IMPROVED GENERATION OF LARGE-SCALE ATOMISTIC REPRESENTATIONS AND PYROLYSIS/COMBUSTION SIMULATIONS OF ILLINOIS COAL AND COAL CHAR USING THE REAXFF REACTIVE FORCE FIELD

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ABSTRACT

A highly automated molecular generation approach was implemented and coupled with reactive force field methods to create a new computational capability that enabled the investigation of structural transformations and chemical reactions involved in coal pyrolysis and char combustion. The present work demonstrated the applicability and utility of this new computational capability for examining at the molecular level the complex chemistry associated with coal pyrolysis and char oxidation and combustion. In this investigation, Illinois no. 6 Argonne Premium coal, the world’s most well-studied coal, was evaluated using atomistic representations of both the coal and the coal char created for this purpose. Orientation and stacking issues were also explored utilizing molecular representations of several Argonne Premium coals and an anthracite coal.

An extensive review of the chemical and physical structural features of Illinois no. 6 coal was created covering aromatic and aliphatic components, functional groups and heteroatoms, molecular weight distribution, nature of the cross-linked network, porosity, surface area and density. Illinois no. 6 coal is vitrinite-rich (85%, dmmf) with a normalized elemental composition of C_{100}H_{77.3}O_{13.1}N_{1.5}S_{1.2} and a high organic sulfur content of 2.5% (dmmf). Nuclear magnetic resonance (NMR) analyses reported an aromaticity of 72% with 15 aromatic carbons (three to four fused aromatic rings) and 5 attachments per cluster, and an average cluster molecular weight of 316 Da. X-ray photoelectron spectroscopy (XPS) determined that organic oxygen, nitrogen, and sulfur forms are primarily ether and phenolic, pyrrolic and pyridinic, and aliphatic and thiophenic type structures, respectively. Small angle neutron scattering (SANS) analyses found that Illinois coal is mostly microporous and ^{129}Xe NMR confirmed that the pore structure of Illinois coal consisted of two distinct regions with average pore diameter of 6 and 10 Å.

These analytical data from the literature were used to construct a large-scale coal molecular model based on an improved automated construction approach in an effort to move toward capturing the continuum structure over a large scale. The model contains 50,789 atoms within 728 diverse molecules and is the largest, most complex coal representation constructed to-date.
The aromatic ring size distribution was based on multiple previously published high-resolution transmission electron microscope (HRTEM) lattice fringe micrographs and was duplicated with automated construction protocols (Fringe3D) in molecular modeling space. Additional structural data was obtained from the abundant literature assessing this Argonne Premium coal. Organic oxygen, nitrogen, and sulfur forms were incorporated primarily into the polyaromatic structures according to XPS and X-ray absorption near-edge structure spectroscopy (XANES) data. Aliphatic carbons were distributed among cross-links and pendant alkyl groups based on the combination of laser desorption ionization mass spectrometry (LDIMS), ruthenium ion catalyzed oxidation, elemental analysis, and NMR data to agree with literature data. Construction of coal molecules was performed using Perl scripts adapted and improved from earlier work in Materials Studio to eliminate personal bias and improve the accuracy and the scale of the structure generated. The Illinois coal model contained >50,000 atoms \( (C_{26860}H_{20897}O_{2502}N_{412}S_{330}) \) in 728 cross-linked aromatic and hydroaromatic clusters exhibiting a broad and continuous molecular weight distribution ranging from 100 to 2850 Da with a sharp peak at \(~350-400~\)Da, calculated values for \( M_n \) and \( M_w \) of 522 and 861 Da respectively, aromaticity of 75\%, and a simulated helium density of 1.32 \( \text{g/cm}^3 \) in agreement with experimental data for Illinois no. 6 coal. A theoretical pyridine extraction yield, determined by a group contribution approach, was in agreement with the experimental value. The extract and residue representations were generated from the large-scale Illinois coal model and showed consistency with NMR, elemental analysis and LDIMS trends. The distribution of heteroatomic classes and double bond equivalents of the extract was consistent with extract experimental data from electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) collected and provided by the National High Magnetic Field Laboratory. These data further constrain the molecular weight of extractable material and was consistent with limited pyridine extractability and model heteroatom classes.

The ReaxFF reactive force field was used to perform pyrolysis simulations at 2000 K on the constructed large-scale molecular model for Illinois coal to examine structural modifications and reactions associated with coal pyrolysis. This high temperature enabled chemical reactions to occur within a practical simulation time. The ReaxFF simulation was performed until about 60\% of the cross-links had been disrupted primarily through thermolysis. For this coal pyrolysis was
mainly initiated by the release of hydroxyl groups, dehydrogenation of hydroaromatic structures, and by cleavage of heteroatom-containing cross-links. The main pyrolysis products were hydrogen, methyl, ethylene, acetylene, formaldehyde, ethynol, alkylphenols, alkynaphthalenes and alkynaphthols, in agreement with experimental observation. During pyrolysis the molecular weight distributions shifted to lower values as expected due to thermal decomposition to form smaller fragments. The thermal degradation of sulfurated and oxygenated cross-links was more substantial than that of alkyl linkages, in accordance with their higher reactivity. Analysis of sulfur form distribution showed that aliphatic sulfur decomposed more rapidly while thiophenic sulfur was more thermally stable in agreement with experimental data. The extent of decomposition for heterocyclic 5-membered rings was: 57 % for pyrrolic, 47% for thiophenic, and 29% for furanic type structures. The ReaxFF simulation was repeated on a sulfur-free model to further analyze the role of organic sulfur forms in Illinois coal pyrolysis. ReaxFF results showed that the rate of generation of light gases and tars was higher in the presence of sulfur. Further analysis of ReaxFF simulations showed that aryl and alkyl C-S bonds are weaker than aryl and alkyl C-C bonds. Hence, cleavage of the C-S bonds resulted in more extensive fragmentation leading to larger quantities of aliphatic and aromatic structures that evolved as light gases and tars within Illinois coal model (sulfur containing) compared to sulfur-free model. Therefore, sulfur atoms enhanced the reaction kinetics during coal pyrolysis.

A devolatilized Illinois no. 6 coal char atomistic representation was generated using published HRTEM lattice fringe images and Fringe3D in conjunction with Perl scripts, and coupled with the ReaxFF reactive force field. Fringe3D facilitates the char structure generation process by producing a distribution of aromatic structures based on HRTEM lattice fringe image analyses. Perl scripts were used for incorporating heteroatom and aliphatic components to aid elimination of investigator bias, and facilitate a more rapid construction process. The char structure was constrained by a combination of elemental and NMR literature data. Chemical and physical parameters were found to be consistent with the experimental data. The ReaxFF force field for hydrocarbon combustion was used to perform simulations to examine the structural transformations and chemical processes associated with char combustion. In this initial work, very high temperatures (3000-4000 K) were selected for ReaxFF simulation under stoichiometric, fuel lean and rich combustion conditions. These elevated temperatures were
chosen to observe chemical reactions proceed to completion within a computationally practical simulation time. It is expected that with computational gains longer simulations at more reasonable combustion temperatures could be obtained. The char oxidation process was mainly initialized by either thermal degradation of char structure to form small fragments, that were subsequently oxidized, or by hydrogen abstraction reactions by oxygen molecules and O and OH radicals. A more rapid oxidation and combustion of the polyaromatic structures occurred at fuel lean (oxygen rich) conditions compared with fuel rich combustion. Char transitions included 6-membered ring conversion into 5- and 7-membered rings that further decomposed or reacted with mostly O and OH radicals.

To further evaluate the applicability of HRTEM as the basis for structural model generation molecular slice models for several Argonne Premium coals (Beulah-Zap, Illinois no. 6, Upper Freeport, Pocahontas no. 3) were also constructed to predict the pair distribution function (PDF) and to evaluate the fine detail of the frequency spectra via examination of intermolecular and intramolecular contributions. Atomistic representations were generated directly from published HRTEM lattice fringe images using Fringe3D and constrained by elemental analysis and NMR data from the literature. The constructed coal models were partially geometry-optimized to achieve realistic bond lengths but without displacement of coal molecules enabling the distribution of fringe length, stacking, and orientations to be duplicated in 3D modeling space. The resulting coal slice models, devoid of cross-links, captured a distribution of turbostratic crystalline dimensions with an average cluster size of about 1 nm, an average interlayer spacing ranging between 0.37 and 0.39 nm, and an average stacking number of ~2-3 in accordance with HRTEM and XRD literature data for Argonne coals. Simulated PDF agreed with experimental data obtained from Argonne National Laboratory. Analysis of the simulated intermolecular PDF contribution showed stronger intensities with increasing coal rank in agreement with the growth in the stacking number and stack height observed from low- to high-rank coals. The simulated intramolecular PDF contribution showed shorter peak amplitudes for low-rank coals in comparison to high-rank coals in agreement with the slight increase in stack width with coal rank in the bituminous range with more extensive increases for anthracite. To further examine these contributions, lattice models composed of pyrene molecules were also constructed via Fringe 3D and manipulated to directly investigate the effect of aromatic orientation distributions and
stacking on the simulated PDF. Peak intensities of simulated intermolecular PDFs at the average interlayer spacing increased with the degree of alignment, consistent with the slight increase in the stacking number observed from low- to high-rank coals with a more dramatic transition for anthracite.

The automated construction protocol enabled generation of large-scale coal molecular models and aided in capturing a wider range of the complex distribution of coal structural features. Linking high-accuracy, large-scale coal model construction approaches improved here with a computational method for large systems with dissociation and formation of chemical bonds enabled obtaining a versatile simulation platform that provided the ability to evaluate the complex chemistry associated with coal pyrolysis and char combustion. The work performed here was aimed at demonstrating the capability of this approach for examining the complex chemistry involved in coal pyrolysis and char oxidation and combustion.
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Chapter 1

Introduction

This chapter provides an overview of the chapters (most being published journal articles) compiling this dissertation. A general background on the composition and structure of coal followed by a brief overview on coal pyrolysis and combustion were presented. Further, a discussion on model construction strategies for coal and char and an introduction to reactive molecular dynamics simulations are provided. The applicability of HRTEM and pair distribution functions as the basis for structural model generation is also evaluated. The final considerations are the research objectives of this investigation.

Composition and structure of Illinois no. 6 coal

The Illinois no. 6 is an industrially relevant coal with the Illinois basin being the largest bituminous basin in the United States.\(^1\) Abundant structural data for Illinois no. 6 are available in the scientific literature. Through extensive research search it was determined that over 150 research journal publications have addressed its behavior, chemical and physical properties. Illinois no. 6 Argonne Premium coal is one of the most extensively studied coal in the world and is the most popular sample of the Argonne Premium coals shipped with almost 3,500 ampoules shipped by 1994.\(^2\) Surprisingly it has not been the subject of a dedicated review paper. Here, an extensive review of chemical and physical structural features of Illinois no. 6 coal was created covering aromatic and aliphatic components, functional groups and heteroatoms, molecular weight distribution, nature of the cross-linked network, porosity, surface area and density. There was conflicting data in the literature, requiring a selection of data deemed more quantitative typically by the nature of the analytical technique for all measured structure parameters. However, a discussion on experimental challenges to a number of characterization techniques was presented and a critical evaluation for the more important chemical and physical structural parameters was performed. This review provided the data to constrain a new large-scale highly automated construction approach for an atomistic representation of Illinois no. 6 coal.
The Argonne Premium Illinois no. 6 coal is a high-volatile bituminous coal with an elemental composition, normalized to 100 carbon atoms, of C$_{100}$H$_{77.3}$O$_{9.4}$N$_{1.5}$S$_{1.2}$ (dmmf) and maceral composition of 85% vitrinite, 10% inertinite, and 5% liptinite. The atomic H/C, O/C and N/C ratios are 0.773, 0.094 and 0.015 respectively. Proximate analysis shows that Illinois coal as-received contains 8.0% moisture, 14.3% ash yield, 36.9% volatile matter, and 39.9% fixed carbon. The major mineral constituents as a percentage of total mineral matter are 19% quartz, 30% pyrite, 10% calcite, and 41% clay minerals (kaolinite and illite). Thus, this coal is relatively high in both organic sulfur and mineral matter.

The aromatic moieties present in coal structures have been characterized using nuclear magnetic resonance (NMR), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and ruthenium ion catalyzed oxidation (RICO). Solum et al., dela Rosa et al., and Alemany et al. used cross-polarization magic angle spinning (CP-MAS) $^{13}$C NMR in studies of Illinois no. 6 coal and reported carbon aromaticity ($f_a$) values of 0.72, 0.70 and 0.68, respectively. Love et al. and Linehan and Franz determined $f_a$ values of 0.75 and 0.70 for Illinois coal utilizing the more quantitative single-pulse excitation (SPE) $^{13}$C NMR approach. Hydrogen aromaticity values of 0.47 and 0.48 were reported as determined by $^1$H NMR with combined rotational and multiple-pulse spectroscopy (CRAMPS). CP-MAS $^{13}$C NMR spectroscopy with dipolar dephasing by Alemany et al. indicated that of the 68±2 aromatic carbons (sp$^2$-hybridized) per 100 carbon atoms in the coal, 18±3 were protonated aromatic carbons, 44±2 were non-protonated aromatic carbons, and 6±1 were carbonyl carbons. Solum et al. conducted quantitative CP-MAS $^{13}$C NMR analyses on eight Argonne Premium coals. Using spin-lattice relaxation, variable contact time and dipolar dephasing 12 structural parameters were derived. Results indicated that there are 72±4 aromatic carbons per 100 carbon atoms in the Illinois coal of which, 26±3 were protonated and 46±3 were non-protonated. In addition, there were 28±2 aliphatic carbons per 100 carbon atoms distributed in 9±3 methyl and 19±2 methylene/methane units. Utilizing the fraction of bridgehead carbons and assuming linear and circular catenations, the average aromatic cluster size was estimated to be 15 carbons (three to four fused aromatic rings), with 5 attachments per clusters, and 316 Da average cluster molecular weight.
Various analytical techniques had characterized the aliphatic portion of coal structures. Obeng and Stock performed RICO experiments to determine the distribution of pendant alkyl groups in the Argonne Premium coals. The oxidation study established that Illinois coal contained 1.76 methyl, 0.29 ethyl, 0.037 propyl, and 0.035 2-propyl groups per 100 carbon atoms. Stock and Wang indicated based on RICO oxidation reactions of Illinois coal that arylmethanes and arylpropanes are primarily responsible for the formation of ethanoic and butanoic acid, and that diarylpropanes contribute significantly to the formation of propanoic acid. In addition, the amount of methyl groups observed in the oxidation reactions was less than that of $^{13}$C NMR analyses for the Illinois No. 6 coal. It was suggested that this difference could arise from additional methyl groups in hydroaromatic structures, for example, 1-methyl-1,2,3,4-tetrahydronaphthalene. Artok et al. determined that RICO reaction of coals generally suffered from low mass balance. Another limitation was the inability to detect monomethylene bridges since the resulting malonic acid from the oxidation reaction was not stable under oxidation conditions. Despite these limitations, RICO provides relatively qualitative information regarding aliphatic structure distribution that cannot be determined by other methods.

Illinois no. 6 coal contains 94 oxygen, 15 nitrogen, and 12 sulfur heteroatoms per 1,000 carbon atoms (dmmf). Various analytical methods have been utilized to examine heteroatoms and functional groups in coals including thermogravimetric Fourier transform infrared spectroscopy (TG-FTIR), X-ray adsorption near-edge structure spectroscopy (XANES), X-ray photoelectron spectroscopy (XPS) and NMR spectroscopy. Kelemen and Kwiatek quantified organic oxygen species from XPS carbon (1s) curve analysis and reported that Illinois coal contained 57 ether, 42 phenolic, 4 carbonyl and 6 carboxyl groups per 1,000 carbon atoms. Winans et al. determined the structural distribution of carbons bonded to oxygen in the Argonne coals by SPE $^{13}$C NMR coupled with high-resolution mass spectroscopy. Illinois coal was found to contain 7.5 phenolic, 1.6 furanic and 0.4 carboxylic groups per 100 carbons atoms. These results are in agreement with CP-MAS $^{13}$C NMR data which indicated aliphatic and aromatic C-O groups as the major types of oxygen structural units in Illinois coal with no significant levels of carboxyl/carbonyl carbons.
Kelemen et al.\textsuperscript{30} utilized XPS for the identification and quantification of the organically bound nitrogen structures present in Argonne Premium suite. The nitrogen type and distribution for Illinois no. 6 coal was: 62\% pyrrolic, 26\% pyridinic and 12\% quaternary. Similar trends were obtained from a XANES study of nitrogen species in Argonne coals where pyrrolic and pyridinic forms were the two most common nitrogen structures in Illinois coal.\textsuperscript{26} XANES data by George et al.\textsuperscript{28} determined that organic sulfur forms in Illinois coal are distributed as: 26\% aromatic (diphenyl sulfide), 33\% aliphatic (dibenzyl sulfide), and 41\% thiophenic (2,5 dimethylthiophene, benzothiphene and dibenzothiophene molecules). It should be noted that XPS permits analysis of the sample surface only, while XANES allows analysis of the bulk of a sample. Furthermore, both techniques require deconvolution of the C\textsubscript{1s}, O\textsubscript{1s} and N\textsubscript{1s} bands for determining functional groups, which is challenging.\textsuperscript{29-31}

Several methods have been utilized for determining the molecular weight of coals including analysis of solvent-extract,\textsuperscript{34, 35} laser desorption ionization mass spectrometry (LDIMS),\textsuperscript{36} and field-ionization mass spectroscopy (FIMS).\textsuperscript{37} Herod et al.\textsuperscript{36} characterized the Argonne Premium coals by matrix-assisted LDIMS. Illinois no. 6 coal spectra showed a sharp peak at 230 – 400 Da followed by another series of smaller peak in the 1500 – 5000 Da. Huai et al.\textsuperscript{38} reported number average molecular weight (M\textsubscript{n}) of 270 Da as determined by pyrolysis gas chromatography mass spectrometry (Py-GCMS) and 367 Da measured by pyrolysis field-ionization mass spectroscopy (Py-FIMS). Techniques reliant on a GC often suffer from larger molecule screening by the column so lower values are expected. Malhotra et al.\textsuperscript{37} analyzed pyridine extracts by FIMS and reported values of 402 and 441 Da for M\textsubscript{n} and weight average molecular weight (M\textsubscript{w}) with a molecular weight distribution ranging from 150 to 1000 Da. It is clear that molecular weight values reported in the literature depend on the experimental techniques. The concept of molecular weight of coal remains elusive and is subject of debate since there is no analytical method available that could isolate the free molecules and leave the macromolecular network intact.\textsuperscript{39, 40}

The structure of bituminous rank coals is usually considered to contain mobile and rigid phases.\textsuperscript{39, 41} The latter is a covalently bonded network of aromatic fragments forming the coal macromolecular structure, whereas the former is trapped and weakly bonded to the
macromolecular structure through hydrogen bond and van der Waals interactions. Larsen et al.\cite{42} conducted solvent swelling/extraction measurements to examine the macromolecular network structure of an Illinois no. 6 coal (likely a non-APS sample) and Bruceton coals. Several associating and non-associating solvents were used to investigate the role of hydrogen bonding in the coal structure. The solvent-swelling data were analyzed by using a non-Gaussian theory that accounts for structural features such as chain stiffness and finite extensibility of the network. The results showed that strong associating solvents replace many of the coal-coal hydrogen bonds with coal-solvent hydrogen bonds resulting in coal swelling. A volumetric swelling ratio of about 2.4 for Illinois coal in pyridine at room temperature was obtained via the usual approach.\cite{42} It was proposed that the Illinois coal structure could best be described as consisted of a covalently bonded network of clusters, which were extensively hydrogen bonded and that the coal-coal hydrogen bonds provided most of the cross-links.\cite{42}

Several techniques have been used for characterization of coal porosity: gas and liquid adsorption,\cite{43} $^{129}$Xe NMR,\cite{44,45} small angle neutron scattering (SANS)\cite{46} and small angle X-ray scattering (SAXS).\cite{43,47} Wernett et al.\cite{45} estimated an average micropore diameter of 5.2 Å for Illinois coal by $^{129}$Xe NMR. Tsiao and Botto\cite{44} also used $^{129}$Xe NMR and found two pore structures of similar size (6 Å in diameter) tentatively assigned to aromatic and aliphatic regions. For Illinois no. 6, an additional pore structure was identified having a larger pore diameter of about 10 Å.\cite{44} Zhu et al.\cite{48} also observed two distinct pore size systems intimately connected in Illinois coal using $^{129}$Xe NMR. Hall et al.\cite{46} performed contrast matching SANS on Argonne coals to investigate their pore structures in wet state. It was obtained that porosity levels decrease with increasing coal rank. Illinois coal showed greater scattering and exhibited microporosity, which appeared to be associated with the presence of water. Norinaga et al.\cite{49} quantified and classified the water sorbed in several coals by differential scanning calorimetry. Water types were experimentally determined from their respective heats of congelation. Illinois coal contained 0.05 and 0.05 g/g-db coal of bound and non-freezable water respectively.

Larsen et al.\cite{43} investigated the pore structure of bituminous coals. The BET surface areas for Illinois no. 6 were: 29 m$^2$/g for N$_2$ (-196 ºC), 132 m$^2$/g for CO$_2$ (-78 ºC), and 38 m$^2$/g for ethane (-78 ºC). Surface areas derived from adsorption methods depend on the characteristic dimension
of the probe molecules used and the magnitude of the interaction forces between them and the coal structure. Lin et al.,\textsuperscript{50} and Spitzer and Ulicky\textsuperscript{51} performed SAXS experiments on Illinois coal and reported surface area values of 151 and 179 m\textsuperscript{2}/g, respectively. Gethner et al.\textsuperscript{52} determined for Illinois coal a surface area of 195 m\textsuperscript{2}/g using SANS. The helium density of Illinois No. 6 is 1.301 g/cm\textsuperscript{3} (dmmf).\textsuperscript{53}

**Model construction strategies for coal and char**

Advances in analytical techniques, molecular modeling approaches and computational power have permitted construction of improved molecular representations of coal structure. Molecular models provide insightful information at atomistic scales that could contribute to improved structure and behavior relationships for coal. According to Mathews and Chaffee more than 125 structural representations of coal exist.\textsuperscript{54} With a few exceptions, the majority of these models are small-scale (<5000 atoms) average structural representations of coal. While useful for revealing some structural features of coals, their application for exploring the structure and behavior relationships of coal are often limited. A review on the utility of coal molecular models is also provided by Mathews et al.\textsuperscript{55} Generation of representative structures is time-consuming, challenging, and requires considerable expertise particularly due to the large range of structural features covering small molecules to very large molecular masses and maceral contributions. Thus, it has long been recognized that coal and many of the extracts and products are a structural continuum over a wide range.\textsuperscript{19, 36, 39, 56-58} These structural features influences coal behaviors including: thermoplasticity,\textsuperscript{59} liquefaction\textsuperscript{60} and pyrolysis.\textsuperscript{57} Despite advances in coal model construction approaches, coal molecular models have yet to capture the continuum of structural features.

Incorporation of structural diversity requires large-scale coal molecular models. The Narkiewicz and Mathews\textsuperscript{61} model for Pocahontas No. 3 low-volatile bituminous coal was the largest molecular coal structure containing ~22,000 atoms in 215 molecules incorporates a molecular weight distribution ranging from 78 to 2420 Da.\textsuperscript{61} The molecular weight distribution accommodates an evaluation of HRTEM lattice fringe images and LDIMS data. The model was used to visualize sequestration issues such as CO\textsubscript{2} and CH\textsubscript{4} sorption capacities, CO\textsubscript{2}-induced swelling, and the pore-blocking role of moisture.\textsuperscript{62} Molecular representations for inertinite-rich
and vitrinite-rich coals constructed by Van Niekerk and Mathews also exhibited a molecular weight distribution ranging from 78 to 1900 Da with model scales being 14,000-18,000 atoms.\textsuperscript{63} These models were utilized to examine solvent-swelling and extractability characteristics of these inertinite-rich and vitrinite-rich coals.\textsuperscript{64} However, all of these previous large-scale models were constructed mostly by-hand (prior to minimization) incurring high expense and requiring considerable time investment (typically months), which limits the scale and severely limits the access of quality coal models for use in the coal research community. Recently, a structure generation approach (Fringe3D) based on HRTEM lattice fringe images has allowed direct inclusion of aromatic stacking and alignment of aromatic moieties in the model space.\textsuperscript{65} Fringe3D enables >20,000 atoms non-cross-linked subbituminous coal slice model representation, containing those structural features, to be produced more easily and more accurately than with the current state-of-the-art model construction approaches.\textsuperscript{55} Basically, the Cartesian location, length, and orientation were determined from image analysis of HRTEM lattice fringes and processed via Fringe3D to duplicate those fringes in molecular modeling space based on a combination of known molecules (such as naphthalenes) to a continuum of larger structures from catenation molecules. Automation (Perl scripts created within the Materials Studio software package) can further populate heteroatoms and aliphatic components to aid in construction and to remove investigator bias. In this manner, structures of larger scale, improved accuracy, and utility can be generated. Here the approach was adapted with the goal of producing the distribution of aromatic structures to form the structural base from which a construction strategy could be implemented. The advantage of this approach was primarily ease of construction. The large-scale also overcomes on the significant challenges of elucidation. Instead with an aromatic base scripting was utilized to distribute the desired frequency of structural features thus avoiding the multiple iterations typically required by other elucidation strategies.

Similar to coal structure representations, structural modeling of char structure is challenging, time-consuming, and demands substantial expertise due to the broad distribution of structural features that often influence the behavior of chars during kinetic controlled conversion reactions. Inorganic species influence char reactivity and have been explored using both experimental\textsuperscript{66} and
small-scale high-level molecular modeling approaches, but are not included in this initial work. Various coal-derived char molecular models have been generated by modifying existing coal molecular structures to reflect structural transformations of coal to char during devolatilization. Alternative approaches using reverse Monte Carlo (RMC) methods have also been used to construct coal-char structural models for exploring char microstructure and dissolution in steel. The RMC approach uses a reconstruction technique that systematically rearranges the position of atoms via Monte Carlo-type moves until close agreement with experimental small angle X-ray diffraction data is achieved. This approach has been utilized for porous carbon structure. However, carbon modeling via RMC methods requires advanced computing capabilities and is more appropriate for highly organized structures.

The work presented here implements an automated model construction approach via Fringe3D and Perl scripts that enables inclusion of structural diversity resulting in making progress toward capturing the continuum of the coal structure and thus better enabling appropriate behavioral observations. The proposed computational protocol was demonstrated with Illinois no. 6 Argonne Premium coal and char. In addition, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) data, provided by the National High Magnetic Field Laboratory, was utilized to further characterize the pyridine extract to capture the diversity in heteroatoms, most specifically oxygen-containing species. Comparison of the FT-ICR MS data to the individual components of the coal molecular model provides a measure of the continuum coverage. Construction of coal molecular model (illustrated in Figure 1.1) consisted of: (1) HRTEM lattice fringe image analysis, (2) construction of the aromatic clusters (benzene to large PAH molecules), (3) inclusion of heteroatoms and functional groups, (4) addition of aliphatic side chains and generation of a cross-linked network structure, and (5) arrangement of cross-linked clusters into a simulation cell. Implementation of an automated construction protocol via Fringe3D and Perl scripts was necessary due to the great structural diversity of Illinois coal and char. This procedure enabled simplifying the model construction process, eliminating researcher structural bias and generating large-scale continuum molecular representations with improved accuracy and utility.
Several Perl scripts within Material Studio were further developed from previous work\textsuperscript{76} to aid in the construction and evaluation of chemical structural parameters (elemental composition, NMR parameters and molecular weight distribution). Essentially, these scripts determine the type and distribution of atoms and functional groups of each molecule. Solubility parameter calculations were conducted to determine the mass that could be theoretically extracted with a specific solvent. Recently, this method was used to evaluate theoretical extraction yields for vitrinite-rich and inertinite-rich coal models.\textsuperscript{64} The group contribution approach developed by Painter et al.\textsuperscript{77} based on aromaticity and elemental composition data was used to estimate the solubility parameter ($\delta$) of coal molecules in the constructed model. These solvent extraction calculations
were performed based on a cutoff value of $\pm 1$ (cal/cm$^3$)$^{0.5}$. The remaining molecules were assumed to form the solid residue. Estimation of solubility parameters was also performed by scripting.\textsuperscript{76} The effects of secondary interaction forces and transport limitations were not considered during solvent extraction calculations.

The compositional continuum of the coal model was evaluated by determining double bond equivalents (DBE) distribution, heteroatom class (numbers of N, O and S atoms) distribution, and van Krevelen diagrams (a plot of H/C vs. O/C atomic ratios). Comparison between model and FT-ICR MS data (provided by the National High Magnetic Field Laboratory) was used to assess the capability of the constructed model in capturing a portion of the continuum structure. DBE corresponds to the number of rings plus double bonds to carbon and thus is a direct measure of unsaturation (higher degree of unsaturation usually indicates increased aromaticity).\textsuperscript{78} Compositional characterization of pyridine coal extracts based on DBE analyses are discussed in detail elsewhere.\textsuperscript{78-80}

The physical evaluation of the coal molecular model comprised determination of simulated helium density, pore size distribution, interlayer spacing, aromatic cluster size, and number of layers per stack. The simulated helium density was calculated from the molar mass and the volume of the coal structure. The latter is the volume not accessible to helium atoms (kinetic radius of 1.29 Å).\textsuperscript{81} Following an approach similar to that presented by Gelb and Gubbin\textsuperscript{s},\textsuperscript{82} the simulation cell was divided into a fine grid composed of cubic cells of 0.05 nm length. A test sphere was placed at every grid point and the distance between the center of the sphere and the center of local atoms was calculated to classify grid points as occupied and unoccupied. The sum of the volume of all occupied grid points defines the volume of the coal structure, while that of all unoccupied grid points corresponds to the pore volume. The pore size distribution was determined from the plot of $-dV_{pore}(r)/dr$ versus $r$, where $V_{pore}(r)$ is the fraction of pore volume that can be enclosed by a test particle of radius $r$. It is important to note that in this study the porosity of the coal model was sampled at the micropore length scale (i.e., not including the macro or mesoporosity). Stacks of aromatic clusters with an angle of inclination within $\pm 10^\circ$ were considered for computing model physical structural parameters (such as stacking number and interlayer spacing). These stacks were classified according to the number of layers per stack.
or stacking number. Interlayer spacing and cluster size were measured as the perpendicular distance between aromatic clusters forming a stack, and the projected length of the layers, respectively, based on molecular modeling software.

While earlier modeling efforts are elucidations requiring comparison and reduction of error between model and data, here our construction protocol starts with an aromatic base and simply add the correct type and distribution of heteroatoms and aliphatics. As such the proposed approach is far more efficient but lacks the traditional validation approaches that commonly occur in smaller-scale atomistic representations. Thus the loop in Figure 1.1 will often consist of a single or perhaps a few tests rather than multiple trial and error iterations. Validation of the model occurs with evaluation and behavior in multiple aspects of coal science. Hence to permit this approach and to further the range of simulations that can be evaluated the atomistic representation (pdb format) is freely available online.

During model construction process, elemental composition, NMR parameters, molecular weight distribution and simulated helium density were adjusted to agree with the available experimental data. However, evaluation of the pore size distribution, interlayer spacing, stacking number, pyridine extraction yield, distribution of DBE numbers and heteroatom classes, and compositional variety of heteroatom classes (frequency of O, N, S in a molecule) explored with van Krevelen diagrams are regarded as a test of the model since these parameters were not fitted in building the coal model.

**Coal pyrolysis and char combustion**

Pyrolysis is the initial reaction step in most coal utilization process and influences the course of any subsequent reactions such as combustion, gasification, or liquefaction. Coal pyrolysis involves several physical and chemical processes in which coal is transformed via heating within inert gas atmospheres into a carbon-rich solid residue (coke or char), and volatile products, tar, light gases, and water.$^{57, 83, 84}$ The evolved gases and volatile products typically comprise CO$_2$, CO, H$_2$O, CH$_4$, C$_2$H$_6$, C$_2$H$_4$, C$_2$H$_2$ and various sulfur- and nitrogen-containing gases. Tars are defined as volatiles (other than water) which condense at room temperature.$^{57}$ The solid residue exhibits a broad distribution of molecular weights. The pyrolysis behavior of coals depends on
temperature, heating rate, particle size, pressure, and coal type, among others.\textsuperscript{25, 57, 83-87} The residence time required for a given degree of completion of coal devolatilization is reduced for higher temperatures. The use of slow heating rates promotes secondary reactions such as cracking and carbon deposition that will tend to reduce the total weight loss. The amount of evolved gases and tars vary broadly with coal rank. In general, low-rank coals produce a high yield of gases and a low yield of tar, while high-rank coals often generate low yields of light gases and tar.\textsuperscript{57, 83, 84}

Coal pyrolysis reactions are highly complex, largely involving bond breaking, vaporization and condensation. The chemistry of coal pyrolysis generally includes the thermal decomposition of surface functional groups to form light gases, and the degradation of the macromolecular network to produce smaller fragments that can evolve as tar. Volatile species and tars are conveyed by mass transport processes to the exterior of the coal particle followed by the formation of char structure due to condensation reactions at high temperature.\textsuperscript{57, 83} Pyrolysis behavior of softening coals has been described as a three-stage process.\textsuperscript{59} During stage I, coal undergoes a disruption of hydrogen bonds and cleavage of labile chemical bonds within the macromolecular network to promote the release of primary gas and liquid components, which are often referred to as metaplast. The metaplast is generally recognized to be responsible for the fluidity of coal upon heating.\textsuperscript{59} At stage I, bond rupture competes with bond stabilization to form char particle. Stage II is characterized by bulk evolution of tar, which is considered the low molecular weight component of metaplast.\textsuperscript{59} The remaining high molecular weight components in the metaplast re-attach to the char structure by condensation reactions. During stage III, char evolves CO and H\textsubscript{2} while continuing to cross-link with further ring condensation.

Coal undergoes rapid loss of moisture and volatiles at high temperatures often followed by thermoplastic transformations resulting in a complex char structure that is dependent on the precursor properties, time-temperature history, and gas pressure employed.\textsuperscript{84, 88-95} Fully devolatilized coal-derived chars are typically highly aromatic (aromaticities of >0.90) and exhibit various degrees of turbostratic crystalline order (stacking, layer size and interlayer spacing), pore size distributions, surface areas, and atomic H/C ratio’s.\textsuperscript{90, 96-98} These variations affect char reactivity.\textsuperscript{84, 91, 99} The structure of char has a significant impact on subsequent conversion
processes such as char gasification and combustion. During combustion, the char structure undergoes several structural transformations and complex chemical reactions. Coal combustion generally involves devolatilization to form char particles with the release of volatiles followed by their combustion (homogeneous gas-phase reaction) and char particle oxidation and combustion (heterogeneous surface reaction with oxygen). The oxidizing agent (O₂, H₂O, CO₂ and H₂) must diffuse to the char particle reaction sites, sometimes through the developing ash layer. The reaction products then diffuse away from the char particle. The ratio of the primary combustion products, CO/CO₂, generally increases with increasing temperatures. Heterogeneous char-gas reactions of industrial relevance occur in one of three temperature zones. In the low-temperature regime (Zone I), the reaction rate is controlled by chemical reaction rather than pore diffusion. As the temperature increases, both chemical reaction and internal pore diffusion become important (Zone II). In the high-temperature regime (Zone III), the reaction controlling mechanism is bulk diffusion.

Despite extensive research, improved understanding of fundamental reaction mechanisms and chemical events involved in coal pyrolysis and char combustion remains desirable. Reactive molecular dynamics simulations can provide insight at the atomistic scale for such reactive events, provided that a representative coal/char structure can be generated and coupled with an appropriately developed reactive force field.

**Reactive molecular dynamics**

Molecular dynamics (MD) is a computer simulation technique in which the time evolution of set of interacting particles is followed by integrating the equations of motion. MD is a statistical method and physical quantities are represented by averaging over the set of configurations distributed according to a certain statistical ensemble. MD approach simulates the dynamic behavior of the system by applying Newton’s equations of motion. A trajectory obtained by MD simulations provide required set of configurations and physical quantities are computed as an arithmetic average of the various instantaneous values assumed during a MD run. The interaction between particles for a covalent system can be classified into bonded and non-bonded interactions. The non-bonded interactions mainly consist of coulomb forces and van der Waals forces while the bonded interactions typically include covalent bonds between two atoms and
valence angle interactions between three atoms and torsion angle interactions between four atoms. These interactions can be calculated using appropriate force fields which incorporates average effects of electronic motion. Force fields can broadly be categorized as non-reactive and reactive. In general, non-reactive force fields consider a rigid connection between atoms and hence they do not describe chemical reactivity. Reactive force fields (RFFs) can simulate the dissociation and formation of chemical bonds during MD simulations. Unlike, non-reactive force field, they are able to properly simulate transition states and barrier energy in chemical reactions. However, they are computationally more expensive than non-reactive force field methods. Since RFF parameters are often derived from quantum mechanics (QM) data and can simulate reaction pathways without any preconditioning, reactive MD simulations via RFF approaches is a useful tool for examining the complex chemistry associated with structural transformations and chemical reactions involved in coal char utilization processes. Among the RFF-schemes that have been developed, the ReaxFF reactive force field has been applied in numerous simulation studies aimed at examining initiation reaction mechanisms and chemical processes relevant to fossil fuel thermolysis processes including pyrolysis, combustion, and oxidation. Thus, the work performed here utilizes the ReaxFF reactive force to conduct MD simulations for the complex and large-scale Illinois coal model. While RFF approaches are less computationally expensive than QM methods, they still require considerable computing resources to provide a detailed description of chemical reaction for large and highly complex systems such as coal and char simulated in this work. With current computational resources, the time scale of reactive simulations is many orders of magnitude shorter than that used in the experiments. Thus, reactive simulations are often performed at temperature ranges extending beyond normal experimental and industrial conditions to enable chemical reactions to occur within a practical computational time. With advances in computing power and software tools, reactive MD simulations over longer time scales and lower temperatures will be reachable. Nevertheless, RFF method coupled with realistic atomistic representations is a versatile computational approach for investigating transformations and modifications relevant to coal conversion and utilization.

ReaxFF reactive force field

ReaxFF is a reactive force field based on the covalent bonding formalism of Tersoff and Brenner in which the bond strength and bond length adjust appropriately in response to
changes in the local chemical environment, resulting in accurate descriptions of bond cleavage and bond formation during chemical reactions. The ReaxFF potential determines the system connectivity based on bond orders calculated from interatomic distances that are updated every iteration, enabling dissociation and formation of chemical bonds during reactive MD simulations. Morse and Coulomb potentials were utilized for modeling the non-bonded interactions (van der Waals and Coulomb), which were calculated between all atom pairs and were shielded at short range. A geometry-dependent charge calculation scheme was used to account for polarization effects. ReaxFF parameters were derived from quantum chemical calculations on bond dissociation and reactions of small molecules as well as heat of formation, transition state energy and geometry data for several simple hydrocarbons. The total potential energy of the system is decomposed into several contributions as:

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdW}} + E_{\text{Coulomb}}$$ (1.1)

where $E_{\text{bond}}$ corresponds to the bond energy, $E_{\text{over}}$ and $E_{\text{under}}$ represent atom under- and over-coordination, respectively. Other terms, including $E_{\text{val}}$, $E_{\text{pen}}$, $E_{\text{tors}}$, $E_{\text{conj}}$, $E_{\text{vdW}}$, and $E_{\text{Coulomb}}$ are the valence angle term, penalty energy term, torsion angle energy, conjugation effects to molecular energy, non-bonded van der Waals interactions and Coulombic interactions, respectively. The potential energy functions of important energy terms are described below. A more detailed description of the ReaxFF potential functions can be found in the work by van Duin et al.

**Bond order and bond energy ($E_{\text{bond}}$)**

ReaxFF assumes that bond order is strictly a function of interatomic distance between two atoms and is given by

$$BO_{ij} = \exp \left[ p_{bo,1} \cdot \left( \frac{r_{ij}}{r_0} \right)^{p_{bo,2}} \right] + \exp \left[ p_{bo,3} \cdot \left( \frac{r_{ij}}{r_0} \right)^{p_{bo,4}} \right] + \exp \left[ p_{bo,5} \cdot \left( \frac{r_{ij}}{r_0} \right)^{p_{bo,6}} \right]$$ (1.2)

where the first, the second, and the third exponential terms determine the single, double (pi bond), and triple (double pi bond) bond order contributions, respectively. Each bonding term, $p$, and each bonding equilibrium distance, $r_0$, have been parameterized so as to yield bond strengths.
and distances that agree with quantum mechanically predicted values for species that are at a distance \( r_{ij} \) apart. From this uncorrected bond order, uncorrected overcoordination is calculated for each atom which is further used in calculating the corrected bond order, \( BO_{ij} \). The corrected bond orders are then used for calculating bond energy which is given by

\[
E_{\text{bond}} = -D_e^e \cdot BO_{ij}^e \cdot \exp\left[p_{be1} \cdot \left(1 - \left(BO_{ij}^e\right)^{p_{be2}}\right) - D_e^\pi \cdot BO_{ij}^\pi - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi}\right]
\]

(1.3)

where \( p_{be1}, p_{be2}, D_e^\pi, \) and \( D_e^{\pi\pi} \) are force field parameters.

Valence angle (\( E_{\text{val}} \)) and torsion angle (\( E_{\text{tors}} \)) interactions

One of the drawbacks of the non-reactive force fields is their rigid description of angle and torsion interactions among atoms within the simulation. These types of interactions are usually described with a simple harmonic relationship, and that same harmonic potential applies regardless of how strong or weak a bond gets. Within ReaxFF, however, these angle and torsion interactions are also bond order dependent. This means that as an atom breaks a bond and leaves a molecule, the force exerted on it due to angle and torsion with respect to the rest of the molecule weakens smoothly along with the bond order. This is shown in Equations 1.4 and 1.5:

\[
E_{\text{val}} = f_7(BO_{ij}) \cdot f_7(BO_{jk}) \cdot f_8(\Delta_j) \cdot \{k_a - k_a \exp[-k_b(\phi_0 - \phi)^2]\}
\]

(1.4)

\[
E_{\text{tors}} = f_{10}(BO_{ij}, BO_{jk}, BO_{kl}) \cdot \sin \phi_{ijk} \cdot \sin \phi_{jkl} \cdot \left\{ \frac{1}{2} V_2 \cdot \exp\left\{p_1 \left(BO_{jk} - 3 + f_{11}(\Delta_j, \Delta_k)\right)^2\right\} \cdot \left(1 - \cos 2\omega_{ijkl}\right) + \frac{1}{2} V_3 \cdot \left(1 - \cos 3\omega_{ijkl}\right) \right\}
\]

(1.5)

where \( BO_{ij} \) and \( BO_{jk} \) are the bond orders for each of the two bonds connecting the three atoms within an angle, \( k_a \) and \( k_b \) are the harmonic force constants that determine the depth and width of the angular potential, respectively, \( \phi \) is the angle, and \( \phi_0 \) is the equilibrium angle. Functional forms for \( f_7 \) and \( f_8 \) can be found elsewhere.\textsuperscript{119}
**Coulomb** ($E_{\text{Coulomb}}$) **and van der Waals** ($E_{\text{vdWaals}}$) **interactions**

Because of the rigid connectivity associated with non-reactive force fields, the Coulomb and van der Waals forces are typically only calculated between the atom pairs that do not share a bond or valence angle with one another. Within the reactive environment of ReaxFF, however, the Coulomb and van der Waals forces are calculated between all the atom pairs, irrespective of their connectivity. To avoid excessive repulsive or attractive non-bonded interactions at short distances, both the Coulomb and van der Waals interactions are shielded in ReaxFF. This is achieved through the use of a shielding term ($f_{13}(r_{ij})$ in eq. 1.6 and $\gamma$ in eq. 1.7) as is shown in the Coulomb and van der Waals terms:

$$E_{\text{vdWaals}} = D_{ij} \cdot \left\{ \exp \left[ \alpha_{ij} \cdot \left( 1 - \frac{f_{13}(r_{ij})}{r_{\text{vdw}}} \right) \right] - 2 \exp \left[ \frac{1}{2} \alpha_{ij} \cdot \left( 1 - \frac{f_{13}(r_{ij})}{r_{\text{vdw}}} \right) \right] \right\}$$

$$E_{\text{Coulomb}} = C \cdot \frac{q_i q_j}{\left( r_{ij}^{\alpha} + (1/\gamma_{ij})^{\beta} \right)^{1/\beta}}$$

where $q_i$ and $q_j$ are the charges of the two atoms, $r_{ij}$ is the interatomic distance, and $f_{13}(r_{ij})$ and $\gamma_{ij}$ is the shielding parameter described above.

**ReaxFF pyrolysis and combustion simulations**

Salmon et al.\textsuperscript{111} utilized the ReaxFF reactive force field to describe the initial chemical processes of thermal decomposition of an aliphatic fossil organic matter (algaenan race L). An algaenan structural model and model compounds containing specific algaenan functional groups (aliphatic and isoprenoid chains, esters, and aldehydes) were constructed based on elemental analysis, IR spectra and NMR data. ReaxFF MD simulations were performed with temperature ramps from 300 to 2500 K at rates of 88, 44, and 22 K/ps to determine the kinetics of the thermal decomposition reactions. High-temperature simulations were conducted to allow the chemical reactions to occur within a reasonable time scale (50 ps). Thermal decomposition of algaenan was found to be initiated with the release of the isoprenoid side chain, followed by the cleavage of a C–O bond in the ester group to produce carbon dioxide. At higher temperature, generation of ethene was observed because of successive $\beta$-cleavage reactions. This degradation mechanism led to products similar to those observed in pyrolysis experiments, demonstrating the
applicability of ReaxFF in accurately modeling initial chemical events of algaenan thermal decomposition.

Early maturation process of Morwell brown coal (lignite) was also simulated by Salmon et al.\textsuperscript{112} via ReaxFF methodology to examine thermal decomposition processes of defunctionalization, depolymerization and rearrangement of the residual lignite structure. A coal molecular model composed of 500 atoms and model compounds (24-33 atoms) containing guaiacyl, syringyl and \(p\)-hydroxyl units to represent specific lignite substructures were constructed based on available experimental characterization data. Structural models were heated up to temperatures ranging from 1000 to 2200 K utilizing heating rates of 88, 44 and 22 K/ps followed by NVT reactive dynamics simulations for 40 ps. The simulation results showed that the decarboxylation and dehydroxylation of the lignin side chain of the Morwell model involved the formation of double bonds conjugated with the aromatic rings. The process of defunctionalization of the methoxy groups led to formation of phenol and methyl radicals. Decomposition of naphtheno-aromatic structures generated ethylene, while linear and branched aliphatic chains formed methane, ethylene, propane and butane. This supported that formation of gas hydrocarbons occurred by cleavage of C–C bonds of the lignin side chain. Agreement with experimental results validated ReaxFF methodology in describing molecular processes related to pyrolysis of complex carbonaceous materials.

ReaxFF simulations on methane thermal decomposition at high temperatures were performed by Lummen\textsuperscript{110} to investigate the subsequent formation of different hydrocarbons by reactions between the decomposition products. A 150-methane molecules model was used to conduct MD simulations at temperatures between 2500 and 3500 K. Formation of molecular hydrogen, a wide range of hydrocarbons and carbon dimers from decomposed methane was observed above of 2500 K. Ethylene and acetylene were the most abundant molecules produced from the decomposed methane, and \(\text{C}_3\text{H}_4\) was the most abundant hydrocarbon based on three carbon atoms. The basic chemical reactions were in agreement with existing models of methane thermal decomposition. An increasing variety of hydrocarbons was obtained with increasing temperature. Much larger molecules were found at temperatures above 3000 K and even the formation of a temporarily stable 6-membered carbon ring structure was observed. These large hydrocarbons
turn out not to be very stable as they were subject to reactions due to the many reactive molecules still present in the system.

Chenoweth et al.\textsuperscript{117} expanded the ReaxFF to investigate the initial chemical events associated with high-temperature gas-phase oxidation of hydrocarbons. High-temperature (2500 K) simulations were performed on various hydrocarbon/O\textsubscript{2} systems including methane/O\textsubscript{2}, propene/O\textsubscript{2}, \textit{o}-xylene/O\textsubscript{2}, and benzene/O\textsubscript{2} mixtures. ReaxFF predicted the correct reactivity trend (propene > \textit{o}-xylene > methane > benzene), following the trend in the C-H bond strength in these hydrocarbons. Chemical reactions during a complete oxidation of isolated methane, propene, and \textit{o}-xylene to a CO/CO\textsubscript{2}/H\textsubscript{2}O mixture were found to be in agreement with carbon chemistry knowledge and QM results. It was observed that the major initiation reaction for oxidation of methane, propene, and \textit{o}-xylene under fuel lean conditions involved hydrogen abstraction of the methyl hydrogen by molecular oxygen forming hydroperoxyl and hydrocarbon radical species. For a mixture of methane, propene, \textit{o}-xylene, and benzene, the initial reactions involved hydrocarbon decomposition or initiation by other radicals in the system.

The initiation mechanisms and kinetics associated with the pyrolysis and combustion of \textit{n}-dodecane\textsuperscript{114} and JP-10 hydrocarbon jet fuel\textsuperscript{113} were investigated using the ReaxFF reactive force field. Chenoweth et al.\textsuperscript{113} utilized a unit cell containing 40 JP-10 molecules to perform simulations at temperatures between 2000 and 2600 K. MD simulations showed that the main decomposition reactions involved either (1) dissociation of ethylene from JP-10, resulting in the formation of a C\textsubscript{8} hydrocarbon intermediate, or (2) the production of two C\textsubscript{5} hydrocarbons, in agreement with experiments. The rate of consumption of JP-10 yielded an activation energy value consistent with the experimental data and with the effects of strain release upon cleavage of the C-C bond in the JP-10 molecule.

Utilizing a system composed of 2 \textit{n}-dodecane molecules and 37 oxygen molecules, Wang et al.\textsuperscript{114} performed ReaxFF simulation to examine the oxidation process of \textit{n}-dodecane. MD simulations were carried out at temperatures from 2000 to 3000 K at an interval of 100 K per 900 ps. Formaldehyde molecules were found to be an important intermediate in the oxidation of \textit{n}-dodecane. ReaxFF simulations showed that \textit{n}-dodecane oxidation proceeded mainly through two
pathways: (1) H-abstraction reactions by small reactive molecules (such as O\textsubscript{2}, H, CH\textsubscript{3} and HO\textsubscript{2}), and (2) the first step of \textit{n}-dodecane pyrolysis that led to formation of small hydrocarbons and then to the reaction with oxygen molecules, in agreement with experiments. The combustion of \textit{n}-dodecane first involved fast thermal cracking of H-abstraction reactions to form small molecules, mainly H\textsubscript{2} and C\textsubscript{1}-C\textsubscript{4} hydrocarbons. Agreement with experimental data validated the use of ReaxFF for modeling the pyrolysis and combustion processes of hydrocarbons.

MD simulations of laser-induced incandescence of soot using an extended ReaxFF force field were performed by Kamat et al.\textsuperscript{115} to evaluate heat transfer from heated soot particles to the surrounding gas. A small-scale (2691 atoms) soot model consisted of a stack of four graphene sheets of 40 Å in diameter linked together using sp\textsuperscript{3} hybridized carbon atoms was used to calculate the thermal accommodation coefficient of various monatomic and polyatomic gases (He, Ne, Ar, N\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4}) with the soot particle. The N\textsubscript{2}-soot parameters were optimized against QM and experimental data. ReaxFF enabled simulating the effects of conduction, evaporation, and oxidation of soot particle on the cooling signal. Accommodation coefficients derived from ReaxFF MD simulations were consistent with experimental values, demonstrating that ReaxFF enables simulation of physical and chemical aspects of soot laser-induced incandescence. ReaxFF simulations on a soot particle for various pressures in the presence of both inert and reactive gases (He, Ne, Ar, N\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4}) were also performed by Kamat et al.\textsuperscript{115} to study the effect of oxidation on the cooling signal. When OH radicals surrounded the soot particle, cooling was observed to be slower than the corresponding case with the same number of argon atoms. This was because the OH radicals oxidized the soot particle, which was an exothermic reaction and hence suppressed the cooling effect to a certain extent.

Agrawalla and van Duin\textsuperscript{123} extended ReaxFF with H\textsubscript{2} molecules to perform simulations for various H\textsubscript{2}/O\textsubscript{2} mixtures and examine the reaction kinetics of H\textsubscript{2} combustion at high-pressure and high-temperature conditions. Hydroperoxyl (HO\textsubscript{2}) radical was found to play a key role in the reaction kinetics. The initiation reaction was predominantly H\textsubscript{2} + O\textsubscript{2} + M → H + HO\textsubscript{2} + M, in agreement with predictions of existing continuum-scale kinetic models for hydrogen combustion. A transition of reaction mechanism was also observed from high pressure, low temperature to low pressure, high temperature. These results can be utilized for enhancing existing continuum-
scale kinetic models for prediction of H₂ combustion kinetics at high-pressure and high-temperature conditions, which are difficult to achieve through experiments.

However, all of these previous ReaxFF pyrolysis and combustion simulations on carbonaceous materials were performed using small-scale systems (<5000 atoms). The work performed here is aimed at demonstrating for the first time ReaxFF integration with improved large-scale atomistic representations of coal and char to examine at the atomistic scale the initial chemical reactions of thermal decomposition processes during pyrolysis and combustion. By combining ReaxFF with realistic large-scale coal and char molecular models that better capture structural diversity generates a versatile and useful computational approach that enables improvement in our current understanding of fundamental reaction mechanisms and chemical events involved in coal pyrolysis and char combustion.

**HRTEM and pair distribution function**

Coal undergoes significant structural transformations with rank. Two useful complementary techniques are HRTEM, particularly in the post lattice fringe extraction period, and the pair distribution function which have been effectively used to provide insights into coal and char structure. The pair distribution function (PDF) is a method that determines the average coordination number or atomic density at a distance r from the center of an arbitrary origin atom. Analysis of peak position and amplitude provides structural information regarding turbostratic crystalline dimensions (aromatic stacking, layer size and interlayer spacing) that can be useful in evaluating coal structure and behavior.⁴⁷, ¹²⁴-¹²⁶

Mathews et al.⁵⁴,⁵⁵ recently reviewed the molecular representations of coal and their utility. In the lignite to medium-volatile bituminous rank range, limited growth in aromatic stacking and a slight growth in aromatic cluster size are expected.¹²⁷ Coalification into the high-rank range, however, is accompanied by significant transitions. For example, Wertz and Bissell¹²⁸ examined short-range structural features of Pocahontas no. 3 coal using X-ray scattering techniques. Interpretation of the experimental PDF data indicated that the average structural unit was 80% aromatic and composed of polycondensed aromatic rings that were predominately planar. The data were consistent with a coronene-like structure composed of seven fused rings. Similarly,
Wertz and Quin investigated the interlayer structure in several Argonne Premium Coals using PDF methods, and found that the number of layers increased with rank, from about 2.3 for Wyodak subbituminous, through about 3 for Pittsburgh no. 8 coal, to 4.5-5 for Pocahontas no. 3. The interlayer spacing decreased with increasing rank. HRTEM lattice fringe image analysis provides structural information on interlayer spacing, layer length and stacking number for carbonaceous materials (including coals, soots and chars) in accordance with the expected coalification trends and crystallography data. HRTEM coupled with image processing were used to determine structural parameters for the Argonne Premium coals.

The average fringe length remained almost the same (~1 nm) for lignite to high-volatile bituminous coal ranks, with a longer average fringe length for Pocahontas low-volatile bituminous coal (1.2 nm) in reasonable agreement with XRD data. A similar result was obtained with the average stacking number, which was observed to increase from two to three for low- to high-rank coals, respectively, consistent with expectations. Interlayer spacing was also evaluated and was found to decrease with increasing coal rank. Thus, HRTEM results support the general trends, but have the advantage of capturing the distribution of structural features.

Grigoriew presented an interpretation of XRD studies on coal structure. Structural models of the coals investigated were generated by fitting simulated PDF to experimental data. The resultant models suggested that sp² carbon atoms formed aromatic layers of 4-20 fused rings, depending on the petrographic component and the rank of coal. The sp³ hybridized atoms units were composed of linked cyclohexane structures. The author further concluded that the amount of disorganized carbon could be neglected. Similarly, Bratek et al. used PDF analysis to determine interatomic distances, and degree and range of structure ordering for different anthracites. A 2D graphene sheet model was used to fit and interpret the experimental PDF data. Results indicated a decrease in the interlayer spacing, and an increase in average size and number of aromatic rings in the basic structural units of the anthracites with increasing rank. Zhang conducted PDF analysis on a brown coal structure model with a moisture content ranging from zero to 60% to evaluate the water and coal interactions in the drying process. Water molecule removal was found to occur successively from the outer hydration shell to the inner hydration shell around the oxygen moieties. Several studies analyzed the morphology of amorphous
asphaltene aggregates using the PDF method, demonstrating the versatility and utility of this approach to characterize and evaluate carbonaceous materials.

The PDF has commonly been used as a structural parameter to validate carbon molecular models. Specifically, the reverse Monte Carlo (RMC) algorithm is a stochastic reconstruction approach that produces structural representations by generating atomic configurations of carbon atoms that are consistent with carbon PDF obtained from X-ray, electron or neutron diffraction experiments. In the RMC approach, changes in the atomic configuration are accepted or rejected based on the agreement between the simulated and experimental PDFs. However, modeling material structures using RMC methods requires considerable computing resources and is more suitable for highly carbonaceous materials. A similar reconstruction approach that uses topological perturbations (addition of non-hexagonal rings) to generate model structures for non-graphitizing carbons was implemented by Smith et al. With this approach, 5- and 7-member rings are randomly incorporated into an extended sp² carbon sheet until reasonable agreement with the experimentally derived PDF was achieved.

In the work presented here HRTEM (coupled with additional constraining data) was the basis for the aromatic distribution. Given the high reliance on this approach it was desirable to further test its applicability by coupling HRTEM observations, the Fringe3D construction strategy with the PDF method. Here, PDFs were evaluated with molecular slice models of the aromatic and aliphatic components for several Argonne Premium coals (Beulah-Zap, Illinois no. 6, Upper Freeport, Pocahontas no. 3) constructed via Fringe3D based on HRTEM lattice fringe images. The constructed coal models were partially optimized to achieve realistic bond lengths but without displacement of coal molecules enabling the distribution of fringe length, stacking, and orientations to be duplicated in 3D modeling space. The effect of turbostratic crystalline parameters such as stacking height, layer size and interlayer spacing on PDFs calculated from the constructed models was examined and compared with experimental data collected and provided by the Advanced Photon Source at the Argonne National Laboratory.


**Research objectives**

The global objective of this investigation was to develop and implement an automated construction approach for generating large-scale coal molecular models that capture the continuum of coal structure and integrate these high-quality coal models with reactive force field methods to obtain a new simulation platform for evaluating highly complex physicochemical processes involved in coal pyrolysis and char combustion. The goal was to create an advanced computational capability that enables probing at the molecular level the complex structural transformations and chemical reactions associated with coal conversion and utilization. In this investigation, Illinois no. 6 Argonne Premium coal was the focus as this is the world’s most extensively studied coal.\(^{140}\)

The objectives of the investigation are:

- To collect and evaluate the available chemical and physical structural data of Illinois no. 6 Argonne Premium coal to serve the need for generating a large-scale molecular model of this coal (Castro-Marcano et al., *Energy and Fuels* **2011**, 25, 845–853).

- To develop and implement an automated model construction approach that enables inclusion of molecular weight distribution and structural diversity to capture the continuum of coal structure (Castro-Marcano et al., *Fuel* **2012**, 95, 35-49).

- To examine structural modifications and reactions associated with coal pyrolysis by performing pyrolysis simulations on a large-scale molecular model for Illinois no. 6 coal using the ReaxFF reactive force field (Castro-Marcano et al., *Fuel Processing Technology* **2012**, to be submitted).

- To investigate the structural evolution of char structure and chemical processes related to combustion under high-temperature conditions by conducting ReaxFF combustion simulations on a molecular representation for a devolutilized Illinois no. 6 coal char (Castro-Marcano et al., *Combustion and Flame* **2012**, 159, 1272-1285).
To evaluate the effect of turbostratic crystalline parameters on pair distribution functions calculated from molecular slice models of Argonne Premium coals and compare with experimental results (Castro-Marcano et al., *Energy and Fuels* **2012**, 26, 4336-4345).

This study implemented an improved computational protocol for generation of large-scale atomistic representations for coal and char (and other carbonaceous materials including soots, asphaltenes, and activated carbons) with improved accuracy, structural diversity and reduced computational cost. The proposed computational approach was demonstrated by building a large-scale (>50,000 atoms) molecular model for Illinois no. 6 coal and an atomistic representation (~7500 atoms) for a devolatilized Illinois no. 6 coal char based on available experimental data. Agreement between model and experimental chemical and physical structural parameters validated the model construction approach. The constructed coal and char models were integrated with ReaxFF reactive force field to create an advanced computational capability that enabled simulation of complex structural transformations and chemical reactions associated with coal pyrolysis and char combustion. This computational capability provides novel insight into the complex chemistry involved in coal pyrolysis and char combustion to enhance current scientific knowledge and support process optimization and efficiency improvements.

**References**


Chapter 2

Constitution of Illinois No. 6 Argonne Premium Coal: A Review*

Abstract

A review of the chemical and physical structural features of the Argonne Premium Illinois No. 6 coal is presented. The topics covered include aromatic and aliphatic components, functional groups and heteroatoms, molecular weight distribution, nature of the cross-linked network, porosity, surface area and density. Nuclear magnetic resonance (NMR) indicated that Illinois No. 6 high-volatile bituminous coal contains 15 aromatic carbons (three to four fused aromatic rings) and 5 attachments per cluster, and an average cluster molecular weight of 316 Da. Methyl units are the most abundant pendant alkyl groups. X-ray photoelectron spectroscopy (XPS) data showed that organic oxygen, nitrogen, and sulfur functionalities are primarily ether and phenolic, pyrrolic and thiophenic groups respectively. Solvent swelling studies suggested that Illinois coal structure is composed of a covalently bonded network of aromatic clusters that are extensively hydrogen bonded. Small angle neutron scattering (SANS) analyses showed that Illinois coal is mostly microporous and $^{129}$Xe NMR indicated that the pore structure of Illinois coal consisted of two distinct regions with average pore diameter of 6 and 10 Å.

Introduction

The Argonne Premium coal (APC) sample program was established in 1985 to provide highly-
uniform, unexposed-to-oxygen coal samples to the coal research scientific community.\(^1\) The full
set of eight U.S. coals includes a rank range from lignite through low-volatile bituminous as well
as a liptinite-rich, an inertinite-rich, and a coking coal. The coals were selected based on
compositional characteristic (primarily carbon content), maceral concentration and geological
age.\(^1\) The Argonne coals have been characterized extensively and have been used as standard and
reference samples in numerous coal studies.\(^2\)–\(^4\) Of all the Argonne coals, Illinois No. 6 high-
volatile bituminous coal is perhaps the most diverse,\(^1\) with more than 10,000 elementally distinct
species present in a single mass spectra.\(^5\) The Illinois No. 6 is an industrially relevant coal with
the Illinois basin being the largest bituminous basin in the United States.\(^6\) Through extensive
research search it was determined that >150 research journal publications have addressed its
behavior, chemical and physical properties. The Illinois No. 6 coal was collected underground
from the Herrin seam in Illinois in 1985. The seam was about 7 ft thick at the collection site, and
the drums were loaded in the mine. The original sample was a block that weighed at least 4 tons.
The initial 3 tons were mechanically mined (resulting in a higher mineral content) and became
the Illinois Basin Coal Sample 105, whereas the final ton was handpicked.\(^1\)

Several reviews have outlined the characteristic of the Argonne coals.\(^2\)–\(^4\) Stock and Muntean\(^2\)
evaluated available structural information on Pocahontas No. 3 Argonne Premium coal and
presented a network schematic structure that accommodate its high aromaticity, abundant methyl
units and bridging biaryl and heterocyclic groups. This paper follows a similar layout to their
review. Winans\(^3\) examined the organic structural components of the Argonne Premium suite of
coals using available analytical data. It was concluded that the aromatic structures were not very
large; heteroatoms were associated with the majority of the clusters; but that there was a need for
more quantitative information on the distribution of cross-links. Davidson\(^4\) published a review on
the structural chemistry of coal including experimental information derived from both APC and
non-APC. Abundant structural data for Illinois No. 6 are available in the scientific literature. It is
also the most popular sample of the Argonne Premium coals shipped with almost 3,500
ampoules shipped by 1994.\(^7\) Surprisingly it has not been the subject of a dedicated review paper.
The objective of this work is to provide a review of chemical and physical structural features of
Illinois No. 6 coal to serve the needs for generating a large-scale molecular model of this coal in an effort to move toward capturing the continuum structure.

**General Data**

The Argonne Premium Illinois No. 6 coal is a high-volatile bituminous coal with an elemental composition, normalized to 100 carbon atoms, of $C_{100}H_{77.3}O_{9.4}N_{1.5}S_{1.2}$ (dmmf) and maceral composition of 85% vitrinite, 10% inertinite, and 5% liptinite.\(^1\) The atomic H/C, O/C and N/C ratios are 0.773, 0.094 and 0.015 respectively. Proximate analysis shows that Illinois No. 6 coal as-received contains 8.0% moisture, 14.3% ash yield, 36.9% volatile matter, and 39.9% fixed carbon.\(^1\) The major mineral constituents as a percentage of total mineral matter are 19% quartz, 30% pyrite, 10% calcite, and 41% clay minerals (kaolinite and illite).\(^8\) Thus, this coal is relatively high (in American terms) in both organic sulfur and mineral matter.

**Aromatic Components**

The aromatic moieties present in coal structures have been characterized using nuclear magnetic resonance (NMR),\(^9\)-\(^13\) X-ray diffraction (XRD),\(^14\) high-resolution transmission electron microscopy (HRTEM)\(^15\)-\(^18\) and ruthenium ion catalyzed oxidation (RICO).\(^19\),\(^20\) Solum et al.,\(^9\) dela Rosa et al.,\(^11\) and Alemany et al.\(^10\) used cross-polarization magic angle spinning (CP-MAS) \(^{13}\)C NMR in studies of Illinois No. 6 coal and reported carbon aromaticity ($f_a$) values of 0.72, 0.70 and 0.68, respectively. Love et al.\(^12\) and Linehan and Franz\(^21\) determined $f_a$ values of 0.75 and 0.70 for Illinois coal utilizing the more quantitative single-pulse excitation (SPE) \(^{13}\)C NMR approach. Hydrogen aromaticity values of 0.47 and 0.48 were reported as determined by \(^1\)H NMR with combined rotational and multiple-pulse spectroscopy (CRAMPS).\(^11\),\(^13\) CP-MAS \(^{13}\)C NMR spectroscopy with dipolar dephasing by Alemany et al.\(^10\) indicated that of the 68±2 aromatic carbons (sp\(^2\)-hybridized) per 100 carbon atoms in the coal, 18±3 were protonated aromatic carbons, 44±2 were non-protonated aromatic carbons, and 6±1 were carbonyl carbons (see Table 2.1). Solum et al.\(^9\) conducted quantitative CP-MAS \(^{13}\)C NMR analyses on eight Argonne Premium coals. Using spin-lattice relaxation, variable contact time and dipolar dephasing 12 structural parameters were derived, shown in Table 2.1. Results indicated that there are 72±4 aromatic carbons per 100 carbon atoms in the Illinois coal of which, 26±3 were protonated and 46±3 were non-protonated. Utilizing the fraction of bridgehead carbons and
assuming linear and circular catenations, the average aromatic cluster size was estimated to be 15 carbons (three to four fused aromatic rings), with 5 attachments per clusters, and 316 Da average cluster molecular weight.

**Table 2.1.** $^{13}$C NMR analyses of Illinois no. 6 coal reported by Alemany et al.$^{10}$ and Solum et al.$^{9}$

<table>
<thead>
<tr>
<th>Sample</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>$f_{al}$</th>
<th>$f_{al}^H$</th>
<th>$f_{al}^*$</th>
<th>$f_{al}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solum et al.</td>
<td>0.72</td>
<td>0.72</td>
<td>0</td>
<td>0.26</td>
<td>0.46</td>
<td>0.06</td>
<td>0.18</td>
<td>0.22</td>
<td>0.28</td>
<td>0.19</td>
<td>0.09</td>
<td>0.05</td>
</tr>
<tr>
<td>Alemany et al.</td>
<td>0.74</td>
<td>0.68</td>
<td>0.06</td>
<td>0.18</td>
<td>0.44</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.32</td>
<td>0.18</td>
<td>0.14</td>
<td>-</td>
</tr>
</tbody>
</table>

Parameters: $f_a$ – total of sp$^2$ carbon, $f_{a'}$ – aromatic carbon, $f_a^C$ – carbonyl/carboxyl carbon, $f_a^H$ – protonated aromatic carbon, $f_a^N$ – nonprotonated aromatic carbon, $f_a^P$ – phenolic ethers, $f_a^S$ – alkylated aromatic carbon, $f_a^B$ – aromatic bridgehead carbon, $f_{al}$ – total sp$^3$ carbon, $f_{al}^H$ – CH or CH$_2$ carbon, $f_{al}^*$ – CH$_3$ carbon, $f_{al}^0$ – aliphatic carbon bonded to oxygen.

HRTEM has been used for characterization of the aromatic portion of the coal and char structure producing structural results in agreement with expected coalification trends, XRD and $^{13}$C NMR.$^{15-18}$ HRTEM lattice fringe images consists of lines termed fringes that correspond to the edges of aromatic rings. Sharp particle edges are usually analyzed to avoid the challenges of microtoming coal samples.$^{22}$ The HRTEM lattice fringe data can be utilized to determine aromatic structural features including average number of fringes per stack, fringe length distribution, and orientation.$^{15, 17, 18, 22}$ Sharma et al.$^{15}$ used HRTEM coupled with image processing and obtained an average fringe length and average stacking number of 1.0 nm and 2.2, respectively, in agreement with earlier XRD results.$^{14}$ An example of HRTEM lattice fringe images of Illinois No. 6 false-colored by length and angle of orientation is shown in Figure 2.1.

Stock and Wang$^{19, 20}$ conducted ruthenium tetroxide (RuO$_4$) catalyzed oxidation experiments. The coal sample, sodium periodate and ruthenium chloride trihydrate were added to a mixture of carbon tetrachloride, acetonitrile, and water. Excess sodium periodate and sodium iodate were collected by filtration and the filtrate was extracted with ether to obtain the reaction products, which were then methylated before characterization by chromatographic and spectroscopic methods. Reactive aromatic compounds were selectively oxidized to produce benzene carboxylic acids, ethanedioic acid and carbon dioxide. High yields of 1,2,3- and 1,2,4-benzenetricarboxylic acid, and 1,2,3,4- and 1,2,4,5-benzenetetracarboxylic acid were obtained in the oxidation
Figure 2.1. HRTEM lattice fringe images of Illinois No. 6 coal false-colored by (a) length and (b) angle of orientation. Adapted from Sharma, A.; Kyotani, T.; Tomita, A., *Energy Fuels* 2000, 14, (6), 1219-1225. Copyright 2000, with permission from the American Chemical Society.

products, as shown in Figure 2.2. These compounds were attributed to the oxidation of naphthalene, phenanthrene, acenaphthenes, anthracene and other more complex polycondensed aromatic structures. These results are consistent with the average NMR data of Solum et al.\(^9\) Quantitatively, the oxidation products accounted for more than 80% of the aromatic carbon atoms in the coal sample with more than 95% of aliphatic structural components recovered unchanged from the oxidation reaction. The RICO method is useful for characterization of aromatic and aliphatic components of organic materials but requires considerable analysis and consideration of multiple pathways to generate the same products.\(^{23}\) Although coal pyrolysis products could be too degraded to provide detailed information regarding the parent coal structure, spectroscopic and chromatographic analyses\(^{24-26}\) of the evolved products during flash-
pyrolysis of Illinois coal indicate the presence of polycyclic aromatic hydrocarbons composed mostly of 2-4 fused rings in agreement with $^{13}$C NMR and RICO results.\textsuperscript{9, 19, 20}

![Figure 2.2](image)

**Figure 2.2.** Yields of benzene carboxylic acids obtained in RuO$_4$ oxidation reactions of Illinois No. 6 coal. Adapted from Stock, L.; Wang, H., *Fuel* 1986, 65, (11), 1552-1562. Copyright 1986, with permission from Butterworth & Co. (Publishers) Ltd.

### Aliphatic Structural Elements

Various analytical techniques had characterized the aliphatic portion of coal structures.\textsuperscript{9, 10, 24, 26-29} Obeng and Stock\textsuperscript{27} performed RICO experiments to determine the distribution of pendant alkyl groups in the Argonne Premium coals. The oxidation study established that Illinois coal contained 1.76 methyl, 0.29 ethyl, 0.037 propyl, and 0.035 2-propyl groups per 100 carbon atoms. Stock and Wang\textsuperscript{29} indicated based on RuO$_4$ oxidation reactions of Illinois coal that arylmethanes and arylpropanes are primarily responsible for the formation of ethanoic and butanoic acid, and that diarylpropanes contribute significantly to the formation of propanoic acid. In addition, the amount of methyl groups observed in the oxidation reactions was less than that of $^{13}$C NMR analyses\textsuperscript{10} for the Illinois No. 6 coal. It was suggested that this difference could arise from additional methyl groups in hydroaromatic structures, for example, 1-methyl-1,2,3,4-
tetrahydronaphthalene. Artok et al. determined that RICO reaction of coals generally suffered from low mass balance. Another limitation was the inability to detect monomethylene bridges since the resulting malonic acid from the oxidation reaction was not stable under oxidation conditions. Despite these limitations, RICO provides relatively qualitative information regarding aliphatic structure distribution that cannot be determined by other methods.

Alemany et al. determined the aliphatic carbon structural distribution in Illinois coal utilizing CP-MAS $^{13}$C NMR with dipolar dephasing. Results indicated that $32\pm2$ aliphatic carbons (sp$^3$-hybridized) per 100 carbon atoms were in Illinois coal with $18\pm2$ aliphatic carbons as quaternary, methyl and high mobile methylene and methine, and $14\pm3$ aliphatic carbons as other methylene and methine. Solum et al. analyzed the Argonne Premium suite of coals with CP-MAS $^{13}$C NMR and obtained several aliphatic structural parameters. Illinois No. 6 coal was found to have $28\pm2$ aliphatic carbons per 100 carbon atoms distributed in $9\pm3$ methyl and $19\pm2$ methylene/methylene units. Aliphatic H/C ratios of 2.1, 1.7 and 1.4 have been reported for Illinois coal as determined by SPE $^{13}$C NMR, CP-MAS $^{13}$C NMR, and CP-MAS $^{13}$C NMR coupled with $^1$H CRAMPS. Xiong and Maciel conducted variable temperature (25, 120, and 180 °C) dipolar dephasing $^1$H CRAMPS experiments on APC coals including Illinois No 6. They were able to construct separate dipolar dephasing curves for protons in aliphatic and aromatic structures by deconvolution of the NMR spectra. It was suggested that a large fraction (65–75%) of the aliphatic structures in high-volatile bituminous coals (Illinois No. 6) were in rigid cross-linked macromolecular networks or were smaller molecules trapped in very tight voids. Chromatographic analysis of Illinois liquefaction products conducted by Carlson et al. detected long-chain paraffinic units (ranging from $n$-$C_{12}$ to $n$-$C_{40}$) presumably originated from polymethylene entities present in the raw coal. Linear alkanes, unattached to the coal structure, containing 16-30 carbon atoms were reported based on deuterium-degradation reactions. These long-chain aliphatics constituted about 1% of the coal. Previous work on RuO$_4$ oxidation products of the macerals from this coal indicated that these alkanes likely arise from the liptinite fraction. They are not observed in the flash pyrolysis of high-purity vitrain coals. Flash pyrolysis of the Illinois density gradient macerals showed that the vitrinite fraction was dominated by alkylbenzenes and alkylphenols, while the inertinite fraction exhibited relatively high amounts of polyaromatic pyrolysis products. Individual macerals were observed to be
characterized by distinct chemical properties such as hydrogen content, heteratom content, and aromaticity, consistent with their different physical behavior.\textsuperscript{25}

**Heteroatom Content**

The Argonne Premium Illinois No. 6 coal contains 94 oxygen, 15 nitrogen, and 12 sulfur heteroatoms per 1,000 carbon atoms (dmmf).\textsuperscript{1} Various analytical methods have been utilized to examine the oxygen functional groups in coals including fast neutron activation analysis (FNAA),\textsuperscript{34} thermogravimetric Fourier transform infrared spectroscopy (TG-FTIR),\textsuperscript{35, 36} X-ray photoelectron spectroscopy (XPS)\textsuperscript{37} and \textsuperscript{13}C NMR.\textsuperscript{9} Kelemen and Kwiatek\textsuperscript{37} quantified organic oxygen species from XPS carbon (1s) curve analysis and reported that Illinois coal contained 57 ether, 42 phenolic, 4 carbonyl and 6 carboxyl groups per 1,000 carbon atoms. Winans et al.\textsuperscript{38} determined the structural distribution of carbons bonded to oxygen in the Argonne coals by SPE \textsuperscript{13}C NMR coupled with high-resolution mass spectroscopy. Illinois coal was found to contain 7.5 phenolic, 1.6 furanic and 0.4 carboxylic groups per 100 carbons atoms. These results are in agreement with CP-MAS \textsuperscript{13}C NMR data\textsuperscript{9} which indicated aliphatic and aromatic C-O groups as the major types of oxygen structural units in Illinois coal with no significant levels of carboxyl/carbonyl carbons.

Nitrogen forms in coals have been mostly investigated by X-ray adsorption near-edge structure spectroscopy (XANES),\textsuperscript{39} XPS,\textsuperscript{40} and \textsuperscript{15}N NMR spectroscopy.\textsuperscript{41} Kelemen et al.\textsuperscript{40} utilized XPS for the identification and quantification of the organically bound nitrogen structures present in Argonne Premium suite. The nitrogen type and distribution for Illinois No. 6 coal was: 62\% pyrrolic, 26\% pyridinic and 12\% quaternary. Similar trends were obtained from a XANES study of nitrogen species in Argonne coals where pyrrolic and pyridinic forms were the two most common nitrogen structures in Illinois coal.\textsuperscript{39} CP-MAS \textsuperscript{15}N NMR data for the Argonne Premium coals reported the presence of pyrrolic but not pyridinic nitrogen species, which could arise from the very low pyridine signal resulting in spectra with poor signal-to-noise-ratios.\textsuperscript{41} Data on acidified derivatives confirmed that pyridinic nitrogen moieties were present in the coal samples but were not detected by standard solid-state \textsuperscript{15}N NMR techniques.\textsuperscript{41}
Characterization and quantification of organic sulfur species in coals has been performed utilizing flash pyrolysis, XPS, XANES, X-ray adsorption fine structure spectroscopy (XAFS), and temperature programmed oxidation (TPO). The distributions of sulfur forms in Illinois No. 6 coal as determined by XPS, XANES and TPO are compared in Table 2.2. These results show that there is a reasonable agreement between techniques; approximately half of the sulfur content in Illinois coal is organic, with thiophene (2,5 dimethylthiophene, benzothiphene and dibenzothiophene) as the most abundant organic sulfur functionality followed by aliphatic (dibenzyl sulfide) and aromatic (diphenyl sulfide). The XPS method, however, could not distinguish the thiophenic from aromatic sulfur. It should be noted that XPS permits analysis of the sample surface only, while XANES allows analysis of the bulk of a sample. Furthermore, both techniques require deconvolution of the C1S, O1S and N1S bands for determining functional groups, which is challenging.

Table 2.2. Organic sulfur species in Illinois No. 6 coal as measured by TPO, XPS and XANES.

<table>
<thead>
<tr>
<th>method</th>
<th>organic sulfur forms (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>aliphatic</td>
</tr>
<tr>
<td>TPO</td>
<td>28</td>
</tr>
<tr>
<td>XANES</td>
<td>33</td>
</tr>
<tr>
<td>XPS</td>
<td>31</td>
</tr>
</tbody>
</table>

Wu et al. used electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to analyze the polar fraction of Illinois coal pyridine extract. This technique enabled assignment of molecular formulas to more than 10,000 elementally distinct species present in a single mass spectrum. The compositional characterization included determination of class compound (heteroatom content), type (number of rings plus double bonds) and alkylation distributions. The distribution of heteroatomic classes (speciation of molecules according to single to multiple heteroatoms and their combinations) showed Ox, NOx and SOx containing molecules as the most abundant class compounds with O2 and O3, NO3 and SO3 classes as the dominant members, as shown in Figure 2.3. The O3 and SO3 distributions were approximately Gaussian, suggesting a single dominant aromatic core structure (rather than two
or more non-fused cores) for these two classes. The O\textsubscript{2} distribution was found to be bimodal with up to six aromatic rings, suggesting the presence of at least two different core structures. Most of the nitrogen- and sulfur-containing moieties that were identified also contained oxygen, suggesting the existence of multiple heteroatom species in Illinois coal. The FT-ICR MS technique has made considerable progress towards defining structural diversity capturing the continuum of the coal structure.

**Figure 2.3.** Distribution of the most abundant heteroatom class identified in Illinois No. 6 coal pyridine extract as determined by FT-ICR MS.\textsuperscript{5} Reprinted from Wu, Z.; Jernstrom, S.; Hughey, C.; Rodgers, R.; Marshall, A., *Energy Fuels* **2003**, *17*, (4), 946-953. Copyright 2003, with permission from the American Chemical Society.
Molecular Weight Distribution

Several methods have been utilized for determining the molecular weight of coals including analysis of solvent-extract,\textsuperscript{51, 52} laser desorption ionization mass spectrometry (LDIMS),\textsuperscript{53} and field-ionization mass spectroscopy (FIMS).\textsuperscript{54} Herod et al.\textsuperscript{53} characterized the Argonne Premium coals by matrix-assisted LDIMS. Illinois No. 6 coal spectra showed a sharp peak ~230 – 400 Da followed by another series of smaller peak in the 1,500 – 5,000 Da. Huai et al.\textsuperscript{55} reported number average molecular weight (M\textsubscript{n}) of 270 Da as determined by pyrolysis gas chromatography mass spectrometry (Py-GCMS) and 367 Da measured by pyrolysis field-ionization mass spectroscopy (Py-FIMS). Techniques reliant on a GC often suffer from larger molecule screening by the column so lower values are expected. Malhotra et al.\textsuperscript{54} analyzed pyridine extracts by FIMS and reported values of 402 and 441 Da for M\textsubscript{n} and weight average molecular weight (M\textsubscript{w}) with a molecular weight distribution ranging from 150 to 1,000 Da.

Larsen et al.\textsuperscript{51} performed extraction measurements to determine the molecular weight distribution of coal extracts. The pyridine extracts were fractionated using gel permeation chromatography and the molecular weight of each fraction was measured using vapor pressure osmometry (VPO). The results indicated M\textsubscript{n} and M\textsubscript{w} values of 1,100 and 2,700 Da. However, these extraction experiments are sensitive to interpretation challenges due to complex associations of the larger molecules. Similarly, Derbyshire et al.\textsuperscript{56} determined molecular mass distributions for pyridine extracts of Argonne coals by size exclusion chromatography (SEC) and obtained values of 640 and 1680 Da for M\textsubscript{n} and M\textsubscript{w}. The results are summarized in Table 2.3 for convenient comparison. It is clear that molecular weight values reported in the literature depend on the experimental techniques. The concept of molecular weight of coal remains elusive and is subject of debate since there is no analytical method available that could isolate the free molecules and leave the macromolecular network intact.\textsuperscript{4, 56} Nevertheless, it is reasonable to recognize a \textit{continuum of structural features}, with more than 10,000 compositionally distinct molecules being identifiable by FT-ICR MS\textsuperscript{5} for the polar extracts alone for Illinois No. 6 and even greater diversity from LDIMS.\textsuperscript{53}
Table 2.3. Number and weight average molecular weights reported for Illinois No. 6 coal from various analytical techniques.

<table>
<thead>
<tr>
<th>sample</th>
<th>method</th>
<th>$M_n$ (Da)</th>
<th>$M_w$ (Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw coal</td>
<td>LDIMS</td>
<td>230-400</td>
<td>-</td>
</tr>
<tr>
<td>raw coal</td>
<td>Py-GCMS</td>
<td>270</td>
<td>-</td>
</tr>
<tr>
<td>raw coal</td>
<td>Py-FIMS</td>
<td>367</td>
<td>-</td>
</tr>
<tr>
<td>pyridine extract</td>
<td>FIMS</td>
<td>402</td>
<td>441</td>
</tr>
<tr>
<td>pyridine extract</td>
<td>SEC</td>
<td>640</td>
<td>1680</td>
</tr>
<tr>
<td>pyridine extract</td>
<td>VPO</td>
<td>1100</td>
<td>2700</td>
</tr>
</tbody>
</table>

**Nature of the Cross-linked Network**

The structure of bituminous rank coals is usually considered to contain mobile and rigid phases.\(^{56, 57}\) The latter is a covalently bonded network of aromatic fragments forming the coal macromolecular structure, whereas the former is trapped and weakly bonded to the macromolecular structure through hydrogen bond and van der Waals interactions. Larsen et al.\(^{58}\) conducted solvent swelling/extraction measurements to examine the macromolecular network structure of an Illinois No. 6 coal (likely a non-APS sample) and Bruceton coals. Several associating and non-associating solvents were used to investigate the role of hydrogen bonding in the coal structure. The solvent-swelling data were analyzed by using a non-Gaussian theory that accounts for structural features such as chain stiffness and finite extensibility of the network. The results showed that strong associating solvents replace many of the coal-coal hydrogen bonds with coal-solvent hydrogen bonds resulting in coal swelling. A volumetric swelling ratio of about 2.4 for Illinois coal in pyridine at room temperature was obtained via the usual approach.\(^{58}\) It was proposed that the Illinois coal structure could best be described as consisted of a covalently bonded network of clusters, which were extensively hydrogen bonded and that the coal-coal hydrogen bonds provided most of the cross-links.\(^{58}\) Later Larsen et al.\(^{59}\) created 2D structural model for Illinois coal, shown in Figure 2.4, to aid in understanding the relationship between coal structure and reactivity. The pentagons in the model represent clusters with an arbitrarily assumed molecular weight of 300 Da. Single lines correspond to rotationally free groups linking clusters. Network branch points, linked to more than two other clusters, are
circled. A feature of the model is the large number of network active hydrogen bonds, denoted by hash marks. At present the Larsen conceptual model is generally accepted. ⁴, ⁶⁰


Shin ⁶¹ utilized detailed chemical analyses of both coal and products from various liquefaction schemes to construct a 2D model that represents vitrinite-rich high volatile bituminous coals such as Illinois No. 6 and 2, Indiana V and Kentucky No. 9 and 11. Larsen and Gurevich ⁶² proposed a model for computing the number of hydrogen bonds in glassy coals based on solvent swelling. It was estimated that about 1/3 of the hydroxyl groups in Illinois No. 6 coal form network-active hydrogen bonds and there were about 1.7 hydrogen bonds per 100 carbon atoms. Nishioka and Larsen ⁶³ reported that solvent swelling of Illinois No. 6 coal was irreversible in pyridine and that the volumetric swelling ratio of the pyridine-extracted coal was lower than that of the raw coal, which was consistent with the decrease in pyridine extractability of 6–12 wt.%. Solvent swelling experiments were performed by Suuberg et al. ⁶⁴ to study the macromolecular structure of several coals including Illinois No. 6 coal. It was found that the extent of the swellability of coals depends strongly on solvent molecule size and shape (steric factors) and coal pretreatment (pre-extraction). The results also indicated that the swelling correlated with the
heat of immersion of coals in solvents, suggesting that the enthalpy of interaction of associating solvents with surface functionalities largely determines the swelling behavior. It was also recognized that moisture removal causes formation of strong internal coal-coal hydrogen-bonding interactions that can actually stress the network structure in the direction of compression.\textsuperscript{64}

Suuberg et al.\textsuperscript{65} reported a volumetric shrinkage of about 8\% for high-volatile bituminous coals on drying at 373 K from the starting moisture content to a fully dry state. Solvent swelling measurements parallel ($Q_{||}$) and perpendicular ($Q_{\perp}$) to the bedding plane were performed by Cody et al.\textsuperscript{66} to investigate the macromolecular network properties. For all coals studied, the solvent swelling was anisotropic, being greater perpendicular to the bedding plane than parallel to it. The solvent-swelling ratios ($Q_{\perp}/Q_{||}$) for Illinois coal were 1.05 for chlorobenzene, 1.19 for tetrahydrofuran, and 1.20 for pyridine.\textsuperscript{66} The anisotropic swelling behavior was attributed to an anisotropy distribution of cross-links (coal structure more highly cross-linked in the bedding plane). Later Larsen et al.\textsuperscript{67} indicated that native coals are strained and glassy materials prevented from rearranging into their most stable configuration. They demonstrated that coal swelling enabled structural rearrangements to a lower free energy and more highly associated state. In addition, anisotropic swelling was observed only in the first swelling of the coal.\textsuperscript{67} Polarized photoacoustic FTIR analysis by Cody et al.\textsuperscript{68, 69} showed that polycondensed aromatic structures are only slightly oriented in Illinois coal. \textsuperscript{13}C NMR work with Illinois No. 6 coal (sample origin is unclear) orientated within the magnetic field also indicated that the preferential orientation of the aromatic rings was slight and that around 3\% lying in the bedding plane. XRD and HRTEM observations also support this view of slight orientation in this coal and coals of similar rank.\textsuperscript{70, 71} Aida et al.\textsuperscript{72} examined steric effects on the kinetics of solvent swelling for Illinois coal. Volumetric swelling ratios obtained at 293 K were 1.04 for benzene, 1.23 for methanol, 1.34 for ethanol, 2.45 for $n$-propylamine, and 2.75 for pyridine. Extraction yields are 25.3 wt.\% (daf) for pyridine,\textsuperscript{24} 19.0 wt.\% (daf) for THF,\textsuperscript{24} and 33.1 wt.\% (daf) for CS$_2$/NMP.\textsuperscript{73}

Solvent swelling techniques have been used as a coal pretreatment for liquefaction reactivity enhancement.\textsuperscript{74, 75} Baldwin et al.\textsuperscript{75} conducted mild liquefaction experiments coupled with coal pretreatment on Argonne coals. Coal samples were swollen in THF for 30 min and then liquefied.
at 390 °C for 15 min. Coal conversion was determined based on THF and hexane solubility. Swelling in Illinois coal was found to have a negligible effect on THF conversion (80% conversion for parent coal vs. 82% for THF-swollen coal) and an appreciable effect on the yield of hexane soluble (16% conversion for parent coal vs. 28% for hexane-swollen coal). This result was attributed to physical loosening of the coal matrix by rupture of some of the weak bonds holding the macromolecules together. Nishioka and Gorbaty examined THF extracts of original and n-butylamine-treated Illinois coal and the pyrolyzed extracts to test the two-phase model for coal, which states that large amounts of low-molecular-weight compounds are physically trapped in the macromolecular network. It was found that low-molecular-weight compounds were not released by n-butylamine treatment but were released by thermal degradation of the extracts of the n-butylamine-treated coal. The authors concluded that most of smaller molecules were not trapped within the network but were both free molecules and partial constituents of macromolecules, thereby inconsistent with the two-phase model.

Nishioka et al. investigated pre-conversion processing for coal liquefaction enhancement under mild conditions (at 430 °C for 1 h). Illinois coal showed a 30% increase in the oil yield and a 15–20% decrease in the gas yield compared with results obtained using conventional methods. Li et al. investigated coal dissolution by heat treatments in NMP and 1,4,5,8,9,10-hexahydroanthracene (HHA) solvents at 175–300 °C under a nitrogen atmosphere. Dissolution yields were obtained using CS$_2$/NMP mixed solvent (1:1 by volume) as an extraction solvent for the heat-treated coals. The soluble fraction obtained was then fractionated into THF-insoluble, the mixed solvent-soluble fraction (TIMS), and THF-soluble fraction (TS). For Illinois coal, the dissolution yields of both NMP and HHA at 300 °C are higher than those at 175 °C, and at 300°C NMP produced a higher dissolution yield (73.0 wt.%) than that (43.0 wt.%) in HHA.

Extraction yield of 63% (at 350 °C for 60 min) was reported by Miura et al. when conducting dissolution/depolymerization experiments in a flowing stream of tetralin at 200–400 °C and 10 MPa. A low-temperature depolymerization procedure consisting of mild hydrotreatment at <290°C followed by base-catalyzed depolymerization (HT-BCD) was applied to various coals by Carlson et al. to produce molecular fragments representative of the parent coal structure. Gas chromatograms of the aliphatic fractions of HT-BCD products for Illinois coal showed a
hydrocarbon distribution ranging from \( n-C_{12} \) to \( n-C_{40} \) with a peak at \( n-C_{27} - n-C_{31} \). These long aliphatic compounds were attributed to polymethylene groups present in the original plant material. Chromatographic analysis of the aromatic HT-BCD fractions indicated the presence of mostly two-four fused aromatic rings compounds. Coal pyrolysis tars and liquefaction extracts prepared from Argonne coals were characterized by Herod et al.\(^80\) using LDIMS. The liquefaction extract was prepared by heating coal samples in a flowing solvent reactor at 5 °C/s to 450 °C with 400 s holding at 450 °C, in a stream of tetralin flowing at 0.9 mL/min under 70 bar pressure. Spectra of liquefaction extract from Illinois coal showed a range of peaks in the mass range of 240–400 amu with traces at up to 5,000 amu.

### Porosity, Surface Area and Density

The physical structure of coals can be characterized in terms of porosity, surface area, and pore size distribution. The pore structure in coals can be complex. Pores are generally well dispersed within the coal matrix with linkages and intersections that may, or may not, be accessible to sorbate molecules depending on their size, nature, and response of the coal (swelling). Larsen et al.\(^81\) measured the fractal dimensionality of pore surfaces in APC using gas adsorption and small angle X-ray scattering (SAXS), and proposed that pores in coals are isolated and could be reached only by diffusion through bulk coal. Coal pores are usually classified into four groups: macropores (>50 nm), mesopores (2–50 nm), micropores (0.4–2 nm), and ultramicropores (<0.4 nm).\(^82\)

Several techniques have been used for characterization of coal porosity: gas and liquid adsorption,\(^81\) \(^{129}\)Xe NMR,\(^83, 84\) small angle neutron scattering (SANS)\(^85\) and SAXS.\(^81, 86\) Wernett et al.\(^84\) estimated an average micropore diameter of 5.2 Å for Illinois No. 6 coal by \(^{129}\)Xe NMR. Tsiao and Botto\(^83\) also used \(^{129}\)Xe NMR and found two pore structures of similar size (6 Å in diameter) tentatively assigned to aromatic and aliphatic regions. For Illinois No. 6, an additional pore structure was identified having a larger pore diameter of about 10 Å.\(^83\) Zhu et al.\(^87\) also observed two distinct pore size systems intimately connected in Illinois coal using \(^{129}\)Xe NMR. Hall et al.\(^85\) performed contrast matching SANS on Argonne coals to investigate their pore structures in wet state. It was obtained that porosity levels decrease with increasing coal rank. Illinois coal showed greater scattering and exhibited microporosity, which appeared to be
associated with the presence of water. Norinaga et al. quantified and classified the water sorbed in several coals by differential scanning calorimetry. Water types were experimentally determined from their respective heats of congelation. Illinois coal contained 0.05 and 0.05 g/g-db coal of bound and non-freezable water respectively.

Coal surface areas are typically determined from gas adsorption isotherms using the Langmuir or Brunauer-Emmett-Teller (BET) equations. Larsen et al. investigated the pore structure of bituminous coals. The BET surface areas for Illinois No. 6 were: 29 m$^2$/g for N$_2$ (-196 °C), 132 m$^2$/g for CO$_2$ (-78 °C), and 38 m$^2$/g for ethane (-78 °C). Surface areas derived from adsorption methods depend on the characteristic dimension of the probe molecules used and the magnitude of the interaction forces between them and the coal structure. Lin et al., and Spitzer and Ulicky performed SAXS experiments on Illinois No. 6 coal and reported surface area values of 151 and 179 m$^2$/g, respectively. Gethner et al. determined for Illinois coal a surface area of 195 m$^2$/g using SANS. The helium density of Illinois No. 6 is 1.301 g/cm$^3$ (dmmf).

**Conclusions**

Illinois No. 6 Argonne Premium coal is vitrinite-rich (85%, dmmf) with an elemental composition of C$_{100}$H$_{77.3}$O$_{13.1}$N$_{1.5}$S$_{1.2}$ and a high organic sulfur content of 2.5% (dmmf). $^{13}$C NMR studies indicated an aromaticity of 72% with 15 aromatic carbons (three to four fused aromatic rings) and 5 attachments per cluster, and an average cluster molecular weight of 316 Da. RuO$_4$ oxidation reactions showed that there are 1.76 methyl, 0.29 ethyl, 0.037 propyl, and 0.035 2-propyl groups per 100 carbon atoms. XANES data indicated that organic sulfur forms are distributed as 26% aromatic (diphenyl sulfide), 33% aliphatic (dibenzyl sulfide), and 41% thiophenic (2,5 dimethylthiophene, benzothiophene and dibenzothiophene molecules). XPS analyses suggested that Illinois No. 6 coal contains 5.2 ether, 3.9 phenolic, 0.4 carbonyl and 0.6 carboxyl groups per 100 carbon atoms. The nitrogen type and distribution derived from XPS experiments were: 62% pyrrolic, 26% pyridinic and 12% quaternary. Solvent-extraction data, LDIMS and FIMS estimated values for M$_n$ and M$_w$ ranging from 402 to 640 and 441 to 2100 Da. Solvent swelling measurements suggested that Illinois coal structure is composed of a covalently bonded network of aromatic clusters highly hydrogen bonded. Volumetric swelling ratios obtained at 293 K are 1.04 for benzene, 1.23 for methanol, 1.34 for ethanol, 2.45 for n-
propylamine and 2.75 for pyridine. Extraction yields are 25.3 wt.% (daf) for pyridine, 19.0 wt.% (daf) for THF and 33.1 wt.% (daf) CS₂/NMP. ¹²⁹Xe NMR studies indicated that the pore structure of Illinois coal consisted of two distinct regions with average micropore diameter of 6 and 10 Å, respectively. SANS experiments showed that Illinois coal porosity is primarily due to the presence of micropores. XRD and HRTEM lattice fringe analyses showed that the interlayer spacing is 0.37 nm, average fringe length is 1.0 nm and average number of layers per stack is 2.2. Gas adsorption measurements showed BET surface areas of 29 m²/g for N₂ (-196 ºC), 132 m²/g for CO₂ (-78 ºC), and 38 m²/g for ethane (-78 ºC).

Acknowledgements
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References


Chapter 3

A Molecular Model for Illinois No. 6 Argonne Premium Coal: Moving Toward Capturing the Continuum Structure*

Abstract

A large-scale molecular model for Illinois No. 6 Argonne Premium coal is generated based on an automated construction approach in an effort to move toward capturing the continuum structure. The model contains 50,789 atoms within 728 molecules and is the largest, most complex coal representation constructed to-date. The aromatic ring size distribution was based on multiple high-resolution transmission electron microscope (HRTEM) lattice fringe micrographs and was duplicated with automated construction protocols (Fringe3D) in molecular modeling space. Additional structural data was obtained from the abundant literature assessing this Argonne Premium coal. Organic oxygen, nitrogen, and sulfur functionalities were incorporated primarily into the polyaromatic structures according to X-ray photoelectron spectroscopy and X-ray adsorption near-edge structure spectroscopy data. Aliphatic carbons were in the form of cross-links (bridges and loops) and pendant alkyl groups based on the combination of laser desorption ionization mass spectrometry (LDIMS), ruthenium ion catalyzed oxidation, elemental analysis, and NMR data in good agreement with the literature. Bound and bulk water was also included. Construction of the coal molecules was performed by use of Perl scripts developed in Materials Studio to eliminate personal bias and improve the accuracy and the scale of the structure generated. The large-scale model captured a broad and continuous molecular weight distribution in accordance with LDIMS data here ranging from 100 to 2850 Da, enabling inclusion of structural diversity to capture a portion of the continuum structure. A theoretical pyridine extraction yield, determined by a group contribution approach, was in agreement with the experimental value. The extract and residue representations were generated from the large-scale Illinois coal model and showed consistency with NMR, elemental analysis and LDIMS trends. The distribution of heteroatomic classes and double bond equivalents was also well-defined experimentally based on electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. These data further constrain the molecular weight of extractable material and was consistent with limited pyridine extractability and model heteroatom classes. Future work will be well served by staying within the limits established by the approach and increasing the structural diversity (sampling frequency through increased scale) to better capture the complex nature of coal structural diversity, i.e., the continuum.

Introduction

The Argonne Premium coals have been extensively studied since being available in 1985. The Illinois No. 6 high-volatile bituminous coal was collected from the Herrin seam in Illinois and is an industrially relevant coal. The Illinois coal basin is the largest in the United States. Of all the Argonne coals, the Illinois No. 6 coal is perhaps the most diverse. However, nearly all coals can be described by a continuum structure, with 10,000 compositionally distinct molecules being identifiable for the polar extracts alone for this Illinois coal and even greater diversity from laser desorption ionization mass spectroscopy (LDIMS). As the Argonne Premium suite of coals has been extensively evaluated, copious structural data are available. A detailed review of the chemical and physical structural features of Illinois No. 6 coal based on the available structural data has been generated.

Advances in analytical techniques, molecular modeling approaches and computational power have permitted construction of improved molecular representations of coal structure. Molecular models provide insightful information at atomistic scales that could contribute to improved structure and behavior relationships for coal. According to Mathews and Chaffee more than 125 structural representations of coal exist. With a few exceptions, the majority of these models are small-scale (100’s of atoms to <5000 atoms) “average” structural representations of coal. Although useful for revealing some structural features of coals, their application for exploring the structure-property and structure-behavior relationships of coal are limited. A review on the utility of coal molecular models is also provided by Mathews et al. Generation of representative structures is time-consuming, challenging, and requires considerable expertise particularly due to the large range of structural features covering small molecules to very large molecular masses and maceral contributions. Thus, it has long been recognized that coal and many of the extracts and products are a structural continuum. These structural features influences coal behaviors including: thermoplasticity, liquefaction and pyrolysis. Despite advances in coal model construction approaches, coal molecular models have yet to capture the continuum of structural features.

Incorporation of structural diversity requires large-scale coal molecular models. The Narkiewicz and Mathews model for Pocahontas No. 3 low-volatile bituminous coal was the largest
molecular coal structure containing ~22,000 atoms in 215 molecules incorporates a molecular weight distribution ranging from 78 to 2420 Da.\textsuperscript{15} The molecular weight distribution accommodates an evaluation of HRTEM lattice fringe images and LDIMS data. The model was used to visualize sequestration issues such as CO\textsubscript{2} and CH\textsubscript{4} sorption capacities, CO\textsubscript{2}-induced swelling, and the pore-blocking role of moisture.\textsuperscript{16} Molecular representations for inertinite-rich and vitrinite-rich coals constructed by Van Niekerk and Mathews also exhibited a molecular weight distribution ranging from 78 to 1900 Da with model scales being 14,000-18,000 atoms.\textsuperscript{17} These models were utilized to examine solvent-swelling and extractability characteristics of these inertinite-rich and vitrinite-rich coals.\textsuperscript{18}

However, all of these previous large-scale models were constructed mostly by-hand (prior to minimization), which limits the scale and severely limits the access of quality coal models for use in the coal research community. Recently, a structure generation approach (Fringe3D) based on HRTEM lattice fringe images has allowed direct inclusion of aromatic stacking and alignment of aromatic moieties in the model space.\textsuperscript{19} Fringe3D enables >20,000 atoms non-cross-linked subbituminous coal slice model representation, containing those structural features, to be produced more easily and more accurately than with the current state-of-the-art model construction approaches.\textsuperscript{7} Basically, the Cartesian location, length, and orientation were determined from image analysis of HRTEM lattice fringes and processed via Fringe3D to duplicate those fringes in molecular modeling space based on a combination of known molecules (such as naphthalenes) to a continuum of larger structures from catenation molecules. Automation (Perl scripts created within Materials Studio) can further populate heteroatoms and aliphatic components to aid in construction and to remove investigator bias. In this manner, structures of larger scale, improved accuracy, and utility can be generated. Recently, Fringe3D coupled with Perl Scripts was used for generation of an Illinois No. 6 coal char atomistic representation that captured a distribution of turbostratic crystalline parameters including stacking height, layer size, and interlayer spacing.\textsuperscript{20} The work here builds upon these recent advances.

Individual maceral fractions exhibit distinct chemical properties\textsuperscript{21} that often influence the behavior of coals during conversion processes.\textsuperscript{7} Structural representations of vitrinite-rich,\textsuperscript{22, 23}
inertinite-rich,\textsuperscript{17} and liptinite-rich\textsuperscript{24} coals have been generated. Here, the constructed coal model corresponds to a data for the whole coal. A significant improvement would consider maceral contributions. As this coal is 85\% vitrinite\textsuperscript{1} the model exhibits much of the vitrinite contribution to coal structure.

Illinois No. 6 high-volatile bituminous coal is vitrinite-rich (85\%, dmmf) with a normalized elemental composition of C\textsubscript{100}H\textsubscript{77.3}O\textsubscript{13.1}N\textsubscript{1.5}S\textsubscript{1.2} and has a high organic sulfur content of 2.5\% (dmmf).\textsuperscript{1} Cross-polarization \textsuperscript{13}C NMR with dipolar dephasing analysis indicated an aromaticity of 72\% with 15 aromatic carbons (approximately three-four fused aromatic rings) and 5 attachments per cluster, and an average cluster molecular weight of 316 Da.\textsuperscript{25} Ruthenium ion catalyzed oxidation (RICO) experiments showed that there are 1.76 methyl, 0.29 ethyl, 0.037 propyl, and 0.035 2-propyl groups per 100 carbon atoms in Illinois No. 6 coal.\textsuperscript{26} Solvent-extraction data,\textsuperscript{9, 27} LDIMS\textsuperscript{4} and field ionization mass spectroscopy (FIMS)\textsuperscript{28} estimated values for number (M\textsubscript{n}) and weight (M\textsubscript{w}) average molecular weights ranging from 402 to 640 and 441 to 2100 Da. Solvent extraction yields have been reported for Illinois No. 6 coal: 25.3 wt.\% (daf) for pyridine,\textsuperscript{29} 19.0 wt.\% (daf) for THF\textsuperscript{29} and 33.1 wt.\% (daf) CS\textsubscript{2}/NMP.\textsuperscript{30}

\textsuperscript{129}Xe NMR studies indicated that the pore structure of Illinois coal consisted of two regions with average micropore diameter of 6 and 10Å, respectively.\textsuperscript{31} Small-angle neutron scattering experiments showed that Illinois coal porosity is primarily due to the presence of micropores.\textsuperscript{32} X-ray diffraction (XRD)\textsuperscript{33} and HRTEM\textsuperscript{34, 35} lattice fringe analyses showed that the interlayer spacing is 0.37 nm, average fringe length is 1.0 nm, and average number of layers per stack is 2.2. Gas adsorption measurements for Illinois No. 6 showed BET surface areas of 29 m\textsuperscript{2}/g for N\textsubscript{2} (-196 °C), 132 m\textsuperscript{2}/g for CO\textsubscript{2} (-78 °C), and 38 m\textsuperscript{2}/g for ethane (-78 °C).\textsuperscript{36} Electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was recently used for chemical compositional characterization for the polar fraction of pyridine Illinois coal extracts, enabling assignment of molecular formulas to more than 10,000 species in a single mass spectrum.\textsuperscript{3, 37} This comprehensive compositional analysis allowed detailed evaluation of class compound (heteroatom content), type (number of ring plus double bonds), and alkylation distributions. This technique determines the elemental composition of the ion and has made
considerable progress toward defining structural diversity and at least partially captures the continuum of the coal structure.

The objective of this work is to implement an automated model construction approach based on analytical data that enables inclusion of structural diversity resulting in making progress toward capturing the continuum of the coal structure and thus better enabling appropriate behavioral observations. The proposed computational protocol is demonstrated with the Illinois No. 6 Argonne Premium coal. Additionally, negative-ion ESI FT-ICR MS was utilized to further characterize the pyridine extract to capture the diversity in heteroatoms, most specifically oxygen-containing species. Direct determination of elemental composition is enabled by accurate mass measurement (100-400 ppb) and allows visualization of the aromaticity and carbon number compositional space occupied by the acidic components of Illinois No. 6 coal. Comparison of the FT-ICR MS data to the individual components of the coal molecular model provides a measure of the continuum coverage.

**Experimental methods**

**Sample preparation**

Eighty mL of HPLC grade pyridine Sigma-Aldrich Chemical Co. (St. Louis, MO) was added to the contents of an ampoule (4.538 g) of Illinois No. 6 coal (Argonne Premium Coal) in a glass flask with backflow condenser and extracted in a sonicator water bath for 50 min. at 50 °C. The flask was cooled to room temperature and the solid particles separated from the pyridine supernatant by vacuum filtration. The filter cake was rinsed with 80 mL of pyridine in small portions. The pyridine solution of extracted materials was concentrated under flow of nitrogen in a fume hood to give a final (wet) weight of 1.37g. Prior to analysis by ESI FT-ICR MS, a solution of 10 mg of sample (concentrated coal extracted materials) was dissolved in 5 mL of pyridine and then diluted with 15 mL of methanol containing 1.3% ammonium hydroxide (NH₄OH). Thus the final solvents and reagents ratio was pyridine: methanol = 25:75 v/v, 1% of NH₄OH. The base is added to facilitate deprotonation of the samples in negative-ion electrospray ionization.
**Mass analysis**

Illinois No. 6 pyridine extracts were analyzed with a custom-built FT-ICR mass spectrometer housed at the National High Magnetic Field Laboratory, and equipped with a 9.4 Tesla horizontal 220 mm bore diameter superconducting solenoid magnet operated at room temperature (Oxford Corp., Oxney Mead, U.K.). A modular ICR data station (PREDATOR) facilitated instrument control, data acquisition and data analysis. Negative ions generated by electrospray ionization were accumulated in an external linear octopole ion trap for 250-1000 ms and subsequently transferred by radiofrequency-only octopoles to a 10 cm diameter, 30 cm long open cylindrical Penning ion trap. Octopoles were operated at 2.0 MHz and 240 V\textsubscript{p-p} amplitude. Broadband frequency sweep (chirp) dipolar excitation was followed by direct-mode image current detection to yield 8 Megaword time-domain data sets. Time-domain data sets were co-added (50-100 acquisitions), Hanning apodized, and zero-filled once before fast Fourier transform and magnitude calculation.\textsuperscript{38}

**Model construction approach**

The construction of the coal molecular model consisted of: (1) HRTEM lattice fringe image analysis, (2) construction of the aromatic clusters (benzene to large PAH molecules), (3) inclusion of heteroatoms and functional groups, (4) addition of aliphatic side chains and generation of a cross-linked network structure, and (5) arrangement of cross-linked clusters into a simulation cell. Implementation of an automated construction protocol via Fringe3D and Perl scripts was necessary due to the great structural diversity of the Illinois No. 6 coal. This procedure enabled simplifying the model construction process, eliminating researcher structural bias and generating large-scale continuum molecular representations with improved accuracy.

**HRTEM lattice fringe image analyses**

Image Processing Toolkit\textsuperscript{39} addition to the Adobe Photoshop was utilized to perform image analyses for a selection of four (one-published and three-unpublished) HRTEM lattice fringe images for Illinois No. 6 coal.\textsuperscript{35} Prior to the image analysis, the image boundaries and fringes connected to it were removed, as was the scale bar following length calibration. Binary images were generated by use of a threshold function and skeletonized features were analyzed. Fringes
smaller than 2.5 Å were assumed to be noise and ignored as well as unrealistic long fringe lengths based on excessive curvature (>90°). Fringes were analyzed for length distribution.

**Aromatic carbon generation**

HRTEM has been used for structural characterization of coal-derived materials producing structural results in agreement with XRD and 13C NMR data. Thus, HRTEM lattice fringe data were utilized to generate a distribution of aromatic moieties for the coal model. The length of the aromatic fringe is dependent on the carbon ring catenation and angle of viewing. Thus, the following structural assignment was used to estimate the size of aromatic moieties: fringes less than 3 Å were assumed benzenes, fringes between 3.0 and 4.5 Å were assigned to naphthalene, and fringes between 4.5 and 6 Å were assigned to phenanthrene/anthracene. A parallelogram shape was assumed for larger aromatic fringes. Thus, a series of parallelogram-shaped aromatic fringes ranging from 2x2 (pyrene) to 10x10 aromatic rings were built and geometry-optimized with molecular modeling software. The two characteristic lengths (short and long fringe lengths) were calculated and then utilized to develop a set of empirical correlations that use the lattice fringe length to determine the number of carbons in parallelogram-shaped fringes as follows:

\[ C_{\text{min}} = 0.8130L^{1.6533} \]  
\[ C_{\text{max}} = 0.5807L^{1.7046} \]

where \( L \) is the lattice fringe length in Å, \( C_{\text{min}} \) and \( C_{\text{max}} \) are the minimum and maximum number of carbon atoms in the aromatic fringe, and \( C_{\text{ave}} \) is defined as \( (C_{\text{min}} + C_{\text{max}})/2 \). These relationships allow the number of carbons in each aromatic fringe to be estimated.

The Fringe3D construction approach was utilized to generate molecular representations for the polycyclic aromatic hydrocarbon (PAH) structures based on HRTEM lattice fringe data. Fringe3D allows for building a molecule in 3D space for each fringe based on its aromatic carbon content. A molecular model (pdb) file is generated containing an entry for every fringe (identified by image analysis) based on either a named or a catenation molecule constructed and geometry-optimized using molecular modeling software. Named molecules were used for small
aromatic fringes (such as benzene, naphthalene and phenanthrene), while catenation molecules were applied to polyaromatic fringes of 2x2 and greater (Fig. 3.1). Fringe3D places these molecules in 3D molecular modeling space. Molecules can be placed at centers of mass (determined by image analysis) of fringes to duplicate HRTEM lattice fringe images, or assembled in a flat arrangement to better show the distribution of structural features. Figure 3.1 shows an example catenation molecule with parallelogram-shaped structures of 2x2 to 3x3. Addition of 6-member rings around the central rings enables larger polyaromatic structures of varying carbon numbers to be generated. Thus, a parallelogram ring-by-ring growth can occur to accommodate the PAH molecular size distribution to match the fringe length distribution. Although parallelogram growth was employed in the current model, alternative catenation styles and their mixtures, such as linear and circular, can be included to enhance model structural diversity.

![Figure 3.1. Examples of aromatic structures generated by named molecule files (left), and parallelogram-shaped structures of 2x2-to-3x3 transitions derived via catenation molecule files (right).](image)

Five-member rings were incorporated into the coal structure via named molecules such as fluorene and indene (Fig. 3.1), and within the polyaromatic structures by converting peripheral 6-member rings into 5-member rings to generate fluorine-type structures. In particular, a protonated aromatic carbon from an outside 6-membered ring was randomly removed and a carbon-carbon covalent bond for ring closure was created followed by geometry optimization. Since protonated aromatic carbons in the generated fluorine structures will often be substituted with heteroatoms to produce furanic, thiophenic and pyrrolic type structures, addition of 5-member rings was conducted using a combination of scripts and manual manipulation until agreement with desired type and distribution of heteroatoms was achieved.
An important structural parameter determined from NMR experiments was the fraction of bridgehead carbons. This parameter is assigned to non-protonated aromatic carbon bonded to other non-protonated aromatic carbon and provides an indication of the portion of aromatic carbons polycondensed. To decrease the bridgehead carbons value to that of experimental NMR data, a trimming procedure was performed on parallelogram-shaped structures of 3x3 and greater, similar to that used by Van Niekerk and Mathews. Here, trimming was conducted by randomly removing peripheral 6-membered rings to form analogs of the original polyaromatic moieties, with hydrogen adjustment performed on the trimmed structure. The trimming process was carried out until agreement with the NMR-derived bridgehead value was obtained. It also has the role of generating more realistic PAH molecules (non-parallelogram shapes). The resulting polyaromatic structures were constructed in order of size in a flat arrangement (Fig. 3.3) to aid communication and visualization of the progress of trimming and structural manipulation.

**Incorporation of heteroatoms and functional groups**

Organic sulfur forms were added to the aromatic structures according to XANES data by George et al. as 26% aromatic (diphenyl sulfide), 33% aliphatic (dibenzyl sulfide), and 41% thiophenic (2,5 dimethylthiophene, benzothiphene and dibenzothiophene molecules). Organic nitrogen was included in the coal model based on XPS data reported by Kelemen et al., where the nitrogen type and distribution was: 62% pyrrolic, 26% pyridinic and 12% quaternary. Addition of organic oxygen groups was consistent with XPS data which indicate 5.2 ether, 3.9 phenolic, 0.4 carbonyl and 0.6 carboxyl groups per 100 carbon atoms.

During the model construction process, sulfur, nitrogen and oxygen heteroatoms were incorporated within the aromatic ring structures or as surface functional groups by selecting specific atoms with a random-number generator and then replacing them by the appropriate functionalities. In particular, aromatic hydrogen atoms were randomly replaced by phenolic, carbonyl, carboxyl and aromatic sulfur groups, whereas aromatic carbons in 5- and 6-membered rings were randomly substituted for heteroatoms to generate furanic, thiophenic and pyrrolic type structures, and pyridinic and quaternary nitrogen, respectively. Phenolics were added in excess to account for aromatic ethers created during cross-linking formation. Aliphatic cross-links
composed of up to three CH$_2$ units (created by covalently connecting aliphatic carbons in pendant positions such as methyl/ethyl groups, with hydrogen adjustment performed on the resulting cross-link followed by geometry optimization) were utilized to include aliphatic ethers (Ph-CH$_2$-O-CH$_2$-Ph) and aliphatic sulfurs (Ph-CH$_2$-S-CH$_2$-Ph). No cross-links longer than three CH$_2$ units were permitted due to the limited contribution of longer chains to the structure.$^{26}$ A Perl script within Materials Studio was developed for incorporating heteroatoms and functional groups. A sensitivity analysis was conducted to examine how the addition of heteroatoms and functional groups in the aromatic moieties affects theoretical pyridine extraction calculations based on a group contribution approach described above. There was no significant variation ($\pm 1.05$) on calculated pyridine extraction yields. The sensitivity analysis results are provided in Appendix C.

**Aliphatic carbon addition**

The coal model was constructed according to the distribution of pendant alkyl groups obtained by Obeng and Stock$^{26}$ based on ruthenium ion catalyzed oxidation experiments. They found 1.76 methyl, 0.29 ethyl, 0.037 propyl, and 0.035 2-propyl groups per 100 carbon atoms. Linear alkanes unattached to the coal structure containing 16-30 carbon atoms were reported for the Illinois No. 6 coal based on deuterium-degradation reactions.$^{48}$ To capture this, four linear alkanes containing 21 carbon atoms were added into the model. Incorporation of aliphatic structures was conducted in the form of cross-links (bridges and loops) and alkyl side chains (with CH$_3$-terminal groups). Cross-links are defined as covalent bonds connecting two different aromatic clusters (bridges). Loops are the hydro portion of hydroaromatic clusters. A Perl script was developed for inclusion of alkyl side chains by randomly substituting aromatic hydrogens for pendant alkyl groups. Aliphatic loops (composed of 2-3 CH$_2$ structural units) were created also via scripting by transforming aromatic rings into saturated rings.

Generation of the cross-linked network structure was based on the approach proposed by Mathews et al.$^{49}$ which enabled estimation of a molecular weight distribution for Pocahontas No. 3 low-volatile bituminous coal in accordance with experimental values from LDIMS. Here, the cross-linking method is applied to a high-volatile bituminous coal, which exhibits higher content of heteroatoms and aliphatic carbons and thus increasing the complexity of cross-linking
formation. In this method, aromatic clusters are randomly distributed and gradually cross-linked until satisfactory agreement with experimental atomic H/C ratio and LDIMS data is achieved. The cross-linking approach was constrained (via exclusion of the largest 25% of aromatic entities) to connect smaller aromatic benzene/PAH molecules to control the growth of cross-linked clusters and reduce the large amount of non-cross-linked smaller moieties. Including the largest 25% would result in some cross-linking between the largest structural entities thus shifting the molecular weight into unreasonably high molecular masses given the scale of the model.

To covalently bond aromatic structures in a cross-linked cluster, PAH molecules were minimized and randomly placed in a rectangular cell by use of Materials Studio Amorphous Cell module; the distances between pairs of bonding sites (mostly aromatic, aliphatic and phenolic hydrogen) were measured and stored in order of increasing close-contact length. All pairs of potential bonding sites that could lead to overlapping were removed from consideration. The closest pairs of bonding sites within a cutoff distance of 6Å were identified and between the corresponding carbon atoms, new covalent bonds were created followed by geometry optimization (Fig. 3.2). If cross-linking did not occur, PAH molecules are further relaxed (by performing MD simulations for 50 ps at constant temperature and volume) and the cutoff distance increased by 0.25Å in the subsequent iteration. Based on known coal chemistry aromatic-aromatic, aromatic-aliphatic, aromatic-oxygen, aliphatic-aliphatic, and aliphatic-oxygen bonding types were all permitted. An example of cross-linking formation is shown in Figure 3.2. A sensitivity analysis was performed to investigate how inclusion of cross-links constrained to connect smaller PAH molecules influences on the model molecular weight distribution. There was no significant variation on estimated $M_n$ and $M_w$ values for these distributions ($\pm 2.4$ for $M_n$ and $\pm 11.4$ for $M_w$), indicating that the constrained cross-linking method is able to consistently generate an appropriate molecular weight distribution. The results of sensitivity analysis can be found in Appendix D. Previous works have also used computational construction protocols; however the automated cross-linking approach implemented here allows removal of investigator structural bias and generation of a larger mass range. Figure 3.4 shows the resulting cross-linked molecules generated by the proposed cross-linking approach.
Figure 3.2. Cross-linked cluster generation example: (a) randomly distributed PAH structures showing distances between potential bonding sites, (b) newly formed covalent bond, and (c) geometry-optimized cross-linked cluster. Atoms are represented by sticks: carbon, green; hydrogen, white; oxygen, red; nitrogen, blue.

Construction of 3D coal molecular model

The cross-linked and non-cross-linked molecules were assembled into 3D molecular model by use of the Theodorous and Suter\textsuperscript{51} method as implemented in the Amorphous Cell module of Materials Studio package.\textsuperscript{44} In this method, molecules are constructed in modeling space by gradually adding atoms and bonds according to a minimum energy criterion. The molecules were located randomly into a simulation cell. We applied standard periodic boundary conditions in all directions to remove possible surface effects.\textsuperscript{52} Prior to construction, 2214 water molecules (corresponding to the 8\% moisture content for this mass of coal) were randomly added to the empty simulation cell to account for the moisture content (bulk and bound water) measured by differential scanning calorimetry (DSC).\textsuperscript{53} Water molecules also acted as small obstacles aiding prevention of spearing and interlocking of molecules during construction. The 3D molecular model was built with an initial low bulk density of 0.5 g/cm\textsuperscript{3} to avoid overlapping of aromatic rings during simulation cell construction. The density was gradually adjusted until close agreement with the experimental value was achieved by applying the density equilibration scheme proposed by Hofmann et al.\textsuperscript{54} According to this procedure, the initially constructed cell is subjected to an energy minimization followed by 12 successive compression, decompression, annealing, and cooling cycles aimed at creating a final relaxed coal structure with a realistic density, as described in Appendix A. In particular, annealing cycles enabled the coal structure to rearrange into a more stable configuration (lower free energy). The water-containing coal model
was built at a density slightly higher than the experimental value of 1.30 g/cm$^3$ (dmmf)$^{55}$ to accommodate the slight density reduction with removal of water molecules and relaxation of coal structure.

**Model evaluation**

Several Perl scripts within Material Studio were further developed from previous work$^{56}$ to aid in the construction and evaluation of chemical structural parameters (elemental composition, NMR parameters and molecular weight distribution). Essentially, these scripts determine the type and distribution of atoms and functional groups of each molecule. Solubility parameter calculations were conducted to determine the mass that could be theoretically extracted with a specific solvent. Recently, this method was used to evaluate theoretical extraction yields for vitrinite-rich and inertinite-rich coal models.$^{18}$ The group contribution approach developed by Painter et al.$^{57}$ based on aromaticity and elemental composition data was used to estimate the solubility parameter ($\delta$) of coal molecules in the constructed model. These solvent extraction calculations were performed based on a cutoff value of ±1 (cal/cm$^3$)$^{0.5}$. Thus, for pyridine ($\delta = 10.7$ (cal/cm$^3$)$^{0.5}$),$^{58}$ coal molecules with calculated $\delta$ values between 9.7 and 11.7 (cal/cm$^3$)$^{0.5}$ were assumed to be theoretically extractable. The remaining molecules were assumed to form the solid residue. Estimation of solubility parameters was also performed by scripting.$^{56}$ The effects of secondary interaction forces and transport limitations were not considered during solvent extraction calculations.

The compositional continuum of the coal model was evaluated by determining double bond equivalents (DBE) distribution, heteroatom class (numbers of N, O and S atoms) distribution, and van Krevelen diagrams (a plot of H/C vs. O/C atomic ratios). Comparison between model and FT-ICR MS results was used to assess the capability of the constructed model in capturing a portion of the continuum structure. DBE corresponds to the number of rings plus double bonds to carbon and thus is a direct measure of unsaturation (higher degree of unsaturation usually indicates increased aromaticity).$^3$ For molecules containing C carbon, H hydrogen and N nitrogen atoms, the corresponding DBE number was calculated from the following equation:$^{59}$

$$DBE = (C+1)-(H-N)/2$$

(3.3)
The physical evaluation of the coal molecular model comprised determination of simulated helium density, pore size distribution, interlayer spacing, aromatic cluster size, and number of layers per stack. The simulated helium density was calculated from the molar mass and the volume of the coal structure. The latter is the volume not accessible to helium atoms (kinetic radius of 1.29Å). Following an approach similar to that presented by Gelb and Gubbins, the simulation cell was divided into a fine grid composed of cubic cells of 0.05 nm length. A test sphere was placed at every grid point and the distance between the center of the sphere and the center of local atoms was calculated to classify grid points as occupied and unoccupied. The sum of the volume of all occupied grid points defines the volume of the coal structure, while that of all unoccupied grid points corresponds to the pore volume. The pore size distribution was determined from the plot of \(-dV_{\text{pore}}(r)/dr\) versus \(r\), where \(V_{\text{pore}}(r)\) is the fraction of pore volume that can be enclosed by a test particle of radius \(r\). It is important to note that in this study the porosity of the coal model was sampled at the micropore length scale (i.e., not including the macro or mesoporosity). Stacks of aromatic clusters with an angle of inclination within ±10º were considered for computing model physical structural parameters (such as stacking number and interlayer spacing). These stacks were classified according to the number of layers per stack or stacking number. Interlayer spacing and cluster size were measured as the perpendicular distance between aromatic clusters forming a stack, and the projected length of the layers, respectively, based on molecular modeling software.

While earlier modeling efforts are elucidations requiring comparison and reduction of error between model and data, here our construction protocol starts with an aromatic base and simply add the correct type and distribution of heteroatoms and aliphatics. As such we use an approach that far more efficient but lacks the traditional validation approaches that commonly occur in smaller-scale atomistic representations. Validation of the model occurs with evaluation and behavior in multiple aspects of coal science. Hence to permit this approach and to further the range of simulations that can be evaluated the atomistic representation (pdb format) is freely available online.

During model construction process, elemental composition, NMR parameters, molecular weight distribution and simulated helium density were adjusted to agree with the available experimental
data. However, evaluation of the pore size distribution, interlayer spacing, stacking number, pyridine extraction yield, distribution of DBE numbers and heteroatom classes, and van Krevelen diagrams are regarded as a test of the model since these parameters were not fitted in building the coal model.

**Results and discussion**

The aromatic fringe distribution based on the structural assignment is listed in Table 3.1. Naphthalene, phenanthrene and 2x2 parallelogram-shaped (pyrene) structures are the most abundant structural entities and a 6x6 aromatic sheet was the largest PAH molecule obtained. A sensitivity analysis was also performed to assess how cutoff values used in the structural assignment modify the fraction of protonated aromatic carbons ($f_a^H$) for the corresponding polyaromatic structures. There was no significant variation ($\pm 0.02$) on calculated $f_a^H$ values. The sensitivity analysis results are provided in Appendix B. Further support for the structural assignment is given by the agreement between the average molecular weight of an aromatic cluster obtained from HRTEM (283 Da) and NMR (316 Da). At this stage of construction, the atomistic representation has only aromatic carbon atoms. Hence, the HRTEM-derived molecular weight value is expected to be slightly lower than that from NMR. The NMR value is calculated from elemental composition and carbon aromaticity, and thus including aromatic carbon, aliphatic carbon and heteroatom contributions.

A total of 1589 polyaromatic structures were generated by Fringe3D in a highly automated manner, capturing the distribution of molecular sizes for the aromatic portion of the coal structure. The PAH structures were constructed in order of size in a flat arrangement (Fig. 3.3) to aid viewing rather than attempting to duplicate the lattice fringe images. Heteroatoms and aliphatics were added by scripting to agree with experimental data. Cross-linking further reduced the atomic H/C ratio and adjusted the molecular weight distribution, producing 728 molecules (>50,000 atoms), shown in Figure 3.4. Examples of cross-links (bridges and loops) that were added to the constructed coal model include: Ph-(CH$_2$)$_n$-Ph, Ph-O-(CH$_2$)$_n$-Ph, Ph-CH$_2$-O-CH$_2$-Ph, Ph-O-Ph, and Ph-S-(CH$_2$)$_n$-Ph. The 728 molecules were geometry-optimized and then
Table 3.1. Structural assignment frequency obtained from HRTEM lattice fringe data of Illinois No. 6 coal.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Frequency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>13.0</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>32.7</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>18.1</td>
</tr>
<tr>
<td>2x2</td>
<td>13.3</td>
</tr>
<tr>
<td>3x3</td>
<td>9.4</td>
</tr>
<tr>
<td>4x4</td>
<td>8.1</td>
</tr>
<tr>
<td>5x5</td>
<td>3.2</td>
</tr>
<tr>
<td>6x6</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Figure 3.3. PAH molecules generated by Fringe3D based on HRTEM lattice fringe data. Incorporation of structural diversity enables capturing a continuous distribution of aromatic moieties in the coal representation. PAH molecules are geometry-optimized and represented by sticks and aligned with the screen.
Figure 3.4. Molecules generated by the cross-linking approach, showing (top) non-cross-linked and (bottom) cross-linked clusters. The model construction approach allows incorporating a distribution of structural features. Molecules are geometry-optimized and represented by sticks and aligned with screen: carbon, green; hydrogen, white; oxygen, red; nitrogen, blue; sulfur, yellow. Cross-linked clusters exhibited a range of orientations.

assembled into a 3D molecular model along with 2214 water molecules (as described above) by use of the Materials Studio Amorphous Cell module. The energy optimized “wet” and “dry” molecular models for Illinois No. 6 coal are shown in Figure 3.5. The length of the cubic simulation cell for the wet and dry models was 86.6 and 82.9 Å. The simulation box containing the moisture component alone is also displayed where water molecules can be seen forming aggregates.

Created 2D slices (with Materials Studio Volume Visualization tool) parallel to the x, y and z-axes show the volume occupied by these water aggregates as a red spots. The coal model exhibited a distribution of water cluster sizes ranging from clusters composed of 2-3 water
Figure 3.5. Molecular model for Illinois No. 6 coal: (a) including moisture component, (b) dry state, (c) showing the 2214 water molecules alone, and (d) 2D slices parallel to the $x$, $y$ and $z$-axes. The occupied volume by the water molecules forming aggregates is shown in red. Atoms are represented by van der Waals spheres and colored as in Figure 3.4. Hydrogens attached to the coal structure are not shown to aid visualization. The length of the periodic cubic box is displayed for (a) and (b).

molecules up to clusters with 6 and 7 water molecules. Since water molecules were randomly distributed into the empty simulation cell, the clustering of water was expected given the mass added and it was caused by water-water hydrogen bond interactions. This also moves toward obtaining “bulk water”, which was desired based on DSC data.$^{53}$ Sheng et al.$^{62}$ determined based on positional disorder theory that the onset of bulk water occurs when the number of water molecules involved is greater than a critical value of about 10-19. The scale of the model here
limits the likelihood of larger water clusters. All water molecules were removed and the coal structure was equilibrated by performing a MD simulation for 100 ps at 300 K and atmospheric pressure. A volumetric shrinkage of 10% was obtained, presumably due to an increasing number of coal-coal hydrogen bonds with the removal of water molecules that directly interact with the coal molecules and thereby stress the network structure in the direction of compression. This result is consistent with experimental observations by Kelemen et al.,\textsuperscript{47} who reported a volumetric shrinkage of 11% for Illinois No. 6 coal on drying at room temperature under ultrahigh vacuum. Suuberg et al.\textsuperscript{63} proposed an empirical correlation for volumetric shrinkage for coals ranging from lignites up to high-volatile bituminous on drying at 373 K from the starting moisture content to a fully dry state. With this empirical correlation, a volumetric shrinkage of 7% was predicted for Illinois coal. Pore size distribution would also be expected to influence the extent of shrinkage; macropores for example are not expected to collapse in this rank of coal.

This coal model has components capturing the two-phase model for coal, which consists of a covalently bound cross-linked network (immobile phase) and low molecular weight compounds (mobile phase) physically trapped within macromolecular networks,\textsuperscript{9, 64} and the associated structure.\textsuperscript{65} The range of structural features captures includes aromatic, aliphatic, heteroatoms and moisture components in a 3D cross-linked network, and is currently the largest coal model generated (having >50,000 atoms). While it is desirable to generate larger structures that better capture the structural diversity for improved structure-behavior-property relationships, the question arises how big is big enough? The answer depends largely on the intended use.\textsuperscript{7} To show a range of structural features, smaller structures are adequate. To explore direct coal-to-chemical or coal-to-liquids approaches the scale needs to be much larger for meaningful results/comparisons. In the case of CO\textsubscript{2} sequestration, the atomistic representation will need to be orders of magnitude larger than the constructed here so the appropriate pore size distribution can be included for CO\textsubscript{2} capacity comparisons, competitive sorption simulations, and the various roles of water forms on the process. To fully capture the continuum, greater scale may be necessary still. However, to reasonably capture the appropriate behavior of interest, structures of this scale are very reasonable starting points until the appropriate scale issues are resolved.
Evaluation of chemical and physical structural parameters

The chemical evaluation of the coal structure comprised elemental analysis, NMR parameters, and molecular weight distribution calculations. The elemental composition, normalized to 100 carbon atoms for the proposed coal model is $\text{C}_{100}\text{H}_{77.4}\text{O}_{9.3}\text{N}_{1.5}\text{S}_{1.2}$, which compares favorably with the experimental value determined by Vorres\textsuperscript{1} for Illinois No. 6 coal on the dmmf basis of 100 carbon atoms as $\text{C}_{100}\text{H}_{77.3}\text{O}_{9.4}\text{N}_{1.5}\text{S}_{1.2}$. Similarly, the atomic H/C ratio of 0.774 from the model agreed with the 0.773 literature value.\textsuperscript{1} A comparison of experimental and model NMR structural parameters for Illinois No. 6 coal is present in Table 3.2. Elemental composition and NMR parameters for the model were determined by scripting.\textsuperscript{56} NMR parameters from the proposed model agreed within the experimental uncertainties, with a few exceptions as discussed below. The model carbon aromaticity ($f_a' = 0.75$) compares well with the 0.72 ± 0.04 determined value by Solum et al.\textsuperscript{25} by cross-polarization $^{13}$C NMR and with the value of 0.75 reported by Love et al.\textsuperscript{66} with single-pulse excitation $^{13}$C NMR. Additionally, NMR parameters related to the aromatic cluster size such as the average aromatic carbons per cluster, the fraction of bridgehead carbons, the coordination number and the number of bridges and loops per clusters are in reasonable agreement with the experimental values. The largest relative errors are obtained in the aliphatic carbon content ($f_{al}$ and $f_{al^*}$) and the carbons associated with oxygen units ($f_{a^P}$ and $f_{a^9}$). As previously discussed, for model construction the aliphatic distribution and oxygen functionalities determined from RICO and XPS data, respectively, were preferred over NMR-derived values since these two techniques were considered to be more quantitative.

<table>
<thead>
<tr>
<th>Sample</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>$f_{al}$</th>
<th>$f_{al}^H$</th>
<th>$f_{al}^P$</th>
<th>$f_{al}^S$</th>
<th>$f_{al}^0$</th>
<th>$\chi_b$</th>
<th>$f_{al/cl}$</th>
<th>$f_{al^cl}$</th>
<th>$f_{al^&amp;l}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solum et al.</td>
<td>0.72</td>
<td>0.72</td>
<td>0.00</td>
<td>0.26</td>
<td>0.46</td>
<td>0.06</td>
<td>0.18</td>
<td>0.22</td>
<td>0.28</td>
<td>0.19</td>
<td>0.09</td>
<td>0.05</td>
<td>0.31</td>
<td>15</td>
<td>5.0</td>
<td>3.1</td>
</tr>
<tr>
<td>Model</td>
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<td>0.75</td>
<td>0.01</td>
<td>0.24</td>
<td>0.51</td>
<td>0.10</td>
<td>0.17</td>
<td>0.24</td>
<td>0.23</td>
<td>0.21</td>
<td>0.02</td>
<td>0.03</td>
<td>0.32</td>
<td>13</td>
<td>4.6</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Parameters: $f_a$ – total of sp$^2$ carbon, $f_a'$ – aromatic carbon, $f_a^C$ – carbonyl/carboxyl carbon, $f_a^H$ – protonated aromatic carbon, $f_a^N$ – nonprotonated aromatic carbon, $f_a^P$ – phenolic ethers, $f_a^S$ – alkylated aromatic carbon, $f_{al}^H$ – aromatic bridgehead carbon, $f_{al}$ – total sp$^3$ carbon, $f_{al}^H$ – CH or CH$_2$ carbon, $f_{al}^P$ – CH$_3$ carbon, $f_{al}^0$ – aliphatic carbon bonded to oxygen, $\chi_b$ – mole fraction of bridgehead carbons, $f_{al/cl}$ – aromatic carbons per cluster, $f_{al^cl}$ – attachments per cluster, $f_{al^&l}$ – bridges and loops per cluster.

The coal model exhibited a broad and continuous molecular weight distribution ranging from 100 to 2850 Da with a sharp peak at ~350 – 400 Da, as shown in Figure 3.6. The corresponding $M_n$ and $M_w$ values are 522 and 861 Da, respectively. This wide and continuous molecular weight
distribution enables inclusion of structural diversity in the coal model resulting in capturing a portion of the continuum of the constitution, a significant improvement over existing coal model construction approaches. Herod et al.\textsuperscript{4} characterized the Argonne Premium coals by matrix-assisted LDIMS and Illinois No. 6 coal spectra showed a sharp peak at \(\approx 230 - 400\) Da followed by another series of smaller peaks in the 1500 – 5000 Da. The shape of both model and experimental molecular weight distribution is very similar. Specifically, both distributions exhibit a short shoulder at low mass followed by a sharp peak and then a long tail. Huai et al.\textsuperscript{67} also characterized Argonne coals by pyrolysis mass spectrometry techniques and reported for Illinois No. 6 values for \(M_n\) of 270 Da as determined by pyrolysis gas chromatography mass spectrometry (Py-GCMS) and 367 Da measured by pyrolysis field-ionization mass spectrometry (Py-FIMS). When compared with experimental data, the calculated \(M_n\) value is found to be somewhat higher. Molecular weight values depend on the experimental technique, making it difficult to assess the model distribution result from this approach. However all the MS results, within their applicable ranges, support a continuum of structural features.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{molecular_weight_distribution.png}
\caption{Molecular weight distribution for the Illinois No. 6 coal molecular model (dry).}
\end{figure}
The physical structure of the coal model was characterized in terms of simulated helium density, pore size distribution and volume shrinkage, as described above. The simulated helium density of the dry coal model was 1.32 g/cm³, in reasonable agreement with the experimentally derived value of 1.30 g/cm³ (dmmf). The difference may be due, in part, to the lack of the slight preferential orientation of coals at this rank. The distribution of micropores for the coal model (Fig. 3.7) was estimated by varying the diameter of a probe molecule. In this simulation, only microporosity can be evaluated due to the size of the simulation cell. The pore size distribution shows smooth transitions as the pore diameter increases with limited fluctuations. The range of pore sizes extends up to about 10Å with a peak at ~2 – 3Å; i.e., the simulated coal structure contains a significant portion of micropores with diameters ranging between 2 and 3Å, somewhat lower than the average micropore diameter of 6Å reported for Illinois No. 6 coal by \(^{129}\text{Xe NMR}\). This is presumably caused by the use of the Theodorous and Suter approach to assemble the PAH molecules into 3D model, which was originally intended for application to amorphous polymeric materials. Future work will implement alternative procedures such as that proposed by Gelb and Gubbins for building simulation cells with controlled-pore sizes. Nevertheless, the coal model successfully captured a continuum of pore sizes mostly in the microporous range (due to scale limitations) in accordance with available experimental data.

![Figure 3.7. Micropore size distribution for the large-scale Illinois coal model (dry).](image-url)
Figure 3.8 shows a qualitative visualization of micropore volume elements for the coal model as a series of 6.92 Å thick slices cut perpendicular to the respective z-axis. The empty regions between the atoms indicate free volume elements. The irregular (amorphous) structure of coal model exhibits a homogenous distribution of void volume. Several PAH molecules are curved and seem to be oriented roughly perpendicular and parallel to the cut. It can be noted that the microcavities have shapes closer to spherical symmetry. Realistically, some distortion due to coalification and burial stresses is expected. In most cases, a microcavity shown in one slice disappears in the subsequent slice; that is, the average size of a free volume element is often lower than the distance between slices. Various PAH molecules can be seen as forming stacks, as shown by enclosed areas (Fig. 3.8). These stacks were extracted for further structural analysis.

**Figure 3.8.** Representation of the micropore volume of dry coal model for Illinois No. 6 coal as a series of 6.92 Å thick slices cut perpendicular to the z-axis (sequence from top left to bottom right). Examples of PAH molecules forming stacks are shown by enclosed areas.
Although small in number compared to all stacks present in the coal model, these stacks are distributed through the simulation cell and thus provide important structural information. The calculated interlayer spacing ranged between 0.34 and 0.39 nm, whereas the average cluster size and average stacking number were 0.8 nm and 2.9, respectively, in agreement with HRTEM and XRD results. Therefore, the coal model was able to capture important physical structural parameters.

*Theoretical pyridine extraction yield*

Theoretical solvent extraction yield calculations were performed to evaluate the capability of the coal model in predicting behavioral observations. Solubility parameters were used to estimate the mass fraction of the coal model that could be theoretically extracted by a specific solvent. Solubility parameters were computed as described previously. The coal model exhibited a distribution of solubility parameters ranging from 9 to 16 (cal/cm$^3$)$^{0.5}$ with a peak at 11 (cal/cm$^3$)$^{0.5}$. Pyridine extraction calculations for the coal model indicated that 241 out of 728 molecules were theoretically extractable. Initially, few extractable molecules (19) exhibited high molecular weights ranging from 800 to 1600 Da, in contrast to mass spectral observations. Painter et al. indicated that calculated $\delta$ values exhibited errors of $\pm$0.6 (cal/cm$^3$)$^{0.5}$ and thus should be regarded as an initial estimate for solubility parameters. Further development of this contribution approach through inclusion of additional structural descriptors such as DBE numbers should result in improved $\delta$ predictions. Therefore, a redistribution of phenolic groups was performed for these molecules to make them less soluble, to better agree with FT-ICR data. NMR parameters, elemental composition, molecular weight distribution, and heteroatoms distribution were recalculated and no significant difference was observed as result of tuning the solubility mass range. Thus, the calculated extraction yield was 22.3 wt.% (dmmf), somewhat lower than the 28 wt.% (dmmf) literature value.

To further investigate the proposed coal model, extractable molecules were removed from the model to construct molecular representations for pyridine extract and residue, as shown in Figure 3.9. The elemental composition, normalized to 100 carbon atoms obtained from these pyridine extract and residue models was $C_{100}H_{86.1}O_{8.8}N_{1.3}S_{0.8}$ and $C_{100}H_{74.9}O_{9.5}N_{1.6}S_{1.3}$, respectively. The atomic H/C ratio was 0.86 for the pyridine extract model and 0.75 for the pyridine residue.
model. There is conflicting data in the literature, which makes difficult to compare model results with experimental values. Miura et al.\textsuperscript{73} conducted pyridine extraction experiments and found that O/C and N/C ratios of the Illinois coal pyridine extract were higher than those of the pyridine residue. However, Erbatur et al.\textsuperscript{74} investigated pyridine extracts and residues for a rank range of coals and found for bituminous coals with carbon content similar to that of Illinois No. 6 that oxygen, nitrogen and sulfur contents of the pyridine extracts were lower than those of the corresponding pyridine residues. Therefore, model results are consistent with experimental data by Erbatur et al.\textsuperscript{74}

\[ (\delta_{\text{solv}} - \delta_{\text{coal}}) > \pm 1 \]

\[ (\delta_{\text{solv}} - \delta_{\text{coal}}) < \pm 1 \]

\textbf{Figure 3.9.} Molecular representations for pyridine extract (c) and residue (b) generated from a large-scale Illinois coal model (a) based on theoretical solvent extraction yields. Hydrogen atoms are not shown to aid visualization. Atoms are colored as in Figure 3.4.
The distribution of heteroatoms and alkyl groups for the coal model and its respective pyridine extract and residue models indicated that the pyridine extract model contained high percentages of pyrrolic nitrogen and phenolic groups. Quaternary nitrogen and long linear alkanes were more prevalent in the pyridine residue model, presumably due to quaternary nitrogen atoms being mainly located in less-soluble, large structural entities, and because the calculated $\delta$ value for the linear alkanes ($7.7 \text{ (cal/cm}^3\text{)}^{0.5}$) was not within the solubility range of $9.7 – 11.7 \text{ (cal/cm}^3\text{)}^{0.5}$. The distribution of aliphatic groups per 100 carbon atoms in the pyridine extract model was 3.0 methyls, 0.2 ethyls and 0.03 propyls, whereas in the pyridine residue model was 1.4 methyls, 0.3 ethyls and 0.05 propyls. These results indicate that short pendant alkyl groups (methyls) were preferentially transferred to the pyridine extract model, whereas longer alkyl side chains (ethyls and propyls) were concentrated in the pyridine residue model. This trend is consistent with experimental observations for bituminous.\(^8, 74\)

NMR parameters were also calculated for the pyridine extract and residue models and the corresponding results are listed in Table 3.3 along with the experimental values published by Fletcher et al.\(^72\) Both experimental and simulation results show in general similar structures with a few exceptions. Specifically, the values for $f_a^N$ and $f_a^H$ are over-predicted by the residue and extract model, respectively. Fletcher et al.\(^72\) obtained for bituminous Argonne coals that carbon aromaticities ($f_a'$) in pyridine extracts were slightly higher than those of the respective pyridine residues. These results are in contrast to other data reported in coal literature\(^29, 30, 74\) where similar $f_a'$ values are found for pyridine extract and residue, as obtained from the constructed models.

The molecular weight distributions for the pyridine extract and residue models were also determined, as shown in Figure 3.10. The molecular weight distribution obtained from the residue model ranges from 300-350 to 2850 Da and is 588 and 988 Da for $M_n$ and $M_w$. The extract model showed values of 373 and 410 Da for $M_n$ and $M_w$, and a molecular weight distribution from 100 to 800 Da with a peak at ~350-400 Da. These results are consistent with those obtained by Malhotra et al.,\(^28\) who characterized pyridine extracts of Argonne coals by FIMS and reported for Illinois no. 6 values of 402 and 441 Da for $M_n$ and $M_w$ with a molecular weight distribution from 150 to 1000 Da.\(^28\) However, experimental studies on the molecular
Table 3.3. Experimental and model NMR parameters for Illinois No. 6 coal pyridine extract and residue.

<table>
<thead>
<tr>
<th>Sample</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>$f_a^R$</th>
<th>$f_{al}$</th>
<th>$f_{al}'$</th>
<th>$f_{al}^0$</th>
<th>$\chi_b$</th>
<th>$f_{al\text{cl}}$</th>
<th>$f_{al\text{cl}}'$</th>
<th>$f_{al&amp;l}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyridine extract</td>
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<td>0.25</td>
<td>12</td>
<td>4.4</td>
</tr>
<tr>
<td>Fletcher et al.</td>
<td>0.77</td>
<td>0.76</td>
<td>0.00</td>
<td>0.32</td>
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<td>0.03</td>
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<tr>
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<td>0.16</td>
<td>0.33</td>
<td>0.24</td>
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<td>0.25</td>
<td>12</td>
<td>4.4</td>
</tr>
<tr>
<td>residue</td>
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<td>0.03</td>
<td>0.25</td>
<td>14</td>
<td>5.1</td>
</tr>
<tr>
<td>Fletcher et al.</td>
<td>0.67</td>
<td>0.62</td>
<td>0.05</td>
<td>0.23</td>
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<td>0.07</td>
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<td>0.16</td>
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<td>0.07</td>
<td>0.25</td>
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<td>4.4</td>
</tr>
<tr>
<td>Model</td>
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<td>0.25</td>
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<td>0.21</td>
<td>0.02</td>
<td>0.03</td>
<td>0.25</td>
<td>14</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Parameters: $f_a$ – total of sp$^2$ carbon, $f_{a'}$ – aromatic carbon, $f_a^C$ – carbonyl/carboxyl carbon, $f_a^H$ – protonated aromatic carbon, $f_a^N$ – nonprotonated aromatic carbon, $f_a^P$ – phenolic ethers, $f_a^S$ – alkylated aromatic carbon, $f_a^R$ – aromatic bridgehead carbon, $f_{al}$ – total sp$^3$ carbon, $f_{al}^H$ – CH or CH$_2$ carbon, $f_{al}^P$ – CH$_3$ carbon, $f_{al}^0$ – aliphatic carbon bonded to oxygen, $\chi_b$ – mole fraction of bridgehead carbons, $f_{al\text{cl}}$ – aromatic carbons per cluster, $f_{al\text{cl}}'$ – attachments per cluster, $f_{al\&l}$ – bridges and loops per cluster.

Figure 3.10. Calculated molecular weight distributions for pyridine extract and residue models.
weight of the pyridine extract for Illinois No. 6 have been reported in the literature showing very different molecular weight values. Larsen et al.\textsuperscript{27} performed extraction measurements to determine the molecular weight distribution of coal extracts. The pyridine extracts were fractionated by gel permeation chromatography and the molecular weight of each fraction was measured by vapor pressure osmometry. The results indicated that Illinois No. 6 has $M_n$ and $M_w$ values of 1100 and 2700 Da. Similarly, Derbyshire et al.\textsuperscript{9} determined molecular mass distributions for pyridine extracts of Argonne coals by size exclusion chromatography and obtained for Illinois coal values of 640 and 1680 Da for $M_n$ and $M_w$. As discussed earlier, it is clear that molecular weight values reported in the literature depend on the method utilized and thus comparison with calculated values is difficult.\textsuperscript{75}

**Compositional continuum evaluation**

To further evaluate the current coal model, the elemental composition for each molecule was determined and then used to sort them by compound heteroatom class (numbers of N, O and S atoms) and type (double bond equivalents). The distribution of DBE values for coal model and their respective pyridine extract and residue models are shown in Figure 3.1. The DBE distributions calculated from coal and pyridine residue models exhibit a sharp peak at 15 and then a long tail extending to ~100, whereas the DBE distribution for the pyridine extract ranges from 5 to 30 (centered at 15) and is approximately Gaussian. This result is consistent with the DBE range (from 3 to 31) reported for the pyridine extract of Illinois No. 6 coal by FT-ICR MS.\textsuperscript{3,37}

The distribution of the most abundant heteroatomic classes found in the coal model and its pyridine extract and residue models was calculated as shown in Figure 3.12. Experimental results obtained by Wu et al.\textsuperscript{3} for Illinois coal pyridine extract are also included for comparison. The heteroatomic distributions were scaled relative to the summed abundances of all species. More than 100 heteroatomic classes (mostly containing oxygen atoms) were identified in the proposed coal model. As seen in Figure 3.12, the coal model and its pyridine extract and residue exhibit similar distributions for O$_x$, NO$_x$ and SO$_x$ class compounds (molecules containing those heteroatoms). The N$_2$ and N$_2$O$_2$ classes are found only in the coal model and its pyridine residue model. Compared with the experimental data, results from pyridine extract model are in
Figure 3.11. Distribution of double bond equivalents (DBE) in the Illinois coal model and pyridine extract and residue models.

Figure 3.12. Distribution of the most abundant heteroatomic classes identified in the coal model and respective pyridine extract and residue models. Experimental data\textsuperscript{3} for the pyridine extract of Illinois No. 6 coal was also included.
reasonable agreement. Specifically, the pyridine extract model is able to predict the most abundant heteroatomic classes experimentally identified and, more important, with O₂ and O₃, NO₃ and SO₃ classes as the dominant members of the Oₓ, NOₓ and SOₓ class compounds. In addition, DBE numbers for O₂, O₃ and SO₂ classes in the pyridine extract model range from 11 to 16, 7 to 26 and 8 to 27, peaking at 15, 15 and 14 – 18, respectively. Wu et al.,³, ³⁷ obtained similar DBE ranges for these classes for compositional analysis of Illinois coal pyridine extract by FT-ICR MS.

Figure 3.13 shows a van Krevelen diagram consisting of a plot of H/C vs. O/C atomic ratios, for O₂ and O₃ class compounds that were the dominant heteroatomic classes in the Illinois coal model. As indicated in Figure 3.13, the coal model predicts trend lines corresponding to the members of a homologous alkylation series (constant DBE value) and vertical lines connecting homologous series with different degree of unsaturation, in agreement with experimental results.⁷⁶ In addition, all trend lines representing alkylation series for both heteroatomic classes intersect the ordinate at an H/C value of 2 (H/C = -a (O/C) + 2), consistent with the experimental value.⁷⁶, ⁷⁷ This remarkable result indicates the structural diversity captured by the molecular model. Although the data points exhibit smooth compositional transitions, there are clear empty spaces, specifically for O/C ratios ranging from 0.069 to 0.077 for the O₂ class and from 0.097 to 0.111 for the O₃ class, presumably caused by the small number of coal molecules belonging to those classes (23 for O₂ and 21 for O₃). Indeed, the number of individual molecules present in the coal model is small, 728 molecules in comparison to the more than 10,000 compositionally distinct compounds identified by ESI FT-ICR MS in the acidic asphaltene fraction (hexane-insoluble fraction), ~5,000 in the acid fraction (hexane-soluble fraction), and more than 10,000 in the pyridine extract of Illinois coal.³⁷ The minuscule scale (~10 nm) of the model structure compared to the macroscopic dimensions of coal particles (typically in the micrometer range) represents a challenging problem for the structural modeler. Under the assumption that the coal structure can be at least partially described by 50,000 unique molecules, the coal molecular model captures an estimated 1% of the structural diversity. Nevertheless, this coal model is representative of coal structure, molecularly diverse, consistent with experimental structural data and represents a significant advancement toward capturing the continuum structure. More importantly, the proposed construction approach offers the potential to facilitate the model
generation process and enable very large continuum representations (>750,000 atoms) to be built with improved accuracy, greater length scale, and minimal computational cost.

**Figure 3.13.** Van Krevelen diagram for compounds of O$_2$ and O$_3$ classes for the Illinois coal model. Trend lines indicate members of a homologous alkylation series (constant DBE value) and vertical lines connect homologous series with different degree of unsaturation.

Compositional analyses of Illinois No. 6 coal pyridine extract were performed by negative-ion ESI FT-ICR MS and the results are presented in Figure 3.14. As previously noted by Wu et al.,$^3$ the most abundant acidic species in the Illinois No. 6 pyridine coal extract are O$_x$ and NO$_x$ classes. Negative-ion ESI analysis highlights the oxygen-containing species, because oxygen is the most abundant heteroatom in the coal and coal extracts. The three-dimensional isoabundance color contour plots of DBE vs. carbon number for the abundant O$_x$ and NO$_x$ classes reveal the aromatic character of the coal pyridine extractable species. For example, at a carbon number of 20, the O$_2$ class has a DBE range of 7-14 (highlighted by the red circle), suggesting 2-3 ring aromatic species. Furthermore, extrapolation of the compositional space (red oval) occupied by the O$_x$ species (O$_2$ and O$_4$ class highlighted in Figure 3.14) supports the average elemental composition of the pyridine soluble species calculated from the pyridine extract model.
Figure 3.14. Three-dimensional isoabundance color contour plots of DBE vs. carbon number for the acidic species identified in the pyridine extract of Illinois No. 6 coal by negative-ion ESI FT-ICR MS, revealing the compositional space occupied by the pyridine-extractable coal components.
Specifically, at a carbon number of 50, the DBE value determined from extrapolation is approximately 30. From the model determined average elemental composition of the pyridine soluble species \( \text{C}_{100} \text{H}_{86.1} \text{O}_{8.8} \text{N}_{1.1} \text{S}_{0.8} \), one would expect a DBE of 29.5. The strikingly similar DBE values suggest that negative-ion ESI is effective in capturing a representative population of species through deprotonation of acidic species. Similar results are obtained for the other \( \text{O}_x \) and \( \text{NO}_x \) classes.

**Conclusions**

An automated construction protocol was applied to construct a large-scale model for Illinois No. 6 Argonne Premium coal based on the available structural data. HRTEM lattice fringe micrographs were used to determine the aromatic fringe size distribution. Organic sulfur, oxygen and nitrogen heteroatom types and distributions were added to the aromatic structures according to X-ray adsorption near-edge structure spectroscopy and X-ray photoelectron spectroscopy data. Incorporation of aliphatic structures was conducted in the form of cross-links (bridges and loops) and alkyl side chains based on laser desorption ionization mass spectrometry (LDIMS), ruthenium ion catalyzed oxidation, bulk elemental analysis, and NMR data. Fringe3D in conjunction with Perl scripts created within Materials Studio were utilized to facilitate the model construction process, remove investigator bias, and generate large-scale representations with improved accuracy and structural diversity. The constructed model exhibited a wide and continuous molecular weight distribution ranging from 100 to 2850 Da and contained 50,789 atoms within 728 molecules. Inclusion of structural diversity allowed capturing a portion of the continuum structure, a significant improvement over existing coal model construction approaches. The proposed computational protocol has great potential to enable the building of very large continuum molecular representations (>750,000 atoms) with no significant increase in computational expense. Furthermore, this approach can be used for structural modeling of other carbonaceous materials such as asphaltenes, soot and activated carbon.

Agreement between model and experimental chemical and physical structural parameters validated the automated model construction protocol. Chemical parameters included elemental
composition, NMR parameters, and molecular weight distribution; whereas physical parameters comprised simulated helium density, micropore size distribution, interlayer spacing, average layer length, and average number of layers per stack. Pyridine extract and residue molecular representations constructed from the large-scale Illinois coal model based on theoretical solvent extraction yields were consistent with NMR, elemental analysis, and LDIMS trends. In addition, double bond equivalents distribution and heteroatom class (numbers of N, O, and S atoms) distribution derived from the coal model captured 1% of the structural diversity determined by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. Increasing the model scale should result in improving the molecular weight diversity and structural diversity to better capture the continuum of structural features. Inclusion of macro and mesopores (concurrent with an increase in model scale), maceral groups, and mineral matter will further help generate yet more accurate and realistic structural models. Future modeling efforts should incorporate these factors.

This Illinois No. 6 coal model based on various analytical structural data is the first molecular representation that captures a broad range of structural features including aromatic, aliphatic, heteroatom, and moisture components in a 3D cross-linked network. Incorporation of these features and their distribution generates state-of-the-art coal atomistic representations. This approach will better enable the coal model to be used in simulation studies that investigate the structure-property and structure-behavior relationships in coal chemistry processes such as liquefaction, CO₂ sequestration, combustion, coalification, and gasification.

**Acknowledgments**

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References


Chapter 4

Pyrolysis of a Large-Scale Molecular Model for Illinois No. 6 Coal
Using the ReaxFF Reactive Force Field*

Abstract

Reactive molecular dynamics simulations are a useful approach for investigating chemical reactions and structural transformations in complex systems. Coal pyrolysis is one such area in which additional insights would be beneficial for utilization improvements and pollution control. Here the ReaxFF reactive force field was used to perform pyrolysis simulations on a large-scale (>50,000 atoms) molecular model for Illinois no. 6 coal to examine structural modifications and reactions associated with coal pyrolysis. The previously constructed large-scale molecular model of Illinois no. 6 coal composed of 728 diverse molecules was used in pyrolysis simulations at 2000 K for 250 ps. This high temperature enabled chemical reactions to occur within a practical simulation time. The ReaxFF simulation was performed until about 60% of the cross-links had been disrupted primarily through thermolysis. For this coal pyrolysis was mainly initiated by the release of hydroxyl groups, dehydrogenation of hydroaromatic structures, and by cleavage of heteroatom-containing cross-links. The main pyrolysis products were hydrogen, methyl, ethylene, acetylene, formaldehyde, ethynol, alkylphenols, alkylnaphthalenes and alkylnaphthols, in agreement with experimental data. During pyrolysis the molecular weight distributions shifted to lower molar mass values as expected due to thermal decomposition to form smaller fragments. The thermal degradation of sulfurated and oxygenated cross-links was more substantial than that of alkyl linkages, in accordance with their higher reactivity. Analysis of sulfur form distribution showed that aliphatic sulfur decomposed more rapidly while thiophenic sulfur was more thermally stable in agreement with experimental observation. The extent of decomposition for heterocyclic 5-membered rings was as follows: 57% for pyrrolic, 47% for thiophenic, and 29% for furanic type structures. The ReaxFF simulation was repeated on a sulfur-free model to further analyze the role of organic sulfur forms in Illinois coal pyrolysis. Analysis of trajectories showed that the rate of generation of light gases and tars was higher in the presence of sulfur. Further analysis of ReaxFF simulations showed that aryl and alkyl C-S bonds are weaker than aryl and alkyl C-C bonds. Hence, cleavage of the C-S bonds resulted in more extensive fragmentation leading to larger quantities of aliphatic and aromatic structures that evolved as light gases and tars within Illinois coal model (sulfur containing) compared to sulfur-free model. Thus, sulfur atoms enhanced the reaction kinetics during coal pyrolysis. This work further demonstrates that ReaxFF integration with representative coal molecular models can be a useful tool for probing complex chemical processes and transformations involved in coal pyrolysis.

**Introduction**

Pyrolysis is the initial reaction step in most coal utilization process and influences the course of any subsequent reactions such as combustion, gasification, or liquefaction. Coal pyrolysis involves several physical and chemical processes in which coal is transformed via heating within inert gas atmospheres into a carbon-rich solid residue (coke or char), and volatile products, tar, light gases, and water.\(^1\text{-}^3\) The evolved gases and volatile products typically comprise CO\(_2\), CO, H\(_2\)O, CH\(_4\), C\(_2\)H\(_6\), C\(_2\)H\(_4\), C\(_2\)H\(_2\) and various sulfur- and nitrogen-containing gases. Tars are defined as volatiles (other than water) which condense at room temperature.\(^1\) The solid residue exhibits a broad distribution of molecular weights. The pyrolysis behavior of coals depends on temperature, heating rate, particle size, pressure, and coal type, among others.\(^1\text{-}^7\) The residence time required for a given degree of completion of coal devolatilization is reduced for higher temperatures. The use of slow heating rates promotes secondary reactions such as cracking and carbon deposition that will tend to reduce the total weight loss. The amount of evolved gases and tars vary broadly with coal rank. In general, low-rank coals produce a high yield of gases and a low yield of tar, while high-rank coals often generate low yields of light gases and tar.\(^1\text{-}^3\)

Coal pyrolysis reactions are highly complex, largely involving bond breaking, vaporization and condensation. The chemistry of coal pyrolysis generally includes the thermal decomposition of surface functional groups to form light gases, and the degradation of the macromolecular network to produce smaller fragments that can evolve as tar. Volatile species and tars are conveyed by mass transport processes to the exterior of the coal particle followed by the formation of char structure due to condensation reactions at high temperature.\(^1\text{-}^2\) Pyrolysis behavior of softening coals has been described as a three-stage process.\(^8\) During stage I, coal undergoes a disruption of hydrogen bonds and cleavage of labile chemical bonds within the macromolecular network to promote the release of primary gas and liquid components, which are often referred to as metaplast. The metaplast is generally recognized to be responsible for the fluidity of coal upon heating.\(^8\) At stage I, bond rupture competes with bond stabilization to form char particle. Stage II is characterized by bulk evolution of tar, which is considered the low molecular weight component of metaplast.\(^8\) The remaining high molecular weight components in the metaplast re-attach to the char structure by condensation reactions. During stage III, char evolves CO and H\(_2\) while continuing to cross-link with further ring condensation.
Despite extensive research, improved understanding of fundamental reaction mechanisms and chemical processes involved in coal pyrolysis remains desirable. Reactive molecular dynamics (MD) simulations can provide atomistic insight for such reactive events. Various coal molecular models have been generated to reflect structural transformations of coal to char during devolatilization. Marzek\textsuperscript{9} constructed models of pyrolyzed coal to investigate the relationship between char structure and pyrolysis temperature. The results showed that oligomerization and dehydrocyclization of aromatic molecules are the predominant reactions during coal pyrolysis, consistent with the chemical description of pyrolysis discussed by Solomon et al.\textsuperscript{10} Mathews et al.\textsuperscript{11} constructed structural representations for two vitrinite-rich coals using Signature program\textsuperscript{12} and simulated rapid-heating devolatilization to examine bond-breaking and bond-forming processes. Similarly, Jones et al.\textsuperscript{13} used a modified Shinn model\textsuperscript{14} to investigate structural conformations of coal molecules in the coal to char pyrolysis reaction. Recently, a novel coarse-graining-like approach was proposed by Alvarez et al.\textsuperscript{15, 16} for systematic simplifications of complex 3D coal molecular models into respective 2D lattice representations via pattern recognition and graph theory to simulate primary bond breaking under mild pyrolysis conditions.\textsuperscript{17} Earlier phenomenological models are also relevant such as FG-DVC,\textsuperscript{10} CPD,\textsuperscript{18} and FLASHCHAIN,\textsuperscript{19} which were developed to predict coal devolatilization yields. These models provide quantitative relationships between parent coal and chemical properties of pyrolysis products (gas, tar, and char) using simplified network models of coal, such as lattices and polymeric chain representations.

Coal has been recognized to have a continuum distribution of structural features over a wide range that influences the behavior of coal during utilization processes.\textsuperscript{1, 20-22} However, most of coal molecular models are small-scale (<5000 atoms) average representations that fail to capture the distribution of structural features and thus their application for exploring the structure-behavior relationship of coal is often limited.\textsuperscript{23} Generation of representative large-scale coal models is challenging, time-consuming, and demands substantial expertise due to the large range of structural features.\textsuperscript{23, 24} Recently, an automated construction approach was implemented to construct a large-scale (>50,000 atoms) coal molecular model based on analytical data.\textsuperscript{25} in an effort to move toward capturing the continuum of Illinois no. 6 Argonne Premium coal.\textsuperscript{26} The work here utilizes this high-quality, large-scale Illinois coal model.
Reactive force fields (RFFs) can simulate the dissociation and formation of chemical bonds during reactive MD simulations of large systems with accuracy similar to quantum mechanical (QM) methods but with significantly reduced computational time and cost. Therefore, RFF methods can provide unique insight into the highly complex chemistry associated with structural transformations and chemical reactions occurring during coal conversion processes. Among the RFF-schemes that have been developed, the ReaxFF reactive force field has been applied in numerous simulation studies aimed at examining initiation reaction mechanisms and chemical processes relevant to fossil fuel thermolysis processes including pyrolysis,\textsuperscript{27-29} oxidation,\textsuperscript{30-32} and combustion.\textsuperscript{32-35} Despite recent advances in computer power and software tools, reactive force fields methods still require extensive computational resources to provide a detailed representation of chemical reactivity in large and highly complex systems such as large-scale Illinois coal model simulated in this work. With current computational capabilities, reactive simulations are often conducted at temperatures higher than experimental conditions to enable chemical reactions to occur within a practical computational time. Nevertheless, ReaxFF method coupled with representative coal representation is a useful computational approach for examining complex coal pyrolysis reactions.

Salmon et al.\textsuperscript{29} simulated early maturation process of Morwell brown coal (lignite) via ReaxFF to examine thermal decomposition processes of defunctionalization, depolymerization and rearrangement of the residual lignite structure. ReaxFF simulations at 2000-2200 K showed that decarboxylation and dehydroxylation of lignin side chains involved the formation of double bonds conjugated with the aromatic rings. The process of defunctionalization of methoxy groups resulted in the generation of phenol and methyl radicals. Agreement with experimental data validated ReaxFF methodology in describing complex chemical processes related to thermal decomposition of carbonaceous materials.

Recently, the ReaxFF reactive force field for hydrocarbon combustion was expanded to include organic sulfur forms and correctly simulate pyrolysis and combustion dynamics of coal molecules and hydrocarbons containing sulfur functionalities. This extended ReaxFF was used to perform combustion simulations on a molecular representation for a devolatilized Illinois no. 6 coal char to investigate the structural evolution of char structure and chemical processes related
to combustion under high-temperature conditions. Here, ReaxFF was utilized for the first time to perform pyrolysis simulations on a large-scale molecular model for Illinois no. 6 coal to examine the complex chemistry associated with coal pyrolysis and further demonstrate ReaxFF integration with coal molecular models for accurate descriptions of chemical processes involved in high-temperature coal pyrolysis.

**Computational Methods**

*Coal model construction*

The Illinois no. 6 Argonne Premium coal is a high-volatile bituminous coal (C = 81%, dmmf) with a normalized elemental composition of C\textsubscript{100}H\textsubscript{77.3}O\textsubscript{13.1}N\textsubscript{1.5}S\textsubscript{1.2} and has a high organic sulfur content of 2.5% (dmmf). Castro-Macano et al.\textsuperscript{25, 36} implemented an automated construction protocol via Fringe3D\textsuperscript{37} coupled with Perl scripts to generate a large-scale molecular model for Illinois no. 6 coal based on available structural data.\textsuperscript{25} The coal model generation approach consisted of: (1) HRTEM lattice fringe images analysis, (2) construction of polyaromatic structures, (3) addition of heteroatoms, alkyl side chains and generation of a cross-linked network structure, and (4) construction of 3D molecular model. Fringe3D was coupled with Perl scripts to facilitate the model construction process, remove structural bias, and enable generation of large-scale structures with improved accuracy and structural diversity. The Illinois coal model contained over 50,000 atoms (C\textsubscript{26860}H\textsubscript{20897}O\textsubscript{2502}N\textsubscript{412}S\textsubscript{330}, atomic H/C=0.778 and O/C=0.093) in 728 cross-linked aromatic and hydroaromatic clusters exhibiting a continuous molecular weight distribution ranging from 100 to 2850 Da with an aromaticity value of 0.75, sulfur distributed among functional groups as 33% aliphatic, 26% aromatic, and 41% thiophenic, and a simulated helium density of 1.32 g/cm\textsuperscript{3} in agreement with experimental data for Illinois no. 6 coal.\textsuperscript{25} A sulfur-free model was generated to analyze the effect of organic sulfur in the pyrolyzed coal structure and final product distribution. This model was created by substituting all sulfurs for carbons in the Illinois coal model with hydrogen adjustment performed on the resulting structures followed by geometry and energy optimization. The sulfur-free model exhibited an elemental composition of C\textsubscript{27190}H\textsubscript{21425}O\textsubscript{2502}N\textsubscript{412} and H/C and O/C atomic ratios of 0.788 and 0.092, respectively. Table 4.1 summarizes the main chemical and physical parameters of Illinois and sulfur-free models.
**Table 4.1.** Chemical and physical parameters for the Illinois and sulfur-free coal models.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Illinois coal model</th>
<th>Sulfur-free model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental composition (dmmf)</td>
<td>C_{26860}H_{20897}O_{2502}N_{412}S_{330}</td>
<td>C_{27190}H_{21425}O_{2502}N_{412}</td>
</tr>
<tr>
<td>Atomic H/C ratio</td>
<td>0.778</td>
<td>0.788</td>
</tr>
<tr>
<td>Atomic O/C ratio</td>
<td>0.093</td>
<td>0.092</td>
</tr>
<tr>
<td>Aromaticity (%)</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Helium density (g/cm³)</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>Number average molecular weight (Da)</td>
<td>522</td>
<td>517</td>
</tr>
<tr>
<td>Weight average molecular weight (Da)</td>
<td>864</td>
<td>854</td>
</tr>
</tbody>
</table>

**ReaxFF reactive force field**

ReaxFF\(^{38}\) is a reactive force field that utilizes a bond order concept to model the chemical and physical interactions of atoms and molecules within complex reactive systems. The use of a general bond order/bond length relationship permits for smooth transitions from non-bonded to bonded systems and thus enabling accurate description of bond-breaking and bond-forming reactions during reactive MD simulations. The ReaxFF potential determines the connectivity of the system based on bond orders calculated from interatomic distances that are updated every iteration allowing a dynamic description of the formation, transition, and complete dissociation of chemical bonds. The bonded interactions (i.e., bonds, angles and torsions) are bond-order dependent so that their energy contributions disappear upon bond dissociation. The non-bonded interactions (van der Waals and Coulomb) are calculated via Morse and Coulomb potentials between all atom pairs and are shielded at short interatomic distances to prevent these interactions from becoming excessive. The electronegativity equalization method is employed for calculating the polarization of charges within molecules.\(^{39}\) This method depends on the system geometry and uses electronegativity and hardness parameters for each element in the system to calculate atomic charges. ReaxFF parameters were optimized against QM calculations and available experimental data and thus enable accurate molecular modeling of reactive systems.\(^{38}\) Further details on the ReaxFF force field have been described previously elsewhere.\(^{38}\)

**Reactive molecular dynamics simulation details**

For the ReaxFF pyrolysis simulations, the Illinois and sulfur-free models were equilibrated at 300 K for 100 ps using NVT-MD simulations with a time step of 0.25 ps. Then, the temperature
of these equilibrated systems was ramped to 2000 K at a rate of ~100 K/ps. The temperature was
controlled using the Berendsen thermostat\textsuperscript{40} with a 0.1 ps damping constant. Thereafter, constant
temperature MD simulations were performed for each system at 2000 K for 250 ps. The total
simulation time for these systems was determined by the extent of ring structures decomposition
and cross-links cleavage. ReaxFF simulations were performed using the ReaxFF program as
implemented in ADF software\textsuperscript{41} with hydrocarbon combustion force field parameters extended
to sulfur. These simulations required ~0.1 ps/h for completion using four processors at the Lion-
XH HPCS of Penn State Research Computing and Cyberinfrastructure.\textsuperscript{42} A typical equilibration
and production run for the complex coal structure examined in this study took about 3-4 months
of simulation time followed by multiple weeks of data analysis. ReaxFF simulations were
conducted at high temperatures (2000 K) to observe chemical reactions within a computationally
practical simulation time, with the expectation that initiation reaction mechanisms are similar to
experiments. Previous studies examining the initial stages of thermal decomposition of
hydrocarbon fuels using elevated temperature (> 2500 K) ReaxFF simulations have been in
accordance with experimental results.\textsuperscript{27-31, 34, 35} Hence, ReaxFF integration with realistic coal
molecular models can provide initial insight into the complex chemical processes related to coal
pyrolysis.

\textbf{Results and Discussion}

ReaxFF pyrolysis simulations of the Illinois coal model at constant temperature of 2000 K were
performed to evaluate the complex chemistry involved in high-temperature coal pyrolysis. The
ReaxFF simulation was repeated on a sulfur-free model to further analyze the role of organic
sulfur forms in Illinois coal pyrolysis. Conducting ReaxFF simulations at elevated temperatures
enabled observation of chemical reactions and structural transformations within the picosecond
range. Previous works have showed that initiation reaction mechanisms associated with thermal
degradation of hydrocarbon fuels utilizing high-temperature (> 2500 K) ReaxFF simulations
qualitatively agree with experimental data.\textsuperscript{27-31, 34, 35} Here ReaxFF was used to examine the
structural changes and fragmentation of the coal structure during the earlier stages of pyrolysis
which involved primary the evolution of light gases and tars. Formation of char structure during
these pyrolysis simulations was not considered. A separate study has been performed using
ReaxFF method to examine the chemistry and structural evolution of char structure during combustion under high temperature conditions for an Illinois no. 6 coal char.\textsuperscript{32}

Snapshots of Illinois coal model at 0, 125, 150 and 250 ps of ReaxFF pyrolysis simulation at 2000 K are shown in Figure 4.1. Coal molecules underwent several transformations via complex network of reaction pathways and decomposed to produce light gases, tars and solid residue, consistent with expectations. Initially, small molecules and fragments (volatiles) escaped from the coal structure followed by the release of larger molecular fragments (tars) and subsequent thermal decomposition of the evolved volatile products and coal matrix structure, in accordance with the fundamental steps of coal pyrolysis.\textsuperscript{1,2} Analysis of trajectories from ReaxFF simulations showed complex initiation chemistry for the coal pyrolysis process. In general, initiation of Illinois coal pyrolysis involved release of hydroxyl groups and dehydrogenation of hydroaromatic structures followed by cleavage of oxygen- and sulfur-containing cross-links, in agreement with experimental expectations.\textsuperscript{1-3,7}

Further analysis of ReaxFF simulations showed a complicated reaction pathway for the thermal decomposition of organic sulfur forms during Illinois coal pyrolysis. Snapshots of thermal degradation for a representative thiophenic type structure observed during ReaxFF simulations of Illinois coal model are presented in Figure 4.2. The results showed that the initial sulfur reactions involved the dissociation of the carbon-sulfur bond, allowing the molecule to twist 180 degrees followed by the formation of a 7-membered ring with the subsequent insertion of the sulfur atom to form a heterocyclic 8-membered ring. Next, ring opening occurred due to C-S bond rupture followed by successive migration of sulfur atom along the new chain leading to one aliphatic chain of 6 carbons with no branching. Finally, the sulfur removed a hydrogen atom from the neighboring CH on the chain to form a thiophenol group. Current kinetic modeling methods based on simplified network models of coal are unable to provide an atomistic description of the initial chemical events associated with coal thermal decomposition process.\textsuperscript{10, 18, 19} The advantage of using the ReaxFF force field is that it provides a detailed, dynamical description of complex pyrolysis reactions for large-scale coal molecular models.
Figure 4.1. Snapshots of Illinois coal model at 0 ps (a), 125 ps (b), 150 ps (c), and 250 ps (d) ReaxFF pyrolysis simulation at 2000 K. Carbon atoms are colored grey, hydrogen atoms are white, oxygen atoms are red, nitrogen atoms are blue, and sulfur atoms are yellow.
Figure 4.2. Example of initiation mechanism for the thermal decomposition of thiophenic type structure observed during pyrolysis of Illinois coal model at 2000 K. Dissociation of the C-S bond, allowing the molecule to twist 180 degrees (a-b), followed by formation of a 7-membered ring with subsequent insertion of the sulfur atom (c-d). Ring opening occurred with migration of sulfur along the new chain (e-g) and subsequently the sulfur atom removing a hydrogen from the neighboring CH on the chain (h).

Figure 4.3 shows the concentration profiles for light gases and tars observed during ReaxFF pyrolysis simulations of the Illinois and sulfur-free coal models at 2000 K. The major gaseous products of Illinois coal pyrolysis were carbon dioxide, steam, hydrogen and light hydrocarbons and oxygenated compounds, which is consistent with experimental data for Illinois coal. In general, the rate of generation of light gases and tars was greater in the presence of sulfur. Analysis of ReaxFF simulations showed that aryl and alkyl C-S bonds are weaker than aryl and alkyl C-C bonds. Hence, cleavage of the C-S bonds resulted in more extensive fragmentation leading to larger quantities of aliphatic and aromatic structures (total number of molecules was 1047 for Illinois coal model and 937 for sulfur-free model) that evolved as light gases and tars within Illinois coal model compared to sulfur-free model. Therefore, sulfur atoms enhanced the reaction kinetics during coal pyrolysis. Solomon et al. analyzed Argonne Premium coal samples (which include Illinois no. 6 coal) by thermogravimetric Fourier transform infrared spectroscopy and reported that functional group composition give rise to variation in gas yields. In particular, coals with a high content of functional groups produced higher pyrolysis gas yields. Furthermore, the evolution profiles of thiophene and methylthiophene obtained from pyrolysis of Argonne Premium coals have been reported to precede benzene and toluene profiles, indicating that aryl C-S bonds are more prone to breakage than aryl C-C bonds in agreement with ReaxFF results.
Figure 4.3. Distribution of light gases and tars and generation of molecular fragments obtained from ReaxFF pyrolysis simulations at constant temperature of 2000 K for 250 ps for Illinois coal model and sulfur-free model. Color version is available online.
Formation of tars (defined as compounds with molar mass between 100 and 700 Da)\textsuperscript{45} follows a similar pattern to that of light gases generation with Illinois coal model producing slight higher tar yields (462 tar molecules for Illinois coal model vs. 444 tar molecules for sulfur-free model) as a result of its higher level of molecular fragmentation largely promoted by C-S bond scission reactions. These results agree with the data of Burnham et al.,\textsuperscript{43} which indicated that tar generation was closely associated with breakdown of oxygen and sulfur functionalities in the coal. Figure 4.3 also shows that the rate of tar formation leveled off at 200 ps and then slightly declined at the later stage of simulation (250 ps). This is due primarily to the thermal degradation of tar molecules that are unstable at 2000 K leading to generation of small fragments that convert to volatiles and light hydrocarbons.

The proportion of organic sulfur and nitrogen between gas, tar and initial solid residue was found to be 11:76:13 and 9:83:8 respectively, indicating that most of the evolved sulfur and nitrogen atoms during Illinois coal pyrolysis were primarily released into the tar fraction. Similar trends were reported by Cai et al.\textsuperscript{46} for pyrolysis of Illinois no. 6 coal in a wire-mesh reactor operated at \~{}1250 K, where the distribution of organic sulfur and nitrogen was 33:50:17 and 13:55:32, respectively. Lee et al.\textsuperscript{5} also found that nitrogen and sulfur species preferentially evolved as tars during Illinois coal pyrolysis at 1190 K and 100-530 psig.

The distribution of the most abundant heteroatomic classes (numbers of N, O and S atoms per molecule) identified in the Illinois gas and tar yields is presented in Figure 4.4. The heteroatomic distributions were scaled relative to the summed abundances of all species. Over 100 heteroatomic classes (mostly containing oxygen atoms) were identified in the Illinois pyrolysis yields. Specifically, the O and O\textsubscript{2}, NO and NO\textsubscript{2}, and SO and SO\textsubscript{2} classes are the dominant members of the O\textsubscript{x}, NO\textsubscript{x} and SO\textsubscript{x} class compounds (molecules containing those heteroatoms) within the tar yield. For the light gases, the O and O\textsubscript{2}, NO and SO classes are the major acidic species of the O\textsubscript{x} and SO\textsubscript{x} heteroatomic classes.
The elemental composition for the tar was $C_{83.2}H_{5.2}O_{1.6}N_{7.7}S_{2.4}$, which compares favorably with the experimental value determined by Lee et al.\textsuperscript{5} for Illinois coal tars (produced using a high-pressure entrained-flow reactor at 1190 K) as $C_{84.7}H_{4.8}O_{5.9}N_{2.2}S_{2.4}$. Applied pressure delays the devolatilization, lowers the volatiles yield and promotes secondary tar reactions.\textsuperscript{5} Similarly, the atomic H/C and O/C ratios of 0.75 and 0.08 from simulated tar yield agreed reasonably with the 0.68 and 0.03 literature values.\textsuperscript{5} Simulated Illinois tar fraction exhibited values for number ($M_n$) and weight ($M_w$) average molecular weights of 265 and 329 Da respectively, in accordance with experimental results for Illinois pyrolysis tars for $M_n$ of 250-400 Da as determined by matrix-assisted laser desorption mass spectrometry\textsuperscript{47} and for $M_w$ of 325 Da measured by size exclusion chromatography.\textsuperscript{48}

The product distribution obtained from ReaxFF pyrolysis simulations for the Illinois no. 6 coal model is given in Table 4.2. The pyrolysis products included light gases and a distribution of alkyl and polyaromatic structures in the carbon number range of $C_1$-$C_6$ and $C_6$-$C_{100}$, respectively. Table 4.2 shows the most abundant pyrolysis products for each compound category. A detailed
list of pyrolysis products containing over 1000 compounds is provided in Supplementary Material. Examples of pyrolysis products are depicted in Figure 4.5. Hydrogen, water, and carbon dioxide were the most prominent light gases; methyl, ethylene, and acetylene were the most abundant C1-C2 hydrocarbons while formaldehyde and ethynol were the predominant light oxygenated compounds. Alkylphenols, alkynaphthalenes, alkynaphthols, and alkylphenanthrenes were the major polyaromatic compounds within the tar yield. Nitrogen-containing compounds (pyrroles), alkylthiophenes and benzothiophenes as well as furanic type structures were also present among pyrolysis products. These results are consistent with experimental data published by Hartgers et al.,44 which characterized flash pyrolysates of Illinois no. 6 coal using Curie-point pyrolysis at 900 K with gas chromatography mass spectrometry. Structural characterization of Illinois pyrolysates showed the presence of alkylphenols, alkylbenzenes, alkylindenes, alkylindanes, alkynaphthalenes, alkynaphthols, alkylanthracenes/-phenanthrenes, greater polycyclic aromatic compounds, isoprenoid hydrocarbons, and homologous series of alkanes and alkenes with phenol and cresol isomers (2-, 3-, and 4-methylphenol) as the most abundant pyrolysis products. Burnham et al.43 reported pyrolysis yields for Argonne Premium coals measured by pyrolysis interfaced to triple-quadrupole mass spectrometry. The yield of gaseous pyrolysis products for Illinois coal was primary composed of hydrogen, carbon dioxide, water, methane, ethylene and ethane, which were the main light gases and volatile products identified in ReaxFF simulations.

Molecular weight distributions were determined from Illinois coal model as a function of time and the results are shown in Figure 4.6. Calculated molecular weight distributions showed progressively lower peak intensity for the main peak (350-400 Da) and shifted to lower molar mass values as a result of thermal decomposition of coal molecules to form smaller fragments. Formation of second and third peaks at 100-149 and 0-49 Da are consistent with the molar mass of naphthalene structures and light gases, respectively. Furthermore, calculated values for $M_n$ and $M_w$ for Illinois coal model decreased during ReaxFF pyrolysis simulations. Specifically, $M_n$ and $M_w$ values declined from 522 to 216 Da and from 864 to 427 Da respectively. The distribution of double bond equivalents (DBE) determined on the initial and pyrolyzed Illinois coal structures are shown in Figure 4.7. DBE corresponds to the number of rings plus double bonds to carbon and thus is a direct measure of unsaturation (higher degree of unsaturation usually indicates
Table 4.2. Summary of main products obtained from ReaxFF pyrolysis simulations of Illinois coal model at 2000 K for 250 ps.

<table>
<thead>
<tr>
<th>light gases</th>
<th>(C1–C6) hydrocarbons</th>
<th>(C1–C6) compounds</th>
<th>(C6–C16) compounds</th>
<th>(C16–C40) compounds</th>
<th>(C40–C100) compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>89 H2</td>
<td>91 C2H4</td>
<td>59 CH2O</td>
<td>18 C7H8O</td>
<td>7 C25H20O2</td>
<td>2 C52H34O4N</td>
</tr>
<tr>
<td>67 H2O</td>
<td>75 C2H2</td>
<td>31 C2H2O</td>
<td>14 C9H7O</td>
<td>6 C26H22O2</td>
<td>1 C40H20O2N</td>
</tr>
<tr>
<td>32 CO2</td>
<td>11 CH3</td>
<td>12 CN</td>
<td>8 C15H13O</td>
<td>5 C26H21</td>
<td>1 C40H2104N</td>
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**Figure 4.5.** Examples of pyrolysis products identified in ReaxFF simulations of Illinois coal model after 250 ps.
Figure 4.6. Molecular weight distributions calculated from Illinois coal model as a function of simulation time during ReaxFF pyrolysis simulations.

increased aromaticity). Compositional characterization of pyridine coal extracts based on DBE analyses are discussed in detail elsewhere.\textsuperscript{49-51} The DBE distributions calculated from the initial Illinois coal structure ranged from 4 to ~100 (not shown) and exhibited a sharp peak at 15, indicating that most of polyaromatic ring structures contained between three and four fused rings. DBE values for the pyrolyzed Illinois coal model showed a distribution spanning from 0 to 40 with major peaks at 2, 4-6, and 14-16, corresponding to light gases and hydrocarbons, benzene and naphthalene, and phenanthrene and pyrene type structures, respectively. These results are consistent with the main peaks at 0-49, 100-149, and 350-400 Da observed in calculated molecular weight distributions and major pyrolysis products obtained from ReaxFF simulations (Table 4.2).

Thermal decomposition of cross-link structures within the Illinois coal model was monitored as a function of time to gain a better understanding of the chemistry during pyrolysis (Figure 4.8).
Figure 4.7. The distribution of double bond equivalents (DBE) in the initial and pyrolyzed (after 250 ps) Illinois coal structures.

Figure 4.8. Time evolution of cross-links within the Illinois coal model observed in ReaxFF pyrolysis simulations at 2000 K.
Almost 64% of all cross-links were cleaved primarily through thermolysis after 250 ps at these conditions. A detailed analysis of ReaxFF trajectories indicated that decomposition of oxygen- and sulfur-containing cross-links was mostly initiated by C-O and C-S thermolysis reactions respectively. Evolution of cross-link distributions indicated that thermal degradation of oxygenated and sulfurred cross-links was more substantial than that for alkyl linkages, in accordance with their higher reactivity. In particular, 86% and 69% of the oxygenated and sulfurred cross-links were disrupted in comparison to 33% alkyl cross-links breakage. Alkyl ethers (Ph-CH$_2$-O-CH$_2$-Ph) and alkyl thioethers (Ph-CH$_2$-S-CH$_2$-Ph) decomposed more rapidly and exhibited the highest degree of thermal decomposition reaching up to 87% and 89% cleavage respectively. Aryl ethers (Ph-O-Ph and Ph-CH$_2$-O-Ph) and aryl thioethers (Ph-S-Ph and Ph-CH$_2$-S-Ph) were more thermally stable and showed lower thermal degradation with 79% and 51% cross-links scission respectively. The thermal stability of sulfurred cross-links was found to decrease in the order: Ph-S-Ph > Ph-CH$_2$-S-Ph > Ph-CH$_2$-S-CH$_2$-Ph. Similar behavior was observed for oxygenated cross-links. This is consistent with the kinetic constrains utilized for numerical lattice-based simulations of coal thermal breakdown.

The evolution of 5- and 6-membered rings as a function of time was also monitored during Illinois coal pyrolysis (Figure 4.9). Analysis of the trajectory from the simulations showed that intermediate ring structures (such as 4-, 7- and 8-membered rings) were formed during coal pyrolysis but these structures were short lived, hence were not included in the analysis shown in Figure 4.9. The Illinois coal model was initially composed of 1329 5-membered rings (394, 544, 135, and 256 containing C, O, S, and N respectively) and 5557 6-membered hydroaromatic rings (5303 containing C and 254 containing N). Figure 4.9 shows that about 18% of all polyaromatic ring structures decomposed over the course of the pyrolysis simulation. Reaction pathway analysis showed that the predominant initial decomposition mechanism of heterocyclic member rings involved dissociation of the C-heteroatom bond to form a carbon radical. The heterocyclic 5- and 6-membered rings were found to decompose more rapidly than hydrocarbon 5- and 6-membered rings (32% vs. 15% respectively), in agreement with expected chemistry. The extent of thermal degradation for heterocyclic 5-membered rings was as follows: 57% for pyrrolic N, 47% for thiophenic S, and 29% for furanic O.
Figure 4.9. Time evolution of 5- and 6-membered rings in the Illinois coal model during ReaxFF pyrolysis simulations at 2000 K.

By combining ReaxFF reactive force field with realistic large-scale coal molecular models that better capture coal structural diversity we obtained a versatile computational approach that enables investigation of the complex chemical reactions and physical transformations associated with high-temperature coal pyrolysis. With computational speed gains it is anticipated that this approach could be utilized at reactor pyrolysis temperatures, over longer simulation times, with very large coal atomistic representations. Both large-scale and long time simulations are required to capture the coal pore size distribution and hence the mass transport effects relevant to coal pyrolysis. Ultimately, many orders of magnitude gains in size and time are necessary to simulate systems of interest. The work presented here provides additional insights into the initial chemical reactions of the thermal decomposition of Illinois coal at high temperature conditions. This simulation approach can be readily extended to incorporate inorganic and aqueous-phase components or coal/catalyst interfaces to enable evaluation of coal liquefaction strategies.
Conclusions

The ReaxFF reactive force field was utilized to perform pyrolysis simulations on a large-scale molecular model of Illinois no. 6 coal to investigate coal pyrolysis chemistry and the effects of organic sulfur content. The large-scale structural model of Illinois coal was created in previous work using an automated construction approach based on available characterization data. ReaxFF pyrolysis simulations were performed on the Illinois coal model at 2000 K to allow chemical processes to occur within the picosecond range (250 ps). The results showed that Illinois coal pyrolysis was mainly initiated by release of hydroxyl groups and dehydrogenation of hydroaromatic structures followed by breakage of heteroatom-containing cross-links. Calculated molecular weight distributions gradually shifted to lower values as expected due to the thermal degradation of coal molecules to produce smaller molecules and fragments. Aliphatic sulfur was observed to decompose more rapidly than thiophenic sulfur, which was more thermally stable. Decomposition of sulfurated and oxygenated cross-links was more extensive than that for alkyl cross-links, consistent with their higher reactivity. A more rapid thermal degradation was observed for heterocyclic 5- and 6-membered rings in comparison to hydrocarbon 5- and 6-membered rings. The ReaxFF simulation was repeated on a sulfur-free model to further evaluate the effect of organic sulfur forms on Illinois coal pyrolysis. The results indicated that the rate of pyrolysis products generation was greater in the presence of sulfur. Analysis of ReaxFF simulations showed that aryl and alkyl C-S bonds are weaker than aryl and alkyl C-C bonds. Hence, C-S bond scission reactions led to more extensive fragmentation producing higher amounts of aliphatic and aromatic moieties that evolved as light gases and tars within Illinois coal model (sulfur containing) compared to sulfur-free model. Therefore, sulfur atoms aided in accelerating pyrolysis reaction kinetics. This work further demonstrates that coupling the ReaxFF reactive force field with large-scale coal molecular models can be a useful simulation approach for examining the complex chemistry associated with structural transformations and chemical reactions involved in coal pyrolysis.

Acknowledgements

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References


42. Penn State Research Computing and Cyberinfrastructure, [http://rcc.its.psu.edu/resources/hpc/](http://rcc.its.psu.edu/resources/hpc/).
Chapter 5

Combustion of an Illinois No. 6 Coal Char Simulated using an Atomistic Char Representation and the ReaxFF Reactive Force Field*

Abstract

Coal or biomass chars are complex carbonaceous materials that are important energy sources for electricity production. Reactive molecular dynamics simulations are a useful tool to examine the chemical reactions occurring in complex processes, providing that a realistic structural representation and an applicable reactive force field can be utilized. Combustion of coal (or biomass) char is one such area where additional insight would be helpful for utilization enhancements and pollution control. In this investigation a devolatilized Illinois No. 6 coal char atomistic representation was generated, using Fringe3D and additional Perl scripts, coupled with the ReaxFF reactive force field for hydrocarbon combustion. Fringe3D facilitates the char structure generation process by producing a distribution of aromatic structures based on HRTEM lattice fringe image analyses. Perl scripts were used for incorporating heteroatoms and aliphatic components to aid elimination of investigator bias, and facilitate a more rapid construction process. The char structure was constrained by a combination of elemental and NMR literature data. Chemical and physical parameters were found to be consistent with the experimental data. The ReaxFF force field for hydrocarbon combustion was used to perform simulations to examine the structural transformations and chemical processes associated with char combustion. In this initial work, very high temperatures (3000 – 4000 K) were selected for ReaxFF simulation under stoichiometric, fuel lean and rich combustion conditions. These elevated temperatures were chosen to observe chemical reactions proceed to completion within a computationally practical simulation time. Analyses indicated that char oxidation process was primarily initialized by either thermal degradation of char structure to form small fragments, that were subsequently oxidized, or by hydrogen abstraction reactions by oxygen molecules and O and OH radicals. A more rapid oxidation and combustion of the polyaromatic structures occurred at fuel lean (oxygen rich) conditions compared with fuel rich combustion. Char transitions included 6-membered ring conversion into 5- and 7-membered rings that further decomposed or reacted with mostly O and OH radicals. This work further demonstrates the utility of ReaxFF force field integration with representative char structural models to investigate physical and chemical transformations of char structure during combustion at high-temperature conditions.

Introduction

Coals are complex carbonaceous structures used as primary combustion fuel sources in electric power generation. Coal supplies 27% of global primary energy needs and currently provides 41% of electricity generation worldwide.\(^1\) The development of realistic atomistic representations can contribute to a better understanding of the structure and behavior relationship of coal char during conversion processes and greatly improve the design strategies for the effective utilization of coal char in gasification and combustion systems. Coal undergoes rapid loss of moisture and volatiles at high temperatures often followed by thermoplastic transformations resulting in a complex char structure that is dependent on the precursor properties, time-temperature history, and gas pressure employed.\(^2-7\) Devolatilized coal-derived chars are typically highly aromatic (aromaticities of >0.90) and exhibit various degrees of turbostratic crystalline order (stacking, layer size and interlayer spacing), pore size distributions, surface areas, and atomic H/C ratio’s.\(^5\)\(^,\)\(^8-10\) These variations affect char reactivity.\(^3\)\(^,\)\(^11\) The structure of char has a significant impact on subsequent conversion processes such as char gasification and combustion.\(^12-15\) During combustion, the char structure undergoes several structural transformations and complex chemical reactions.\(^16\) Coal combustion generally involves devolatilization to form char particles with the release of volatiles followed by their combustion (homogeneous gas-phase reaction) and char particle oxidation and combustion (heterogeneous surface reaction with oxygen).\(^16-18\) The oxidizing agent must diffuse to the char particle reaction sites, sometimes through the developing ash layer. The reaction products then diffuse away from the char particle.\(^16-18\) For coal char combustion by oxygen, the ratio of the primary combustion products, CO/CO\(_2\), generally increases with increasing temperatures.\(^18\)

Despite extensive research, understanding the fundamental reaction mechanisms and chemical events involved in coal char combustion is desirable. Reactive molecular dynamics (MD) simulations can provide insight at the atomistic scale for such reactive events, provided that a representative char structure can be generated and coupled with an appropriately developed reactive force field.

Structural modeling of char structure is challenging, time-consuming, and requires considerable expertise due to the distribution of structural features that often influence the behavior of chars
during kinetic controlled conversion reactions. Inorganic species influence char reactivity and have been explored using both experimental\textsuperscript{19} and small-scale high-level molecular modeling approaches,\textsuperscript{20-22} but are not included in this initial work. Various coal-derived char molecular models have been generated by modifying existing coal molecular structures to reflect structural transformations of coal to char during devolatilization.\textsuperscript{23-25} Alternative approaches using reverse Monte Carlo (RMC) methods have also been used to construct coal-char structural models for exploring char microstructure and dissolution in steel.\textsuperscript{26} The RMC approach uses a reconstruction technique that systematically rearranges the position of atoms via Monte Carlo-type moves until close agreement with experimental small angle X-ray diffraction data is achieved. This approach has been utilized for porous carbon structure.\textsuperscript{26-29} However, carbon modeling via RMC methods requires advanced computing capabilities and is more appropriate for highly organized structures. Recently, a more rapid alternative structure generation approach (Fringe3D) has enabled inclusion of nanostructural features and their distributions in model space for carbon materials such as coals, chars and soots directly from HRTEM lattice fringe images.\textsuperscript{30, 31} With this approach and additional Perl scripts, very large continuum representations (>60,000 atoms) better capturing structural diversity can be generated rapidly with improved accuracy, greater length scale, and minimal computational cost.\textsuperscript{31} Fringe3D coupled with Perl scripts for structural manipulation and evaluation was recently utilized in the generation of a large-scale coal molecular model in an effort to move toward capturing the continuum of an Illinois No. 6 coal.\textsuperscript{32} Here Fringe3D was used for microstructural modeling of crystalline regions of an Illinois No. 6 coal char atomistic representation from HRTEM micrographs to demonstrate the model construction approach in capturing turbostratic crystalline parameters such as stacking height, layer size and interlayer spacing. These structural nuances influence kinetically controlled char reactivity. For the first time a coal-char molecular model was coupled with a reactive force field to perform reactive MD simulations of char combustion. Coupling ReaxFF combustion with coal-char structural models will greatly improve our design strategies for coal and biomass combustion applications, and air pollution control.\textsuperscript{14, 33-35}

Development of reactive force fields (RFFs) enable description of the formation, transition, and complete dissociation of chemical bonds during reactive MD simulations with accuracy close to quantum mechanics (QM) but with significantly reduced computational expenses. Since RFF
parameters are often derived from QM data and can simulate reaction pathways without any preconditioning, reactive MD simulations via RFF approaches is a powerful tool for examining complex reactive systems. Furthermore, recently developed parallel ReaxFF schemes enable simulations at scale for highly complex structures. Several RFF schemes have been developed and applied to a wide range of materials and applications. In particular, the ReaxFF reactive force field has been utilized in several studies to investigate initial reaction mechanisms and kinetics associated with hydrocarbon, fuels, soot and coal thermolysis processes including pyrolysis, combustion, and oxidation. While reactive force fields are less computationally expensive than QM methods, they still require considerable computing resources to provide a detailed description of chemical reaction for large and highly complex systems such as coal chars simulated in this work. With current computational resources, the time scale of reactive simulations is many orders of magnitude shorter than that used in the experiments. Thus, reactive simulations are often performed at temperature ranges extending beyond normal experimental/industrial conditions to enable chemical reactions to occur within a practical computational time. With advances in computing power and software tools, reactive MD simulations over longer time scales and lower temperatures will be reachable. Nevertheless, ReaxFF method coupled with a more realistic coal char representation is a useful initial computational approach for examining complex char oxidation and combustion reactions.

Chenoweth et al. expanded the ReaxFF reactive force field training set to include additional transition states and chemical reactivity of systems relevant to hydrocarbon oxidation and optimized the force field parameters against a QM-based training set. They demonstrated that ReaxFF simulations on various hydrocarbon/O$_2$ systems reproduced the correct reactivity trend, following the trend in the C-H bond strength in these hydrocarbons. Analysis of trajectories from simulations also showed that pathways predicted by ReaxFF were in agreement with QM results and available experimental data.

Recently, the ReaxFF reactive force field for hydrocarbon combustion was extended to incorporate sulfur-containing hydrocarbons. ReaxFF parameters were determined through optimization against an extensive training set obtained from QM data describing reaction barriers and energies associated with C/H/O/S compounds. The newly trained ReaxFF was found to
correctly simulate pyrolysis and combustion dynamics of coal molecules and hydrocarbons containing sulfur functionalities.\textsuperscript{52} Castro-Marcano et al.\textsuperscript{53} utilized the newly trained ReaxFF to perform pyrolysis simulations on a large-scale molecular model for Illinois No. 6 coal constructed based on experimental data\textsuperscript{54} to investigate the effect of sulfur content and local sulfur chemistry on the pyrolyzed coal structure. These and previous reactive MD simulations\textsuperscript{46} demonstrated the feasibility of ReaxFF integration with coal molecular models and the capability of the newly implemented ReaxFF to provide accurate descriptions of initial reactive events associated with coal pyrolysis. Here ReaxFF was used to perform combustion simulations on a molecular representation for a devolatilized Illinois No. 6 coal char to examine the structural evolution of char structure and chemical processes related to combustion under high-temperature conditions. This work provides an improved char construction methodology and further demonstrates ReaxFF combustion with coal char structural models.

\textbf{Computational Methods}

\textit{Char model generation}

The Fringe3D\textsuperscript{31} construction approach was applied to generate atomistic representations for the polyaromatic sheets of the char structure based on HRTEM lattice fringe data and constrained by elemental analysis.\textsuperscript{9, 55} HRTEM has been used for characterization of coal and char structures producing structural results in agreement with several analytical techniques but with the advantage of capturing the distribution of nanostructural features.\textsuperscript{10, 11, 55-58} HRTEM lattice fringe image analysis provides structural information on the degree of turbostratic crystalline order (length and stacking of parallel polyaromatic layers as indicated by the fringes) in carbons.\textsuperscript{55, 56} The methodology of application of HRTEM technique and image processing approach utilized to extract lattice fringes are discussed elsewhere.\textsuperscript{57, 59}

Image Processing Toolkit\textsuperscript{60} coupled with Adobe Photoshop was used to perform image analysis for a HRTEM lattice fringe micrograph of an Illinois No. 6 coal char sample heat-treated at 800 °C for 5 min (heating rate: 30 °C/min).\textsuperscript{55} The extracted fringe lengths along with a specific catenation growth were used by Fringe3D to place fringes in 3D molecular modeling space with the assumption that the fringes are all in the same \textit{z}-plane. Molecules can be placed at the correct Cartesian location, rotated and pitched to duplicate HRTEM lattice fringe images stacking, or
assembled in a flat arrangement to better show the distribution of structural features. Currently, fringe curvature was not considered and all fringes were duplicated as flat molecules. Assumption for the shape of the polyaromatic sheets (catenation style) creating the fringes allowed conversion of fringe length to the number of rings in the molecule.\(^{31}\) Here circular catenation was considered for building the polyaromatic layers of char model. Figure 5.1 shows an example catenation molecule with polyaromatic structures of \(C_{24}\) to \(C_{54}\). Addition of 6-member rings around the central rings enables larger polyaromatic structures of varying carbon numbers to be generated. Thus, a circular ring-by-ring growth can occur to accommodate the fringe length distribution. With this construction approach, polyaromatic structures with zigzag and armchair sites, which have been found to exhibit different reactivities,\(^{61, 62}\) are created and thus enhancing model structural (and reactive) diversity. In this manner, polyaromatic sheets with a range of sizes and shapes were generated in accordance with known coal char chemistry.

Five-membered rings were manually incorporated into the polyaromatic layers to contain heteroatoms by randomly removing a protonated carbon from an edge 6-membered ring and then creating the respective carbon-carbon covalent bond for ring closure and geometry optimization. Non-hexagonal rings (containing only carbon atoms), recognized as important structural features of the char structure,\(^{63}\) have been incorporated into RMC-derived char models on amounts of up to \(15\%\).\(^{26-28, 64}\) Here, about 6\% of non-hexagonal aromatic rings (5- and 7-membered rings) were distributed randomly throughout the largest sheets. Incorporation of aliphatic structures was conducted in the form of hydroaromatic units and cross-linking bridges between layers until agreement with desired aromaticity value of \(>0.90\) was achieved.

**Figure 5.1.** Examples of polyaromatic structures of \(C_{24}\)-to-\(C_{54}\) transitions generated from a circular catenation molecule.
Elemental analysis data for an Illinois No. 6 coal char prepared at similar conditions to the sample used for HRTEM analyses, 800 °C for 5 min with heating rate of 50 °C/min, was utilized to further constrain the char model. Unfortunately, information regarding the type and distribution of heteroatoms in the coal char sample was not available. Hence, oxygen functionalities were restricted primarily to phenolic, carbonyl and furanic structures, whereas nitrogen and sulfur atoms were placed in pyrrolic and quaternary, and thiophenic type structures respectively, which is consistent with known coal char chemistry. Heteroatoms were incorporated into polyaromatic layers by selecting specific atoms using a random-number generator and then replacing them by appropriate functionalities. Specifically, aromatic hydrogens were randomly replaced by phenolics and carbonyls, whereas aromatic carbons in 5- and 6-membered rings were randomly substituted for heteroatoms to generate furanic, thiophenic and pyrrolic structures, and quaternary nitrogen, respectively. A trimming procedure similar to that utilized in previous works was performed by randomly removing outer aromatic rings from polyaromatic layers until agreement with the experimental atomic H/C and O/C ratios was achieved. Incorporation of heteroatom and aliphatic components with limited cross-linking was conducted using Perl scripts to remove researcher structural bias, improve accuracy of the structure generated and facilitate a more rapid model construction process.

The resulting polyaromatic layers were geometry-optimized and then assembled into 3D molecular model using the Theodorous and Suter method, which randomly distributed the constructed layers into a periodic simulation cell based on a minimum energy criterion. The 3D molecular model was constructed with an initial low bulk density of 0.5 g/cm³ to prevent overlapping of polyaromatic layers in the final structure. The density of the system was then adjusted using successive compression and annealing cycles. Energy minimizations and compression and annealing cycles were performed within Materials Studio package using the consistent-valence force field. Since the structural information employed for char model construction was derived from data sets at different time-temperature histories, the resulting structural model corresponds to a generic representation for the crystalline portion of a devolatilized Illinois No. 6 coal char.
Model evaluation

Perl scripts developed for coal structural modeling\textsuperscript{32, 68} were modified and utilized to facilitate model construction and evaluation of chemical and physical structural parameters. These Perl scripts calculate the type and distribution of atoms and functional groups present in the char model. Chemical parameters included elemental composition, carbon aromaticity and molecular weight distribution; whereas physical parameters comprised simulated helium density, pair correlation function, pore size distribution, and turbostratic crystalline dimensions. The simulated helium density was calculated from the molar mass and the volume of the char structure following an approach similar to that presented by Gelb and Gubbins.\textsuperscript{73} The simulation cell is divided into a fine grid and a probe particle is placed at every grid point to determine if an overlap occurs with the char structure. The grid points are sorted as occupied and unoccupied. The sum of the volume of all occupied grid points defines the volume of the char structure, while that of all unoccupied grid points corresponds to the pore volume. The pore size distribution was determined from the plot of -$dV_{\text{pore}} (r)/dr$ versus $r$, where $V_{\text{pore}} (r)$ is the fraction of pore volume that can be enclosed by a probe particle of radius $r$. It is important to note that the porosity of the char model was sampled at the micropore length scale (i.e., not including the macro or mesoporosity) due to the scale of the atomistic representation. Macro- and mesoporosity are expected to influence coal char reactivity and mass transfer during oxidation and combustion, since the oxidizing agents must diffuse to the char reaction sites and the reaction products must diffuse away from the char particle.\textsuperscript{74} Unfortunately, the small-scale of the char model ($\sim 5$ nm) compared to coal char particles sizes (typically in the micrometer range) represents a challenging problem for the structural modeler. A simple calculation shows that approximately $15000 \times 15000 \times 15000$ models ($3.4 \times 10^{12}$ models) would be required to fill the same volume as a single $65$ $\mu$m particle (assuming a cubic particle for ease of calculation). Thus, macro and mesopores were not included and mass transport within the simulated char structure cannot be realistically considered.

The pair correlation function, $g(r)$, provides the probability of finding an atom at a given distance $r$ from another atom. The $g(r)$ function can be calculated from $g(r) = 4\pi r^2 [\rho(r) - \rho_0]$, where $\rho(r)$ and $\rho_0$ are the pair density at distance $r$ and the average number density, respectively. Stacks of polyaromatic sheets with an inclination angle within $\pm 10^\circ$ were considered for calculation of
turbostratic crystalline parameters. These stacks were manually classified according to the number of layers per stack or stacking number. Interlayer spacing and layer length were manually measured as the perpendicular distance between layers forming a stack, and the projected length of the layers, respectively, using molecular modeling software.

**ReaxFF reactive force field**

ReaxFF is a reactive force field based on the covalent bonding formalism of Tersoff and Brenner in which the bond strength and bond length adjust appropriately in response to changes in the local chemical environment, resulting in accurate descriptions of bond cleavage and bond formation during chemical reactions. The total potential energy of the system is decomposed into several contributions as:

\[
E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}
\]  

(5.1)

where \(E_{\text{bond}}\) corresponds to the bond energy, \(E_{\text{over}}\) and \(E_{\text{under}}\) represent atom under- and over-coordination, respectively. Other terms, including \(E_{\text{val}}, E_{\text{pen}}, E_{\text{tors}}, E_{\text{conj}}, E_{\text{vdWaals}},\) and \(E_{\text{Coulomb}}\) are the valence angle term, penalty energy term, torsion angle energy, conjugation effects to molecular energy, non-bonded van der Waals interactions and Coulombic interactions, respectively. The ReaxFF potential determines the system connectivity based on bond orders calculated from interatomic distances that are updated every iteration, enabling dissociation and formation of chemical bonds during reactive MD simulations. Morse and Coulomb potentials were utilized for modeling the non-bonded interactions (van der Waals and Coulomb), which were calculated between all atom pairs and were shielded at short range. A geometry-dependent charge calculation scheme was used to account for polarization effects. ReaxFF parameters were derived from quantum chemical calculations on bond dissociation and reactions of small molecules as well as heat of formation, transition state energy and geometry data for several simple hydrocarbons. A more detailed description of the ReaxFF potential functions can be found in the work by van Duin et al.
Molecular dynamics simulation details

For the oxidation/combustion simulations, three periodic cubic boxes of 140, 165 and 195 Å box length were built containing the char structure composed of 7458 atoms along with 3500, 7000, and 14000 O₂ molecules, respectively. These periodic systems (char + oxygen) with different oxygen concentrations were generated to analyze the effect of combustion environment on the final products distribution. The equivalence ratio (ϕ) for these systems was 0.5, 1.0, and 2.0, which correspond to fuel lean, stoichiometric, and fuel rich combustion. The equivalence ratio being defined as the fuel/oxygen ratio normalized with respect to the stoichiometric fuel/oxygen ratio. These systems were energy-optimized using the conjugate gradient method and equilibrated via low-temperature (100 K) ReaxFF simulations (time step of 0.25 fs) to prevent chemical reactions from occurring during equilibration. The temperature was controlled using the Berendsen thermostat with a 0.1 ps damping constant. The temperature of these equilibrated systems was ramped up to 4000 K at a rate of ~24 K/ps with the system states (i.e. atomic positions, velocities and accelerations) saved at 3000, 3500 and 4000 K. Thereafter, constant temperature MD simulations were conducted for each periodic system for 250 ps at temperatures of 3000, 3500 and 4000 K. The highly complex char representation generated in this study required reactive simulations at elevated temperatures to enable complete combustion of the char structure within 250 ps.

Although fuel combustion processes often occurs within a few seconds at flame temperatures up to 2000 K, ReaxFF simulations were performed at higher temperatures to allow chemical reactions to occur within a reasonable time scale (in the picoseconds range) with the expectation of exhibiting similar initiation mechanisms to experiments. Previous works have showed that initial reaction mechanisms and kinetics associated with fossil fuel thermolysis processes via high-temperature ReaxFF MD simulations are in qualitative agreement with experimental data, although the elevated temperature has to be considered in the quantitative analysis of the reaction kinetics. The current simulations were performed within the ReaxFF program as implemented in ADF software using 36 processors on an Intel Xenon X5560 Quad-Core 2.8 GHz at the Lion-XH HPCS of Penn State Research Computing and Cyberinfrastructure. A typical equilibration and production run for the systems investigated in this study took about 4-6 weeks of simulation time (each simulation occupying four processors) followed by multiple
weeks of data analysis. With increase in computing resources, longer reactive simulations under conditions of lower temperature will be manageable. Nevertheless, by linking ReaxFF method with representative char models can provide initial insight into complex chemical processes related to coal char combustion. Fortran scripts were developed to create separate trajectories of all polyaromatic sheets in the system to track the structural transformations and chemical reactions during oxidation and combustion.

**Results and Discussion**

A total of 72 polyaromatic sheets were generated by Fringe3D coupled with Perl scripts in a highly automated manner, capturing a distribution of structural features in the char structure. The layers were created in order of molecular size and arranged in a flat grid (Figure 5.2) to allow visualization of the model construction process. Limited cross-linking produced 66 polyaromatic hydrocarbon structures. Heteroatom and aliphatic components were incorporated by scripting to agree with experimental data. The resultant polyaromatic (and heteroatom containing) structures were geometry-optimized and assembled into a cubic 3D molecular model using Materials Studio Amorphous Cell module. The energy-optimized model for an Illinois No. 6 coal char is shown in Figure 5.3. The turbostratic char structure contains 7458 atoms (C\textsubscript{5743}H\textsubscript{1511}O\textsubscript{131}N\textsubscript{61}S\textsubscript{12}) within 66 polyaromatic molecules and captures a range of structural features including aromatic, aliphatic and heteroatoms components as well as molecule sizes, degree of stacking, and interlayer spacing. The length of the cubic simulation cell was 43Å.

**Evaluation of chemical and physical structural parameters**

The chemical evaluation of the char structure comprised, elemental analysis, aromaticity, and the molecular weight distribution. The elemental composition, normalized to 1000 carbon atoms for the char structural model was C\textsubscript{1000}H\textsubscript{263}O\textsubscript{23}N\textsubscript{11}S\textsubscript{2}, in reasonable agreement with the experimental value C\textsubscript{1000}H\textsubscript{252}O\textsubscript{24}N\textsubscript{11}S\textsubscript{2}. The char model aromaticity was 0.96 in accordance with experimental data for devolatilized coal chars. The char molecular model exhibited a molecular weight distribution ranging from 239 to 3454 Da with a peak at ~250 – 500 Da, and calculated values for number and weight average molecular weights of 1095 and 1605 Da, respectively.
Figure 5.2. Polyaromatic hydrocarbon molecules generated by Fringe3D coupled with Perl scripts based on HRTEM lattice fringe data, showing (top) non-cross-linked and (bottom) cross-linked polyaromatic layers. Carbon atoms are colored green, hydrogen atoms are white, oxygen atoms are red, nitrogen atoms are blue, and sulfur atoms are yellow.
Figure 5.3. Atomistic representation for the crystalline regions of a devolatilized Illinois No. 6 coal char composed of 7458 atoms \( (C_{5743}H_{1511}O_{131}N_{61}S_{12}) \) within 66 polyaromatic layers. The length of the periodic cubic box is 43Å.

The physical structure of the char model was characterized in terms of several analytical parameters. The simulated helium density of the char model was 1.81 g/cm\(^3\), consistent with the helium density value of 1.7 – 1.9 g/cm\(^3\) (dmmf) corresponding to coal chars generated at 800 °C.\(^{82,83}\) The helium density of coal chars is usually expected to be greater than that of parental coals (1.30 g/cm\(^3\) on dmmf for Illinois No. 6 coal)\(^{84}\) mostly due to an ordering of polyaromatic layers within the coal char matrix along with an increase in aromaticity and release of aliphatic carbons, hydrogen and oxygen during devolatilization. The pair correlation function for carbon atoms within the char model is shown in Figure 5.4 with total \( g(r) \) being the sum of the
Figure 5.4. Pair correlation function for carbon atoms within the Illinois char model. The total $g(r)$ function is the sum of intermolecular (inter $g(r)$) and intramolecular (intra $g(r)$) contributions.

Intermolecular and intramolecular contributions. The first three peaks in the total $g(r)$ function correspond to separation distances between pairs of atoms within the same polyaromatic layer due to the intermolecular contribution to total $g(r)$ is zero. Specifically, the first peak appears at 1.40Å due to the presence of sp$^3$ and sp$^2$ carbons. This result is consistent with the model aromatic and aliphatic carbon content of 96 and 4% (using 1.39Å for aryl C-C bonds and 1.54Å for alkyl C-C bonds result in $1.40Å = 0.96 \times 1.39Å + 0.04 \times 1.54Å$). The second and third peaks are at around 2.40 and 2.85Å, similar to the second and third peaks for graphite located at 2.46 and 2.86Å. Peaks located at $r > 3Å$ are also affected by the stacking and neighboring layers (intramolecular contribution) and thus analysis of the total $g(r)$ function becomes more complex. However, no peaks appeared at $\sim 3.4Å$, the layer separation in graphite consistent with shorter polyaromatic layers that are more turbostratic.
Figure 5.5 shows the distributions of pore size and turbostratic crystalline parameters (stacking number, layer size and interlayer spacing). The pore size distribution showed smooth transitions as the pore width increases with limited fluctuations. The range of pore sizes extends up to about 7Å with a peak at ~1 – 2Å; i.e., the simulated char structure contains a significant portion of micropores with pore widths ranging between 1 and 2Å. Kulaots et al.\textsuperscript{8} examined the role of porosity during char combustion for Argonne coals and reported for an Illinois coal char (prepared at 1000 °C for 1h in pure He) a pore size distribution ranging from 4 to 60Å with the char being mostly microporous.\textsuperscript{8} Since the simulation cell length employed here was 43Å, the char model porosity can only be evaluated at the micropore length scale. Nevertheless,
increasing the length scale should result in a char model that better accommodates the pore size distribution and molecular diffusion issues. The average interlayer spacing between stacked sheets was \( \sim 3.8\text{Å} \), consistent with XRD data for an Illinois coal char prepared at 1300 °C.\(^\text{10}\) The stacking number distribution indicated that the majority of polyaromatic layers are either single or in stacks composed of 2-3 layers with an average value of 2.4, which is in reasonable agreement (given the limited scale) with the values of 3.0 and 3.2 as determined by HRTEM\(^\text{55}\) and XRD\(^\text{10}\) analyses for Illinois coal char samples. The layer size distribution ranged from 5 to 32.5Å with an average value of 14Å, in accordance with reported values of 12 and 14Å from HRTEM\(^\text{55}\) and XRD\(^\text{10}\) studies for Illinois coal chars. Therefore, the char model generated exhibits the distinct advantage of representing the distribution of nanostructural features observed in HRTEM lattice fringe images and in capturing the turbostratic crystalline dimensions measured by XRD and HRTEM.

**ReaxFF combustion simulations**

A series of ReaxFF combustion simulations of the char structure under fuel lean, fuel rich and stoichiometric conditions at high temperatures (3000, 3500 and 4000 K) were performed to evaluate the effects of combustion environment and temperature on the final product distribution. Conducting combustion simulations with different oxygen levels can provide structural information associated with the competitive role of thermal decomposition and direct oxidation by oxygen molecules. However, at these temperatures it is expected that initiation of char oxidation will be a competition between hydrogen abstraction reactions and direct thermolysis. At lower practical temperatures the char oxidation process will be mainly initialized by thermal decomposition and reactions with radicals in the fuel rich system while direct oxidation of the char structure by oxygen molecules and O and OH radicals under fuel lean combustion.\(^\text{42}\)

Snapshots of the equilibrated and final configurations of the combustion products after 250 ps of ReaxFF simulation at 3000 K for the fuel rich (a-b), stoichiometric (c-d) and fuel lean (e-f) systems are shown in Figure 5.6. Initially, small molecules and fragments were released from the char structure followed by O and OH radical attacks on polyaromatic sheets and molecular fragments in the system (char oxidation) and subsequent combustion of the evolved gases and char structure, in accordance with the fundamental steps of char combustion.\(^\text{16-18}\) Snapshots of combustion for a representative polyaromatic sheet \((\text{C}_{117}\text{H}_{24}\text{O}_{2}\text{N}_{1}\text{S}_{1})\) observed during ReaxFF
Figure 5.6. Snapshots of the equilibrated and final configurations after 250 ps ReaxFF combustion simulation at 3000 K for the fuel rich (a – b), stoichiometric (c – d) and fuel lean (e – f) systems containing the char structure (C_{5743}H_{1511}O_{131}N_{61}S_{12}) surrounded by 3500, 7000 and 14000 O_2 molecules, respectively. Molecular oxygen is represented by sticks and the char structure is represented by the ball-and-stick model with atoms colored as in Figure 5.2.
simulations under fuel rich and lean conditions at 3000 and 4000 K are presented in Figure 5.7. The char sheet underwent several changes and structural transformations during combustion. As seen in Figure 5.7, the polyaromatic sheet decomposed more rapidly during fuel lean conditions in comparison to fuel rich combustion, and thermal decomposition became more significant with increasing temperature as expected. In general, the radical species (mostly O and OH radicals) were seen to surround and attack the peripheral atoms promoting oxidation/combustion of ring structures.

**Figure 5.7.** Snapshots of the combustion process for a representative polyaromatic sheet (C_{117}H_{24}O_{2}N_{1}S_{1}) observed during ReaxFF combustion simulations under fuel rich conditions at 3000 K (a – f) and 4000 K (g – l), and in fuel lean at 3000 K (m – r) and 4000 K (s – y). The char sheet is represented by the ball-and-stick model with atoms colored as in Figure 5.2.
Analysis of trajectories from ReaxFF simulations showed complex initiation chemistry for the char oxidation process for all combustion conditions studied. In most cases, char oxidation was mostly initialized by either thermal decomposition of char structure to produce small fragments that were subsequently oxidized or hydrogen abstraction reactions by O\textsubscript{2} molecules, and O and OH radicals. An example of initial chemical events observed for the oxidation of a polyaromatic sheet (C\textsubscript{54}H\textsubscript{18}O\textsubscript{4}N\textsubscript{1}) in the fuel rich system at 3000 K is shown in Figure 5.8. The initial reaction involved dissociation of the furanic C-O bond to form a carbon radical (Fig. 5.8a-b) that reacts with molecular oxygen to generate a carbon-oxygen complex (Fig. 5.8c-d) followed by release of a hydroxyl radical resulting in formation of two semiquinone groups (Fig. 5.8e). Subsequent oxidation of the neighboring carbon produced a semiquinone (Fig. 5.8f) and then cleavage of the C-C bond generated a carbon radical that was oxidized to carboxylic group (Fig. 5.8g-h), followed by decarboxylation leading to CO\textsubscript{2} formation.

**Figure 5.8.** Example of initial chemical events observed for the oxidation of a polyaromatic sheet (C\textsubscript{54}H\textsubscript{18}O\textsubscript{4}N\textsubscript{1}) in the fuel rich system at 3000 K. Dissociation of the C-O bond produced a carbon radical (a – b) that reacted with O\textsubscript{2} molecule to form a carbon-oxygen complex (c – d). Next, release of a hydroxyl radical resulted in formation of two semiquinone groups (e). Subsequent oxidation of the neighboring carbon produced a semiquinone (f), then cleavage of the C-C bond generated a carbon radical that was oxidized to carboxylic group (g – h), followed by decarboxylation leading to CO\textsubscript{2} formation. Atoms are represented using the ball-and-stick model and colored as in Figure 5.2.
Current kinetic modeling methods based on single- or multi-step combustion reaction do not provide an atomistic description of the initial chemical events associated with char oxidation.\textsuperscript{35, 85, 86} Alternative approaches using density functional theory (DFT) calculations on simplistic carbon structures (<50 atoms) have been used to examine carbon-oxygen complexes formed during char gasification.\textsuperscript{87-89} These DFT-based studies have showed that initially molecular oxygen is adsorbed on active carbon sites (zigzag and armchair edges) forming peroxide complexes that then transformed into two stable semiquinone groups (by dissociating the O-O bond), which decomposed to release CO by breaking two C-C bonds.\textsuperscript{87-89} The advantage of using the ReaxFF force field is that it provides a detailed, dynamical description of complex oxidation reactions for larger and more complex systems over longer time scales.

A Fortran script was created to monitor the major types of oxygen attacks (O\textsubscript{2} molecules, and O and OH radicals), to gain a better understanding of the chemistry during combustion. The number of successful attacks (defined as reactive collisions producing covalent bonds lasting more than 5 ps) observed after 250 ps of simulation is summarized in Table 5.1. Oxygen attacks on small fragments generated from thermal decomposition of polyaromatic sheets were identified as “decomp”, whereas attacks on large polyaromatic sheets (> 30 atoms) were considered as direct oxidation by O/O\textsubscript{2}/OH species. As seen, oxygen attacks on small fragments seem to be more predominant than direct oxidation of large sheets for all combustion environments at the temperature range investigated. In addition, the O and OH radical attacks exhibited the highest rate of success (defined as the ratio of successful attacks and the total number of collisions), which can be attributed to the highly reactive nature of these radical species. Under fuel rich conditions, the radical attack successful rates were higher in comparison to fuel lean because of the lower total number of collisions.

\textbf{Table 5.1.} Number of successful oxygen attacks (O\textsubscript{2} molecules, and O and OH radicals) observed after 250 ps ReaxFF combustion simulation.

<table>
<thead>
<tr>
<th>Combustion environment</th>
<th>3000 K</th>
<th>3500 K</th>
<th>4000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
<td>O\textsubscript{2}</td>
<td>OH</td>
</tr>
<tr>
<td>Fuel rich</td>
<td>798</td>
<td>107</td>
<td>282</td>
</tr>
<tr>
<td>Stoichiometric</td>
<td>916</td>
<td>124</td>
<td>166</td>
</tr>
<tr>
<td>Fuel lean</td>
<td>896</td>
<td>132</td>
<td>133</td>
</tr>
</tbody>
</table>

\hspace{1cm}
Figure 5.9 shows the concentration profiles for oxygen and the major combustion products (CO₂, H₂O, CO and H₂) observed during ReaxFF combustion simulations at constant temperature (after the temperature of the system was ramped up) and thus initial amounts of CO₂ and O₂ molecules differ with temperature. In general, the rate of combustion products generation was greater when fuel lean in comparison to fuel rich conditions, in agreement with observations of faster char burning rates for progressively higher O₂ levels. At fuel lean combustion (φ = 0.5), CO₂ concentration was higher than that of CO due to an excess of oxygen resulting in a more

![Distribution of major combustion products](image)

**Figure 5.9.** Distribution of major combustion products obtained from ReaxFF MD simulations of char combustion at temperatures of 3000, 3500 and 4000 K under fuel rich, stoichiometric and fuel lean conditions.
complete transformation of the char structure to carbon dioxide and water at 250 ps. Under fuel rich conditions ($\phi = 2.0$), there would be incomplete conversion to combustion products and thus CO and H$_2$ would remain as combustion gases.\textsuperscript{16} However, at the end of the simulation, there were around 500 – 700 molecules of CO in the fuel rich system compared to about 900 – 1600 CO molecules in the fuel lean system. This is presumably caused by the short time scale (250 ps) used in the ReaxFF simulations. Carbon monoxide oxidation to CO$_2$ is a relatively slow process among combustion reactions.\textsuperscript{18} Thus, it is expected that at longer time scales a portion of CO molecules in the fuel lean system would be oxidized to CO$_2$.

Figure 5.9 also shows that the rate of increase of combustion products was almost linear during simulations at the lower temperature (3000 K). This can be contrasted with combustion at 4000K, where rapid char conversion to combustion products occurred and the concentration of reaction products reached a peak and subsequently leveled off at a relative constant value. In addition, the rate of decrease of O$_2$ was more rapid and the char structure exhibited shorter initiation reaction times. This is due to char combustion reactions proceed rapidly with increasing temperature.\textsuperscript{14,35} Formation of CO was facilitated by high temperatures whereas CO$_2$ production was favored at the lower temperature studied, as expected because CO is more stable than CO$_2$ at temperatures higher than 2000 K.\textsuperscript{16-18} Small amounts of water and hydrogen were formed during char combustion mostly because of the limited hydrogen content of the char.

A Fortran script was developed to track the evolution of 5-, 6- and 7-membered rings in the char structure, as a function of time, to gain a better understanding of the chemistry during combustion (Figure 5.10). Analysis of the trajectory from the simulations showed that intermediate ring structures (such as 3-, 4- and 8-membered rings) were formed during char combustion but these structures were short lived, hence were not included in the analysis shown in Figure 5.10. The char structure was initially composed of 130 5-membered rings (6, 98, 11, and 15 containing C, O, S, and N respectively), 2166 6-membered hydroaromatic rings (135 containing N) and four 7-membered rings containing only C and H atoms. Figure 5.10 shows the transformations in ring structures corresponding to ReaxFF combustion simulations at constant temperature and thus the initial number of polyaromatic ring structures is different for each temperature. As shown, all ring structures decomposed more rapidly in fuel lean (oxygen rich) in
comparison to fuel rich environment, at the temperature range used. This can be attributed to the limited oxygen availability in the fuel rich system leading to incomplete combustion of polyaromatic sheets. In fuel lean environment, however, there was sufficient oxygen and time (at this temperature) for complete combustion of the char structure.

Figure 5.10. Time evolution of 5-, 6- and 7-membered rings in the char structure observed in ReaxFF combustion simulations at temperatures of 3000, 3500 and 4000 K under fuel rich, stoichiometric and fuel lean environments.
At 3000 K, the number of 6-membered rings steadily decreased over the course of the simulations (Figure 5.10). The 5-membered rings with O decreased significantly during the earlier stages of the simulation (between 75 and 100 ps) but changed little thereafter. The amount of 7-membered rings and 5-membered rings with C atoms reached peaks before decreasing close to its initial low value. The location of these peaks coincided with a more rapid decomposition of the 6-membered rings suggesting that these ring structures decomposed to form 5- and 7-membered rings, as shown in Figure 5.11. Initially, an oxygen radical attacked a 6-membered ring leading to cleavage of the edge C-C bond and formation of the respective carbon-oxygen complex (Fig. 5.11a-b). Next, the bonded O atom connected to a carbon radical generating a heterocyclic 7-member ring (Fig. 5.11c), which afterward decomposed to form two semiquinone groups (Fig. 5.11d). Subsequent intramolecular rearrangement of the C-O bond formed a 5-membered ring (Fig. 5.11e-f). Kinetic Monte Carlo simulations of graphene-edge growth in combustion environments showed that high temperatures (> 2500 K) lead to kinetic instability of 5-membered rings and thus prevent them from forming in the growing graphene sheet.90

Figure 5.11. Example of conversion of 6-membered ring into 5- and 7-membered rings observed during fuel rich combustion at 3000 K. An O radical attack caused 6-membered ring opening and formation of carbon-oxygen complex (a – b). An intermediate heterocyclic 7-membered ring is generated (c), which decomposed to form two semiquinone groups (d). Subsequent intramolecular rearrangement of the C-O bond led to formation of the 5-membered ring (e – f). Atoms are represented using the ball-and-stick model and colored as in Figure 5.2.
As the temperature increases (Figure 5.10), the number of 6-membered rings and 5-membered rings containing O declined rapidly, and 7-membered rings and 5-membered rings with C atoms reached peaks that were more pronounced. Combustion reactions were accelerated at these high temperatures resulting in ring structures fragmenting. Ultimately, with computational speed gains it is anticipated that this approach could be utilized at boiler combustion temperatures, over long simulation times, with very large-scale char representations. Both large-scale and long time simulations are necessary to capture the char pore size distribution and hence the mass transport issues important in zones III and II. Catalytic influences, important in some chars, could also be included. The work presented here is an initial exploration of the approach while ultimately many orders of magnitude gains in size and time is necessary to simulate particle systems of interest.

Conclusions
Fringe3D coupled with Perl scripts were used to generate a structural representation of the crystalline portion of a devolatilized Illinois No. 6 coal char based on HRTEM lattice fringe images and constrained by elemental analysis data. Agreement between model and experimental chemical and physical structural parameters validated the constructed coal char representation. Chemical parameters included elemental composition, carbon aromaticity, and molecular weight distribution; whereas physical parameters comprised simulated helium density, pore size distribution, pair correlation function, and turbostratic crystalline parameters (stacking height, layer size and interlayer spacing).

The ReaxFF reactive force field was applied to perform combustion simulations of the constructed char model under fuel lean, fuel rich and stoichiometric conditions at temperatures of 3000, 3500, and 4000 K to investigate the effects of combustion environment and temperature on the oxidation/combustion process and product distributions. Analysis of trajectories from ReaxFF simulations showed that char oxidation was mainly initialized by either thermal degradation of char structure generating small fragments that were subsequently oxidized, or by hydrogen abstraction reactions by O₂ molecules and O and OH radicals. The ratio of the major combustion products, CO/CO₂, was found to increase with increasing temperature consistent with expectations. Furthermore, ring structures were observed to disintegrate more rapidly in fuel
lean conditions in comparison to the fuel rich environment, and 6-membered rings were transformed into 5- and 7-membered rings that subsequently decomposed into smaller fragments. This work demonstrates that coupling the ReaxFF reactive force field with more realistic char molecular models can be a useful simulation approach for examining the complex chemistry associated with structural transformations and chemical reactions involved in char combustion.

Acknowledgements
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Chapter 6

Fine Structure Evaluation of the Pair Distribution Function with Molecular Models of the Argonne Premium Coals*

Abstract

The pair distribution function (PDF) is one means of evaluating the atomic spatial arrangements of coals. Analysis of PDF based on X-ray diffraction data provides structural information on turbostratic crystalline parameters that can be utilized to further characterize coal structure. With coalification, expectations are of limited growth in aromatic stacking and a slight growth in the aromatic cluster size over the lignite to medium-volatile bituminous range. The PDF can be also used to construct and validate atomistic representations for carbonaceous materials including coal. Here, the PDF was evaluated with molecular slice models of several Argonne Premium coals (Beulah-Zap, Illinois No. 6, Upper Freeport, Pocahontas No. 3), also a non-Argonne Hon Gai anthracite, and compared with experimental observations. Atomistic representations were generated directly from high-resolution transmission electron microscope (HRTEM) lattice fringe images. The Fringe3D approach populates aromatic moieties matching the distributions of fringe: length, layers per stack, interlayer spacing, and orientations to produce an aromatic slice model of limited depth. Perl scripts incorporated appropriate aliphatic and heteroatom components. This approach creates atomistic representations with greater ease, improved accuracy, and reduced computational expense than other construction approaches. The constructed coal models were partially geometry-optimized to achieve realistic bond lengths but without displacement of coal molecules enabling the distribution of fringe length, stacking, and orientations to be duplicated in 3D modeling space. The resulting coal slice models, devoid of cross-links, captured a distribution of turbostratic crystalline dimensions with an average cluster size of about 1 nm, an average interlayer spacing ranging between 0.37 and 0.39 nm, and an average stacking number of ~2-3 in accordance with HRTEM and XRD data for Argonne coals. These structural models were used to predict PDFs and to evaluate the fine detail of the frequency spectra via examination of intermolecular and intramolecular contributions. Analysis of the simulated intermolecular PDF contribution showed strong intensities with increasing coal rank in agreement with the growth in the stacking number and stack height observed from low- to high-rank coals. The simulated intramolecular PDF contribution showed shorter peak amplitudes for low-rank coals in comparison to high-rank coals in agreement with the increase in stack width as coal rank increases. To further examine these contributions, lattice models composed of pyrene molecules were also constructed via Fringe 3D and manipulated to directly investigate the effect of aromatic orientation distributions and stacking on the simulated PDF. Peak intensities of simulated intermolecular PDFs at the average interlayer spacing increased with the degree of alignment (ϕ) according to \( g(r)_{\text{inter}} = 0.0014\phi^2 + 0.0107\phi + 4.2784 \). This result was consistent with the slight increase in the stacking number observed from low- to high-rank coals with a more dramatic transition for anthracite.

Introduction

Coal undergoes significant structural transformations with rank. One useful technique that can be used to provide insights into coal structure is the pair distribution function (PDF) method, which determines the average coordination number or atomic density at a distance $r$ from the center of an arbitrary origin atom. Analysis of peak position and amplitude provides structural information regarding turbostratic crystalline dimensions (aromatic stacking, layer size and interlayer spacing) that can be useful in evaluating coal structure and behavior.\textsuperscript{1-4}

Mathews et al.\textsuperscript{5,6} recently reviewed the molecular representations of coal and their utility. In the lignite to medium-volatile bituminous rank range, limited growth in aromatic stacking and a slight growth in aromatic cluster size are expected.\textsuperscript{7} Coalification into the high-rank range, however, is accompanied by significant transitions. For example, Wertz and Bissell\textsuperscript{8} examined short-range structural features of Pocahontas No. 3 coal using X-ray scattering techniques. Interpretation of the experimental PDF data indicated that the average structural unit was 80\% aromatic and composed of polycondensed aromatic rings that were predominately planar. The data were consistent with a coronene-like structure composed of seven fused rings. Similarly, Wertz and Quin\textsuperscript{4} investigated the interlayer structure in several Argonne Premium Coals\textsuperscript{9} using PDF methods, and found that the number of layers increased with rank, from about 2.3 for Wyodak subbituminous, through about 3 for Pittsburgh #8 coal, to 4.5-5 for Pocahontas No. 3. The interlayer spacing decreased with increasing rank. HRTEM lattice fringe image analysis provides structural information on interlayer spacing, layer length and stacking number for carbonaceous materials (including coals, soots and chars) in accordance with the expected coalification trends and crystallography data.\textsuperscript{10-17} HRTEM coupled with image processing were used to determine structural parameters for the Argonne Premium coals.\textsuperscript{18,19} The average fringe length remained almost the same ($\sim$1 nm) for lignite to high-volatile bituminous coal ranks, with a longer average fringe length for Pocahontas low-volatile bituminous coal (1.2 nm) in reasonable agreement with XRD data.\textsuperscript{18} A similar result was obtained with the average stacking number, which was observed to increase from two to three for low- to high-rank coals, respectively, consistent with expectations. Interlayer spacing was also evaluated and was found to decrease with increasing coal rank. Thus, HRTEM results support the general trends, but have the advantage of capturing the distribution of structural features.
Grigoriew\textsuperscript{20} presented an interpretation of X-ray diffraction (XRD) studies on coal structure. Structural models of the coals investigated were generated by fitting simulated PDF to experimental data. The resultant models suggested that sp\textsuperscript{2} carbon atoms formed aromatic layers of 4-20 fused rings, depending on the petrographic component and the rank of coal. The sp\textsuperscript{3} hybridized atoms units were composed of linked cyclohexane structures. The author further concluded that the amount of disorganized carbon could be neglected. Similarly, Bratek et al.\textsuperscript{2} used PDF analysis to determine interatomic distances, and degree and range of structure ordering for different anthracites. A 2D graphene sheet model was used to fit and interpret the experimental PDF data. Results indicated a decrease in the interlayer spacing, and an increase in average size and number of aromatic rings in the basic structural units of the anthracites with increasing rank. Zhang\textsuperscript{21} conducted PDF analysis on a brown coal structure model with a moisture content ranging from zero to 60\% to evaluate the water and coal interactions in the drying process. Water molecule removal was found to occur successively from the outer hydration shell to the inner hydration shell around the oxygen moieties.\textsuperscript{21} Several studies analyzed the morphology of amorphous asphaltene aggregates using the PDF method,\textsuperscript{22-24} demonstrating the versatility and utility of this approach to characterize and evaluate carbonaceous materials.

The PDF has commonly been used as a structural parameter to validate carbon molecular models.\textsuperscript{25-28} Specifically, the reverse Monte Carlo (RMC) algorithm is a stochastic reconstruction approach that produces structural representations by generating atomic configurations of carbon atoms that are consistent with carbon PDF obtained from X-ray, electron or neutron diffraction experiments.\textsuperscript{26-28} In the RMC approach, changes in the atomic configuration are accepted or rejected based on the agreement between the simulated and experimental PDFs. However, modeling material structures using RMC methods requires considerable computing resources and is more suitable for highly carbonaceous materials. A similar reconstruction approach that uses topological perturbations (addition of non-hexagonal rings) to generate model structures for non-graphitizing carbons was implemented by Smith et al.\textsuperscript{29} With this approach, 5- and 7-member rings are randomly incorporated into an extended sp\textsuperscript{2} carbon sheet until reasonable agreement with the experimentally derived PDF was achieved.
Structural modeling of coal structure is challenging, time-consuming, and requires considerable expertise due to the structural continuum of coal. Common construction approaches fail to capture the distribution of structural features, such as the orientation and stacking of aromatic entities, that often influence coal conversion processes. Recently, a structure generation approach (Fringe3D) has enabled inclusion of structural features and their distributions in 3D molecular modeling space for carbonaceous materials directly from HRTEM lattice fringe images. HRTEM has been used for characterization of coal and char structure, producing structural results consistent with various analytical techniques but with the advantage of capturing the distribution of nanostructural details. With the Fringe3D construction approach, atomistic representations containing >50,000 atoms can be generated rapidly with improved accuracy, that capture the aromatic stacking and alignment of aromatic coal moieties. Scripting populates aliphatic entities in a similarly efficient approach. Fringe 3D was recently used to build a large-scale Illinois No. 6 coal molecular model based on analytical data in an effort to move toward capturing the structure continuum. An atomistic representation for an Illinois No. 6 coal char was also generated from HRTEM micrographs using Fringe3D to perform reactive molecular dynamics simulations of char combustion at high-temperature conditions. Here, PDFs were evaluated with molecular slice models of the aromatic and aliphatic components for several Argonne Premium coals constructed via Fringe3D based on HRTEM lattice fringe images. The effect of turbostratic crystalline parameters such as stacking height, layer size and interlayer spacing on PDFs calculated from the constructed models was examined and compared with experimental results obtained from the Advanced Photon Source at the Argonne National Laboratory.

**Methods**

**Coal model construction**

The Fringe3D approach was applied to generate atomistic representations of the polycondensed aromatic hydrocarbon (PAH) structures directly from HRTEM lattice fringe images, constrained by elemental analysis and $^{13}$C NMR data. The methodology of the application of the HRTEM technique and image processing approach applied to extract lattice fringe data are discussed elsewhere. Basically, an estimation of the carbon numbers within the PAH were generated assuming the fringe is as deep as it is long. All fringes were assumed to be in the same
Image Processing Toolkit\textsuperscript{42} coupled with Adobe Photoshop was utilized to perform image analyses (fringe length, center of mass, angle of momentum) for HRTEM lattice fringe micrographs of the Argonne Premium Beulah-Zap, Illinois No. 6, Upper Freeport, and Pocahontas No. 3 coals, and a non-Argonne Hon Gai anthracite. The non-Argonne anthracite Hon Gai was included to complete the rank range from lignite to anthracite. The extracted lattice fringe data, along with an assumed parallelogram catenation were used to place molecules in molecular modeling format at centers of mass (determined by image analysis) of fringes to duplicate HRTEM lattice fringe micrographs. Molecules were rotated and pitched to capture the appropriate momentum angles enabling the aromatic alignment, stacking, and fringe length/size to be duplicated in 3D modeling space creating “slice” models of limited depth (all molecules being centered in the same \( z \) plane). Fringe curvature was not considered, and thus all molecules were linear. Figure 6.1 shows an example calibration molecule with parallelogram-shaped catenation PAH growth. Addition of 6-member rings around the central rings enables larger polyaromatic structures of varying carbon numbers to be generated. Thus, a parallelogram, ring-by-ring addition can be used to accommodate the PAH molecular size distribution to match the fringe length distribution.

![Figure 6.1. Polyaromatic ring growth from a parallelogram catenation molecule.](image)

Obeng and Stock\textsuperscript{43} conducted ruthenium ion catalyzed oxidation experiments to determine the distribution of pendant alkyl groups in the Argonne Premium coals. The oxidation study showed that methyl was the most abundant alkyl group for high-rank coals (low-volatile bituminous and greater), with minor contributions from ethyl and propyl units. For low-rank coals, a broader aliphatic distribution with methyl as the most frequent was observed. Coal molecular models were constructed according to the distribution of alkyl side chains obtained by Obeng and
Stock. Table 6.1 contains the relative abundances of aliphatic groups per 100 carbons in Argonne coals used for model construction. Since experimental data for the non-Argonne Hon Gai anthracite were scarce, alkyl groups were added in the form of methyl units, consistent with expectations of anthracite coal. Incorporation of aliphatic structures was conducted by scripting until agreement with NMR-derived aromaticity was achieved.

Argonne Premium coals exhibit a high organic oxygen content of 1.7-19.1 wt.% (dmmf) and relatively low organic nitrogen (1.1-1.7 wt.%, dmmf), and sulfur (0.4-2.4 wt.%, dmmf) contents. Since oxygen is typically far more abundant than other heteroatoms in Argonne coals, nitrogen and sulfur forms were not considered for model construction. Kelemen and Kwiatek quantified organic oxygen species from X-ray photoelectron spectroscopy (XPS) carbon (1s) curve analysis and observed that the number and types of oxygen functionalities presented on Argonne coals declined with increasing rank. Specifically, the amount of organic oxygen per 100 carbons ranged from 16.9 to 18.8 for low-rank coals and from 3.2 to 4.5 for high-rank coals. Addition of organic oxygen forms into coal molecular models was consistent with XPS data reported by Kelemen and Kwiatek. Table 6.1 summarizes organic oxygen types and distributions per 100 carbons utilized during model generation. Unfortunately, information regarding the type and distribution of oxygen heteroatom in the non-Argonne Hon Gai anthracite was not available. Hence, an organic oxygen content corresponding to anthracite with carbon content similar to that of Hon Gai was employed, with oxygen functionalities restricted to furanic structures in accordance with known coal chemistry. Since cross-links were not considered, ether structures were incorporated into molecular models as closed ethers. Inclusion of oxygen groups

<table>
<thead>
<tr>
<th>Coal Models</th>
<th>Organic oxygen forms</th>
<th>Alkyl side chains</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ether</td>
<td>phenolic</td>
</tr>
<tr>
<td>Beulah-Zap</td>
<td>4.8</td>
<td>6.4</td>
</tr>
<tr>
<td>Illinois No. 6</td>
<td>5.7</td>
<td>4.2</td>
</tr>
<tr>
<td>Upper Freeport</td>
<td>3.9</td>
<td>0.0</td>
</tr>
<tr>
<td>Pocahontas</td>
<td>3.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Hon Gai</td>
<td>1.7</td>
<td>0.0</td>
</tr>
</tbody>
</table>
was performed by custom Perl scripts within Materials Studio environment until agreement with experimental data was reached.

The resultant coal molecular models were partially geometry-optimized using the conjugate gradient method as implemented in the Materials Studio Discover module\textsuperscript{47} to obtain realistic bond lengths but not displace the aromatic molecule locations, to retain the aromatic stacking and alignment of aromatic coal moieties from the HRTEM lattice fringe micrographs in molecular modeling format. Maceral differences, mineral matter, and cross-links, that are known as important structural components of coal, were not included in this work since the primary interest was in aromatic stacking and aromatic orientation. Future modeling efforts should include these structural features. Thus, the resulting slice models correspond to atomistic representations of the aromatic, aliphatic, and heteroatom contributions of coals studied. Model construction was performed on a personal computer and required about 90 sec of computational time for generating each coal aromatic slice molecular model with some additional time ~10 min for aliphatic and oxygen functionality additions prior to the partial geometry optimization step.

**Coal model evaluation**

In model construction, elemental composition and NMR-derived aromaticity were adjusted to agree with the available experimental data. Evaluation of coal molecular models was carried out by calculating turbostratic crystalline parameters (interlayer spacing, average cluster size and number of clusters per stack). Stacks of aromatic clusters with an angle of inclination within ±10° were considered for calculating model physical structural parameters (stacking height and interlayer spacing). These stacks were manually classified according to the number of clusters per stack or stacking number. Interlayer spacing and cluster size were manually measured as the perpendicular distance between aromatic clusters forming a stack, and the length of the molecules, respectively, using molecular modeling tools. The intramolecular pair distribution function $g(r)_{\text{intra}}$ is given by

$$g(r)_{\text{intra}} = (1 - \delta_{\text{ary}}) \left[ \delta \left( r - r^{\text{rr}} + r^{\gamma} \right) \right]$$

(6.1)
where \( r_i^\alpha \) is the instantaneous position of the \( \alpha \)th reference atom in the \( i \)th coal molecule, the angle brackets stand for the equilibrium ensemble average, and the factor with the Kronecker delta ensures that we are referring to different atoms (i.e., \( \alpha \neq \gamma \)) within the same molecule. The intermolecular pair distribution function \( g(r)_{\text{inter}} \) is defined as

\[
g(r)_{\text{inter}} = \rho^{-2} \left\langle N(N-1)\delta(r_i^\alpha)\delta(r_j^\gamma - r) \right\rangle
\]

where \( \rho = \left\langle N/V \right\rangle \) is the average number of molecules per unit volume in the system. Eq. (6.2) gives the intermolecular probability density between atoms \( \alpha \) and \( \gamma \) on molecules \( i \) and \( j \). The simulated total pair distribution function \( G(r) \) is the sum of the intramolecular and intermolecular contributions:

\[
G(r) = g(r)_{\text{intra}} + \rho g(r)_{\text{inter}}
\]

Thus, \( G(r) \) indicates the probability distribution of finding an atom \( \gamma \) at a given distance \( r \) from an atom \( \alpha \). The \( G(r) \), \( g(r)_{\text{intra}} \) and \( g(r)_{\text{inter}} \) functions were calculated using Materials Studio software. During model construction process, elemental composition and aromaticity were adjusted to agree with the available experimental data. Validation of the constructed models was performed by evaluating turbostratic crystalline parameters (interlayer spacing, layer length and stacking number) and comparing against experimental results. Further model validation occurred with comparison of simulated and experimental PDFs, which was not fitted during model generation.

**Coal samples**

Beulah-Zap, Illinois No. 6, Upper Freeport, and Pocahontas No. 3 coal samples (-100 mesh particle size) were obtained in sealed ampoules from the Argonne Premium Coal Sample Program and were used as received. The carbon content, low temperature ash yield, and aromaticity of selected Argonne Premium coals and the non-Argonne Hon Gai anthracite are shown in Table 6.2. Additional characterization data can be found elsewhere.
Table 6.2. Carbon content, low temperature ash yield and aromaticity of investigated coals.\textsuperscript{9,40}

<table>
<thead>
<tr>
<th>Coal</th>
<th>Rank</th>
<th>Carbon content (dmmf)</th>
<th>Low Temp Ash (%)</th>
<th>Aromaticity ($^{13}$C NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beulah-Zap</td>
<td>lignite</td>
<td>74.1</td>
<td>8.7</td>
<td>0.61</td>
</tr>
<tr>
<td>Illinois No. 6</td>
<td>hv bituminous</td>
<td>80.7</td>
<td>18.1</td>
<td>0.72</td>
</tr>
<tr>
<td>Upper Freeport</td>
<td>mv bituminous</td>
<td>88.1</td>
<td>15.3</td>
<td>0.81</td>
</tr>
<tr>
<td>Pocahontas</td>
<td>lv bituminous</td>
<td>91.8</td>
<td>5.5</td>
<td>0.86</td>
</tr>
<tr>
<td>Hon Gai</td>
<td>anthracite</td>
<td>94.0</td>
<td>-</td>
<td>0.95</td>
</tr>
</tbody>
</table>

**X-ray experimental approach**

Samples of the Argonne Premium Coals investigated (Beulah-Zap, Illinois No. 6, Upper Freeport, and Pocahontas No. 3), were sealed in cells constructed of two 2.75\textsuperscript{°} ConFlat\textsuperscript{®} flanges with 1 mm spacing between the Kapton\textsuperscript{®} windows\textsuperscript{1} that were glued over holes drilled in the flanges to allow penetration by the X-ray beam. The cell was mounted on the instrument at beamline 11-ID-B at the Advanced Photon Source, Argonne National Laboratory with the incident (and scattered) beam directed through the hole in the cell. High-energy X-rays (90.48 keV, $\lambda = 0.1370$ Å) were used in combination with a MAR-345 image plate detector to record diffraction images\textsuperscript{48} to high values of momentum transfer ($Q \sim 20$ Å\textsuperscript{-1}). Raw images were processed using Fit-2D.\textsuperscript{49,50} The sample-to-detector distance was refined using a CeO$_2$ NIST standard. The PDF was extracted using PDFgetX2,\textsuperscript{51} subtracting the contributions from the sample environment and background. Corrections for multiple scattering, X-ray polarization, sample absorption, and Compton scattering were then applied to obtain the structure function $S(Q)$. Direct Fourier transform of the reduced structure function $F(Q) = Q[S(Q) - 1]$ up to $Q_{\text{max}} \sim 20$ Å\textsuperscript{-1} produced the experimental PDF values, which are calculated as follows:

$$G( r ) = 4\pi r^2[\rho( r ) - \rho_0] = \frac{2r}{\pi} \int_0^\infty Q[S( Q ) - 1] \sin( Qr )dQ$$ \hspace{1cm} (6.4)

where $\rho( r )$ is the microscopic pair density, $\rho_0$ is the average number density. Experimentally it is not possible to measure data up to infinite $Q$, and the cutoff at finite values of $Q_{\text{max}}$ decreases the real space resolution of the PDF. This causes some aberrations in the form of “termination ripples” which propagate through PDF as high frequency noise. For both X-ray scattering experiments, high energies (> 60 keV) are required to access high values of $Q_{\text{max}}$ to obtain as accurate Fourier transform of the reduced structure function $F(Q)$. 

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Results and Discussion

The atomistic representations constructed for the Argonne Premium coals and the Hon Gai anthracite are shown in Figure 6.2. As seen in Figure 6.2, coal molecular models captured the expected increase in the aromatic stacking and alignment of aromatic coal moieties observed from low- to high-rank coals. These partially energy-optimized slice models contained 22,000-30,000 atoms in 500-600 PAH structures and captured a range of structural features including aromatic, aliphatic, and heteroatom components (added by scripting) as well as molecule sizes, degree of stacking, and interlayer spacing as discussed below. The model construction approach enables inclusion of structural diversity resulting in capturing a distribution of fine-structural details as shown in Figure 6.3 for the atomistic representation of Illinois No. 6 coal. The coal model captured turbostratic crystalline dimensions measured by XRD and HRTEM techniques. These molecular slice models are of limited depth but reproduced the lattice-fringe micrograph height and width. Only the edge-view of benzene-PAH structures perpendicular to the electron beam can effectively be seen on image-processed HRTEM lattice fringe images. The HRTEM approach using a singular micrograph would also be improved by increasing the number of micrographs evaluated. Aliphatics and heteroatoms were included via a scripting approach to agree with RICO\textsuperscript{43} and XPS\textsuperscript{44} data, respectively.

![HRTEM images](image_url)

**Figure 6.2.** HRTEM skeletonized images and the corresponding molecular model generated by Fringe3D for (a,b) Beulah-Zap coal, (c,d) Illinois No. 6 coal, (e,f) Upper Freeport coal, (g,h) Pocahontas No. 3 coal, and (i,j) Hon Gai anthracite. Carbon atoms are colored green, hydrogen atoms are white, and oxygen atoms are red.
Evaluation of chemical and physical structural parameters

The chemical evaluation of the constructed coal models consisted of aromaticity, average aromatic cluster size and molecular weight, and average number of aromatic carbons per cluster. The aromaticities were 0.62, 0.77, 0.82, 0.87, and 0.94, for Beulah-Zap, Illinois No. 6, Upper Freeport, and Pocahontas No. 3 coals and Hon Gai anthracite, respectively, in accordance with $^{13}$C NMR and expected trends.\textsuperscript{40, 52-54} The aromatic carbons per cluster and aromatic cluster molecular weights ranged from 20 to 28 and from 258 to 354 Da respectively, in agreement with NMR analyses for Argonne coals,\textsuperscript{40} where the average number of aromatic carbons per cluster was between 14 and 20, and the molecular weight of a cluster ranged from 299 to 359 Da.

The model average aromatic cluster size was 1-3 fused rings for Beulah-Zap and Illinois No. 6, 3-4 for Upper Freeport and Pocahontas No. 3, and 4-5 for Hon Gai anthracite, in accordance with the cluster sizes reported by Solum et al. of 1-3 fused rings for subbituminous coals, 3-4 for high-volatile bituminous coals, and 4-5 for low-volatile bituminous coals.\textsuperscript{40} Thus, the construction approach was able to capture the increase in the average aromatic cluster molecular weight and average number of aromatic carbons per cluster with increasing coal rank. These results are consistent with $^{13}$C NMR studies for the Argonne Premium coals where the aromatic carbon content and aromatic cluster size slight increased from low-rank to bituminous rank range with more significant transitions occurring after low-volatile bituminous.\textsuperscript{40, 52-54}
The physical structure of the generated coal models was characterized in terms of turbostratic crystalline parameters. The distributions of stacking number, layer length and interlayer spacing determined from the coal models are shown in Figure 6.4. The model stacking numbers ranged from 1 to 5 (Figure 6.4a) with the majority of polyaromatic layers being either single or in stacks of 2-3 layers. Specifically, the average stacking numbers were 2.0 for Upper Freeport, Illinois No. 6 and Beulah-Zap coals, 2.4 for Pocahontas No. 3, and 2.9 for Hon Gai anthracite. There is considerable diversity in the distribution of layer lengths (Figure 6.4b). This distribution showed a sharp peak at 0.25-0.50 (the appropriate size for naphthalene and phenanthrene) with a long tail. Average cluster size was 1.0 nm for Upper Freeport, Illinois No. 6, Beulah-Zap and Pocahontas No. 3 coals, and 1.1 nm for Hon Gai anthracite. The interlayer spacing distributions determined from the models ranged from 0.30 to 0.48 nm, peaking around 0.37-0.39 nm for all coals. The results obtained are in qualitative agreement with HRTEM (analysis of several micrographs including the ones used in model generation) and XRD analyses for Argonne Premium coals where the average layer size ranged from 1 to 1.3 nm, the interlayer spacing ranged between 0.36 and 0.38 nm, and the average stacking number was 2-3. In general, the coal models showed a decrease in interlayer spacing, an increase in aromatic cluster size, and an increase in stacking number with transition from lignite to anthracite, consistent with expectations. Therefore, the constructed molecular models exhibit the distinct advantage of representing the distribution of nano-structural features observed in HRTEM lattice fringe.

Figure 6.4. Distributions of turbostratic crystalline parameters: (a) stacking number, (b) layer length, and (c) interlayer spacing determined from the coal molecular models.
images and in capturing the turbostratic crystalline dimensions determined by XRD and HRTEM.

**Evaluation of simulated and experimental PDFs.**

The simulated $G(r)$ functions for carbon atoms for the constructed coal models are shown in Figure 6.5 with $G(r)$ being the sum of the intermolecular and intramolecular contributions. Experimental $G(r)$ data for selected Argonne coals are also included for comparison (unfortunately the anthracite sample from the HRTEM analysis was not available for experimental PDF analysis). As shown in Figure 6.5a, the peak location and peak amplitude of simulated $G(r)$ functions were in reasonable agreement with the experimental results. High-rank coals exhibited slightly greater peak intensity than low- and medium-rank coals. The peak amplitude increased with increasing rank (lignite to anthracite) in agreement with the growth in the average aromatic cluster size. The first three peaks in the $G(r)$ functions correspond to separation distances between pair of atoms within the same polyaromatic structure. Specifically, the first peaks appear at ~1.40Å due to the presence of sp$^3$ and sp$^2$ carbons. This result is consistent with the models aromatic and aliphatic carbon content and carbon bond lengths (1.39Å for aryl C-C bonds and 1.54Å for alkyl C-C bonds). The second and third peaks are at around 2.45 and 2.85Å, similar to the second and third peaks for coal samples located at 2.46 and 2.86Å. Peaks located at $r >$3Å are also affected by the stacking and neighboring clusters (intramolecular contribution) and thus the analysis of the $G(r)$ function becomes more complex. The experimental $G(r)$ for lignite Beulah-Zap showed fluctuations within a larger range of pair distances, presumably due to the mineral matter and the fact that there are much less larger aromatics which can align with each other. The medium- and high-rank coals will show more aromatic carbon pairs at these longer distances. The simulated $G(r)$ for Beulah-Zap would not capture mineral matter influences.

The $g(r)_{inter}$ function can provide structural information associated with interlayer spacing and stacking number (the fine structure). As seen in Figure 6.5b, the first peaks appeared at ~3.7-3.9Å consistent with the model average interlayer spacing. The $g(r)_{inter}$ functions exhibited similar shapes and strong intensity as the coal rank increased in accordance with the growth in
Figure 6.5. Comparison of (a) simulated and experimental $G(r)$ functions, (b) simulated intermolecular contributions ($g(r)_{\text{inter}}$), and (c) simulated intramolecular contributions ($g(r)_{\text{intra}}$). Simulated values are in colored solid lines and experimental data are in black solid lines.
the stacking number and stack height observed from low- to high-rank coals. Analysis of the $g(r)_{\text{intra}}$ function provides information on the stack width. As shown in Figure 6.5c, the peak amplitude for low-rank coals is smaller than that of high-rank coals, which is consistent with the increase in the calculated average aromatic cluster size with increasing coal rank (1-3 condensed rings for Beulah-Zap and Illinois No. 6, 3-4 for Upper Freeport and Pocahontas No. 3, and 4-5 for anthracite Hon Gai).

Atomistic representations containing PAH molecules composed of four fused rings (pyrene) were also constructed to investigate the effect of alignment and stacking of aromatic entities, in a controlled manner, on the simulated PDF. The use of pyrene as the basic structural unit simplifies the model construction process and is consistent with the average aromatic cluster size for medium- and high-rank coals. Fringe3D was used to place pyrene molecules in 3D modeling space at grid points separated by 8Å. This separation distance, based on the pyrene size of ~6-7Å, was used to avoid overlapping of aromatic rings. Molecules were randomly rotated using Fringe3D within orientation angles between 0 and 360º using a random-number generator. Lattice models of different sizes ranging from 10x10 up to 30x30 were generated to determine the influence of lattice size on the respective simulated PDF. Figure 6.6 shows the $g(r)_{\text{inter}}$

![Figure 6.6. Simulated $g(r)_{\text{inter}}$ functions for coal lattice models of molecular sizes ranging from 10x10 up to 30x30.](image)
functions calculated from the constructed lattice models. The simulated $g(r)_{\text{intra}}$ functions are expected to be insensitive to the lattice size since the aromatic cluster size is constant. As seen in Figure 6.6, a significant variation in the simulated $g(r)_{\text{inter}}$ function for lattice grid size <15x15 was found. The first peaks are located at ~8Å in accordance with the separation distance between grid points. Based on the sensitivity analysis, the minimum lattice model size should be $\geq$ 15x15 to reduce the occurrence of artifacts introduced by the use of smaller models.

The 15x15-lattice model was altered to create several variations with different degrees of alignment of PAH molecules as shown in Figure 6.7. These model variants were generated by rotating a portion of the pyrene molecules to an angle of 180° until agreement with desired alignment values of 30, 60 and 90% of the molecules. Rotation of PAHs to 180° was conducted by selecting pyrene molecules with a random-number generator. Figure 6.8 shows the simulated $g(r)_{\text{inter}}$ functions for the 15x15-lattice coal model with varying degree of aromatic alignment. The $g(r)_{\text{inter}}$ functions exhibited similar shape with significantly more peaks and fluctuations as the degree of alignment increased. This is accompanied with a reduction in the frequency of certain separation distances resulting in a progressively discrete distribution. The simulated $g(r)_{\text{inter}}$ function for the lattice model with random orientation angles exhibited a smooth trend reflecting a continuous distribution of separation distances between PAH molecules. The peak intensity of $g(r)_{\text{inter}}$ increased with the degree of aromatic alignment, thereby permitting further quantification. The correlation for the peak intensity of simulated $g(r)_{\text{inter}}$ functions at the average interlayer spacing as a function of the degree of aromatic alignment can be expressed as:

$$g(r)_{\text{inter}}^{\text{cluc}} = 0.0014\phi^2 + 0.0107\phi + 4.2784 \quad (6.5)$$

where $\phi$ is the degree of aromatic alignment (%). This relationship is a potential means of evaluating aromatic alignment on coal structure. The distributions of stacking number calculated from the 15x15-lattice coal model are shown in Figure 6.9. The calculated stacking numbers ranged from 1 to 10 with a sharp peak at 2-3 indicating that most PAH molecules are forming stacks composed of 2-3 layers. The stacking number distribution for the case of 90% alignment extended up to 15, as expected (not shown in Figure 6.9). The average stacking numbers were 2.1 for random and 30% aligned, 2.8 for 60% aligned, and 6.9 for 90% aligned.
Figure 6.7. Visualization of a 15x15-lattice coal model with PAH molecules showing: (a) random orientation angles, (b) 30% alignment, (c) 60% alignment, and (d) 90% alignment.
Figure 6.8. Simulated $g(r)_{\text{inter}}$ functions for a 15x15-lattice coal model with varying degree of alignment of PAH molecules.

Figure 6.9. Distributions of stacking number determined from the 15x15-lattice coal model with varying degree of alignment of PAH molecules.
The Fringe3D approach enabled generation of coal atomistic representations with simulated \( G(r) \) functions in reasonable agreement with the experimental data. Addition of maceral influences, mineral matter, and cross-links into molecular models should result in enhancing the structural diversity to improve the agreement with the experimental \( G(r) \) values. Generation of volumetric rather than slice representations would further aid in creating yet more realistic structural models. The construction approach can be coupled and constrained by additional structural data to generate atomistic representations that better capture the distribution of coal structural features. Nevertheless, the model construction approach offers the distinct advantage of representing the distribution of nano-structural features observed in HRTEM lattice fringe images and in capturing the turbostratic parameters (aromatic stacking, layer size and interlayer spacing). This approach will better enable coal models to be used in simulation studies to probe the structure-behavior relationship in coal chemistry processes such as CO\(_2\) sequestration, coalification, combustion, gasification, and liquefaction. Future modeling efforts should pursue Fringe3D integration with another reconstruction protocol such as RMC by utilizing Fringe3D-generated models as starting templates in RMC simulations. This hybrid construction approach offers great potential to enable the generation of representative molecular models that better capture coal structural diversity. Additional simulations approaches such as simulated HRTEM images from atomistic representations\(^{56, 57}\), small angle X-ray scattering\(^{58}\) or small angle neutron scattering\(^{59}\) can also aid in probing structure and our atomistic representation accuracy and utility.

**Conclusions**

The pair distribution function (PDF) was evaluated with molecular models of several Argonne Premium coals (Beulah-Zap, Illinois No. 6, Upper Freeport, and Pocahontas No. 3) and a non-Argonne Hon Gai anthracite generated directly from HRTEM lattice fringe images using Fringe3D and constrained by elemental analysis and NMR data. Aliphatic and heteroatom components were included by scripting to agree with available experimental data. These atomistic representations were partially geometry-optimized to capture and duplicate the distribution of structural features in molecular space from HRTEM lattice fringe images. The constructed coal models exhibited an average cluster size of \(~1\) nm, an average interlayer spacing ranging from 0.37 to 0.39 nm, and an average stacking number of about 2-3 in agreement with HRTEM and XRD data for Argonne coals. These atomistic representations, devoid of mineral
matter and cross-links, were used to predict the respective PDFs and to evaluate the fine structure of the frequency spectra. Simulated PDFs exhibited a reasonable agreement with experimental PDF data. Evaluation of the simulated intramolecular PDF contribution showed shorter peak amplitudes for low-rank coals than high-rank coals in accordance with the increase in stack width with increasing coal rank. The simulated intermolecular PDF contribution showed strong intensities with increasing coal rank in agreement with the growth in the stacking number and stack height observed from low- to high-rank coals. Further examination of these contributions was conducted by creating coal lattice models consisting of pyrene molecules generated via Fringe3D to explore the effect of aromatic stacking and alignment of polyaromatic molecules on simulated intermolecular PDFs. The results showed that peak intensities at the average interlayer spacing increased with the degree of alignment \((\phi)\) as \(g(r)_{\text{inter}}^{\phi_0} = 0.0014\phi^2 + 0.0107\phi + 4.2784\), consistent with the slight increase in the aromatic cluster size and stacking number observed from low- to high-rank coals.

**Acknowledgments**

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**References**

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Chapter 7

Summary and Conclusions

A highly automated molecular construction approach was developed and implemented to generate high-quality, large-scale coal and char models with improved accuracy and utility, greater length scale, and significantly reduced computational expense. This construction approach enabled simplifying the model generation process, eliminating researcher structural bias and generating very large-scale continuum molecular representations. A significant advance enabled by this large-scale approach is the avoidance of iterative trial and error undertaking. Utilizing a base distribution of aromatic and hydroaromatic cores to which the desired distribution of functionality was applied. Automatic cross-linking approach produced a molecular weight distribution in agreement with the literature demonstrating a major progression toward capturing the continuum of coal structure. This computational protocol was effectively demonstrated with the Illinois No. 6 Argonne Premium coal and char. The constructed coal and char models were coupled with reactive force field methods to create a specialized simulation tool that enabled an atomistic-scale investigation of the complex structural transformations and chemical processes associated with coal pyrolysis and char combustion. The work performed here was aimed at demonstrating the capability of this approach in gaining additional insights into the initial chemical reactions of the thermal decomposition of Illinois coal and char during pyrolysis and combustion.

An extensive review of the chemical and physical structural features of the Argonne Premium Illinois no. 6 coal was created. The topics covered include the relative contributions of the aromatic and aliphatic components, functional groups and heteroatoms, molecular weight distribution, nature of the cross-linked network, porosity, surface area and density. Illinois no. 6 Argonne Premium coal is vitrinite-rich (85%, dmmf) with an elemental composition of $C_{100}H_{77.3}O_{13.1}N_{1.5}S_{1.2}$ and a high organic sulfur content of 2.5% (dmmf). Nuclear magnetic resonance (NMR) analyses reported an aromaticity of 72% with 15 aromatic carbons (three to four fused aromatic rings) and 5 attachments per cluster, and an average cluster molecular weight of 316 Da. Ruthenium ion catalyzed oxidation (RICO) experiments determined that there are
1.76 methyl, 0.29 ethyl, 0.037 propyl, and 0.035 2-propyl groups per 100 carbon atoms. X-ray absorption near-edge structure spectroscopy (XANES) studies found that organic sulfur forms are distributed as 26% aromatic (diphenyl sulfide), 33% aliphatic (dibenzyl sulfide), and 41% thiophenic (2,5 dimethylthiophene, benzothiphene and dibenzothiophene molecules). X-ray photoelectron spectroscopy (XPS) analyses demonstrated that Illinois no. 6 coal contains 5.2 ether, 3.9 phenolic, 0.4 carbonyl and 0.6 carboxyl groups per 100 carbon atoms. The nitrogen type and distribution derived from XPS experiments were: 62% pyrrolic, 26% pyridinic and 12% quaternary. Solvent-extraction data and laser desorption ionization mass spectrometry (LDIMS) estimated values for number ($M_n$) and weight ($M_w$) average molecular weights ranging from 402 to 640 and 441 to 2100 Da. $^{129}$Xe NMR studies confirmed that the pore structure of Illinois coal consisted of two distinct regions with average micropore diameter of 6 and 10 Å, respectively. X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) lattice fringe analyses determined that the interlayer spacing is 0.37 nm, average fringe length is 1.0 nm and average number of layers per stack is 2.2.

An automated construction protocol was implemented to construct a large-scale model for Illinois no. 6 Argonne Premium coal based on available analytical data. Previously published HRTEM lattice fringe micrographs were used to determine the aromatic ring size distribution. Organic sulfur, oxygen and nitrogen heteroatom types and distributions were added to the aromatic structures according to XANES and XPS data. Incorporation of aliphatic structures was conducted in the form of cross-links and alkyl side chains based on LDIMS, RICO, bulk elemental analysis and NMR data. Fringe3D program in conjunction with Perl scripts created within the Materials Studio software package were utilized to facilitate model construction process, remove investigator bias, and generate large-scale representations with improved accuracy and structural diversity. The Illinois coal model contained more than 50,000 atoms ($C_{26860}H_{20897}O_{2502}N_{412}S_{330}$, atomic H/C=0.778 and O/C=0.093) in 728 cross-linked aromatic and hydroaromatic clusters exhibiting a continuous molecular weight distribution ranging from 100 to 2850 Da with a sharp peak at ~350-400 Da and 522 and 861 Da for $M_n$ and $M_w$, aromaticity value of 0.75, and a simulated helium density of 1.32 g/cm$^3$ in agreement with experimental data for Illinois no. 6 coal. This Illinois coal model is the first molecular representation that captures a broad range of structural features including aromatic, aliphatic, heteroatom, and moisture.
components in a 3D cross-linked network. Agreement between model and experimental chemical and physical structural parameters validated the automated model construction protocol. During model generation process, elemental composition, NMR parameters, molecular weight distribution and simulated helium density were adjusted to agree with the available experimental data. However, evaluation of the pore size distribution, interlayer spacing, stacking number, pyridine extraction yield, distribution of double bond equivalents and heteroatom classes, and van Krevelen diagrams were regarded as a test of the model since these parameters were not fitted in building the coal model. Improved data was obtained in collaboration with the National High Magnetic Field Laboratory for this comparison. Pyridine extract and residue molecular representations constructed from the large-scale Illinois coal model based on theoretical solvent extraction yields were consistent with NMR, elemental analysis and LDIMS trends. In addition, double bond equivalents distribution and heteroatom class distribution (numbers of N, O, and S atoms) derived from the coal model captured 1% of the structural diversity determined by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry.

Fringe3D coupled with Perl scripts were used to generate a structural representation of the crystalline portion of a devolatilized Illinois no. 6 coal char based on HRTEM lattice fringe images and constrained by elemental analysis data. The constructed char structure contained ~7500 atoms within 66 polyaromatic molecules and exhibited a molecular weight distribution ranging from 239 to 3454 Da with a peak at ~250-500 Da, and calculated values for $M_n$ and $M_w$ of 1095 and 1605 Da, respectively. The average interlayer spacing, average layer size, and average stacking number were 3.8Å, 14Å, and 2.4 respectively, which were in reasonable agreement (given the limited scale) with the reported values of 3.7-3.9Å, 12-14Å, and 3.0-3.2 from HRTEM and XRD analyses for Illinois coal char samples. Thus, this char model exhibits the distinct advantage of representing the distribution of nanostructural features observed in HRTEM lattice fringe images and in capturing the turbostratic crystalline dimensions measured by XRD and HRTEM.

The ReaxFF reactive force field was utilized to perform pyrolysis simulations on the large-scale molecular model of Illinois no. 6 coal to investigate coal pyrolysis chemistry and the effects of organic sulfur content. ReaxFF pyrolysis simulations were performed at 2000 K to allow
chemical processes to occur within the picosecond range (250 ps). The results showed that Illinois coal pyrolysis was mainly initiated by release of hydroxyl groups and dehydrogenation of hydroaromatic structures followed by breakage of heteroatom-containing cross-links. Calculated molecular weight distributions gradually shifted to lower values as expected due to the thermal degradation of coal molecules to produce smaller molecules and fragments. Aliphatic sulfur was observed to decompose more rapidly than thiophenic sulfur, which was more thermally stable. Decomposition of sulfurated and oxygenated cross-links was more extensive than that for alkyl cross-links, consistent with their higher reactivity. A more rapid thermal degradation was observed for heterocyclic 5- and 6-membered rings in comparison to hydrocarbon 5- and 6-membered rings. The ReaxFF simulation was repeated on a sulfur-free model to further analyze the role of organic sulfur forms in Illinois coal pyrolysis. The results indicated that the rate of generation of pyrolysis products was greater in the presence of sulfur. Analysis of ReaxFF simulations showed that aryl and alkyl C-S bonds are weaker than aryl and alkyl C-C bonds. Hence, C-S bond scission reactions produced more extensive fragmentation resulting in higher amounts of aliphatic and aromatic moieties that evolved as light gases and tars within Illinois coal model (sulfur containing) compared to sulfur-free model. Thus, sulfur atoms aided in accelerating pyrolysis reaction kinetics.

The ReaxFF reactive force field was used to conduct combustion simulations of a devolatilized Illinois no. 6 coal char under fuel-lean, fuel-rich and stoichiometric conditions at 3000, 3500, and 4000 K to investigate the effects of combustion environment and temperature on the gasification process and product distribution. These elevated temperatures were chosen to observe chemical reactions proceed to completion within a computationally practical simulation time. Analysis of trajectories from ReaxFF simulations confirmed that further char degradation occurs under these conditions, generating small fragments that were subsequently oxidized; alternatively, hydrogen abstraction reactions by O_2 molecules and O and OH radicals may be the dominant gasification events. The ratio of the major combustion products, CO/CO_2, was found to increase with increasing temperature, consistent with expectations based on well-known experimental facts. Furthermore, ring structures were observed to disintegrate more rapidly in fuel-lean conditions than in a fuel-rich environment, and 6-membered rings were transformed into 5- and 7-member
rings (mostly via intramolecular rearrangement of aryl C-C bonds) that subsequently decompose into smaller fragments.

As a test of the applicability of HRTEM, the pair distribution function (one means of examining the atomic spatial arrangements of coals) was evaluated with molecular models of several Argonne Premium coals (Beulah-Zap, Illinois no. 6, Upper Freeport, and Pocahontas no. 3) and a non-Argonne Hon Gai anthracite generated directly from HRTEM lattice fringe images using Fringe3D and constrained by elemental analysis and NMR data. The constructed coal models exhibited an average layer size of ~1 nm, an average interlayer spacing ranging from 0.37 to 0.39 nm, and an average stacking number of about 2-3 in agreement with HRTEM and XRD data for Argonne coals. These atomistic representations, devoid of mineral matter and cross-links, were used to predict the respective pair distribution function (PDF). Simulated PDFs exhibited reasonable agreement with experimental PDF data. Evaluation of the simulated intramolecular PDF contribution showed shorter peak amplitudes for low-rank coals in accordance with the increase in stack width with increasing coal rank from literature HRTEM observations. The simulated intermolecular PDF contribution showed stronger intensities with increasing coal rank, in agreement with the growth in the number of layers per stack and stack height observed from low- to high-rank coals. Further examination of these contributions was conducted by creating coal lattice models consisting of pyrene molecules (generated via Fringe3D) to explore the effect of aromatic stacking and alignment of polyaromatic molecules on simulated intermolecular PDFs. The results showed that peak intensities at the average interlayer spacing increased with the degree of alignment, consistent with the slight increase in aromatic cluster size and stacking number observed from low- to high-rank coals.

This investigation thus demonstrated that, by coupling improved-quality, large-scale coal models based on a highly automated construction approach with reactive molecular dynamics enables obtaining a versatile and powerful computational tool that can be used effectively and efficiently to examine atomistic-scale transformations and chemical events occurring during coal pyrolysis and combustion. It is expected that such an approach will not only be capable of reproducing key experimental facts but also of predicting new phenomena in coal conversion processes.
Chapter 8

Recommendations for future work

- Improve the molecular representation via increasing the model scale to enhance the molecular weight distribution and structural diversity to better capture the continuum of structural features over a large scale including an evaluation of how much diversity is warranted to obtain important structure/behavior/property relationship. Inclusion of macro and mesopores (concurrent with an increase in model scale), maceral groups, and mineral matter will further improve the usefulness of structural models. Future modeling efforts should incorporate these factors.

- Fringe3D integration with reconstruction protocol such as reverse Monte Carlo (RMC) by utilizing Fringe3D-generated models as starting templates in RMC simulations. This hybrid construction approach offers great potential to enable the generation of realistic molecular models that better capture coal structural diversity. Additional simulations approaches such as simulated HRTEM images from atomistic representations, small angle X-ray scattering or small angle neutron scattering can also aid in probing structure and atomistic representation accuracy and utility.

- Future work should explore conducting ReaxFF simulations over longer time scales and lower temperatures to better capture temperature influences. With current computational resources, the time scale of reactive molecular dynamics (MD) simulations is many orders of magnitude shorter than that used in the experiments. Therefore, reactive simulations are often performed at temperature ranges extending beyond normal experimental and industrial conditions to enable chemical reactions to occur within a practical computational time. The work performed here was aimed at demonstrating the capability of this approach for examining the complex chemistry involved in coal pyrolysis and char oxidation and combustion. Despite these time and temperature differences between simulation and experiment, initial reaction mechanisms and product distribution of ReaxFF simulations on
thermal decomposition of hydrocarbon fuels are in qualitative agreement with the available experimental data.

- Progress to more advanced computational power and software tools. While nonreactive MD simulations can be performed within a reasonable time scale using a single CPU, reactive MD simulations are computationally more demanding and often require super computer/cluster facilities with multiple processor cores and parallel-processing. A typical equilibration and production run for the complex systems investigated in this study took 3-4 months of simulation time for coal pyrolysis and about 4-6 weeks for char combustion followed by multiple weeks of data analysis. An alternative strategy for reducing computational and elucidation efforts could be the use of hybrid reactive lattice/ReaxFF approaches recently explored by Alvarez et al. (2012) as discussed in Chapter 4.

- Improve solvent extraction results by comparison with experimental observations. Theoretical solvent extraction yield calculations were performed based on a group contribution approach for solubility parameters (δ) which yield errors of ±0.6 (cal/cm^3)0.5 and thus should be regarded as an initial estimate for δ values. Further development of this contribution approach through inclusion of additional structural descriptors such as double bond equivalents should be pursued to improve δ predictions. In addition, the effects of secondary interaction forces and transport limitations during solvent extraction calculations should also be considered.

- The proposed large-scale Illinois no. 6 coal model will better enable conducting further simulation studies that investigate the structure-property and structure-behavior relationships in coal chemistry processes such as liquefaction, CO₂ sequestration in coal, solvent swelling/extraction, coalification, and gasification. This coal model is available online (see journal article) and other researchers are encouraged to use it for these purposes.
Appendix A

Density Equilibration Scheme

The density equilibration scheme proposed by Hofmann et al. (2000) was utilized for gradually adjusting the density of coal model. According to this procedure, the initially constructed simulation cell is subjected to an energy minimization followed by succession of 12 molecular dynamics stages, consisting of NVT and NPT simulations (corresponding to compression, decompression, annealing, and cooling cycles under various conditions of temperature and pressure), aimed at creating a final relaxed coal structure with realistic density. The successive stages and the conditions imposed at each simulation step are listed in Table A1. The advantage of this method is that the generated coal structure is fully relaxed during the successive stages of the equilibration cycle. Specially, the annealing cycles enable the coal structure for rearranging into its most stable configuration (lower free energy). Hence, the resulting coal structure is energy optimized. It was observed that 50 ps was enough to equilibrate the coal structure in a low-energy configuration. For all NVT MD simulations, the energy decreased only during the first 20 ps of simulations and then remained approximately constant. Energy minimizations and compression and annealing cycles were performed within Materials Studio package using the consistent-valence force field (cvff) with van der Waals and electrostatic interactions modeled via Lennard-Jones and Coulomb potentials, respectively. All energy minimizations were conducted using the classical conjugate gradient algorithm, and temperature and pressure were controlled by a Nose-Hoover thermostat and barostat.
Table A1. Successive steps in the equilibration cycle used to generate a structural model with realistic density.

<table>
<thead>
<tr>
<th>Equilibration step</th>
<th>Simulation conditions</th>
<th>Duration (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NVT, 600 K</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>NVT, 300 K</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>NPT, 10000 bar, 300 K</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>NVT, 600 K</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>NVT, 300 K</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>NPT, 30000 bar, 300 K</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>NVT, 600 K</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>NVT, 300 K</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>NPT, 50000 bar, 300 K</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>NVT, 600 K</td>
<td>50</td>
</tr>
<tr>
<td>11</td>
<td>NVT, 300 K</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>NPT, 1 bar, 300 K</td>
<td>500</td>
</tr>
</tbody>
</table>
Appendix B

Structural Assignment Sensitivity Analysis

A sensitivity analysis was conducted to evaluate how cutoff values used in the structural assignment modify the fraction of protonated aromatic carbons ($f_a^H$) for the corresponding polyaromatic structures. Fringe 3D was used to create molecular representations for the aromatic fringes and protonated aromatic carbons were determined using molecular modeling software. The cases 1 – 3 in Table B1 correspond to 90, 95 and 105% of the initial structural assignment defined as grouping in Table B1. The distribution of PAH molecules obtained from these cases is shown in Figure B1. As seen, all the cases considered exhibit similar distributions of aromatic moieties with naphthalene, phenanthrene and 2x2 parallelogram-shaped structures as the most abundant structural entities and a 6x6 aromatic sheet representing the longest PAH molecule observed. The calculated $f_a^H$ values for case 1, 2 and 3 were 0.685, 0.693 and 0.702, respectively, indicating that there is no significant variation on $f_a^H$ values between the cases.

Table B1. Structural assignment for aromatic fringes obtained from HRTEM lattice fringe images.

<table>
<thead>
<tr>
<th>Aromatic fringe</th>
<th>Grouping (Å)</th>
<th>Case 1 (Å)</th>
<th>Case 2 (Å)</th>
<th>Case 3 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.5-3.0</td>
<td>2.50-2.95</td>
<td>2.50-2.98</td>
<td>2.50-3.03</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>3.0-4.5</td>
<td>2.95-4.21</td>
<td>2.98-4.31</td>
<td>3.03-4.50</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>4.5-6.0</td>
<td>4.21-5.65</td>
<td>4.31-5.83</td>
<td>4.50-6.18</td>
</tr>
<tr>
<td>2x2</td>
<td>6.0-7.5</td>
<td>5.65-7.27</td>
<td>5.83-7.54</td>
<td>6.18-8.07</td>
</tr>
<tr>
<td>3x3</td>
<td>7.5-9.5</td>
<td>7.27-9.07</td>
<td>7.54-9.44</td>
<td>8.07-10.17</td>
</tr>
<tr>
<td>4x4</td>
<td>9.5-13.0</td>
<td>9.07-11.32</td>
<td>9.44-11.81</td>
<td>10.17-12.79</td>
</tr>
<tr>
<td>5x5</td>
<td>13.0-16.0</td>
<td>11.32-14.92</td>
<td>11.81-15.61</td>
<td>12.79-16.99</td>
</tr>
</tbody>
</table>
Figure B1. Distributions of PAH molecules generated from the cases studied in the structural assignment.
A sensitivity analysis was performed to examine how the addition of functional groups within the polyaromatic structures affects theoretical pyridine extraction calculations (Table C1). This sensitivity analysis tested the algorithm for randomly incorporating heteroatoms and functional groups by replacing selected atom types with appropriate functionality. Solubility parameters were used to estimate the mass fraction of the coal model that could be theoretically extracted by pyridine. The solubility parameter for each polyaromatic molecule was calculated from aromaticity and elemental composition data (as described in Chapter 3). Fringe 3D was used to generate atomistic representations for polyaromatic structures followed by addition of functional groups. Pyridine extraction yield calculations were performed to estimate the number of extractable molecules. Theoretically extractable molecules were assumed to have a solubility parameter difference (between coal molecule and solvent) within ±1 \((\text{cal/cm}^3)^{0.5}\). Note that high extraction yields are anticipated because the aromatic molecules have not yet been cross-linked and thus have a higher atomic H/C ratio and are more soluble. As seen in Table C1, no significant difference exists in the pyridine extract yields for these aromatic structures, because values range between 48 and 51% for the four cases. Thus, the random approach for heteroatoms and functional groups addition was deemed reasonable.

**Table C1.** Sensitivity analysis for heteroatoms and functional groups addition effect on calculated pyridine extraction yields (cutoff = ±1 \((\text{cal/cm}^3)^{0.5}\)).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of extracted molecules</th>
<th>Molecular weight extracted</th>
<th>Calculated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>877</td>
<td>200,806</td>
<td>50.8</td>
</tr>
<tr>
<td>Case 2</td>
<td>846</td>
<td>191,819</td>
<td>48.5</td>
</tr>
<tr>
<td>Case 3</td>
<td>858</td>
<td>196,031</td>
<td>49.6</td>
</tr>
<tr>
<td>Case 4</td>
<td>852</td>
<td>192,416</td>
<td>48.7</td>
</tr>
</tbody>
</table>
A sensitivity analysis was conducted to investigate how generation of cross-links influences the frequency of PAH structures per cross-linked cluster for molecular weight distributions generated by the constrained cross-linking approach described in section 2.3.4. Fringe 3D was used to build molecular representations for polyaromatic structures followed by cross-linking to obtain a molecular weight distribution based on LDIMS data. Based on known coal chemistry aromatic-aromatic, aromatic-aliphatic, aromatic-oxygen, aliphatic-aliphatic, and aliphatic-oxygen bonding types were all permitted. The distribution of PAH structures in a cross-linked cluster is listed in Table D1. The cases 1 – 3 correspond to different initial (random) locations of PAH structures in the simulation cell. All cases exhibited a high frequency of cross-linked molecules containing between two and seven PAH structures and a few clusters containing a larger number, with examples of 15, 16 and 17 PAH structures in a molecule. Further support to this cross-linking approach is provided by the calculated values for number ($M_n$) and weight ($M_w$) average molecular weights for these distributions (±2.4 for $M_n$ and ±11.4 for $M_w$), indicating that the constrained cross-linking method is able to consistently generate an appropriate molecular weight distribution.
Table D1. The frequency of PAH structures in a cross-linked cluster for molecular weight distributions generated by cross-linking constrained to connect small aromatic moieties.

<table>
<thead>
<tr>
<th>PAH structures per cross-linked cluster</th>
<th>Frequency (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Case 1</td>
<td>Case 2</td>
<td>Case 3</td>
</tr>
<tr>
<td>2</td>
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VITA

EDUCATION

PhD in Fuel Science and Engineering
Pennsylvania State University | PA, USA | 2012

MSC in Chemical Engineering
Universidad Simon Bolivar | Caracas, Venezuela | 2005

BS in Chemical Engineering
Universidad Simon Bolivar | Caracas, Venezuela | 2001

AWARDS AND HONORS

Honorable Mention Award for Technical Paper
29th Annual International Pittsburgh Coal Conference | Pittsburgh, PA | 2012

Charles B. Darrow Award for Excellence in Fuel Science
Pennsylvania State University | University Park, PA | 2012 & 2011

Honorable Mention Award for Technical Paper
28th Annual International Pittsburgh Coal Conference | Pittsburgh, PA | 2011

Graduate Student Travel Award | ACS Fuel Chemistry Division | Denver, CO | 2011

PEER-REVIEWED PUBLICATIONS


