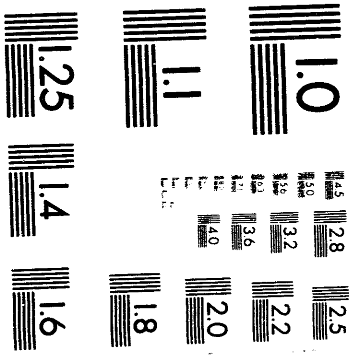
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APPLICATIONS OF MOLECULAR MODELING IN COAL RESEARCH

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Over the past several years, molecular modeling has been applied to study various characteristics of coal molecular structures. Powerful workstations coupled with molecular force-field-based software packages have been used to study coal and coal-related molecules. Early work involved determination of the minimum-energy three-dimensional conformations of various published coal structures (Given, Wiser, Solomon and Shinn), and the dominant role of van der Waals and hydrogen bonding forces in defining the energy-minimized structures. These studies have been extended to explore various physical properties of coal structures, including density, microporosity, surface area, and fractal dimension. Other studies have related structural characteristics to cross-link density and have explored small molecule interactions with coal. Finally, recent studies using a structural elucidation (molecular builder) technique have constructed statistically diverse coal structures based on quantitative and qualitative data on coal and its decomposition products. This technique is also being applied to study coalification processes based on postulated coalification chemistry.

The three-dimensional molecular structure of coal is of considerable interest because of the relationship between structure and reactivity (especially as related to coal liquefaction). Recently, a new technique, computer-aided molecular design (CAMD), or computer-aided molecular modeling (hereafter called simply molecular modeling), has been developed and used to study the structural characteristics of complex molecular systems (1). Initially used to aid in the design of pharmaceutical molecules, the technique is now being applied in many fields such as biochemistry, materials science, polymer science, and fuel science. In the area of coal research, molecular modeling has been used to study coal and coal-related molecules and the interactions of coal with solvents and other molecular species. This paper reviews the use of the molecular modeling technique for this latter application.

The molecular modeling methods used for most coal-related studies are molecular mechanics and molecular dynamics calculations. These use a classical force field approximation to simulate the interactions of atoms within and between molecules (2). With these techniques, the minimum-energy three-dimensional structures of molecules can be determined, as well as a number of other physical properties. There are a number of commercial software packages that include energy-minimization capabilities based on force field calculations, coupled with graphical interfaces for visualization of molecules in three dimensions. These packages are described in the various papers that form the basis for this review, and will not be discussed in more detail here.

The earliest use of molecular modeling for fossil fuel applications that the authors are aware of was a structural elucidation study by Oka, Chang and Gavalas in the 1970s directed at coal-derived compounds (3). Their method used analytical data to determine appropriate combinations of structural groups that were then combined to build molecules. Ten years later, Robinson published a study of heavy coal liquids (4), in which the three-dimensional structures were explored but not the energetics. Soon after, Faulon and coworkers (5) constructed molecular representations of kerogen macromolecules, utilizing a structural elucidation technique to build the macromolecules.

The first use of molecular modeling to study coal structures was by Carlson and Granoff (6, 7), who studied a series of previously-postulated bituminous coal structures (Given, Wiser, Solomon and Shinn) and compared their minimum energy structures, physical densities and hydrogen bond interactions. Good agreement with experimental data was obtained for density and hydrogen bonding. Carlson also explored the specific interactions that define the tertiary structure of coal (hydrogen bonding and van der Waals interactions), finding that the much weaker (but ubiquitous) van der Waals interactions actually dominated the energy-minimization driving force for coals of bituminous rank (8, 9). A method of calculating porosities as well as physical densities from the computer modeling data utilizing a grid system was presented (9), and microporosities were determined for the coal structures studied.

Carlson also addressed the concept of coal as a three-dimensionally cross-linked (network) solid, attempting to compare results with the experimental and theoretical relationships found between coal cross-link density and degree of solvent swelling (10). Previous coal molecular models (Given, Shinn, etc.) did not include cross-linking explicitly. In unpublished work (11), Carlson found that structures constructed with widely-varying cross-link densities showed no significant variations in energy, physical density or microporosity, suggesting that cross-links were not important sources of rigidity in coal structures.

In 1992, Faulon *et al.* published an extension of his original molecular builder program (12), and applied the method to build representative structures for vitrinite from bituminous coal (13, 14). In this work, the analytical data on which the structures were based were derived from elemental analysis, NMR studies and flash pyrolysis/gc/ms data from coalified wood of bituminous rank. It was found that constraints had to be introduced into the builder program to develop models with reasonable energy and physical properties (the builder had to be constrained to generate models with the maximum number of new five and six membered rings--i.e., hydroaromatic structures); otherwise, the energies were much too high, and the degree of cross-linking was excessive. In extensions of this work (15, 16), Faulon *et al.* showed that, although the number of possible coal structures that could be generated from analytical data was very high (over 300,000 for a structure of 650 total atoms), a statistical sampling of 15 structures was sufficient to provide representative results for vitrinite macerals of bituminous coal. Minimized energies, physical densities and micropore volumes for the 15 structures were essentially the same, within the statistical uncertainty. Since the cross-link densities of the 15 structures varied ten-fold, but the physical characteristics of the structures did not appreciably change, these results confirmed the previous observations by Carlson (11) that cross-link density is not a strong driver for rigidity in coal structures.

Faulon and coworkers have extended the post-modeling analysis of three-dimensional coal molecular structures, exploring porosity, surface area and fractal dimension at a molecular level for vitrinite maceral models. Results consistent with experimental measurements of microporosity and CO_2 and N_2 surface areas have been obtained. Additionally, fractal dimensions of 2.7 for coal structures, in agreement with experiment, were observed (17).

Hatcher and Faulon have also used the builder methodology to study the coalification process (18), beginning with a lignin structure and proceeding stepwise through brown coal, to lignite coal, to subbituminous coal and finally to bituminous coal structure. At each step appropriate chemical transformations of the molecular structure were used and computer results were matched to experimental data. In this study and a more extensive companion study (19), it was determined that the most probable tertiary structure for lignin in wood, as well as for isolated lignin following degradation of the cellulosic component of wood, is a helical structure.

Recently, Nakamura, Murata *et al.*, have developed a new method to simulate the physical density of coal structures using molecular modeling (20-22). The method, which involves utilizing the periodic boundary conditions available in certain modeling packages, allows a coal macromolecule to be replicated in adjacent physical locations and thus to interact with its replicates. By shrinking the size of the periodic boundaries, it is possible to estimate the optimal packing arrangement for the structure, and from this, the density. The technique has been used to study model polymers and simulated structures of four Japanese coals of varying carbon content (72-87%). The densities determined for the coal structures to date are somewhat lower (4-20%) than experimental values. For one of the coals, several structural modifications were made in the links between molecular clusters and the effects on density determined (23). In contrast to the studies referenced earlier, cross-linked structures were found to have a significant influence (reduction of ~10%) on density.

Takanohashi *et al.* have investigated the association of coal soluble constituents using molecular modeling (24). Molecules typical of pyridine soluble and pyridine insoluble fractions were simulated and found to form relatively stable three-dimensional structures, held together by non-covalent interactions, perhaps similar to the structures and interactions in the parent coal.

Kumagai and coworkers have studied the interactions of a lignite molecular model with water molecules (25). By adding water to the lignite structure before and after energy minimization, they were able to simulate the native coal-water interactions as well as the heat of desorption of water from the lignite and the tendency of the lignite structures not to reverse the conformational changes that occurred upon drying.

In other rather different applications of molecular modeling, Vorpagel and Lavin utilized molecular mechanics calculations to explore the most stable geometric arrangements of associated polynuclear aromatic hydrocarbons (26). These studies, with a focus on the behavior of pitches, could have relevance to the stacking of polynuclear aromatic structures within coal structures as well. In another study, Budzinski *et al.* modeled the enthalpies of formation of alkylnaphthalenes using several modeling methods (27). These results are cited because of the similarity of the studied molecules to components of coal structure. Finally, as the power of available computers grows, the application of semi-empirical and even quantum mechanical methods to coal research has become more practical. For example, Ades and coworkers have recently used a molecular orbital method to study cleavage mechanisms of model compounds related to direct coal liquefaction (28). Currently, Li *et al.* are studying small molecule adsorption on nanocluster metal catalysts utilizing density functional quantum mechanical methods adapted to massively parallel computers (29). It appears likely that within the next few years, significant advances in catalysis modeling will be made utilizing these powerful new techniques.

In summary, molecular modeling has become a valuable technique for the investigation of the three-dimensional conformations and physical properties of coal molecular structures, coal-small molecule interactions and coal soluble constituents. Modeling results generally agree with experimental results, and provide additional insight beyond that from experiments alone. With the advent of new high-speed massively parallel computers, it will be possible to model significantly larger macromolecular structures, as well as to begin to utilize quantum chemical methods more effectively.

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