other atomic representations were edited to aid view.
Conclusions

Prior to this work only a few small-scale molecular representations of subbituminous coals existed despite the economic importance of Powder River coals to the U.S. electric utility system (produced >40% of the US coal supply). The required expertise, cost and time invested, in even small-scale subbituminous coals models, has been prohibitive for computational simulations. Large-scale models, capturing the structural diversity of the coal, will be beneficial for structural-behaviors simulation and exploring coal conversion approaches. To accommodate this need large-scale subbituminous coals model need to include a diverse molecular mass range, oxygen functionalities, and water forms among others structural parameters. Here, a new approach, named Fringe3D, was created to construct large-scale subbituminous coal slice models directly from HRTEM lattice fringe images. The combination of HRTEM lattice fringe image analysis with FRINGE3D techniques effectively generated aromatic molecules while keeping coal microstructure properties. Such properties captured distribution of aromatic molecules size, stacking, interlayer spacing, and orientation improved model accuracy physical properties while meeting many average properties derived from NMR and other analytical approaches. This new approach enabled the construction of the largest low-rank coals model generated (24,672 atoms) with improved structural accuracy. Some, 544 aromatic molecules, were generated from a single HRTEM lattice fringe images. Furthermore, reasonable correlation between model aromatic average molecular weight of 289 amu (HRTEM prediction) and 299 amu ($^{13}$C-NMR) was obtained. The slice model generated, capture structural features such as spatial orientation (stacking), fraction of aromatic bridgehead carbons, aromatic molecular size distribution, and aromatic molecular weight distribution. Cross-linking and inclusion of aliphatic, heteroatom (enabled with scripting), water forms, coupled with manual fragment manipulation generated a
3D representation in good agreement generally with multiple analytical approaches. The aromaticity of the model was 63% in close agreement to the Argonne Premium coal and other Powder River basin coals (~64%). Other NMR parameters were also in reasonable agreement. The molecular weight distributions was constructed to match the profile of laser desorption ionization spectroscopy. Some 262 molecules were formed from the 544 aromatic moieties. Evaluation of theoretical extraction generated (9wt% ~30 molecules) in agreement with experimental data (average ~7wt %) It is expected that this model will aid in progressing coal science for subbituminous coals via various simulation approaches.

References


CHAPTER 4: SUMMARY, CONCLUSIONS & FUTURE WORK

Summary and conclusions

The combination of HRTEM lattice fringe image analyses with an innovative model generation approach was used to construct a 3D molecular “slice” graphene-like structure model for soot, chars, and subbituminous coals that captured the observed structural features implicitly. Such an approach reduces the time to generate structural models, it enables larger-scale models to be generated that capture the continuum of structural features of size, alignment and stacking. Since aromatic fragments are made by hexagonal structure (condensed benzene rings) allows distinction of periodic structures (graphite structures) to be observed from polycyclic aromatic hydrocarbon molecules as resemble graphene-like structure. Evidence of aromatic structural features in carbonaceous matters was demonstrated by XRD analyses, and distribution of the aromatic structural features was observed by TEM techniques. Unfortunately, no HRTEM lattice fringe of Wyodak-Anderson subbituminous coals has been reported. Therefore, HRTEM lattice fringe image of Beulah-Zap lignite coals found in literature were used to generate aromatic structural features for WY subbituminous coals molecular representation from a single micrograph.

Suggested future applications

This unique new method to generate 3D models directly from HRTEM lattice fringe image analysis can be used to develop 3D models for carbonaceous matter. The combination of HRTEM lattice fringe image analyses with an innovative model generation approach was used to construct a 3D coal molecular “slice” model that captured the observed structural features implicitly. Such an approach will be useful in reducing the time to generate structural models of
coals, chars, cokes, soot, and activated carbon, see Figure 4-1, and Figure 4-2. It will also allow for larger-scale models to be generated that capture the structural features of alignment and stacking. The more realistic coal molecular models will be useful in relating structure to behaviors such as CO$_2$ sequestration, coal solvent interaction, coal-to-liquids, and gasification among others. Future work will further address curvature, slice to cubic model transformations, heteroatom and aliphatic carbon, and cross-linking inclusion.

**Figure 4-1. New era in model construction are expected.** Coal aromatic structural features compose of HRTEM lattice fringe images can be used to generate models of more than million molecules.
Figure 4-2. **Landmark**, primary soot particles models (diameter above 300Å) can be constructed directly from experimental data (fuel chemistry/combustion environments). Here, approximately, 3,000 centroid were used to generate atomistic scale soot primary particles.
APPENDIX A: Directly capturing aromatic structural features in coal via “Fringe 3D” generating 3D molecular models directly from HRTEM lattice fringe images


DIRECTLY CAPTURING AROMATIC STRUCTURAL FEATURES IN COAL VIA “FRINGE 3D” GENERATING 3D MOLECULAR MODELS DIRECTLY FROM HRTEM LATTICE FRINGE IMAGES

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Introduction

Generating meaningful representations of coal is time consuming and resource intensive. An approach that is simpler, quicker, and yet is able to capture structural diversity while removing considerable investigator structural bias is proposed. Early HRTEM work generated fuzzy images from which a discerning eye could distinguish some structural features. Advances in lattice fringe images algorithm analysis allows a clear picture, and characterization of lattice fringe parameters, such as fringe orientation, stacking behaviors, interlayer spacing, morphology, and length distribution to be obtained¹-³. There is confidences in HRTEM lattice fringe image analyses from applications such as microtexture analysis of coal char⁴, ⁵, soot formation⁶, ⁷, asphaltene stacking⁸, activated carbon⁹-¹¹, coals³, ¹², and coal-derivates¹, ³, ¹²-¹⁴. Furthermore, close agreement between XRD aromatic parameters, and 2D HRTEM lattice fringe image measurements have been observed for phenol formaldehyde resin chars¹⁰. However, these micrographs may also prove useful in the direct generation of 3D coal models. This is the objective of the current investigation. Future work will focus on producing full 3D coal
molecular structure based on multiple slice models, and the necessary addition of aliphatic carbons, heteroatoms, and cross-linking.

Currently, coal model generation occurs with amorphous construction approaches and any structural alignment is happenstance. Coal modeling requires considerable construction expertise and investigator time. While some computer-aided construction has been utilized for coals\textsuperscript{15, 16} and carbon models\textsuperscript{17, 18} these have still tended to be small. Only a few large-scale (>20,000 atoms) coal models have been generated\textsuperscript{19,20}. The scale allows for molecular-weight distribution incorporation and attempted induced molecular orientation\textsuperscript{20}.

**Experimental**

A HRTEM lattice micrograph consists of lines and squiggles representing the edges of aromatic rings. With calibration, the image can be analyzed and a variety of structural features, and their distribution, can be determined. One such image is shown in Figure A-1a. Small straight lines of lengths between 3.0 and 4.75Å are of the appropriate scale for benzene, and naphthalene molecules (depending on the molecules rotational orientation in the case of naphthalene). Many of the fringes are longer than 5Å, large amounts have some degree of curvature, stacking of similar length fringes and preferential orientation can also be discerned. It is possible to determine the center of fringes and the relative position of each fringe. This information, determined from image analyses using Photoshop with Image Processing Tool Kit plug-in, was rewritten in an appropriate format for displaying molecular models in 3D space. Thus, the relative position of each fringe is captured and duplicated in 3D space. Figure 1b shows a 3D view of the fringe centroid, extracted from Upper Freeport bituminous coal lattice fringe image analysis\textsuperscript{12}.
The flow of information necessary for model construction is shown in Figure 2. Essentially, the HRTEM lattice fringe image is a 2D x-y “graph”. The fringe center of mass in Cartesian coordinates was formatted in 3D space via the Protein Database (pdb) file format via simple text manipulation with spreadsheet software assuming a constant z-axis position of zero. The fringe centers are all aligned in the z-direction. A PERL script (Fringe3D) populates each of the fringe centers with either a named molecule, or a specified number of carbon atoms from a calibration file with specific catenation. These calibrations and named molecules were constructed, their center of mass determined computationally, and placed in 3D space such that the molecule centroid was located at the x,y,z coordinates of 0,0,0. The flat molecules were oriented such as the molecules lay in the z-plane. Thus, the Fringe3D script places a molecule of the appropriate size (determined from image analyses and assumptions of molecule shape or depth) at the appropriate x,y,z coordinates via simple mathematical addition (each atoms x,y,z location plus the x,y,z centroid location).
The molecules are also pitched around their centroid to match their fringe moment angle, thus capturing fringe stacking and alignment. Also to generate “natural” looking models, the molecules can also be rotated at their centroid. Both pitch and rotation are shown in Figure 3a. To ensure that the complexity of coal and other carbonaceous material can be captured, it is desirable to generate molecules that represent a range of sizes and shapes in accordance with known coal/carbon chemistry. Similar approaches have been utilized in petroleum process modeling\textsuperscript{21,22}. Here calibration molecules with circular, parallelogram and other catenation were created. However, it was necessary to renumber the carbon atoms in these models such that the first six atoms comprised the central benzene ring. This is shown in Figure 3b. As larger ring systems (rafts) are required, it is a simple process to increase the number of carbon atoms and
Fringe3D generates molecules of the appropriate size. Preferential raft growth can be controlled by catenation selections. Alternatively, a named molecule can be positioned at the x,y fringes center coordinates. This is the preferred approach for small molecules such as phenanthrene.

![Diagram of benzene rings](image)

**Figure 3.** (a) Show, 25 central benzene rings each individual benzene ring was generated by named molecules method. (b) Benzene-Circumcononene C₅₄H₁₈, circular growth method generated from central (gray color) benzene ring.

### Results and Discussion

The HRTEM micrograph and resulting slice model of Hon Gui anthracite coal are shown **Figure 4a and 4b**. This transformation method successfully captures 3D structural features for the aromatic portion of the coal structure. Figure 4c and 4d shows distribution of interlayer spacing (d-space) values in 3D space, range in 3.50-3.60Å, characteristics of high-rank coals. The slice model is shown with benzene, rather than the distribution of molecular sizes, because utilizing the appropriate aromatic raft without first accommodating fringe/model curvature resulted in molecular impingement.
Figure 4. (a) HRTEM lattice fringe image of Hon Gui anthracite coal. (b) 3D model mirror image of fringes shown with benzene molecules. (c) Expanded view of the lower box region of image b shows stacking of molecules represented by benzene. (d) Expanded view of the upper box region of image b shows stacking of molecules represented by benzene.

It is assumed that curved fringes are generated from molecules that contain 5, and 5,7-member rings and are shown Figure 5. For many of these fringes, the appropriate curvature could be obtained with molecule containing such configurations. More extreme curvature may be produced by overlapping fringes, disclinations, or from structural features reminiscent of Bucky ball and nanotube fragments. In Figure 6 a more pronounced curve is formed with 5-7-7-5 rings.
Figure 5 (a) 5-member ring curvature calibration file view form z-plane. (b) 5,7-member ring curvature calibration file, view from z-plane.

Figure 6. (a) 5-7-7-5 member ring combination, side view z-plane. The red sphere represents the centroid location in the 5-7-7-5 member ring calibration files.

Conclusions

The combination of HRTEM lattice fringe image analyses with an innovative model generation approach was used to construct a 3D coal molecular “slice” aromatic moiety model that captured the observed structural features implicitly. Such an approach will be useful in reducing the time to generate structural models of coals, chars, cokes, soot, and activated carbon. It will also allow for larger-scale models to be generated that capture the structural features of alignment and stacking. The more realistic coal molecular models will be useful in relating structure to behaviors such as CO₂ sequestration, coal solvent interaction, coal-to-liquids, and gasification.
among others. Future work will further address curvature, slice to true 3D model transformations, heteroatom and aliphatic carbon, and cross-linking inclusion.

Acknowledgement

Dr. Atul Sharma for helpful discussions.

References


APPENDIX B: File format/application for Protein Data Base

PDB FILE FORMAT

The PDB file format provides flexibility to transfer and store large volume of information. In addition it is supported by numerous molecular modeling software as well as viewers. Another advantage of PDB is the ability to manipulate or create single bond (C-C) if the distance between the atoms is less than 2.0 Å.

Figure B-7. (a) Raw information extracted by HRTEM skeleton lattice fringe image analysis. (b) Raw PDB file format created in Excel.

Figure B-8. (a) Shows a Protein Data Base file characterize 606 benzene molecules in 606 Model. (b) Protein Data Base file characterize 606 benzene molecules within a single Model 1.
APPENDIX C: Transformation Matrix brief overview

The HRTEM lattice fringe skelotonized digital images contain information relevant to aromatic structural components. For the purpose of this research, skelotonized lattice fringe lengths are used to determine fraction of aromaticity based on polycyclic aromatic hydrocarbons molecular lengths are referred to chemical properties. Other skelotonized lattice fringe image features are fringe centroid coordinates, inclination angles, and rotational angle characteristics of physical properties. Thus experimental data are captured by 3D model. In addition both chemical and physical properties were directly generated from HRTEM lattice fringe images. For example, Equations – (1)-, and – (2) – describes rotation for aromatic compound specific for each fringe as a function of rotational angles (θ°). The arithmetical operation used simple transformation matrix.

\[
\begin{bmatrix}
X_\theta \\
Y_\theta \\
Z_\theta
\end{bmatrix} = \begin{bmatrix}
\cos(\theta) & -\sin(\theta) & 0 \\
\sin(\theta) & \cos(\theta) & 0 \\
0 & 0 & 1
\end{bmatrix} \begin{bmatrix}
X_i \\
Y_i \\
Z_i
\end{bmatrix} \quad \text{Named compound or Catenation Files}
\]

The coordinates from named molecules and catenation files are uploaded by Fringe3D, and the angel of rotation (θ) are imported from image analyses data. The (i) is the atoms sequence number or herachiral for molecule construction.

\[
X_{\theta i} = (X_i \cos(\theta) - Y_{\theta i} \sin(\theta)) \quad Y_{\theta i} = (X_i \sin(\theta) + Y_{\theta i} \cos(\theta)) \quad Z_{\theta i} = 0
\]

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The momentum angle was provided by experimental data from lattice image processing. This provide 3D molecules specific spatial orientation, avoiding overlapping during model constructions due to close arrangements. The molecules construction approach simultaneously combine geometrical configuration with skeletonize lattice fringe image structural features such as moment angle, and spatial orientation. Example of mathematical operations used for molecule (atoms) rotation and inclination. The cartesian coordinates of each atom in the molecule are set in xy-plane, and the z-coordinates is constant (ΔZ=0) during rotational angle from 0°<θ<360°. The elevation (or inclination angle) was integrated by converting cartesian coordinates to spherical coordinates, Equation-(3).

\[ \rho = \sqrt{X^2 + Y^2 + Z^2} \quad \tan \theta = \frac{Y}{X} \quad \phi = \cos^{-1}\left(\frac{Z}{\rho}\right) \quad - (3) - \]

The conversion from radians to degrees is required to add the angle from the input lattice fringe image analyses are described by Equation-(4). Followed by converting degrees back to radians.

\[ \phi^* = \phi + \text{Ascension Angle} \quad \theta^* = \theta + \text{Declination Angle} \quad - (4) - \]

This angles are used to change the plane angle of the atoms in the aromatic molecules from (X,Y,Z) to (X*, Y*, Z*) was obtained from Equation-(5), and Equation-(6).

If \( \phi^* \) is zero, then.

\[ X^* = \rho \times \cos \theta \quad Y^* = \rho \times \sin \theta \quad Z^* = 0 \quad - (5) - \]

For \( \phi^* \neq 0 \), Equation-(6) are used to convert plane angles.
\begin{align*}
X^* &= \rho \cdot \sin \varnothing \cdot \cos \theta \\
Y^* &= \rho \cdot \sin \varnothing \cdot \sin \theta \\
Z^* &= \rho \cdot \cos \varnothing
\end{align*}
\text{--- (6) ---}
APPENDIX D: Aromatic raft growth

AROMATIC RAFT GROWTH

In Figure D-10, “calibration files” are used to generate different polycyclic aromatic hydrocarbons basis on experimental data. For example, here, both aromatic molecules have the same number of aromatic carbons, C24. Figure D-11(a) show aromatic molecule of C54H18 combine symmetry/ statistical graphics methods. The initial benzene ring (Ai) is observed in Figure D-11(b).

Figure D-10. Simple transformation matrix and format modifications enable different aromatic rafts growths for C24.

Figure D-11. (a) Circumcononene, aromatic carbon nomenclature for raft growth. (b) Ring nomenclature also used for raft growth.
APPENDIX E: Exchange fraction, protocol

EXCHANGE FRACTION

Atoms were systematically added to the model, converted to appropriate isotope ratios for subsequent conversion into CNOS atoms with appropriate functionality. This was necessary given the large-scale of the model. Manual manipulation was impractical.

\[ \text{X}_t = \text{Total initial } [\text{H}], \text{ (value is provided from “Force Field parameters Number of aromatic carbon protonated } [\text{H}]: \text{SaroH.}) \]

\[ x_1 = \text{fraction aromatic carbons that are protonated , replace } [\text{H}] \rightarrow [\text{He}] \text{ at input (x1 = “0.30”).} \]

\[ \text{X}_a = \text{fraction aromatic carbons that are non-protonated, replace } [\text{H}]-[\text{Ne}] \text{ at (Xa = “1-}x_1”). \]

\[ x_{c1} = \text{fraction of carboxylic acid, value of } x_{c1} \text{ is provided from “Experimental input values, (f}_{\text{C}_a*\text{TotC}}-(\text{Input amount of carbonyl})/(\text{Xa})”}. \text{ Output (carboxylic acid Fraction exchange) } [\text{Ne}] \rightarrow [\text{Se}] \]

\[ x_{c2} = \text{fraction of carbonyl, value of } x_{c2} \text{ is provided from “Experimental input values, (f}_{\text{C}_a*\text{TotC}}-(\text{Input amount of carboxylic acid})/(\text{Xa})”}. \text{ Output (carboxylic acid Fraction exchange) } [\text{Ne}] \rightarrow [\text{B}]. \]

\[ \text{X}_a = \text{Total number of aromatic carbon protonated available to exchange } [\text{Ne}] = \text{X}_t - \text{X}_a(x_{c1}+x_{c2}) \]

\[ x_{1a} = \text{fraction of all } (x_{aC}=\text{CH3}) + (x_{aC2}=\text{CH2}) + (x_{aC3}=\text{CH2-CH3}) + (x_{aC4}=\text{CH2-CH2-CH3}) = [\text{Se}]. \text{ Value is provided from “Experimental input values, (f}_{\text{S}_a*\text{TotC}}/(\text{Xal}) = x_{a1} \]

\[ x_{aC} = \text{fraction of CH3 attached to aromatic carbons that are protonated. } ((x_{aC})*(f}_{\text{S}_a*\text{TotC}}) / (\text{Xal}). \]

\[ x_{aC2} = \text{fraction of CH2- attached to aromatic carbons that are protonated. } ((x_{aC2})*(f}_{\text{S}_a*\text{TotC}}) / (\text{Xal}). \]

\[ x_{aC3} = \text{fraction of CH2-CH3 attached to aromatic carbons that are protonated. } ((x_{aC3})*(f}_{\text{S}_a*\text{TotC}}) / (\text{Xal}). \]

\[ x_{aC4} = \text{fraction of CH2-CH2-CH3 attached to aromatic carbons that are protonated. } ((x_{aC4})*(f}_{\text{S}_a*\text{TotC}}) / (\text{Xal}). \]

\[ x_{a2} = \text{fraction of all } (x_{aH2}=x_{aC2}=\text{CH2}) + (x_{aH3} = \text{CH2-CH3}) + (x_{aH4}=\text{CH2-CH2-CH3}) = [\text{Se-H}]. \text{ Values is provided from “Experimental input values, (f}_{\text{ai}*\text{TotC}})/(x_{a1}*\text{Xal}) = x_{a2}. \]
x2= oxygen functions (phenolic and methoxy and aryl-o-crosllinks).

x2a= methoxy fraction of phenoloic + methoxy +aryl-o-crosllinks.

x2b= phenolic fraction of phenoloic + methoxy +aryl-o-crosllinks.

x2c= aryl-O crosslink fraction of phenoloic + methoxy +aryl-o-crosllinks.

1. Select $atom1 “H”, Exchange with $atom2 “He”; Fraction exchange “x1”. Lock [H] with [He] to represent number of aromatic Hydrogen aromatic carbons “He” ([H] eq [He] lock).*

2. Repeat $atom1 “H”, Exchange with $atom2 “Ne”; Fraction exchange “l-x1”. Only use [Ne].

3. Carboxylic acid. Select $atom1 “Ne”, Exchange with $atom2 “Se”; Fraction exchange “xc1”

4. Loop to generate Carboxylic acid in selected [Se].

   (4a) Hydrogen adjusts (1st) output; [Ar-Se-H]. (This step is done manually).
   # Add hydrogen atoms
   $document->AddHydrogenAtoms();
   $document->UpdateViews();

   (4b) Select $atom1 “H”, Replace with $atom2 “O”; Fraction exchange “1.0”.
   # Add hydrogen atoms
   $document->AddHydrogenAtoms();
   $document->UpdateViews();

   (4c) Hydrogen adjusts (2nd) output; [Ar-Se-O-H]. (This step is done manually).
   # Add hydrogen atoms
   $document->AddHydrogenAtoms();
   $document->UpdateViews();

   (4d) Select $atom1 “H”, Replace with $atom2 “He”; Fraction exchange “1.0”. Output [Ar-Se-O-He].
   (4e) Select $atom1 “Se”, Replace with $atom2 “B”; Fraction exchange “1.0”. Output [Ar-B-O-He].
   (4f) Hydrogen adjusts (3rd) output; [Ar-B-H-O-He].

   # Add hydrogen atoms
   $document->AddHydrogenAtoms();
   $document->UpdateViews();

   (4g) Select Satom1 “H”, Replace with Satom2 “Se”; Fraction exchange “1.0”. Output [Ar-B- Se-O-He].
   (4h) Select Satom1 “B”, Replace with Satom2 “C”; Fraction exchange “1.0”. Output [Ar-C-Se-O-He].

   (4i) Bond type selection, [Se-C], change to Double bond.
   (4j) Select Satom1 “Se”, Replace with Satom2 “O”. Output
   (5a) Bond type selection, [C-B], change to Double bond.
   (5b) Select $atom1 “B”, Replace with $atom2 “O”. Output [C=O].

6. Select $atom1 “Ne”, Exchange with $atom2 “Se”; Fraction exchange “xa1”.
   (6a) H-adjusts (4th) output; [Ar-Se-H]. (This step is done manually).
   # Add hydrogen atoms
   $document-&gt;AddHydrogenAtoms();
   $document-&gt;UpdateViews();
   (6b) Select $atom1 “H”, Replace with $atom2 “He”; Fraction exchange.

4. Convert [H] to [O] at (my $xc1). Will be Carbonyl (C=O) and Carboxylic (COOH) acid.
5. H-adjust, convert [H] to [O] acid (1-$xc2); BOND SELECTION double bond.
6. H-adjust, now have (COOH).
7. Convert [H] to [Se]; Input (my $b1).
8. H-adjust at (xa3), convert [H] to [Se] (b1).
9. Keep going until no more (xa1) (xa2).
13. Replace [H] with [He] (1-x2a), (phenols).
14. Replace [H] with [Cl] (1-x3a), (aryl-O-linkages).
15. Replace certain [O] with [S] and [N]