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Title: Applications Of Molecular Modeling To The Design And Characterization Of Materials

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ABSTRACT

A variety of new molecular modeling tools are now available for studying molecular structures and molecular interactions, for building molecular structures from simple components using analytical data, and for studying the relationship of molecular structure to the energy of bonding and non-bonding interactions. These are proving quite valuable in characterizing molecular structures and intermolecular interactions and in designing new molecules. In this paper, we will describe the application of molecular modeling techniques to a variety of materials problems, including the probable molecular structures of coals, lignins, and hybrid inorganic-organic systems (silsesquioxanes), the intercalation of small gas molecules in fullerene crystals, the diffusion of gas molecules through membranes, and the design, structure and function of biomimetic and nanocluster catalysts.

INTRODUCTION

A new technique, computer-aided molecular design (CAMD), or computer-aided molecular modeling (hereafter called simply molecular modeling), has recently been developed for studying the structural characteristics of complex molecular systems (Bajorath *et al.*, 1991). Initially used 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. This paper reviews the use of the molecular modeling technique for a number of diverse applications.

The methods used for most of these 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 (Fruhbeis, Klein and Wallmeir, 1987). With these techniques, the minimum-energy three-dimensional structures of molecules can be determined, as well as a number of

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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 referenced herein, and will not be discussed in more detail here.

Our earliest use of molecular modeling was for the design of biomimetic (biological mimic) catalysts (Shelnutt, 1989). Some enzymes, which are naturally-occurring catalysts, contain metalloporphyrins as the specific catalytic sites within a complex, rigid macromolecular structure. We have used molecular modeling to design metalloporphyrin-based catalysts that are much simpler than enzymes, but that maintain the desirable features of the enzymes. Figure 1 shows a metalloporphyrin that has been designed to have catalytic activity for CO_2 reduction. The porphyrin is sterically crowded, forming a binding pocket to hold the CO_2 in place near the catalytic metal center. Additionally, the peripheral substituents have been designed to have appropriate surface properties (partial charge, etc.) to enhance catalytic activity.

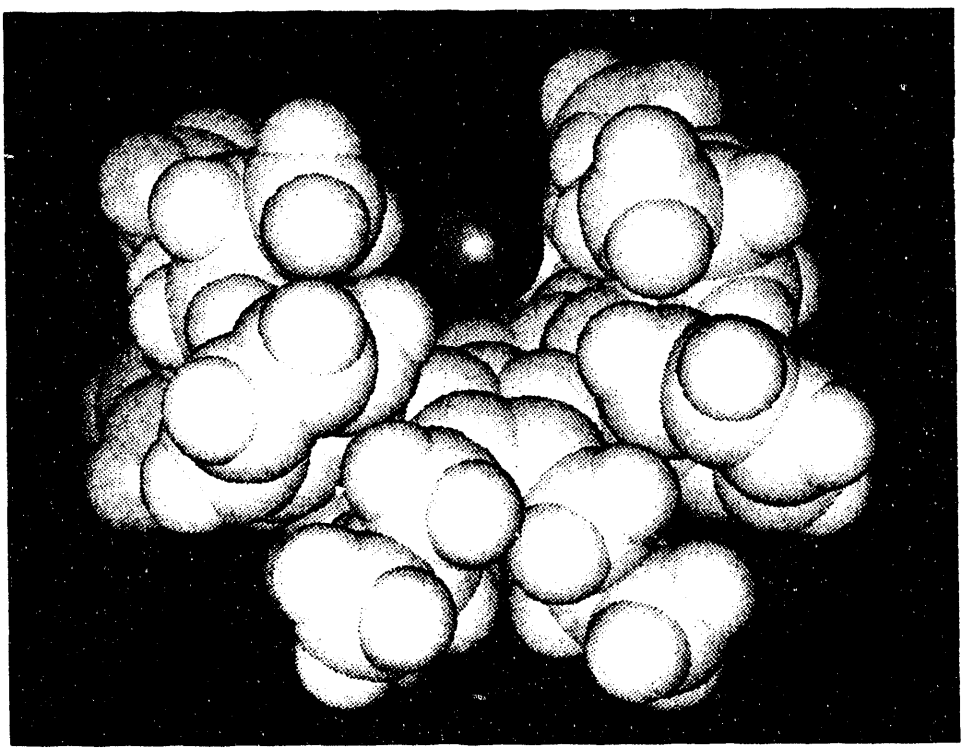

Figure 1. Solid-filled representation of a nickel octaethyltetraphenyl porphyrin. The molecule contains a binding pocket (groove) created by steric crowding of the peripheral groups. A CO_2 molecule is shown in the binding pocket, where the catalytic reaction will take place.

Tests have shown that the synthesized catalysts in fact do have the geometry indicated by the computer models, and that they show catalytic activity enhancements as predicted.

We have used molecular modeling extensively to study coal and related macromolecules. Initially, we studied a series of previously-postulated bituminous coal structures (Given, Wiser, Solomon and Shinn models) and compared their minimum energy structures, physical densities and hydrogen bond interactions (Carlson and Granoff, 1989, 1991). Good agreement with experimental data was obtained for density and hydrogen bonding. We 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 (Carlson, 1991, 1992). Figure 2 shows the Shinn macromolecular structure as it was input to the computer, and then after treatment by molecular dynamics and energy minimization. The folding of the structure into a quasi-three-dimensional solid is apparent after minimization.

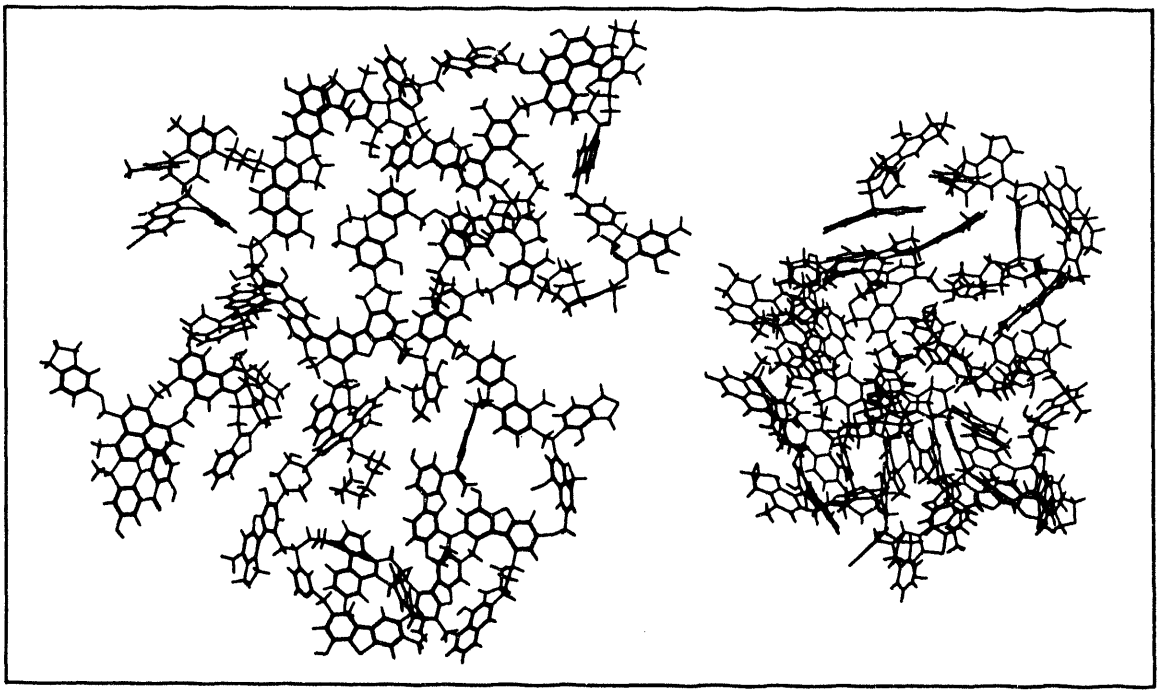

Figure 2. Computer model of bituminous coal structure after Shinn. On the left, the structure as input to the computer is roughly planar. On the right, after 40 ps of molecular dynamics and energy minimization, the structure has folded into a three-dimensional form.

We have also developed a unique macromolecular builder routine, the SIGNATURE program, that creates molecules based on quantitative and qualitative experimental data (atomic composition, NMR analysis, gc/ms pyrolysis fragments, etc.) and specific rules of bond formation. This program has been used in the study of statistical samples of coal structure (Faulon, Carlson and Hatcher, 1993). Other studies related to coal structure include studies of the

structure of lignin, one of the main constituents of vascular plants, and also the precursor to coal (Faulon, Carlson and Hatcher, 1994). In these studies, a model of lignin was constructed based on the known concentrations of the lignin building blocks that are present in wood. When the model was subjected to molecular dynamics calculations, an alpha-helical structure resulted. Figure 3 shows an initially linear lignin molecular fragment as it folds in response to the intramolecular forces, and finally forms a tightly-coiled alpha-helical structure. This ordered structure had not been postulated previously; in fact, it was always assumed that lignin in wood had a random structure. Experimental studies are now underway to compare with the calculated molecular model of lignin.

Figure 3. Lignin structure. As originally input (left), the molecule is relatively linear. As molecular dynamics calculations are performed, the molecule begins to fold (center two figures), finally reaching a fully-collapsed, alpha-helical structure as the minimum energy conformation.

We have also used molecular modeling to study the coalification process (Hatcher, Wenzel and Faulon, 1993). By starting with a lignocellulose (wood) model and applying appropriate degradation chemistry supplemented by NMR data on coals of various maturities, we have been able to determine the effect of maturation on the tertiary structure of the coal macromolecules. Interestingly, as shown in Figure 4, the original structure of the lignin is preserved during initial stages of coalification (center image, lignite coal), and is only substantially lost in more mature (bituminous) coal structures. This is in agreement with experimental observations of microscopic coal particles, which often show residual plant structures.

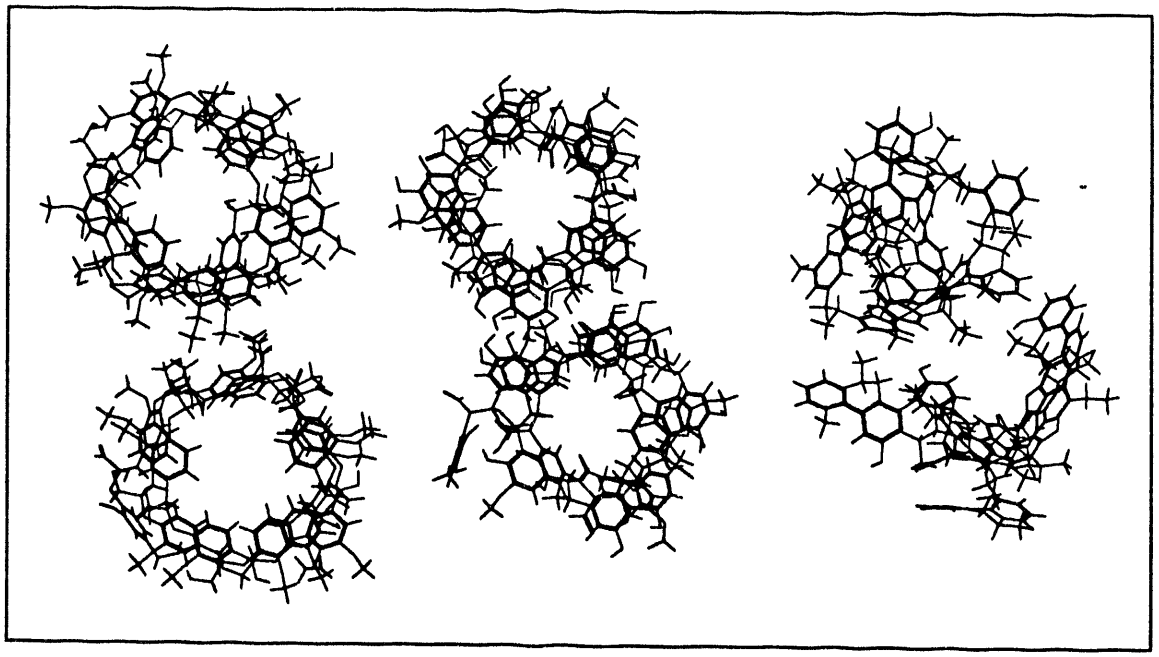

Figure 4. Molecular modeling of the coalification process. At the left is a lignin structure, similar to that which might result from plant decomposition. The center image is a structure of lignite, a low-rank coal, reached by modifying the lignin structure using appropriate decomposition chemistry. The image on the right represents bituminous coal, the structure obtained once again by applying appropriate coalification chemistry to the previous structure.

In other applications of molecular modeling, we are studying the structure and properties of porous materials. Figure 5 shows the structure of imogolite, an inorganic crystalline material whose structure is related to zeolites. The image is of a periodic system, based on crystal structure, with a full cylindrical structure shown in vector form in the central part of the figure, and partial repeat units of the cylindrical structure at the four corners. We are using the computer models to study diffusion of small molecules within the cylindrical pores. We have also developed a method to image the porosity in the structure, as shown by the cylindrical arrays of spheres inside the imogolite pore structure. This method also enables the determination of surface area and fractal dimension of molecular models, a technique that has also been applied to coal structures (Faulon *et al.*, 1994).

Figure 6 shows another application, the determination of structure of an engineered porous material, triphenylene-bridged polysilsesquioxane (Faulon *et al.*, unpublished data). This hybrid inorganic-organic material is observed experimentally to consist of aggregated particles that exhibit high surface area (~250-1000 m^2/g) and microporosity. Our molecular models, constructed to match the known composition of the materials, provided microstructure with surface area and porosity that agree with the experimental findings. Extrapolations of these models to different organic bridging groups will allow us to design novel materials.

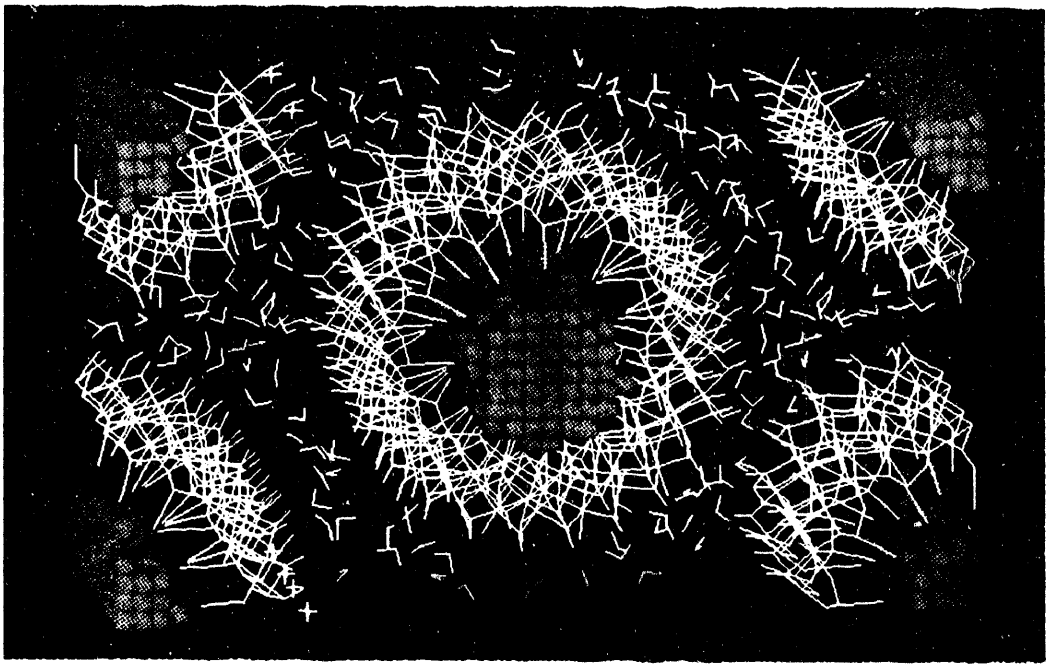

Figure 5. Imogolite, a crystalline inorganic material, displayed as a periodic system. A full crystalline representation can be constructed by combining several units of the periodic structure. Also shown is a representation of cylindrical porosity in the imogolite, shown as solid balls filling the pore volumes.

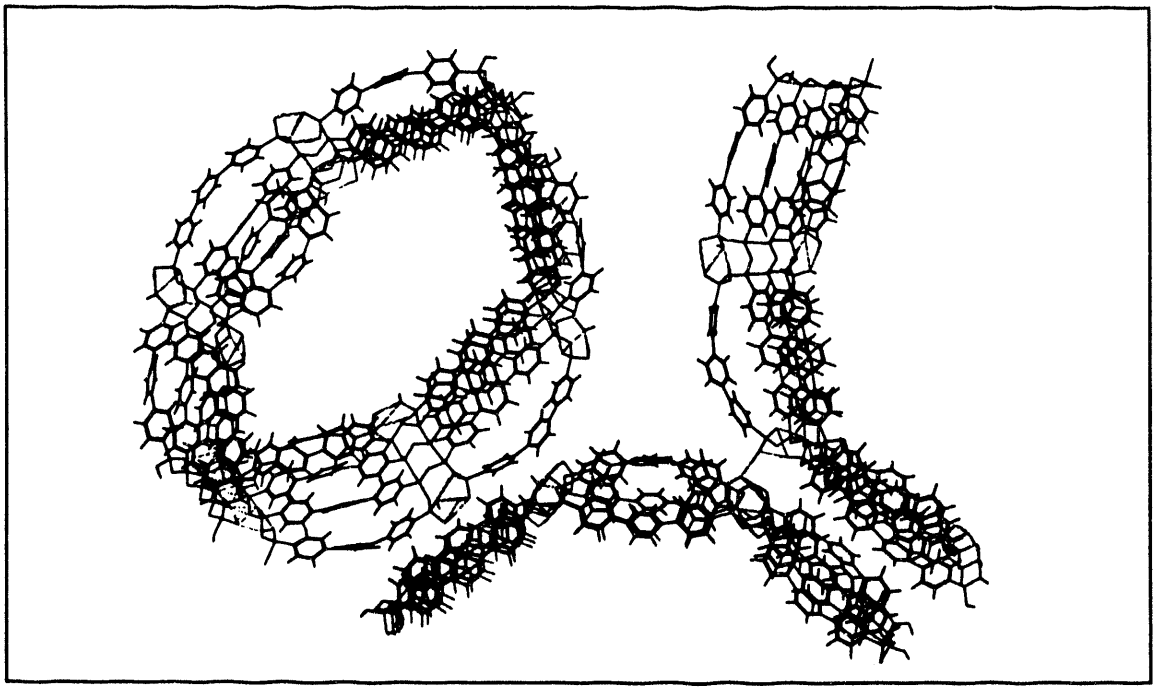

Figure 6. Molecular modeling of an engineered porous material, triphenylene-bridged polysilsesquioxane. The models showed a complex mesostructure with high surface area and significant porosity, in agreement with experimental results.

In a final application of molecular modeling, Figure 7 shows a buckminsterfullerene crystal containing oxygen molecules in interstitial octahedral sites. Experimental NMR evidence had shown up to six O_2 molecules coordinated with each C_{60} molecule. The molecular models were helpful in confirming that O_2 would fit comfortably in the six octahedral sites associated with each C_{60} but not in the four smaller tetrahedral sites in the C_{60} crystals (Assink *et al.*, 1992).

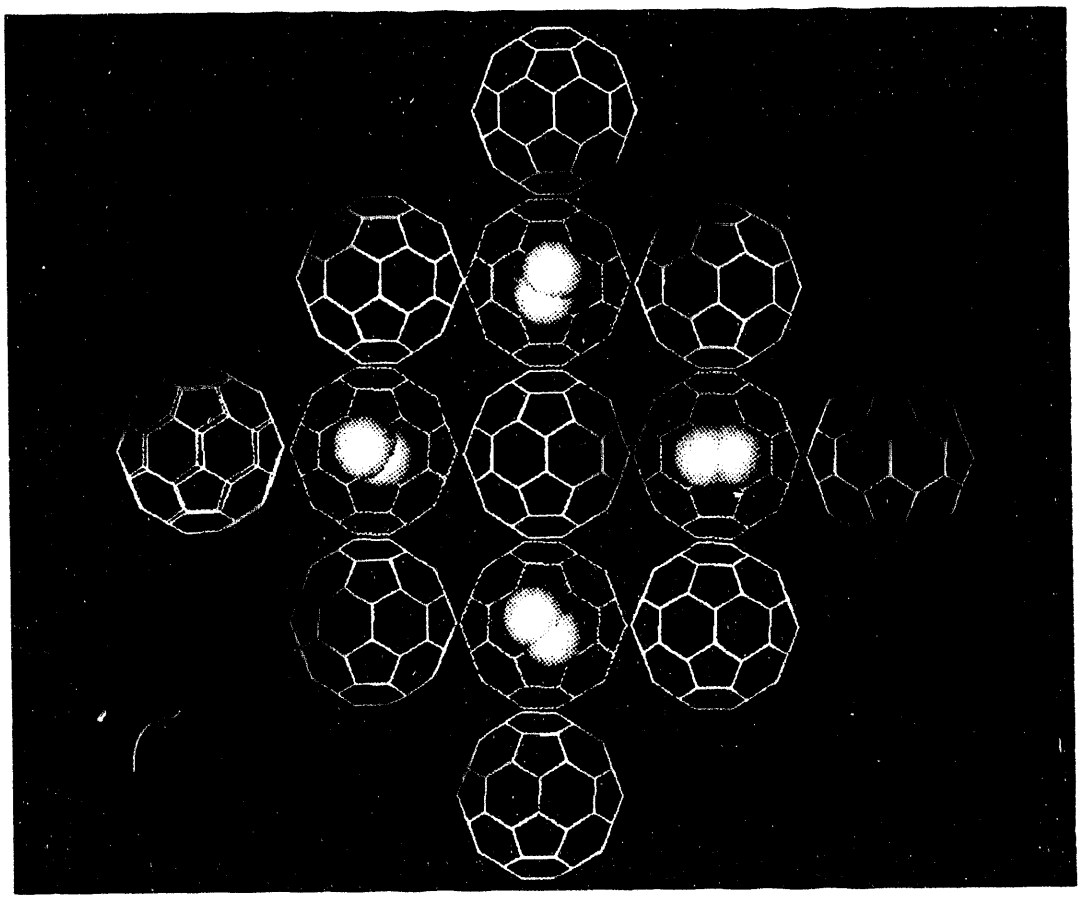

Figure 7. Buckminsterfullerene crystal, shown with oxygen in octahedral sites in the crystal lattice.

In summary, molecular modeling has become a valuable technique for the investigation of the three-dimensional conformations and physical properties of a wide variety of molecular structures, for molecular design and for intermolecular interactions. Modeling results generally have agreed well with experimental results, and often provided additional insight beyond that from experiments alone. With the recent availability of new high-speed massively parallel computers, it will soon be possible to model significantly larger macromolecular structures, as well as to begin to utilize quantum chemical methods more effectively.

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References

Assink, R. A., Schirber, J. E., Loy, D. A., Morosin, B., Carlson, G. A., *J. Mater. Res.* **1992**, *7*, 2136-2143.

Bajorath, J.; Kraut, J.; Li, Z.; Kitson, D. H.; Hagler, A. T., *Proc. Natl. Acad. Sci.* **1991**, *88*, 6423-6426.

Carlson, G. A.; Granoff, B., *Am. Chem. Soc. Div. Fuel Chem. Preprints* **1989**, *34(3)*, 780-786.

Carlson, G. A.; Granoff, B., "Modeling of Coal Structure Using Computer-Aided Molecular Design," Coal Science II, Ed. H. H. Schobert, K. D. Bartle and L. J. Lynch, *ACS Symposium Series* **1991**, *461*, 159-170.

Carlson, G. A., *Am. Chem. Soc. Div. Fuel Chem. Preprints* **1991**, *36(1)*, 398-404.

Carlson, G. A., *Energy and Fuels* **1992**, *6*, 771-778.

Faulon, J. L.; Carlson, G. A.; Hatcher, P. G, *Energy and Fuels* **1993**, *7*, 1062-1072.

Faulon, J. L.; Mathews, J. P.; Carlson, G. A.; Hatcher, P. G, *Energy and Fuels* **1994**, *8*, 408-414.

Faulon, J. L.; Carlson, G. A.; Hatcher, P. G., "A Three-Dimensional Model for Lignocellulose," accepted for publication in Organic Geochemistry (1994).

Fruhbeis, H.; Klein, R.; Wallmeir, H., *Angew. Chem. Intl. Ed. Engl.* **1987**, *26*, 403-418.

Hatcher, P. G.; Wenzel, K. A.; Faulon, J. L.,. *Am. Chem. Soc. Div. Fuel Chem. Preprints* **1993**, *38(4)*, 1270-1274.

Shelnutt, J. A., "Photochemically-Driven Biomimetic Oxidation of Alkanes and Olefins," *Am. Chem. Soc. Div. Fuel Chem. Preprints* **1989**, *34*, 1402.

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