ABSTRACT

The Illinois bituminous coal basin is the largest in the United States. Its coals have been extensively studied generating copious chemical, physical, and behavioral data. With current advances in coal molecular modeling construction approaches, and more importantly, in reactive force field development it was evaluated if it was possible to generate very large-scale molecular models of an Illinois coal and an Illinois coal char and utilize those models for advancing Illinois coal and coal-char chemistry. Thus a review of Illinois no. 6 Argonne Premium bituminous coal was performed and utilized in the construction of a large-scale (50,000 atom) atomistic representation created with an efficient highly-automated construction/evaluations protocols that enabled moving towards a continuum structural representation inclusive of a wide molecular weight distribution. The model is the largest, and most accurate structural representation of coal currently and is freely available to better enable future Illinois coal investigations.

To enable large-scale (>1000 atoms) molecular dynamics simulations of sulfur-induced pyrolysis reactions we added sulfur-containing functional groups to the ReaxFF reactive force field. DFT calculations of S containing molecules were used to train the ReaxFF force field parameters. The force field was subsequently utilized to investigate the thermolysis of the coal representation (and variants highlighting various sulfur forms, and one free of sulfur). The presence of S-forms increased the rate of formation and quantity of light gases produced while retarding the extent and rate of tars. The S-variant of ReaxFF is available to the ReaxFF community and is expected to yield additional insight into sulfur chemistry.

The oxidation and combustion of an Illinois coal char was also investigated with ReaxFF at 3000 to 4000 K. These simulations allow tracking the effect of local char structure on reactivity. A high-temperature reactive dynamics run was performed to allow the chemical reactions to occur within a reasonable time scale (a few picoseconds). During oxidation, the reactive sites become oxygenated and ring opening occurs often followed by reorganization into a 5-membered ring. The number of 6-membered aromatic rings reduces with increasing iterations (or time steps) due to the molecular fragmentation.
EXECUTIVE SUMMARY

Objectives
A large-scale molecular model for Illinois No. 6 Argonne Premium coal was to be created, based on an automated construction approach, in an effort to move toward capturing the continuum structure. Sulfur chemistry was to be incorporated into the ReaxFF force field to be used in reactive molecular dynamic simulations to study pyrolysis/liquefaction of the coal model, and various S-rich forms. An Illinois coal char model was also to be created and used in ReaxFF oxidation and combustion studies.

Structural Information
A review of the structural information of Illinois no. 6 bituminous coal was generated (Castro-Marcano and Mathews 2011). 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. $^{13}$C NMR indicated that Illinois No. 6 high-volatile bituminous coal contains on average 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. 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. SANS analyses showed that powdered Illinois coal is mostly microporous.

Coal Model Generation
The large-scale model generated contains 50,789 atoms within 728 cross-linked aromatic clusters and is the largest coal representation constructed to-date. The aromatic fringe size distribution was determined from 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 Illinois no. 6 coal. Organic oxygen, nitrogen, and sulfur functionalities were incorporated primarily into the aromatic clusters 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 literature data. 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 researcher structural 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 2,850 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 reasonable 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 and are consistent with the limited scale of the pyridine extract model heteroatom classes. It is expected that the model, which is freely available from ICCI, will continue to provide insight into coal behavior and structure property relationships. It is currently the largest structure generated to-date and the most appropriate coal representation created.

**Sulfur Inclusion into ReaxFF**

ReaxFF (van Duin et al. 2001) is a reactive force field based on the bond distance/bond order formalism of Tersoff (Kelires and Tersoff 1988) and Brenner (Brenner 1990) in which the bond orders and bond strengths adjust appropriately in response to changes in the local chemical environment, resulting in accurate descriptions of bond cleavage and bond formation during chemical reactions. Quantum chemical calculations of S-containing molecules were used to train the ReaxFF force field as it is recognized that the high S content of Illinois coal influences its behavior. Good agreement with quantum calculations were obtained for both reaction energies, geometries as well as reaction barriers, indicating that ReaxFF can describe both the reaction products as well as the reaction kinetics related to sulfur-chemistry in coals. The ReaxFF force field is available to its international community (van Duin 2011) for further utilization.

**Coal Model Pyrolysis/Liquefaction**

The original coal model was altered to create several variations with high concentrations of various sulfur forms, aliphatic, aromatic (S-bound to an aromatic carbon), and thiophenic sulfur forms which along with the original model and a non-S containing model was used in ReaxFF pyrolysis/liquefaction simulations. The computationally intense calculations were performed at a cluster facility using multiple processors for periods of several weeks to obtain picosecond simulation times. High temperatures (2000 K) were used to speed the process. The presence of S-forms increased the rate of formation and quantity of light gases produced while retarding the extent and rate of tars (defined as molecular weights in the 100 to 700 Da range).

**Illinois Coal Char Model Creation**

The Fringe3D approach was applied to generate molecular representations for the graphitic sheets of the char structure based on HRTEM lattice fringe data and constrained by elemental analysis. Image analysis for a HRTEM lattice fringe image of an Illinois No. 6 coal char sample heat-treated at 800 °C for 5 min (heating rate: 30 °C/min) was used from the literature (Sharma et al. 2001b). The extracted fringe lengths along with a specific catenation growth were used by Fringe3D to construct graphitic sheets with a range of sizes and shapes were generated in accordance with known coal char chemistry. Limited non-hexagonal rings (5- and 7-membered rings), recognized as important structural features of the char, were distributed randomly throughout the sheets. Incorporation of aliphatic structures was conducted in the form of hydroaromatic units and cross-linking bridges between graphitic layers until agreement with desired aromaticity >0.90. Elemental analysis data for an Illinois No. 6 coal char prepared at 800
°C for 5 min (heating rate: 50 °C/min) (Matsuoka et al. 2008) was utilized to further constrain the coal char structural model.

**Coal Char Oxidation and Combustion Simulation with ReaxFF**

The resulting char structure along with oxygen molecules behavior were observed utilizing ReaxFF oxidation simulation at 3000 to 4000 K. These simulations allow tracking the effect of local char structure on reactivity. A high-temperature reactive dynamics run was performed to allow the chemical reactions to occur within a reasonable time scale (a few picoseconds). During oxidation, the reactive sites become oxygenated and ring opening occurs often followed by reorganization into a 5-membered ring. The number of 6-membered aromatic rings reduces with increasing iterations (or time steps) due to the molecular fragmentation associated with the thermal decomposition at high-temperature (4000 K) simulation of char oxidation.

Coupling the current ReaxFF-methodology with realistic Illinois coal and char models, constructed based on available experimental data, will improve the design strategies for coal utilization. New approaches were utilized to rapidly generate an Illinois no. 6 coal model and char model with relative ease. The new construction protocols were demonstrated producing structures with good agreement with a wide variety of chemical and physical analyses. They were successfully utilized in ReaxFF simulations to examine coal thermolysis (pyrolysis/liquefaction) and char oxidation and combustion.
OBJECTIVES

Molecular simulations are valuable tools in many scientific evaluations, but their use with coal and char were often limited due to challenges and difficulties in capturing the structural diversity and the accompanying transformations. To overcome these challenges a large-scale molecular model for Illinois No. 6 Argonne Premium coal was to be created, based on efficient and automated construction protocols, in an effort to move toward capturing the continuum structure. Sulfur chemistry was to be incorporated into the ReaxFF force field to be used in reactive molecular dynamic simulations to study pyrolysis/liquefaction of the coal model, and various S-rich forms. An Illinois coal char model was also to be created and used in ReaxFF oxidation and combustion studies.

INTRODUCTION AND BACKGROUND

The Illinois bituminous coal basin is the largest in the United States. Its coals have been extensively studied generating copious chemical, physical, and behavioral data. With current advances in coal molecular modeling construction approaches, and more importantly, in reactive force field development it is now possible to generate very large-scale molecular models of coal and utilize those models for advancing Illinois coal chemistry. No molecular representations of Illinois coal models exist. Had one been generated it is likely that they would have been of limited scale (100’s of atoms) and because of that limited in their applicability to coal chemistry processes such as coal-to-liquids, coal char formation (combustion and gasification), carbon dioxide, water, and methane sorption (sequestration/coalbed methane related) etc. We have a new approach to generate large-scale models (>20,000 atoms) that enables inclusion of a molecular weight diversity, directly captures aromatic ring stacking, and enables better porosity and pore size distribution inclusion. We utilize image analysis from HRTEM lattice fringe images to directly populate 3D models of the aromatic portion of the coal. Constrained by NMR data, and including elemental composition, mass spectroscopy data, known coal chemistry, heteroatom functionality, cross-linking, bound and bulk water, an automated construction protocol creates the large-scale model. Physical parameters, such as helium density and pore size distribution, further constrain the model. Capturing all of these features and the distribution of such features generates state-of-the-art coal atomistic representations. Thus the model can synthesize and present the available Illinois coal data in a visual manner and the model also has great utility for Illinois coal chemistry studies. Here specifically the interests are in the intitial stages of pyrolysis/liquefaction for the Illinois coal and the reactions occurring in char oxidation/combustion utilizing a reactive force field dynamics simulation (ReaxFF).

To demonstrate the utility of this realistic large-scale coal model in predicting coal chemistry we extended the ReaxFF reactive force field, which has been previously applied to study hydrocarbon combustion, with the sulfur functionalities present in Illinois coal. This extension was performed by training the force field parameters against a quantum chemistry (QM)-based data set describing geometry, energies, and key reaction barriers associated with S/C/H containing molecules. Thereafter, this extended ReaxFF description was employed in combination with the large-scale Illinois coal models to perform massively parallel, fully reactive, molecular dynamics (MD)
simulations on the pyrolysis/liquefaction of Illinois coal. In these simulations the key coal input parameters, like sulfur content and local sulfur chemistry, were studied to determine their influence on the process. A char structure was also evaluated in a similar manner by observing the transitions accompanying oxidation/combustion during a reactive dynamics run with oxygen.

By combining a QM-trained ReaxFF description with a realistic coal model that is constrained by experimental data we obtain a versatile, multi-scale simulation platform for predicting the chemistry in complicated materials. This simulation platform can be straightforwardly extended to incorporate an aqueous and catalyst component, making it into a useful tool for evaluating coal conversion and coal use strategies.

**EXPERIMENTAL PROCEDURES**

**ILLINOIS No. 6 COAL MODEL CONSTRUCTION**
The construction of the coal molecular model consisted of: (1) HRTEM image analysis, (2) construction of the aromatic clusters, (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 enabled simplifying the model construction process, eliminating researcher structural bias and generating large-scale continuum molecular representations with improved accuracy.

HRTEM has been used for structural characterization of coal-derived materials producing structural results in agreement with XRD and \(^{13}\)C NMR data (Sharma et al. 2000b; Sharma et al. 2000c; Sharma et al. 2000a; Sharma et al. 2001a; Sharma et al. 2002; Mathews et al. 2007). 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 smaller fringes: <3Å benzene, <4.5Å naphthalene, and <6Å phenanthrene/anthracene. A parallelogram shape was assumed for larger aromatic fringes. Centers of mass (determined by image analysis) of fringes are placed in 3D format and then appropriate named or catenation molecules are located at the appropriate Cartesian coordinates with the assumption that the molecules are all in the same \(z\)-plane. A trimming procedure was performed on aromatic fringes of 3x3 and greater until reasonable agreement with the experimental NMR value was achieved, similar to that employed previously (Van Niekerk and Mathews 2010a). Here trimming was conducted by randomly selecting aromatic hydrogen atoms then removing the corresponding aromatic ring. The constructed model contained a continuous distribution of aromatic moieties.

Sulfur, nitrogen and oxygen were incorporated within the aromatic ring structures or as surface functional groups by selecting specific atoms using a random-number generator and then replacing them by the appropriate functionalities. In particular, aromatic hydrogen atoms were randomly replaced by phenolic, carbonyl, carboxyl, aromatic ether
and aromatic sulfur groups, whereas carbons in 5- and 6-member rings were randomly substituted for furanic, thiophenic and pyrrolic type structures, and pyridinic and quaternary nitrogen, respectively. Similarly, aliphatic carbons were also added utilizing the distribution of pendant alkyl groups based on ruthenium ion catalyzed oxidation experiments (Obeng and Stock 1996). Generation of the cross-linked network structure was based on the approach proposed previously (Mathews et al. 2010), which utilizes LDIMS and HRTEM data. This cross-linking approach is constrained to connect smaller aromatic fringes by excluding (here) the largest 25% of aromatic fringes. In this method, aromatic clusters were randomly distributed and cross-linked until satisfactory agreement with LDIMS data (Herod et al. 1994) was obtained. To covalently bond aromatic fringes in a cross-linked cluster: aromatic fringes were minimized and randomly placed in a rectangular cell using Materials Studio Amorphous Cell module.

The cross-linked aromatic clusters were assembled into 3D molecular model using the Theodorous and Suter (Theodorou and Suter 1985) method as implemented in the Amorphous Cell module of Materials Studio package (Klose and Suginobe 1985). Prior to construction, 2,214 water molecules were randomly added to the empty simulation cell to account for the moisture content (bulk and bound water) measured by differential scanning calorimetry (DSC) (Norinaga et al. 1998). The 3D molecular model was built with an initial low bulk density of 0.5 g/cm³ 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 an equilibration scheme (D. Hofmann et al. 2000). According to this procedure, the initially constructed cell is subjected to an energy minimization followed by successive MD simulations aimed at creating a final equilibrated coal structure with realistic density. Scripts were utilized to determine the level of agreement with chemical structure data.

REAXFF INCORPORATION OF S AND TRAINING

A ReaxFF force field which is capable of modeling the pyrolysis and combustion of pure hydrocarbons had been developed previously by the van Duin group (Chenoweth et al. 2008). To accurately model the dynamics of the sulfur containing coal compounds (important in Illinois coals), a range of the typical structures and reactions associated with the presence of sulfur in coal was desired. A collection of such structures, and their reactions were created and used to train the hydrocarbon/oxygen force field to include the addition of sulfur chemistry. Each of the respective energies for these molecules was calculated using DFT in either the Gaussian or Jaguar program with the B3LYP hybrid functional and 6-311G++** basis set.

This training set contains the following elements:

1) Single- and double (if relevant) bond dissociation curves for C-S, S-S and S-H bonds.
2) Charge distributions for sulfur-functionalized hydrocarbon compounds.
4) Rotational barriers around X-C-S-X dihedrals.
5) Hydrogenation energies for a series of sulfur functional groups relevant to coal chemistry.

6) Equations of state for elemental sulfur (both molecular and crystalline configurations).

7) Reaction barriers for sulfur hydrogenation and sulfur radical rearrangement reactions.

The force field used within the ReaxFF program contains a large array of parameters such as the van der Waals radius and electronegativity, as well as bond strengths, angles, and dihedrals to describe both the individual elements as well as their interaction with one another. By iteratively varying these parameters and comparing the relative calculated ReaxFF energies for the given structures to the quantum calculated energies, it is possible to tune the force field to reproduce these quantum results.

ILLINOIS COAL MODEL PYROLYSIS/LIQUEFACTION SIMULATION

An important step in both pyrolysis and liquefaction is thermolysis to produce lower molecular weigh soluble or volatile components (Snape 1991). Here the S including ReaxFF force field created in the early task was used to evaluate the thermolysis of the Illinois coal model, and coal model variants with higher concentrations of the various S-forms (loading was 80% singular form of the organic S content) for aliphatic, aromatic (S-bound to an aromatic carbon), and thiophenic sulfur forms which along with the original model and a non-S containing model was used in ReaxFF pyrolysis/liquefaction simulations. The computationally intense calculations were performed at a cluster facility using multiple processors for periods of several weeks to obtain picosecond simulation times. High temperatures (2000 K) were used to speed the process. The constructed coal structure was placed into a 130Å cubic simulation box under periodic boundaries conditions. The system was energy minimized using the steepest descent method and equilibrated at a temperature of 300 K for 100 ps using a NVT-MD simulation with a time step of 0.25 fs. The equilibrated system was then subjected to a production run of 200 ps simulation time, where the temperature of the system was ramped up using the Berendsen thermostat (damping constant = 0.1 ps) from 300 to 2000 K at a rate of 800 K/ps. Formation of light gases, tars and char were determined as well as S form evolution, molecular weight distribution and cross-linking through molecular modeling tools.

ILLINOIS CHAR MODEL CONSTRUCTION

The Fringe3D approach (Fernandez-Alos et al. 2011) was applied to generate molecular representations for the graphitic sheets of the char structure based on HRTEM lattice fringe data and constrained by elemental analysis. Image analysis for a HRTEM lattice fringe image of an Illinois No. 6 coal char sample heat-treated at 800°C for 5 min (heating rate: 30°C/min) was used (Sharma, Kyotani and Tomita 2001b). The extracted fringe lengths along with a specific catenation growth were used by Fringe3D to construct graphitic sheets with a range of sizes and shapes were generated in accordance with known coal char chemistry. Limited non-hexagonal rings (5- and 7-membered rings), recognized as important structural features of the char, were distributed randomly throughout the sheets. Incorporation of aliphatic structures was conducted in the form of
hydroaromatic units and cross-linking bridges between graphitic layers until agreement with the desired aromaticity >0.90.

Elemental analysis data for an Illinois No. 6 coal char prepared at 800°C for 5 min (heating rate: 50 °C/min) (Matsuoka et al. 2008) was utilized to further constrain the coal char structural 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 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 (Van Krevelen 1993a; Cai et al. 1993; Solomon et al. 1990). Heteroatoms were incorporated into the graphitic 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, whereas the aliphatic carbon in 5- and 6-membered rings were randomly substituted for heteroatoms to generate furanic, thiophenic and pyrrolic structures, or quaternary nitrogen. A trimming procedure similar to that utilized in previous work (Castro-Marcano et al. 2011) was performed by randomly removing outer aromatic rings from “graphitic” layers until agreement with the experimental atomic H/C and O/C ratios was achieved. Incorporation of heteroatom and aliphatic components was performed using Perl scripts to remove researcher structural bias, improved the accuracy of the structure generated and facilitate the model construction process. The resulting graphitic sheets were assembled into 3D molecular model using the Theodorous and Suter method (Theodorou and Suter 1985) which randomly distributed graphitic layers into a 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 avoid overlapping of the graphitic sheets with the density being gradually adjusted using successive compression and annealing cycles (Dieter Hofmann et al. 2000) Since the structural information employed for char model construction was derived from data sets at different heat treatment conditions, the resulting structural model corresponds to a generic representation for the crystalline portion of a devolatilized Illinois No. 6 coal char.

CHAR OXIDATION/COMBUSTION SIMULATIONS

For the oxidation simulations, the constructed char structure was surrounded with 1500 O₂ molecules in a cubic simulation cell of 120 Å box length under periodic boundaries conditions. The system was minimized using the conjugate gradient method and equilibrated at a temperature of 500 K for 100 ps using a NVT-MD simulation with a time step of 0.1 fs. The temperature was controlled using a Berendsen thermostat (Berendsen et al. 1984) with a 0.1 ps damping constant. The equilibrated system was then subjected to a production run of 250 ps simulation time, in which the temperature of the system was ramped up using the Berendsen thermostat (damping constant = 0.1 ps) from 500 to 4000 K at a rate of 13 K/ps. MD simulations were conducted at two separate temperatures (3000 and 4000 K) to observe char oxidation at constant temperature. ReaxFF simulations were performed at high temperatures to allow the chemical reactions to occur within a reasonable time scale (in the picoseconds range) with the expectation of exhibiting similar mechanisms than experiments. Previous works have showed that initiation mechanisms and kinetics associated with fossil fuel thermolysis processes via high-temperature ReaxFF simulations are in qualitative agreement with experimental data.
(Jiang et al. 2009; Lummen 2010; Salmon et al. 2009; Chenoweth et al. 2009; Wang et al. 2011; Kamat et al. 2010; Agrawalla and van Duin 2011; Chenoweth, van Duin and Goddard 2008). Scripts (Fortran) were created and utilized to follow transitions in 5- and 6-membered rings quantities. Concentrations of oxygen, carbon monoxide, carbon dioxide and water were similarly monitored.

RESULTS AND DISCUSSION

TASK 1. LARGE-SCALE ILLINOIS COAL MODEL GENERATION AND GASIFICATION/COMBUSTION CHAR MODEL GENERATION

The model construction and evaluation are discussed in more detail in the journal article (Castro-Marcano et al. 2011). Figure 1 shows the Illinois coal model molecule distribution (728 cross-linked aromatic clusters) and the generated structure both wet (2,214 water molecules) and dry (with the expected volume contraction). This is the largest molecular representation of coal yet constructed (50,789 atoms) and captures a molecular weight distribution and moves towards capturing a continuum representation.

The chemical evaluation of the coal structure comprised elemental, NMR parameters and molecular weight distribution calculations. The elemental composition, normalized to 100 carbon atoms for the proposed coal model is $C_{100}H_{77.4}O_{9.3}N_{1.5}S_{1.2}$, which compares favorably with $C_{100}H_{77.3}O_{9.4}N_{1.5}S_{1.2}$ (Vorres 1990). A comparison of experimental and model NMR structural parameters is present in Table 1. NMR parameters from the proposed model agree within the experimental uncertainties, with a few exceptions as discussed below. The model carbon aromaticity ($f_{a'} = 0.75$) compares well with the $0.72 \pm 0.04$ determined value by Solum et al. (Solum et al. 1989) using cross-polarization $^{13}$C NMR and with the value of 0.75 reported by Love et al. (Love et al. 1993) using 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 carbons content ($f_{al}$ and $f_{al^+}$) and the carbons associated with oxygen units ($f_{a}^o$ and $f_{al}^o$). During 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.
Figure 1. Molecular model for Illinois No. 6 coal: Flat view of the molecules comprising the model (a) representation including moisture (b) dried-state.

Table 1. NMR Experimental and Illinois coal model data

<table>
<thead>
<tr>
<th>Sample</th>
<th>$f_6$</th>
<th>$f_8$</th>
<th>$f_5^C$</th>
<th>$f_7^H$</th>
<th>$f_5^S$</th>
<th>$f_7^B$</th>
<th>$f_7^R$</th>
<th>$f_9^H$</th>
<th>$f_9^R$</th>
<th>$f_{10}$</th>
<th>$f_{12}$</th>
<th>$f_{13}$</th>
<th>$f_{16}$</th>
<th>$f_{17}$</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>
</tr>
<tr>
<td>Model</td>
<td>0.75</td>
<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>
</tr>
</tbody>
</table>

Parameters: $f_6$ – total of sp$^3$ carbon, $f_8$ – aromatic carbon, $f_5^C$ – carbonyl/carboxyl carbon, $f_7^H$ – protonated aromatic carbon, $f_7^S$ – nonprotonated aromatic carbon, $f_7^B$ – phenolic ethers, $f_7^R$ – alkylated aromatic carbon, $f_9^R$ – aromatic bridgehead carbon, $f_9^H$ – total sp$^3$ carbon, $f_{10}$ – CH or CH$_2$ carbon, $f_{12}$ – CH$_3$ carbon, $f_{13}$ – aliphatic carbon bonded to oxygen, $f_{16}$ – mole fraction of bridgehead carbons, $f_{17}$ – aromatic carbons per cluster, $f_{18}$ – attachments per cluster, $f_{19}$ – bridges and loops per cluster.
The coal model exhibited a broad and continuous molecular weight distribution ranging from 100 to 2,850 amu with a sharp peak around 350 – 400 amu. The corresponding Mn and Mw values were 522 and 861 amu, 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, a significant improvement over other coal model construction approaches. Herod et al. (Herod et al. 1994) characterized the Argonne Premium coals by matrix-assisted LDIMS and Illinois No. 6 coal spectra showed a sharp peak around 230 – 400 mass range followed by another series of smaller peak in the 1,500 – 5,000 mass range. The shape of both model and experimental molecular weight distribution are similar.

Theoretical solvent extraction yield calculations were performed to evaluate the capability of the coal model in predicting behavioral observations (Van Niekerk and Mathews 2010b). Solubility parameters were used to estimate the mass fraction of the coal model that could be theoretically extracted by a specific solvent. Pyridine extraction calculations on 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 1,600 amu, in contrast to mass spectra observations (Fletcher et al. 1993; Carlson et al. 1992; Malhotra et al. 1991). Painter et al. (Painter et al. 1990) indicated that calculated δ values exhibited errors of ±0.6 (cal/cm³)⁰.⁵ and thus should be regarded as an initial estimate for solubility parameters. Therefore, a redistribution of phenolic groups was performed on these molecules to make them less soluble to better agree with FT-ICR data (Wu et al. 2004). 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 (Derbyshire et al. 1989). Comparison between elemental composition, molecular weight, compound class, and double bond equivalency between the FT-ICR data for pyridine soluble extract and predicted soluble model cut was in good agreement demonstrating progress towards capturing a continuum representation. The physical structure of the coal model was characterized in terms of simulated helium density, pore size distribution and volume shrinkage. 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) (Huang et al. 1995).

Similarly, a devolatilized Illinois coal char was constructed and is shown in Figure 2. Char structure is typically highly aromatic (aromaticities of >0.90) and exhibits various
Figure 2. Graphitic sheets generated by Fringe3D and Perl scripts and char structural model for crystalline regions of a devolatilized Illinois No. 6 coal char composed of 6993 atoms within 66 polyaromatic layers. Atoms are represented by van der Waals spheres.
degrees of turbostratic crystalline order (stacking, layer size and interlayer spacing), pore size distributions, surface area, and atomic H/C ratio (Kulaots et al. 2007; Lu et al. 2000; Matsuoka et al. 2008; Davis et al. 1995). These structural variations affect char reactivity in subsequent utilization processes such as char oxidation and combustion (Cai et al. 1996; Hurt 1993; Alonso et al. 2001; Liu and Niksa 2004; Solomon et al. 1992). During char oxidation, the structure anneals forming a more ordered and more aromatic structure that is less reactive (Solomon et al. 1993). Chemical evaluation of the char model included elemental composition, aromaticity and molecular weight distribution; physical evaluation comprised simulated helium density, pair correlation function, and turbostratic crystalline dimensions with good agreement.

The char molecular model exhibited a molecular weight distribution ranging from 240 to 3250 Da with a peak at ~250 – 500 Da, and calculated values for number and weight average molecular weights of 985 and 1504 Da, respectively. The elemental composition, normalized to 1000 carbon atoms for the char structural model was C_{1000}H_{264}O_{23}N_{10}S_{0.2}, in reasonable agreement with the experimental value of C_{1000}H_{252}O_{24}N_{11}S_{0.1} (Matsuoka et al. 2008). The char model exhibited an aromaticity value of 0.96 in accordance with experimental data for devolatilized coal chars (Pugmire et al. 1991; Lu, Sahajwalla and Harris 2000). The physical structure of the char model was characterized in terms of several analytical parameters. The simulated helium density of the char model was 1.72 g/cm^3, in reasonable agreement with the expected value (Van Krevelen 1993b; Jones et al. 1999). The average interlayer spacing was ~3.8 Å, consistent with XRD data (Davis et al. 1995) and the fourth peak of the total g(r) function (atom pair correlation) located at ~3.8 Å. The stacking number distribution indicated that the majority of polyaromatic layers are either singly or forming 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 (Sharma, Kyotani and Tomita 2001a) and XRD (Davis et al. 1995) analyses.

**TASK 2. REAXFF FORCE FIELD TRAINING**

Figure 3 shows a selection of the compounds used to optimize the ReaxFF C/S, H/S and S/S parameters. These compounds were chosen to represent the sulfur-containing functional groups encountered in coal. As described in the Methods-section, we performed bond dissociation, angle and dihedral distortion and hydrogenation reaction simulations on these compounds, using DFT at the B3LYP/6-311G**++-level of theory, and used this DFT-based training set to derive ReaxFF parameters.

![Figure 3. Examples of compounds included in the ReaxFF training set for S/C/H compounds.](image-url)
There was excellent agreement between ReaxFF and DFT for the bond-dissociation, angular distortion and rotational barrier analysis, indicating that ReaxFF can describe the single, double, and aromatic bond energies associated with sulfur-functionalized hydrocarbons. Figure 4 shows the hydrogenation reaction energies for a series of coal-relevant C/S/H compounds, indicating that ReaxFF gives an accurate description (generally within 5 kcal/mol of the DFT results) of these reaction energies, which are relevant to pyrolysis reactions.

![Figure 4. ReaxFF- and DFT hydrogenation energies for a range of coal-relevant sulfur-substituted hydrocarbon compounds.](image)

Figure 5 shows the ReaxFF and DFT- reaction energies and reaction barriers for three reactions relevant to sulfur-initiated pyrolysis events, including hydrogen transfer, sulfur insertion and hydrogen removal. For all these reactions and barriers we found good agreement between ReaxFF and DFT, indicating that ReaxFF can not only reproduce the reaction products but also the reaction kinetics associated with pyrolysis events.
Figure 5. Sulfur radical reaction energies via quantum and reaxFF calculations. a) Internal hydrogen transfer in a C₂H₅S molecule. b) Aromatic ring attack/insertion by a sulfur radical. c) Methyl-radical removing a hydrogen from H₂S to become methane plus an HS radical.

TASK 3. COAL PYROLYSIS/LIQUEFACTION SIMULATIONS
The constructed Illinois coal model along with its model variants containing high concentration of sulfur forms (aliphatic, thiophenic, aromatic and a variant without sulfur) were used to perform pyrolysis simulations using ReaxFF to examine the effect of sulfur forms on the Illinois coal pyrolysis. High-temperature (2000 K) simulations were
conducted to allow the chemical reactions to occur within a reasonable time scale (in the picoseconds range). During the first 100 ps of these pyrolysis simulations, small molecules were observed to be released from the coal structure representing light gases followed by a molecular fragmentation resulting in larger molecules to be formed (tar). The distribution of the major light gases and tar products observed are showed in Figure 6. As seen, the concentration of pyrolysis products increases as the simulation progresses with H₂O, H₂, and light oxygenated hydrocarbons as the most abundant pyrolysis products for all cases. The coal model containing high content of aliphatic S form exhibited the highest concentrations for H₂S and light sulfurated hydrocarbons mainly since aliphatic sulfurs (aryl-CH₂-S-CH₂-aryl) are expected to cleave first during thermolysis process, leaving sulfur atoms exposed to react with hydrogen and small hydrocarbon radicals. The corresponding coal models for aromatic and thiophenic S functionalities showed lower concentrations of sulfurated compounds as these S forms are less likely to break at the initial stages of the simulated pyrolysis.

Molecular weight distributions as a function of time were determined for all coal models. All coal models initially exhibited molecular weight distributions ranging from 100 to 2850 Da with sharp peaks at ~350-400 Da. However, at 50 and 100 ps all model molecular weight distributions were more narrow and shifted toward lower mass ranges in accordance with the molecular fragmentation occurring as pyrolysis simulation progresses. Specifically, several small peaks appeared at molecular weight values of ~50-200 Da along with a decrease in the intensity of 350-400 Da peaks. For all coal models, molecular fragments with molecular masses >2100 and >1700 Da were not observed at 50 and 100 ps, respectively.

Figure 6. Distribution of light gases and tar products obtained from ReaxFF pyrolysis simulations on original, aliphatic, aromatic, thiophenic, and without sulfur forms coal models.
TASK 4. COAL CHAR COMBUSTION SIMULATIONS
Two constant temperature runs at 3000 and 4000 K were conducted on the char model surrounded by 1500 O₂ molecules. To study the rate of oxidation, concentrations of oxygen, carbon monoxide, carbon dioxide and water were monitored during both temperature runs. Figure 8 shows that, at 3000 K, the rate of oxidation of char is almost linear, as is evident from the rate of decrease of the O₂ concentration, as well as increase in the concentrations of stable combustion products such as water, carbon monoxide and carbon dioxide. This can be contrasted with oxidation at 4000 K (Figure 7), where the rate of decrease of O₂ is much steeper and water and carbon dioxide concentrations reach a maximum value before trailing off to zero. At 4000 K, combustion is accelerated due to the higher temperature. However, these combustion products are not stable (except for CO, which is more stable than CO₂ at such a high temperature) and disintegrate into smaller molecules.

![Figure 7. Concentration of reactants and products of char oxidation at 3000 and 4000 K.](image)

To better understand the chemistry of aromatic rings in char during oxidative pyrolysis, a FORTRAN script was written to track the evolution of the number of 5 and 6 member rings in the char structure as a function of time. This allowed the comparison of the stability of 5 and 6 member rings at two different temperatures. As seen in Figure 8, at 3000 K, the number of 6-member rings steadily decreases to about 50 % of its original value in 0.25 nanoseconds. The number of 5-member rings, however, exhibits a maximum value before decreasing to its initial value. This is due to 6-member rings decomposing to form 5-member rings; however after this initial surge the 5-member rings begin decomposing. No such trend is seen at 4000 K (Figure 8), wherein both 5 and 6 member rings rapidly decompose possibly into smaller aliphatic molecules.
CONCLUSION AND RECOMMENDATIONS

A review of the structural information available for the Argonne premium Illinois no. 6 coal was generated covering a wide variety of chemical and physical evaluations. A large-scale (50,000 atom) structural representation of Illinois no. 6 coal was generated, with highly efficient automated approach. The atomistic representation was used to demonstrate utility in exploring coal transformations. Sulfur functional groups relevant to coals were included in the ReaxFF reactive force field and thermolysis was explored with the original coal model, with various higher concentrations of the different sulfur forms and in a structure without sulfur. The presence of S-forms increased the rate of formation and quantity of light gases produced while retarding the extent and rate of tars (defined as molecular weights in the 100 to 700 Da range). Such explorations have utility in coal liquefaction and coal pyrolysis. This coal model and the S-inclusive variant of ReaxFF will be made available to the international ReaxFF community. It is expected that the availability of a large-scale and accurate representation of Illinois coal will initiate its use in other simulations by other institutions and lead to a better understanding of Illinois coal structure and behavior. The S-inclusive ReaxFF variant will also lead to a better understanding of sulfur chemistry and, eventually, a better position for the effective use of Illinois coal.

An Illinois coal char model was also developed (~7000 atoms) and used to explore the oxidation and combustion process. During oxidation, the reactive sites become oxygenated and ring opening occurs often followed by reorganization into a 5-membered ring. The frequency of 6-membered aromatic rings reduces with increasing iterations (or time steps) due to the molecular fragmentation associated with the thermal decomposition at high-temperature (4000 K) simulation of char oxidation. The char construction approach and transitional chemistry can now be followed with computational simulations thus gasification and combustion can be better explored.

Molecular modeling improvements in construction protocols and in reactive simulations has better positioned coal and char chemistries to be explored and utilized. Coupling the current ReaxFF-methodology with realistic Illinois coal and char models, constructed
based on available experimental data, will improve the design strategies for coal utilization. New approaches were utilized to rapidly generate an Illinois no. 6 coal model and char model with relative ease. The new construction protocols were demonstrated producing structures with good agreement with a wide variety of chemical and physical analyses. They were successfully utilized in ReaxFF simulations to examine coal thermolysis (pyrolysis/liquefaction) and char oxidation and combustion.

REFERENCES


Mathews, J. P., V. Fernandez-Also, A. D. Jones, and H. H. Schobert. "Determining the Molecular Weight Distribution of Pocahontas No. 3 Low-Volatile Bituminous


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