STRUCTURE-BASED PREDICTIVE MODEL FOR COAL CHAR COMBUSTION

**Quarterly Technical Progress Report
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Principal Investigators:

**Robert Hurt
J.M. Calo**

**Brown University
Brown University**

**Robert Essenhight
Christopher Hadad**

**Ohio State University
Ohio State University**

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**Submitted by: Brown University
Division of Engineering, Box D
Providence, RI 02912**

**Ohio State University
Department of Mechanical Engineering and
Department of Chemistry
206 W. 18th Ave.
Columbus, OH 43210-1107**

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EXECUTIVE SUMMARY

During the past quarter of this project, significant progress continued was made on both major technical tasks.

Progress was made at OSU on advancing the application of computational chemistry to oxidative attack on model polyaromatic hydrocarbons (PAHs) and graphitic structures. This work is directed at the application of quantitative *ab initio* molecular orbital theory to address the decomposition products and mechanisms of coal char reactivity. Previously, it was shown that the “hybrid” B3LYP method can be used to provide quantitative information concerning the stability of the corresponding radicals that arise by hydrogen atom abstraction from monocyclic aromatic rings. In the most recent quarter, these approaches have been extended to larger carbocyclic ring systems, such as coronene, in order to compare the properties of a large carbonaceous PAH to that of the smaller, monocyclic aromatic systems. It was concluded that, at least for bond dissociation energy considerations, the properties of the large PAHs can be modeled reasonably well by smaller systems. In addition to the preceding work, investigations were initiated on the interaction of selected radicals in the “radical pool” with the different types of aromatic structures. In particular, the different pathways for addition *vs.* abstraction to benzene and furan by H and OH radicals were examined. Thus far, the addition channel appears to be significantly favored over abstraction on both kinetic and thermochemical grounds.

Experimental work at Brown University in support of the development of predictive structural models of coal char combustion was focused on elucidating the role of coal mineral matter impurities on reactivity. An “inverse” approach was used where a carbon material was doped with coal mineral matter. The carbon material was derived from a high carbon content fly ash (Fly Ash 23 from the Salem Basin Power Plant. The ash was obtained from Pittsburgh #8 coal (PSOC 1451). Doped samples were then burned in a high temperature flame reactor fitted with rapid quench extractive sampling. It was found that the specific reaction rate *decreased* with increasing ash content by about an order of magnitude over the ash content range investigated. In this case, it was concluded that at least one of the primary reasons for the resultant observation was that an increasing amount of carbon becomes inaccessible to oxygen by being covered with a fused, “protective,” ash layer.

Progress continued on equipment modification and testing for the combustion experiments with widely varying flame types at OSU.

PROJECT DESCRIPTION

The problem of excessive unburned carbon in fly ash could be better managed if designers and users of combustion systems could determine the reactivity of a given char from basic coal properties, avoiding the need to resort to expensive full-scale testing. Establishing a mechanistic link between coal properties and fuel behavior has long been a goal of the coal research community, as such a capability would find numerous uses in predictive tools and optimization tools for coal technologies. Such a predictive capability will not likely be achieved through incremental improvements to current models — new, more fundamental approaches are needed such as the structure-based approach, which we believe has the long term potential to make the required mechanistic links between coal properties and char behaviors.

The overall objective of this project is to carry out the fundamental research needed to develop a first-generation, structure-based model of coal char combustion. The project involves combustion experimentation at a variety of scales, theoretical treatments of surface chemistry, and the development and refinement of advanced modeling techniques describing solid-state transformations in coal chars. The fundamental modeling approaches taken here may also produce auxiliary benefits for other coal technologies, including cokemaking, liquefaction, activated carbon production and use, and carbon materials manufacture (fibers, composites, graphite, etc.). The crystalline structure of carbons and its evolution during processing plays an important role in each of these diverse applications.

This combined experimental and theoretical approach will result in a first-generation, structure-based model that is a significant improvement over empirical models in its ability to:

- Predict, from fundamental principals, the rank-dependence of char reactivity
- Predict the dependence of char reactivity on heat treatment conditions
- Describe reaction kinetics in a wide variety of combustion / gasification environments

Task Structure

This project consists of the following three interrelated tasks:

Task 1. Project Management

This task involves reporting, documentation, coordination of effort at the two participating universities, and interactions with the advisory board.

Task 2. Development of Structure-Based Models

The objective of this task is the development of new models that describe the combustion process on a more fundamental basis. Dynamic models will be formulated that describe the evolution of char crystal structures in flames, and fundamental computational treatments of oxidative attack on model PAH and graphitic structures will be carried out. This task also includes laboratory-scale experiments designed to establish link between char structure and oxidation reactivity, and a direct investigation of carbon crystalline rearrangements by in-situ, hot-stage HRTEM.

Task 3. Experiments in Practical Combustion Systems

This represents a parallel effort to investigate and document the importance of thermal history effects on char structure and reactivity in well-controlled and characterized coal flames. Comparative experiments will be carried out on two reactor facilities with widely varying flame type and the properties and reactivities of the chars characterized.

Project Team

The project involves Brown and Ohio State Universities with expertise in coal combustion and carbon science, and modern computational chemistry. The multidisciplinary team will apply modern scientific tools to the challenging technological problem of linking char combustion behavior with coal properties and processing conditions.

The project is supported by an advisory panel assembled from industry, academia, and the national laboratories with a wide range of expertise. The panel members are:

Hamid Farzan	Babcock and Wilcox Co.
Alan Kerstein	Sandia National Laboratories
Harry Marsh	University of Alicante
Arun Mehta	Electric Power Research Institute
Richard McCreery	Ohio State University
Nsakala Nsakala	ABB Combustion Engineering
Stuart Daw	Oak Ridge National Labs

DISCUSSION OF PROGRESS THIS PERIOD

Section I. Computational Chemistry of Oxidative Attack on Model PAH and Graphitic Structures (within Task 2 at OSU)

In the most recent quarter, we have embarked on calculating some thermochemical properties of some larger polycyclic aromatic hydrocarbons (PAHs) by density functional theoretical methods.[1,2,3,4] Previously, we have shown that the “hybrid” B3LYP[2] method can be used to provide quantitative information on the stability of the corresponding radicals that arise by hydrogen atom abstraction from monocyclic aromatic rings. We have extended our previous efforts to larger carbocyclic ring systems, such as coronene, in order to compare the properties of a large carbonaceous PAH to that of the smaller, monocyclic aromatic systems. Also, in this quarter, we have examined the mechanism of attack of radicals with aromatic ring systems. We have considered a number of radicals which are found in the typical combustion “radical pool.”

We have extended our calculation of bond dissociation energies (BDEs) to bicyclic and large PAHs. In Figure 1, we present the BDE for each C-H bond in a variety of heteroatom-substituted bicyclic PAHs. The “plain” values are the absolute BDE (H°) at 298 K in kcal/mol, while the values in brackets are determined as the *difference* between the C-H bond in the compound and the “identical” C-H bond in the monocyclic analog. So for naphthalene, the C-H bond in the 1-position (adjacent to the bridge C-C bond) is only 0.3 kcal/mol greater than that of a C-H bond in benzene. In Figure 1 one can see that, in general, the C-H bonds in the bicyclic aromatic compounds are very similar (within 1 kcal/mol) to that of the parent monocyclic analogs. However, there are a few exceptions. In benzofuran, benzoxazole, and quinoline, the C-H bond in the 6-membered ring near to the heteroatom has a BDE that is ~2 kcal/mol greater than that of a C-H bond in benzene.

We have begun to analyze the origins of these effects. In particular, we have analyzed how much of the excess radical spin density resides on the location where the hydrogen atom was abstracted for the monocyclic aromatic hydrocarbons. In principle, a low BDE will be expected when the unpaired spin in the radical can be spread out over a number of atomic centers rather than localized on the center of abstraction. Previously we presented a good correlation between BDE and the excess radical spin density on the location of abstraction for the monocyclic rings. The spin density was evaluated *via* Bader’s Theory of Atoms in Molecules [5], which should be quantitatively accurate. We have extended our efforts to examine the BDE correlation in the bicyclic ring systems. A plot of the BDE *vs* the spin density at the abstraction center is presented in Figure 2. A good correlation is observed, but there seems to be two trends. Abstraction from the 6-

BDEs of HETEROCYCLIC AROMATIC HYDROCARBONS

Figure 1: C-H Bond Dissociation Energies for bicyclic aromatic hydrocarbons.

Figure 2: C-H BDE vs. the spin density at the abstraction center in bicyclic aromatic hydrocarbons.

BDEs OF POLYCYCLIC AROMATIC HYDROCARBONS

Figure 3: Bond dissociation energies for carbonaceous polycyclic aromatic hydrocarbons.

membered ring seems to be slightly different from abstraction from the 5-membered ring.

Larger PAH systems are certainly more appropriate for comparison to coal chars. We have calculated the BDEs in some larger carbonaceous PAHs, and that data are presented in Figure 3. As before, the “plain” number is the absolute BDE at 298 K, while the number in brackets is the deviation between the calculated C-H bond and a C-H BDE in benzene. In all cases, the C-H BDE is within 1 kcal/mol of the benzene analog. Therefore, at least for BDE considerations, the properties of the large PAHs can be modeled by smaller systems. Other theoretical data, albeit at a different level of density functional theory, also provided similar conclusions.[4]

We have continued to explore the potential energy surfaces for oxidative decomposition of aromatic radicals with oxygen. We are particularly interested in the transition states which lead to the intermediates involved in the combustion process and to understand the requirements for efficient reactivity of a coal char.

Morokuma and Lin have recently published calculations on the vinyl radical with O₂ using B3LYP geometries.[6] They have also published calculations in the past few years on intermediates of relevance to the oxidation of benzene.[7] Carpenter has also presented computational results, but at a lower level of theory.[8] The results by Morokuma and coworkers suggest that the B3LYP method provides results which are in good qualitative and quantitative agreement with higher levels of theory on the potential energy surfaces.[6,7]

In this quarter, we have focussed significant effort to understand the interaction of radicals in the “radical pool” with the different types of aromatic structures. In particular we have begun to explore the different avenues of attack that might be available for interaction of radicals with PAHs. Above, we presented data on the thermochemistry of cleavage of a C-H bond to generate an organic radical. Let us begin with some transition state information for H atom abstraction.

In Figure 4, we present a schematic of the transition states and free energies (G° , 298 K) for H atom abstraction by a H atom (from the radical pool) to form the corresponding aromatic radicals. Furan has the highest C-H BDE (118.3 kcal/mol) and also has the highest barrier to H-atom abstraction (21.3 kcal/mol). Pyridine has the lowest C-H BDE (105.6 kcal/mol) and also has the lowest barrier to H-atom abstraction (13.0 kcal/mol).

There are many radicals that might be able to cleave a C-H bond and in Figure 5, we have investigated the cleavage of the C-H bond in benzene by hydroxyl radical (OH), hydrogen (H) atom and an oxygen atom in the ³P state. Of the three radicals, OH has the most favorable transition state with an activation energy of 8.1 kcal/mol (G° , 298 K). However, the worst case of the three (H atom) has a transition state barrier of only 13.3 kcal/mol, and it should also be very accessible in typical combustion environments.

Interaction of OH radical with different monocyclic aromatic rings is presented in Figure 6.

H ATOM ABSTRACTION BY H ATOM

Figure 4: C-H bond cleavage by H atom for furan, benzene and pyridine.

TRANSITION STATES FOR H ATOM ABSTRACTION FROM BENZENE

B3LYP / 6-31G*
 $\Delta\text{G}^\circ(298 \text{ K})$, kcal/mol

$\text{C}_6\text{H}_5 + \text{H}_2$ and $\text{C}_6\text{H}_6 + \text{H}$:
 A.M. Mebel, M.C. Lin, T. Yu, and K. Morokuma
J. Phys. Chem. A 1997 **101** 3189-3196

Figure 5: C-H bond cleavage in benzene by OH radical, H atom, and O (³P) atom.

H ATOM ABSTRACTION BY OH RADICAL

Figure 6: C-H bond cleavage by OH radical for furan, benzene and pyridine.

In general, the picture is a bit more complicated as the H_2O molecule which is generated from H-atom abstraction can create a complex with the aromatic radical. However, the transition state data are very similar to that in Figure 4 but the activation energies are about 5 - 8 kcal/mol lower for OH radical as compared to H atom as the abstracting agent. The activation energy ($G^\ddagger$) for C-H bond cleavage in furan is about 13 kcal/mol, while the $G^\ddagger$ for C-H bond cleavage in pyridine is lower in energy (6.1 kcal/mol).

Thus far, we have postulated that interaction of species in the radical pool will only generate H atom abstraction products. It is well known from atmospheric chemistry studies that species such as OH radical will *add* to aromatic rings instead of abstracting a hydrogen atom.[9]

We have examined the different pathways for addition *vs.* abstraction to benzene and furan by H and OH radicals. In Figure 7, one can see that the addition of OH to the benzene ring is favored both by thermochemistry ($\Delta G^\circ \sim 7$ kcal/mol) and also by activation energies ($G^\ddagger \sim 3$ kcal/mol). We are especially intrigued by this result as the formation of phenoxy radical ($\text{C}_6\text{H}_5\text{O}^\bullet$) is a very important process in combustion flames and the addition of OH to benzene provides a possible route to the phenoxy radical.

We have also investigated H atom reactions with furan at both the 2 and 3 positions, and the information is presented in Figure 8. The transition state for H atom addition to the furan ring is lower in energy as compared to the abstraction channel. In particular, the addition product is significantly more stable as compared to the abstraction product. With regard to interaction at both the 2 and 3 positions for the furanyl radical, the addition channel is significantly favored over abstraction on both kinetic and thermochemical grounds.

We will continue to probe the effects of abstraction *vs.* addition channels in these systems. We are currently exploring the reaction products that could arise after addition of a radical to the aromatic rings. In addition, we will continue our efforts to understand the stability effects in the organic radicals as well as the mechanism for O_2 addition and decomposition.

BENZENE + OH: ABSTRACTION vs. ADDITION

Figure 7: Abstraction vs . addition by OH radical with benzene.

FURAN + H: ABSTRACTION vs. ADDITION

Figure 8: Abstraction vs addition by H atom at the 2 and 3 positions of furan.

References:

- [1] Ziegler, T. *Chem. Rev.* **1991**, *91*, 651. *Density Functional Methods in Chemistry*; Labanowski, J.; Andzelm, J., Eds.; Springer-Verlag: New York, 1991. Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
- [2] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648 and references therein. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Stephens, P. J.; Devlin, F. J.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623. (d) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612 - 5626.
- [3] Sulzbach, H. M.; Schleyer, P. v. R.; Jiao, H.; Xie, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1995**, *117*, 1369.
- [4] Cioslowski, J.; Liu, G.; Martinov, M.; Piskorz, P.; Moncrieff, D. *J. Am. Chem. Soc.* **1996**, *118*, 5261.
- [5] (a) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893. (b) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1990.
- [6] Mebel, A. M.; Diau, E. W. G.; Lin, M. C.; Morokuma, K. *J. Am. Chem. Soc.* **1996**, *118*, 9759 - 9771.
- [7] (a) Mebel, A. M.; Lin, M. C. *J. Am. Chem. Soc.* **1994**, *116*, 9577-9584. (b) Liu, R.; Morokuma, K.; Mebel, A. M.; Lin, M. C. *J. Phys. Chem.* **1996**, *100*, 9314 - 9322.
- [8] Carpenter, B. K. *J. Am. Chem. Soc.* **1993**, *115*, 9806.
- [9] Atkinson, R. *Atmos. Environ.* **1990**, *24A*, 1. Tully, F. P.; Ravishankara, A. R.; Thompson, R. L.; Nicovich, J. M.; Shah, R. C.; Kreutter, N. M.; Wine, P. H. *J. Phys. Chem.* **1981**, *85*, 2262.

Section II. The Effect of Mineral Matter on Carbon Burn-Out (within Task 2 at Brown).

One of the important issues that remains to be addressed in developing models of structure development in coal chars is the role of mineral matter impurities. It has often been suspected that the presence of mineral matter can affect the structure and ordering of carbons [1,2]. Mineral matter can also affect reactivity *via* such mechanisms as “blocking” of active sites and reducing carbon surface density. Here we report on the first efforts in this project at exploring the effects of coal-derived ash on carbon ordering and reactivity.

One of the most common approaches used to explore the effects of mineral matter impurities on reactivity has been to demineralize coals and chars by washing in strong acids [3]. One of the drawbacks of this technique is that it almost certainly causes significant alterations of the structure of the resultant material. Consequently, an “inverse” approach was used here; that is doping of a “pure” carbon with mineral matter. The carbon material was derived from a high carbon content fly ash (Fly Ash 23 from the Salem Basin Power Plant), which was further enriched by sieving to 84% carbon. The ash was obtained from Pittsburgh #8 coal (PSOC 1451) which was pyrolyzed and ashed in oxygen at 773K. The resultant particle size fraction $<40\mu\text{m}$ was used to dope the carbon samples.

The final doped samples were dried at 383K for 2h, and then burned in a high temperature flame reactor fitted with rapid quench extractive sampling [4]. The reactor was fed by a Hencken burner fueled with a $\text{CH}_4/\text{O}_2/\text{Ar}$ mixture, producing a post-flame oxygen concentration of 14 mol%. The mean residence time was 140ms, and the centerline temperature was 1280K. Particle temperatures were estimated to range from 1650-1800K. The sample feed rate was less than 1 g/h. Additional details of the apparatus are described elsewhere [4]. A schematic of the apparatus is presented in Figure 1.

The average reaction rate on a carbon basis in the flame reactor was determined by dividing the mass loss by the initial carbon content and the mean residence time. Figure 2 shows that this average reaction rate for the doped samples as a function of initial ash content. As shown, the specific reaction rate *decreases* with increasing ash content by about an order of magnitude over the ash content range investigated. It is also interesting to note that the shape of this curve is reminiscent of isothermal TGA reactivity curves for Pittsburgh #8 coal char (pyrolyzed at 1573K for 4h) in oxygen at lower temperatures.

Figure 1. Schematic of Hencken burner/reactor system.

Figure 2. Average reaction rate per mass of original carbon content for Fly Ash 23 doped with varying amounts of ash derived from Pittsburgh #8 coal.

(a)

(b)

Figure 3. SEM micrographs of undoped sample FA1.1 (8% ash), before (a) and after (b) reaction.

(c)

(d)

Figure 4. SEM micrographs of sample FA1.4 (68% total ash) before (c) and after (d) reaction.

The SEM micrographs for the undoped sample FA1.1 (8% total ash content), before and after the flame reactor are presented in Figures 3(a) and 3(b), respectively. From these figures, it is apparent that the mean carbon particle size was reduced due to reaction, while the ash particles appear to have agglomerated and coalesced, creating larger particles of about 2-3 μm in size. A closer examination reveals that the carbon has been reacted away, creating more irregularly shaped openings and a rougher texture than for the previously smooth carbon surfaces.

Figures 4(c) and 4(d) show the corresponding SEM micrographs for the doped sample FA1.4 (68% total ash content). The micrograph for the freshly prepared sample shows that the added ash particles effectively cover the surfaces of the carbon particles. The added ash can be distinguished from the smooth, pearl-like ash particles original to the fly ash by their irregular shape. The micrograph in Figure 4(d), taken after reaction, shows not only an increase in the relative amount of ash, but that some of the ash has fused and covered carbon particles. This latter mechanism may be the primary reason for the observed decrease in specific reaction rate with increasing ash content; i.e., an increasing amount of carbon becomes inaccessible to oxygen by being covered with a fused, “protective,” ash layer.

References:

- [1] Kang, S.G., A.F. Sarofim, and J.M. Beer, *Twenty Fourth Symp. (Int.) Combustion*, The Combustion Institute, Pittsburgh, PA, 1992, pp. 1153-1159.
- [2] Srinivasachar, S., Senior, C.L., Helble, J.J., and Moore, J.W., *Twenty Fourth Symp. (Int.) Combustion*, Combustion Institute, Pittsburgh, PA, 1992, pp.1179-1187.
- [3] Morgan, M.E., Jenkins, R.G., and Walker, P.L., Jr. *Fuel* **60**, 189, 1981.
- [4] Hachmann, L., Burnett, A., Gao, Y.-M., Hurt, R.H., and Suuberg, E.M., to be presented at the *Twenty Seventh Symp. (Int.) Combustion*, 1998.

Section III. Experiments in Practical Combustion Systems - Combustion Laboratory Activities (Task 3 at OSU)

Reconstruction of the High Intensity furnace is now complete and firing will be started shortly. This has required major reconstruction. The reactor (furnace) and exhaust system have been completely rebuilt. The chimney is complete. The solid sampling system is operational. We are now ready set to begin experiments.

As set forth below, TGA reactivities will be determined on the solid (char) samples using equipment available in the Chemistry Department. The temperature measurement procedures are being reviewed.

Separately, the Poster Paper given at the Penn State Carbon Conference has been written up, submitted to and accepted for presentation at the 27th International Combustion Symposium in Boulder this coming August.

Furnace Status Summary

1. High Intensity (HIT) Tower Furnace

The rebuilt furnace is substantially an exact copy of the original. It was rebuilt since the original was in such poor shape. Some minor modifications have been made. At this time, the secondary air staging has been omitted. This will be the prime source of char samples for analysis. The major process of analysis will be determinations of reactivity by TGA.

2. 1-D Tower Furnace

This furnace will be kept in reserve. It is anticipated that it will be needed to test developing concepts.

3. Jet Mixed Reactor

The jet mixed reactor is operational and is in use to test and modify ancillary equipment. When the HIT furnace comes on line which is anticipated shortly it will be kept in reserve and used as needed.

Ancillary Equipment Status Summary

1. Thermogravimetric Analysis (TGA).

A TGA system has been located in the Analytical Chemistry Department. This is to be used to determine reactivity of char samples obtained from the HIT furnace. Training on use of the equipment under the direction of the Laboratory Supervisor is essentially complete.

2. Exhaust System.

The exhaust system shared by the 1-D tower and large high intensity furnaces has been relocated, partially rebuilt, and completely overhauled. The bricks were removed and remortared; the hoses have been replaced; a more secure frame has been installed; and the flue has been straightened.

3. Coal Feeder.

The feeder system is now operational following its repositioning, and replacement of the potentiometer for the calibration dial. It has been slightly modified in order to make the calibration process easier.

4. Solid Sampling Probes.

The solid sampling probes are operational, and the sampling procedure has been successfully tested using the jet mix reactor.

5. Temperature Measurement Equipment.

Wall temperatures will be obtained with thermocouples; gas temperatures with optical pyrometry. The installation of the wall thermocouples is nearly complete; re-connection to the data logging system is in progress. The suction pyrometer and 2-color pyrometer both require overhaul. This is now in planning.

6. Gas Analysis.

Analyses of CO, CO₂, O₂, and NO_x are planned. The CO₂, O₂, and NO_x analyzers are on site. We are currently reviewing available CO analyzers. The CO₂ and O₂ analyzers are operational.

**U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MILESTONE PLAN**

1 Program: DE -FC22-96PC96249

2. Program/Project Title: Structure-Based Model of Coal Char Combustion

3. Performers: Robert Hurt, Division of Engineering, Brown University
182 Hope Street,
Providence, RI 02912

Project start date: 9/30/96

Project completion date: 9/30/99

Number	Task / Subtask	Activity	Project Duration	Comments / notes / performer
1.	general	selection of test coals	<div><div>1</div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div>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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MILESTONE PLAN (PAGE 2)

1 Program: DE -FC22-96PC96249		2. Program/Project Title: Structure-Based Model of Coal Char Combustion		
3. Performers: Robert Hurt, Division of Engineering, Brown University 182 Hope Street, Providence, RI 02912		Project start date: 9/30/96		
		Project completion date: 9/30/99		

Number	Task / Subtask	Activity	1998	1999	Project Duration	Comments / notes / performer
1.	general	selection of test coals	complete			Brown / OSU
2.	2.1	development of dynamic structural models				
2a.		<i>nonbonded</i>	Δ ¹²			BU / Brown
2b.		<i>graphene layers</i>	Δ ¹³			BU / Brown
2c.		<i>linked networks</i>				
		<i>model synthesis</i>			Δ ¹⁴	Brown
3.	2.	in-situ, hot-stage fringe imaging	Δ ¹⁵			Brown
4.	2.2	computational chemistry of surface oxidation		Δ ¹⁶		OSU
5.	3	experiments in contrasting flame types		Δ ¹⁷		OSU
6.	3	analyses of char samples from part 5.		Δ ¹⁸		OSU
7.	2.1	establishment of secondary correlations:				
7a.		<i>structure / reactivity</i>	Δ ¹⁹			Brown
7b.		<i>structure / fluidity</i>	complete			Brown

**U.S. Department of Energy
Milestone Log**

Project title: Structure-based models for char combustion

Milestone Number	Description	Planned Completion Date	Actual Completion Date	Comments
1	Coals selected for laboratory and OSU furnace testing	April, 1997	June, 1997	coals also selected for laboratory testing at Brown, AFR, and BYU
2	First successful simulation of structural ordering in nonbonded graphene layers	Sept., 1997	June, 1997	
3	Completed set of simulations of growth and hindered motion based on hard lines	Sept. 1997	Sept. 1997	
4	Enhancement of algorithm in 3 to produce simulated structures comparable to HRTEM fringe images.	May., 1998		
5	First successful demonstration of in-situ, hot-stage fringe imaging	Sept. 1997	July 1997	in progress
6	First set of thermochemical computations complete for model organic structures	Dec. 1997	Oct. 1997	
7	Shakedown / testing of OSU furnace facilities complete	Oct. 1997	Jan 98	
8	First set of char generation experiments complete on OSU furnaces	Apr. 1998		
9	First set of char samples characterized -- major differences in flame types identified	Sept. 1998		
10	Structure-based prediction concept developed for fluidity and char macromorphology	Sept. 1998		
11	Reactivity / structure link assessed for mineral-free model carbon	Sept. 1998		

U.S. Department of Energy
Milestone Log (page 2)

Project title: Structure-based models for char combustion

Milestone Number	Description	Planned Completion Date	Actual Completion Date	Comments
12	Modeling activities on non-crosslinked networks complete	Dec. 1998		
13	Modeling activities on cross-linked networks complete	Dec. 1998		
14	Unified model developed from parallel modeling efforts in 12, 13	Sept. 1999		
15	Completion of in-situ HRTEM studies - insights into structural dynamics included in models	Dec. 1998		
16	Thermochemical computations complete, likely oxidation pathways identified. Implications for modeling identified.	April. 1999		
17	Flame experiments complete	Jul. 1999		
18	Char analyses complete. Impact of annealing and heating rate on burnout from various flame types identified and quantified.	Jul. 1999		
19	Auxiliary correlations complete	Dec. 1998		