STRUCTURE-BASED PREDICTIVE MODEL FOR COAL CHAR COMBUSTION

**Quarterly Technical Progress Report
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TABLE OF CONTENTS

EXECUTIVE SUMMARY	4
PROJECT DESCRIPTION.....	5
PROGRESS THIS PERIOD	6
Brief Summary of Activities	6
Detailed Discussions of Progress	
Section I: Computational Chemistry	7
Section II: Carbon Structural Modeling Based on Mesophase Thermodynamics	14
Section III: Combustion Experiments in Contrasting Flame Types	26
MILESTONE PLAN... ..	30
MILESTONE LOG	32

EXECUTIVE SUMMARY

During the third quarter of this project, progress was made on both major technical tasks. Progress was made in the chemistry department at OSU on the calculation of thermodynamic properties for a number of model organic compounds. Modelling work was carried out at Brown to adapt a thermodynamic model of carbonaceous mesophase formation, originally applied to pitch carbonization, to the prediction of coke texture in coal combustion. This latter work makes use of the FG-DVC model of coal pyrolysis developed by Advanced Fuel Research to specify the pool of aromatic clusters that participate in the order/disorder transition. This modelling approach shows promise for the mechanistic prediction of the rank dependence of char structure and will therefore be pursued further. Crystalline ordering phenomena were also observed in a model char prepared from phenol-formaldehyde carbonized at 900 °C and 1300 °C using high-resolution TEM fringe imaging. Dramatic changes occur in the structure between 900 and 1300 °C, making this char a suitable candidate for upcoming *in situ* work on the hot stage TEM. Work also proceeded on molecular dynamics simulations at Boston University and on equipment modification and testing for the combustion experiments with widely varying flame types at Ohio State.

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 three participating universities, and interactions with the advisory board.

Task 2. Development of Structure-Based Models

The objective of this 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 three universities (Brown, Ohio State, and Boston University), in order to couple engineering experts in coal combustion and carbon science (at Brown and Ohio State) with research groups in the pure sciences specializing in modern computational chemistry (OSU) and in solid state physics (BU). 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

PROGRESS THIS PERIOD

Brief Summary of Activities

During this quarter, progress was made on each of the major technical tasks. First, a meeting was held at Advanced Fuel Research on June 12 to plan the technical approach for the new modeling initiative within Task 1. Among the attendees at the meeting were R.

Hurt, J. Calo, and E. Suuberg at Brown; M. Serio, M. Wojtowicz, Y. Chen, and S. Charpenay of AFR, and two Brown students L. Hachman and M. Ruskovsky.

The goal of the new modeling initiative is to describe the rank dependence of coal char structure by combining a model of mesophase thermodynamics (described in part 3) with AFR's network pyrolysis model FG-DVC. FG-DVC predicts the amount of liquid phase present during coal pyrolysis and the molecular, weight distribution of the liquid products, while the mesophase model uses the MW distribution to predict the occurrence and amount of ordered carbon. Based on the results of the meeting, AFR made modifications to the output files in its code and transferred the code to Brown. Martin Ruskovsky then undertook a summer project examining test cases involving high-heating-rate pyrolysis of four U.S. coals of widely varying rank. The initial results are promising and this initiative will be continued in the fall (see detailed discussion in section 3).

In addition, Nancy Yang paid a visit to discuss the collaboration with Sandia on mineral effects and annealing. Chi Man from Imperial College also visited to discuss carbon burnout. The list of test coals was finalized this quarter, and arrangements were made to acquire the international coals from New England Power, Babcock and Wilcox, and the University of Stuttgart. This included a trip by Hurt and Ruskovsky to New England Power to make the arrangements for a South American coal sample. A letter was written to Harry Teng to begin preparations for coal grinding and classifying.

Significant progress was also made at OSU on the estimation of thermodynamic properties for model organic compounds. Tests were run on the combustion facilities at Ohio State University in preparation for the main test matrix in project year 2. These activities are discussed in detail in later sections.

Progress was made on developing collaborations with other groups. Contacts were made at the University of Stuttgart, the University of Queensland, the University Federico Secondo in Naples, and in Minsk in the former Soviet Unions (R. Essenhigh).

DETAILED DISCUSSIONS OF PROGRESS

Section I: Computational Chemistry (within Task 1 at OSU)

Modern computational chemistry is able to address conformational, thermochemical and even kinetic issues for a variety of chemical questions¹. Via high level *ab initio* molecular orbital theory we are assisting the experimental approach on coal char combustion by calculating thermochemical properties of representative moieties of coal, such as polyaromatic hydrocarbons (PAHs).

The oxidation and combustion of coal is certainly a very complicated problem. Even the chemical structure of coal is variable². Experimental studies on combustion have provided Arrhenius information for the kinetic properties of some small organic reactive intermediates³. Coal, with its complexity, has attracted much less attention for specific kinetic or computational study. Furthermore, a computational approach is also difficult.

The molecular systems are very large, and there are many potential reaction channels. In addition, the theoretical models need to be of high level and quality. However, in order to understand the combustion of coal, one vitally needs this information for kinetic models. These kinetic models have been very useful for combustion of gaseous fuels², and we are testing the application of this approach to coal combustion.

There have been some recent computational studies of reactions of O₂ with small organic radicals, like vinyl and phenyl radicals². These recent studies have shown that semi-empirical levels (such as the PM3 method²) are useful for estimating qualitative chemical behavior, but higher (and more expensive) theoretical levels, such as *ab initio* molecular orbital theory,^{1,2} are required for quantitative information.⁴

We wish to study the reaction channels for O₂ attack on PAHs such as benzene, naphthalene and larger polyaromatic hydrocarbons. In the past few months, we have also focused on heteroatomic ring systems, such as furan, thiophene, pyrrole, pyridine and pyrazine (Scheme I), which are typically found in coal, and we have included these structures in our studies.

Our theoretical studies have utilized *ab initio* calculations at the Hartree-Fock (HF) level for generating minimum energy geometries as well as further theoretical calculations in order to obtain more accurate energetic information. For these calculations, we have focused on electron correlation methods such as Møller-Plesset (MP) perturbation theory² and density functional theory³. Electron correlation will be very important for the chemical properties that we will attempt to calculate, and both perturbation and density functional theories will be most useful. The DFT calculations, in particular, seem most promising as the B3LYP functional² has shown success in predicting *accurate* chemical phenomena and at a *reasonable cost* for large systems². Some DFT calculations have been presented in the literature on PAHs,² and these types of calculations reveal tremendous promise. It is important to calibrate our theoretical models for accuracy prior to exploring the complicated coal combustion system.

From March 1997 to the present, we have calculated a number of different thermochemical properties for simple models of coal containing units. In order to calibrate our results for these computational systems, we need to have accurate calculations or experiment data to guide the theory. Unfortunately there are very few experimental values of important thermodynamic properties for aromatic systems. One recent, accurate piece of information is that the C-H homolytic bond dissociation energy (BDE) of benzene is 112.0 ± 0.6 kcal/mol². In our approach, we have therefore relied on proven accurate theoretical methods for calibration as well as the limited experimental data where available.

In order to probe the effect of theoretical level, we have proceeded with a variety of theoretical methods. In particular, there are a few recent methods, Complete Basis Set (CBS)², Gaussian-2 (G2),² and G2MP2², that have been shown to be very accurate (less than 2 kcal/mol) for a host of chemical properties. These methods range in the degree of computational expense, and they sacrifice computer time for accuracy. At the heart of each method is an attempt to perform a very large basis set calculation and also correct for

complete electron correlation. The CBS and G2 methods differ on how they approach those limits. However, the CBS methods and G2 methods are “recipes” and require multiple calculations; the results of which are then added together in increments to provide the final energy of the system. Many of these recipe methods will be difficult to apply in probing the potential energy surface; therefore, we have also utilized relatively “cheap” methods such as HF, MP2, B3LYP (DFT) for geometry optimization. In principle, these latter methods will be more applicable to larger systems and if they show reasonable accuracy, we will be able to examine large PAHs.

Table I shows representative information for our calculated bond dissociation energies (BDE) for representative aromatic ring systems. Each of these energies, of course, is an energy difference between the starting hydrocarbon and the specie with a hydrogen lost at the designated position. Scheme I shows the molecules under discussion and the location numbering for the hydrogen atom loss.

Scheme I. Aromatic systems and the numbered location (see Table I) for hydrogen atom loss.

Analysis of the data presented in Table I shows a few trends. With regard to the computational methods, the CBS-4, CBS-q, CBS-Q, G2MP2 and B3LYP/6-31G(d) calculations tend to give similar results for the bond dissociation energies. The B3LYP/6-31G(d) BDEs tend to be slightly lower than the other (more accurate) methods. In the only case (benzene) where an experimental datum is available, the calculated BDEs for the CBS levels, G2MP2 and B3LYP methods are in good agreement with experiment. The HF/6-31G(d) and MP2/6-31G(d) methods yield very poor results in comparison to the experiment data and also to the more accurate CBS and G2MP2 methods. In addition, the HF and MP2 methods suffer badly from “spin contamination” in the radical species -- the radical (doublet) wave function is mixed with wave functions from higher spin states. The B3LYP calculations are not spin contaminated, in general, and yield good BDEs. This feature about DFT calculations and aromatic systems has been noted previously,¹² but not applied to a larger data set.

There are some relative trends with regard to hydrogen atom abstraction that is evident in Table I. The BDE is relatively similar (about 115 kcal/mol) between all of the monocyclic aromatic compounds, and only the H-atom abstraction at position 1 of pyridine has a lower BDE than for benzene. Comparing between positions in the same molecule, there is no special preference for hydrogen atom abstraction in furan and pyrrole, but there is a significant effect between the different positions of abstraction for thiophene and pyridine.

There is approximately a 5 kcal/mol preference for abstraction of the hydrogen immediately adjacent to the nitrogen in pyridine; however, there is a 2 kcal/mol preference for abstraction of the hydrogen away from sulfur in thiophene. We are currently investigating the origin of these preferences.

We are particularly excited by the good performance of a very inexpensive B3LYP method as compared to the more accurate CBS and G2MP2 methods. In Table II, we have compiled the relative cpu time needed to run these different kinds of calculations with the furan and 1-furanyl radical systems. In particular, open shell systems, i.e. radicals, are typically more expensive calculations. One can see that the B3LYP calculations are significantly cheaper than the other more accurate methods. In addition, the B3LYP calculations are even better on larger systems as the B3LYP calculations scale as ON^3 (O =occupied molecular orbitals and N =total number of molecular orbitals), while many of the other methods scale as ON^4 or much greater.

Since we have shown that the B3LYP method can be well applied to calculating accurate energies for these systems, we have begun an exploration of some larger PAHs. In particular we have BDEs for naphthalene at the B3LYP level of about 117.6 kcal/mol, a value that is larger than for benzene. We will explore to see if the C-H BDE is consistently larger for bigger PAHs compared to benzene.

We have also begun to explore the potential energy surfaces for some simple systems in order to calculate the intermediates involved in combustion. We have begun with the CH_4 and O_2 system and we have obtained a transition state structure and energy for H-atom abstraction similar to previous calculations². We have also done similar comparisons with the oxidation of $CH_2=CH_2$ (ethylene) with hydroxyl radical (OH), O (3P) atom, and O_2 . We have found transition states with relative energies of about 28, 36 and 63 kcal/mol at the HF/6-31G(d) level, and we are currently pursuing these systems at the B3LYP level. These systems can all be examined at very high levels of theory (such as the above) in order to further calibrate the efficacy and accuracy of using the B3LYP method to examine the potential energy surfaces of O_2 addition to PAHs. Thus far, all indications suggest that the B3LYP method will be very useful in this regard. Transition state energies at the HF level for the OH, O (3P) and O_2 initiated hydrogen-atom abstraction from benzene are 24, 33, and 60 kcal/mol, respectively. These values are very similar to that for ethylene above. We are continuing to explore the oxidation of benzene.

In addition to these calculations, we have been examining the structure of the coal chars from Professor Essenhight's furnace via the different spectroscopic methods available in the Chemistry department here at Ohio State University. We have examined a few coal char samples by Nuclear Magnetic Resonance (NMR), using toluene- d_8 as the solvent. Our 1H NMR experimental spectra show a variety of chemical shift resonances and therefore, a significant number of different kinds of hydrogens are still evident in the coal char samples. Our attempts at ^{13}C NMR were not successful due to insufficient concentration in solution. One caveat of the NMR studies is that we are only able to examine the components of the coal char that dissolve in the solvent samples. We are exploring other solvent systems for consistency and also other analytical methods here at Ohio State in order to probe these

samples. More on this will be presented at a later time. However, Professor Essenhigh will discuss the exciting results that have been obtained from solid state microscopy of some of the coal char samples.

For the near future, we will continue to explore BDEs of higher PAHs, such as anthracene and pyrene. We hope to address if the hydrogen atom abstraction process has converged to a similar BDE regardless of size of the PAH. We will further calibrate the B3LYP method for examining the potential energy surface for the simple ethylene system and then also examine possible mechanisms of O₂ addition and combustion of benzene and some heteroaromatic hydrocarbons. We, in particular, will probe the O₂ mechanism for benzene oxidation that was recently postulated by Carpenter.⁵ We hope to further explore how O₂ adds to PAHs and contributes to the size distribution of the resulting coal chars. Experimentally we will continue to explore the coal char samples and examine the chemical composition of the coal chars. Such an experimental characterization will provide tremendous insight into the combustion process.

Table I. Bond Dissociation Energies (kcal/mol) for Aromatic Hydrocarbons

	radical	CBS-4	CBS-q	CBS-Q	G2MP2	HF ^a	B3LYP ^a	MP2 ^a	Expt ^b
benzene		116.9	117.5	113.1	115.6	78.5	109.2	127.7	112.0 ± 0.6
furan	1	120.1	119.1	119.5	121.5	89.1	116.7	122.5	
	2	120.5	119.0	119.9	121.6	89.6	116.7	123.2	
thiophene	1	118.8	117.6	117.7	120.0	86.3	115.0	123.3	
	2	116.5	114.7	115.4	117.8	84.7	112.1	120.8	
pyrrole	1	120.3	118.4	119.2	120.9	90.2	116.3	119.1	
	2	120.1	118.0	118.9	120.4	90.0	116.0	119.1	
pyridine	1	111.9	110.4	108.7	111.6	77.3	103.9	131.2	
	2	118.8	118.9	115.0	116.9	80.2	108.4	128.0	
	3	116.7	116.6	113.7	115.9	79.3	104.1	129.4	
1,4-pyrazine		115.2	113.3	110.2	112.8	77.4	104.1	129.4	

^a Completely optimized geometries using the 6-31G(d) basis set.

^b Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590.

Table II. Comparison of CPU times for Furan and 1-Furanyl Radical (minutes)^a

	Furan	1-Furanyl Radical
	-----	-----
CBS-q	38	140
CBS-Q	138	597
G2MP2	123	727
HF/6-31G(d)	16	21
B3LYP/6-31G(d)	68	128
MP2/6-31G(d)	44	102

^a Actual CPU times are from a Silicon Graphics PowerChallenge using Gaussian-94.

References: Section I

1. Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. Ab initio Molecular Orbital Theory ; John Wiley & Sons: New York, 1986.
2. For a representative structure, see: Essenhigh, R. H. Chemistry of Coal Utilization, Volume II, Wiley: New York, 1981; Elliott, M. A., Ed.; pp. 1153 - 1312.
3. Gardiner, W. C., Jr., Ed., Combustion Chemistry; Springer-Verlag: New York, 1984. Sloane, T. M. The Chemistry of Combustion Processes; American Chemical Society: Washington, DC, 1984. Benson, S. W.; Nangia, P.S. Acc. Chem. Res. 1979, 12, 223. Slagle, I. R.; Ratajczak, E.; Gutman, D. J. Phys. Chem. 1986, 90, 402.
4. Markatou, P.; Wang, H.; Frenklach, M. Combust. Flame 1993, 93, 467. Emdee, J. L.; Brezinsky, K.; Glassman, I. J. Phys. Chem. 1992, 96, 2151. Olsson, J. O.; Olsson, I. B. M. J. Phys. Chem. 1992, 96, 690.
5. Carpenter, B. K. J. Am. Chem. Soc. 1993, 115, 9806.
6. Stewart, J. J. P. J. Comput. Chem. 1989, 10, 209.
7. Gaussian 94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A., Jr.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1995.

8. Møller, C.; Plesset, M. S. *Phys. Rev.* 1934, 46, 618. Binkley, J. S.; Pople, J. A. *Int. J. Quant. Chem.* 1975, 9, 229. Pople, J. A.; Binkley, J. S.; Seger, R. *Int. J. Quant. Chem., Symp.* 1976, 10, 1.
9. 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.
10. Becke, A. D. *J. Chem. Phys.* 1993, 98, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* 1988, 37, 785. Stephens, P. J.; Devlin, F. J.; Frisch, M. J. *J. Phys. Chem.* 1994, 98, 11623.
11. Sulzbach, H. M.; Schleyer, P. v. R.; Jiao, H.; Xie, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* 1995, 117, 1369.
12. Cioslowski, J.; Liu, G.; Martinov, M.; Piskorz, P.; Moncrieff, D. J. *Am. Chem. Soc.* 1996, 118, 5261.
13. Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* 1995, 117, 2590.
14. (a) Ochterski, J.; Petersson, G.; Wiberg, K. B. *J. Am. Chem. Soc.* 1995, 117, 11299. (b) Ochterski, J.; Petersson, G.; Montgomery, J. A., Jr. *J. Chem. Phys.* 1996, 104, 2598.
15. Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* 1991, 94, 7221.
16. Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* 1993, 98, 1293.
17. Hamilton, T.; Schaefer, H. F., III *J. Chem. Phys.* 1989, 90, 6391.

Section II: Carbon Structural Modeling Based on Mesophase Thermodynamics (within Task 1 at Brown)

The previous report presented initial results of a simulation-based technique for describing crystalline order development in chars from coals of different rank. These "mobility/growth" models are being developed further. In parallel, a new modeling initiative was begun this quarter based on the thermodynamics of carbonaceous mesophase. A model of the phase transitions in fluid carbonizing media was recently developed at Brown and initially applied to petroleum pitch as a precursor to carbon materials. The model can be adapted to coal problems if it is coupled with a detailed network pyrolysis model, such as FG-DVC, developed at Advanced Fuel Research. In the section below, the mesophase thermodynamics model and its application to pitch are discussed briefly, followed by a presentation of initial results on the adaption of the model to coal carbonization and combustion.

Carbonaceous mesophase

It is widely accepted in carbon science that long-range crystalline order in carbons is established early in the carbonization process, and that subsequent rearrangements occurring at higher temperature serve only to enhance or perfect the initial order. Long range order is usually established in the fluid phase of carbonization through development concerted alignment of large, approximately planar PAH that make up the fluid carbonizing medium. This intermediate liquid crystalline state is referred to as carbonaceous mesophase, and when it solidifies through crosslinking, its orientational order is preserved as anisotropic solid coke[Marsh and Walker, 1979].

Carbonaceous mesophase is believed to consist of a liquid state mixture of approximately planar substituted and unsubstituted PAH, with strong preferential but statistical alignment of the planar units along a common orientational vector. This ordered liquid has been described as a nematic phase (possessing long range orientational but no long-range positional order) but has also been shown to possess some columnar nature (possessing long range orientational order and partial positional order in the form of stacked columns of planar units).

The optical properties of the planar building blocks differ in directions parallel and perpendicular to the planes, and as a result, carbonaceous mesophase is optically anisotropic and easily identified by polarized light microscopy. For precursors that are initially isotropic (having no orientational order over length scales visible by light microscopy), carbonaceous mesophase typically appears following a period of heat treatment as spherical regions suspended in an isotropic medium.

The induction time is believed to be related to the kinetics of molecular-weight growth processes which are necessary to produce the large (> 1000 MW) polyaromatic species with a tendency to align. The spheres may grow, coalesce, and/or deform by shear forces to form elongated, optically active regions. Extensive coalescence can lead to consumption and disappearance of the isotropic matrix and the formation of "bulk mesophase".

As molecular weight growth processes proceed further, mobility is lost and a solid semi-coke is formed that retains the optical characteristics of the liquid phase precursor. The solid coke may be entirely ordered (from bulk mesophase), partially ordered (containing anisotropic domains interspersed in a continuous isotropic solid, or entirely disordered (isotropic coke). It is usually observed that a material which is optically isotropic upon solidification remains isotropic upon further heat treatment. Heat treatment of solid phases can cause local rearrangements that lead to increased short range order, but is apparently incapable of concerted ordering processes that align layers in a common direction over long length scales ($> 1 \mu\text{m}$). This is not surprising as $1 \mu\text{m}$ corresponds to one thousand 1 nm planar units end-to-end — such a massive concerted ordering process typically occurs only in highly fluid medium.

The formation of anisotropic carbons via mesophase is key to the production of quality carbon materials, namely graphites and fibers [Marsh, H., and Walker, 1979]. The initial order established in the liquid phase can be perfected by local rearrangements at high temperatures ($2500 - 3000 \text{ C}$) to form a graphite with large crystallites. In the case of fibers, mesophase formation is necessary for the planar units to align during the spinning process with the basal planes parallel to the fiber axis, leading to high tensile strength and modulus. The formation of this phase is also believed to be important for the reactivity of carbons to oxidizing gases. The ordered phase results in lower surface areas (poorer site accessibility), since crystal disorder is the origin of micropores in carbons. Highly ordered domains can likely be attracted only from the edges. Figure 1 shows a plot of char reactivity in steam vs. the size of the ordered domains [Rouzaud and Oberlin, 1980].

Figure 1 Steam reactivities of various carbon samples from Rouzaud and Oberlin. Example of the dependence of reactivity on size of the optically anisotropic domains.

Description of the mesophase formation process is one key to the structure-based approach being pursued in this project. In the absence of crosslinks, the mesophase formation process may be regarded as a liquid/liquid-crystal phase transition in a liquid mixture of PAH of various molecular weight. The mobility/growth simulations presented in the previous quarterly report suggest that the rearrangements to ordered carbon are very fast if the ordering medium has liquid-like mobilities. In the absence of crosslinks, therefore, ordering is not dependent on rearrangement kinetics, but on the thermodynamic tendency to form the ordered phase.

Equilibrium is a reasonable assumption, and if the thermodynamic properties of the two liquid phases (isotropic and anisotropic) could be determined, the formation of carbonaceous mesophase could perhaps be predicted. This approach is valid in the absence of crosslinks, and thus has applications to pitches, and, perhaps, the fluid *fraction* of carbonizing coals.

Brief description of the mesophase thermodynamic model

Liquid crystal theory was used to develop a model of carbonaceous mesophase formation, based on the molecular weight distribution in a liquid carbonizing medium. The model was developed under an NSF project at Brown and is described briefly in an abstract for the 23rd Conference on Carbon [Hurt and Hu, 1997] and in more detail in a manuscript under preparation. Some example results and conclusions from the model development are given in the following paragraphs.

The modeling work began with the recognition that the known, pure PAH do not form discotic liquid crystals. It is therefore very difficult to describe carbonaceous mesophase (a liquid crystal mixture) in terms of pure PAH properties. A model was built based on pseudo-properties of pure PAH, in particular the liquid crystal-forming tendency of a compound expressed as a "clearing temperature", the temperature at which the liquid crystal "melts" into an isotropic liquid. Some highly substituted PAH have real clearing temperatures, but for the known pure PAH these transitions are virtual ones, lying beneath the melting point of the pure crystalline solid. Only in multicomponent mixtures, therefore, where the solid phases are suppressed, can the liquid crystalline phase be directly observed.

Figure 1 illustrates these ideas for a hypothetical binary mixture consisting of a low molecular weight, nonmesogenic[†] PAH, component A, and a higher molecular weight mesogenic PAH, component B. Note for pure A that the melting temperature lies above the clearing temperature, consistent with the trends discussed earlier. Therefore as the isotropic liquid A is cooled from high temperature, the first phase transition observed is the

[†] The compounds that form liquid crystals or mesophases are called mesogens, and a nonmesogen is a compound that does not exhibit a liquid crystal state as a single component.

formation of the crystalline solid. For A/B mixtures, certain regions on the phase diagram do include mesophase (shaded regions), including a pure (bulk) mesophase region, a two-phase region with coexisting isotropic liquid, and a two phase region with coexisting solid B. The freezing point depression associated with the binary system does expand the mesophase-containing regions, but only slightly. Calculations were also carried out for the case when both A and B are nonmesogenic. Although it is possible in principal to achieve mesophase in this class of systems [DeGennes and Prost, 1993], it proved very difficult in this binary model to achieve a mesophase region of any appreciable size using reasonable values for the transition enthalpies.

Overall, the binary model reproduces some major features of carbonizing systems, but was quantitatively deficient in a number of ways. Much of the phase diagram is still occupied by solid phases and the mesophase-containing zones are restricted to a relatively narrow range of temperature and composition, and to cases in which the high molecular weight component is mesogenic. The model we seek should yield mesophases easily, under a wide range of conditions, to be consistent with the prevalence of mesophase phenomenon in carbonization, and the fact that mesophase formation is not unduly sensitive to the details of molecular size and composition [Marsh and Walker, 1979]. The next section paragraphs describe a multicomponent model capable of predicting mesophase over a much wider range.

Figure 2 Example binary phase diagram for generic PAH of low (~500) and high (~1500) molecular weight. This example calculation assumes ideal solution behavior, a heat of fusion of 110 J/gm, a clearing enthalpy of 9 J/gm.

The multicomponent mesophase model is based on the classical picture of pitch as an intrinsic solution, rather than a micellar colloid, the latter view preferred by some researchers [Riggs and Diefendorf, 1980]. Second, for these complex whole pitches with numerous components we ignore crystalline solid phases, and third (for the time being) we consider ideal solutions ($\gamma_i^N = \gamma_i^I = 1$). The model then requires information on the clearing temperatures and enthalpies of pure components of varying molecular weight. For the clearing enthalpy we adopt a constant, but unknown value of the mass-specific H_{cl} as a model parameter (implying a linear relationship with molecular weight for the molar H_{cl}). We then adopt a linear relationship between the absolute clearing temperature and the molecular weight:

$$T_{cl} = a + b (MW)$$

This particular functional form is chosen largely for convenience, but is also suggested by the modeling results of Bates and Luckhurst [1996] considering that V (molecular volume) and h (well depth per molecule) can be expected to show an approximately linear scaling with molecular weight. The model is now completely defined if we specify the three parameters: H_{cl} , a , and b , or alternatively, H_{cl} and clearing temperatures at two different molecular weights.

The three parameters were assigned in the following way. The point of unity partition coefficient in Fig. 9 (MW ~ 1000) fixes the clearing temperature of the 1000 MW fraction at the system temperature (400 °C). This fact is easily seen by examination of Eqs. 8 and 9 with T equal to T_{cl} , and it establishes one of the three parameters. The second parameter needed to define the T_{cl} / MW relationship cannot be determined precisely, but can be assigned a reasonable value based on the following considerations. Clearing temperatures for lower molecular weight components must be low enough to ensure that the PAH structures in Fig. 3 are nonmesogenic, as observed. This limits T_{cl} to less than about 100 °C for a molecular weight of 400. Also, the estimated virtual T_{cl} for coronene (300 MW) is 120 °C and a virtual clearing temperature for the triphenylene core (MW 228) has been estimated at 55 °C by Queguiner et al., [1980]. Based on this information, a reasonable choice for the clearing temperature of MW 400 species is 100 °C. Altering this value by ± 100 °C does not greatly alter the model predictions.

The final parameter, H_{cl} , then determined by comparison of model predictions to the pitch carbonization data of Greinke and Singer [1988] in Fig. 3. The best fit is shown as a line, and the resulting value of H_{cl} is 9 J/gm. This value is much less than typical heats of fusion for known PAH; for example it is about 8% of 110 J/gm, an average heat of fusion computed for 14 PAH. Calorimetric studies of phase transitions in pure liquid crystalline systems show, with few exceptions, that the clearing enthalpies are indeed much smaller than the heats of fusion. All the model parameters are summarized in Table 3.

Figure 3 Application of the multicomponent model to the pitch carbonization data of Greinke and Singer [1988]. Measured vs. predicted partition coefficients.

Table 3
Model Parameters and
Best Values for Greinke and Singer Data

Clearing temperature: $T_{cl} \text{ (K)} = a + b \text{ MW}$

$a = 0.5$

$b = 173$

Mass-specific clearing enthalpy: $H_{cl} = 9 \text{ J/gm}$

Activity coefficients: $i^N = i^I = 1$

Conclusions from the initial development and testing of the mesophase thermodynamic model can be briefly stated as follows.

1. The set of known fully-condensed PAH do not form discotic liquid crystals in their pure state. The temperature ceilings for the liquid crystalline phases (clearing temperatures) are virtual transitions that lie below solid melting points and/or chemical decomposition temperatures. The known liquid crystalline nature of carbonaceous mesophase can only be rationalized by considering

partially condensed structures (e.g. aryl-linked oligomers of small polyaromatic cores) and/or multicomponent mixtures.

2. A quantitative model of a generic carbonizing system has been developed based on solution thermodynamics. Equations of phase equilibrium dictate the amount and composition of the coexisting isotropic (liquid) and anisotropic (liquid crystal) phases for a fixed molecular weight distribution of carbonization products. Example phase diagrams are given for binary and ternary systems. In multicomponent mixtures, crystalline solid phases are suppressed revealing the underlying liquid crystalline phase. Mixture effects are shown to be key to the understanding of carbonaceous mesophase.
3. The thermodynamic model describes the complete phase behavior a given material if the clearing enthalpy and clearing temperatures are specified as a function of molecular weight. The model successfully describes the pitch carbonization data of Greinke and Singer, implying a clearing temperature of 400 °C for 1000 MW species and a clearing enthalpy of about 9 J/gm (less than 10% of a typical heat of fusion for fully condensed PAH). The model and optimal parameter set can be used to explore the effects of molecular weight distribution, temperature, and blending processes on the formation and composition of carbonaceous mesophase.

Adaptation to coal carbonization / combustion

The optical properties of coal chars vary greatly across the rank spectrum, revealing a highly variable degree of order that is one key to understanding their properties and combustion behavior. Unfortunately, coal is a highly substituted, cross-linked, polyaromatic network that cannot be treated as simple as pitches. One approach to coals is the two phase approximation, in which the viscous carbonizing melt is divided into a rigid crosslinked solid phase (which cannot form mesophase) and a liquid phase consisting of mobile PAH that rapidly partition into equilibrium amounts of the isotropic liquid and the anisotropic carbonaceous mesophase.

For this approach, one needs to couple the mesophase thermodynamic model with a prediction of the amount of liquid phase liberated during carbonization, and its molecular weight distribution. The network pyrolysis models developed over the past several years, CPD, FLASHCHAIN, FG-DVC, each provide a prediction of the amount and molecular weight distribution of liquid products from the pyrolytic depolymerization of coal. It was undertaken this quarter to conduct a feasibility study of the coupling of the mesophase thermodynamic model and FG-DVC, the network pyrolysis model developed at Advanced Fuel Research.

The model concept is illustrated in Fig. 4. FG-DVC describes the depolymerization and re-crosslinking of the macromolecular network and the production and transport of gases, liquid, and solids. The mesophase thermodynamic model partitions the liquid into two phases, predicting the composition (MW distribution) and amount of each phase. At some

point, molecular weight growth processes lead to a glass transition, which prevents equilibrium and transport across the phase boundaries.

A technique for describing the resolidification process is under development and will be discussed in a future report. The initial feasibility studies focused on high heating rate pyrolysis typical of combustion (50,000 K/sec) of four coals of various rank (Beulah lignite, Illinois #6, Pittsburgh #8, and Pocahontas). These four coals make useful modeling targets as the basic features of the optical texture of their flame chars is known.

Char Structure Prediction from Mesophase Thermodynamics

Figure 4. Flow of logic in the prediction of coal char structure based on FG-DVC and mesophase thermodynamics

The Pocahontas flame char is highly anisotropic, Illinois is isotropic, and the Pittsburgh char intermediate between the two. The lignite undergoes solid-state carbonization to form an all-isotropic carbon. A detailed study of the optical textures of flame chars from these coals is underway, based on extractive sampling from the Brown entrained flow reactor followed by reflected light microscopic analysis. In the meantime, the basic features of the flame chars from these benchmark U.S. coals as known from the literature and can be used to guide model development.

FG-DVC was used to make predictions of the liquid fraction as a function of temperature for each of the four coals being heated at $5 \cdot 10^4$ k/s. The results are shown in Figs. 5 - 7. The coals vary greatly the amount of liquid they yield upon pyrolysis (see Fig. 5). Note

that significant "liquid" fraction at low temperatures for Illinois and Pittsburgh represent the extractable material in the raw coals that is interpreted as organic material that is not covalently bonded to the macromolecular network.

The lignite produces very little liquid, and will therefore form a largely isotropic char regardless of the behavior of the liquid phase. In contrast, the Illinois and Pocahontas coals represent an interesting challenge for the modelling work — although Illinois produces abundant liquid, its chars are isotropic, while the Pocahontas with its lower liquid fraction is highly ordered.

Figure 5. FG-DVC predictions of liquid fraction during high heating rate pyrolysis of four U.S. coals of varying rank.

Figures 6 and 7 shows the prediction of the mesophase thermodynamic model. This solution uses the same thermodynamic parameters found for pitches (see Table 3), so no adjustable parameters were involved in this calculation. The Illinois coal is predicted to form only an isotropic phase during the main part of pyrolysis (near the peak liquid fraction in Fig 5) in agreement with the known isotropic nature of its flame chars. The bulk of the molecular weight distribution is too low to favor carbonaceous mesophase (the

thermodynamic tendency to form discotic liquid crystalline phases increases greatly with increasing aspect ratio of the disk-like objects, corresponding to increasing molecular weight of the oligomers of aromatic clusters.) The dashed line in Fig. 5 gives the prediction prior to the onset of primary pyrolysis — the extractable material in coal is predicted to be ordered. This latter prediction is not believed to be relevant, as these oligomers have not undergone sufficient thermal processing to rearrange into nearly planar structures. This apparent order is lost between 400 and 600 °C, giving way to the isotropic phase during primary pyrolysis.

Figure 6. Predictions of mesophase and isotropic liquid fractions during high heating rate pyrolysis of Illinois #6 coal based on the combined use of FG-DVC and the mesophase thermodynamics model.

The same model parameters, when used to make predictions for Pocahontas #3, predict the formation of some carbonaceous mesophase. At 1050 K the liquid phase is equally partitioned into isotropic phase and mesophase. As temperature increases to 1200 K, the carbonaceous mesophase disappears yielding isotropic liquid. At the point of peak liquid fraction, the isotropic phase accounts for about 80% of the liquid. There is clearly a difference between the Illinois and Pocahontas, with the Pocahontas showing a high tendency toward carbonaceous mesophase during to the larger molecular weights in its liberated fragments. At present, however, the absolute amounts of carbonaceous mesophase for Pocahontas are too low. Much more mesophase is predicted to form if the

Figure 7. Predictions of mesophase and isotropic liquid fractions during high heating rate pyrolysis of Pocahontas #3 coal based on the combined use of FG-DVC and the mesophase thermodynamics model.

liquid crystal forming tendency is enhanced by modifying the coefficients in the clearing temperature / molecular weight relations. It was found however, that large modifications were needed to make carbonaceous mesophase dominate in the late stages of pyrolysis. It is currently believed that the underprediction of mesophase formation will be solved when a proper description of the solidification process is developed and included.

A method of treating solidification is needed before a complete assessment of this approach can be made. Detailed examination of the model outputs reveals that the carbonaceous mesophase disappears in the middle-to-late stages of pyrolysis due to the long shift in the oligomer population toward low molecular weights. This is believed to be due to the completion of depolymerization, which yields many small fragments, and the formation of solid through oligomer-oligomer attachment or oligomer-network attachment. The high molecular weight products of these two events are removed from the liquid pool, and if the attached oligomers are themselves high in molecular weight, the remaining liquid can become lighter in the calculation. Thus solid formation suppresses mesophase production in the late stages of pyrolysis by removing high molecular weight material from the liquid phase equilibrium calculation. This effect is not desired and can likely be eliminated by

proper description of the solidification process. Overall this approach is very promising, but a final assessment must await the inclusion of a theoretical technique for handling solidification.

References: Section II

- Bates, M.A., Luckhurst, G.R. *J.Chem. Phys.* 104 (17) 6696 (1996).
- De Gennes, P.G., Prost, J. *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 1993.
- Greinke R. A., and Singer, L.S. *Carbon* 26 665 (1988).
- Hurt, R.H. and Hu, Y.; "Thermodynamics of Carbonaceous Mesophase" 23rd Biannual Conference on Carbon, Penn. State University, The American Carbon Society, 1997.
- Marsh, H., and Walker, P.L.Jr., Chap. 3 in *Chemistry and Physics of Carbon, Vol. 15*, (Walker and Thrower, eds.). Marcel Dekker, New York, 1979.
- Queguiner, A., Zann, A., Dubois, J.C., Billard, J., "Mesogenic Disc-Like Molecules with Twofold Symmetry Axis", in *Liquid Crystals*, S. Chandrasekhar, ed., Heyden, London, 1980.
- Riggs, D.H., and Diefendorf, R.J., *Carbon '80 Int. Carbon Conf. Preprints*, (1980).
- Rouzaud J.N. and Oberlin A., Ch. 17 in "Advanced Methodologies in Coal Characterization," (Charcosset ed.) Elsevier, Amsterdam, 1980.

Section III: Combustion Experiments in Contrasting Flame Types (within Task 2 at OSU)

Full time work on the Combustion Laboratory activities has not yet been possible; this is waiting on appointment of a full time GRA (Graduate Research Assistant). A suitable candidate, just graduated, is now available, and the GRA appointment is expected to be made in July. In the interim, progress has been made during the Spring Quarter (April-June) utilizing undergraduate students enrolled in the ME 581 Mechanical Engineering Laboratory course. The task given to the students was to determine the state of the equipment, fire the furnace, and initiate the sampling processes to obtain solid samples. Time put in was two 2-hour periods per week for 9 weeks, and this task was, broadly, completed. First char samples were obtained. Some of these were examined by SEM by Mr. Michael Thompson as part of a course: Geol. Sci. 675 Use of the Electron Microscope. Other samples were supplied to the OSU Chemistry group under the direction of Dr. Chris Hadad, and he has reported separately on his findings. These results have just become available.

Furnace activities

The furnace consists of a vertical refractory tunnel topped by a water-cooled tube bank, with a conical distributor above the tube bank. The coal-air mixture to fire the furnace is supplied at the top of the cone along with secondary air for separate control of the stoichiometry. The coal-air mixture is fed to the cone from a mechanical feeder feeding into a jet-injector pick-up point. Primary and secondary air are supplied from the university compressed air system, and are separately metered. The coal feed into the primary line is through a funnel to the jet-injector pick up point where the compressed air expanding through the jet reduces the local pressure and allows the coal to enter the air line. The reduced pressure is sufficient to draw in substantial quantities of unmetered air. To control this, the pick up point is enclosed in a plexiglass box, and some of the metered primary air is fed into the box at a controlled rate to balance the pressure in the box (to prevent unmetered infiltrating air). During firing there is also draft control for the furnace by use of compressed air jets into the exhaust flue.

The furnace temperature profile is monitored by thermocouples in the walls, with the tips flush with the inside wall. Measurements in the furnace are obtained (mostly) by intrusive sampling for solid and gas samples, and for temperature by suction pyrometer and by 2-color pyrometry. The suction pyrometer measurements approximates the gas temperatures, and the 2-color approximates an (average) temperature for the particles where the particles are known to be burning at different temperatures, substantially dependent on particle size, so far as is known at this time. The different particle sizes are known to be responsible for part of the burn-out "tail" at the end of the flame.

For input measurement purposes, the air rates and coal feed rates must be known. The air rates are metered during firing (on-line) by standard flow meters. The coal feed rate must be measured by calibrating the feeder off-line, by feeding into a weighing cup for a known period of time. For wall temperature measurements from the wall thermocouples, the set-

up is designed for continuous input into an A/D converter and logged into a PC recorder, with read-out on call-up for monitoring. For internal gas analysis measurements, these are designed for O₂, CO₂, and CO by continuous sampling, with feed to the on-line analyzers through wash bottles and dryers. Likewise, the suction and 2-color pyrometers as designed are also on-line. Solid samples are obtained in batches, by continuous sampling (as for gas analyses), but with filters in the sampling line so that samples are obtained over periods of a minute or several minutes depending on solids concentration in the flame.

The solid samples can then be analyzed in several ways. Past analyses in previous projects have included: PSD using a MicroTracII, and internal surface by BET; also, VM (residue) and ash by treatment in VM and ashing furnaces, and in some cases, elemental analysis. New measurements, as identified above, will include SEM, and other measurements as reported by Dr. Hadad, and specifically NMR.

Status of Experimental Activities

Operation of this equipment is not a "press-button" action. It takes substantial time for training and development for familiarity with the equipment. For the new student this is expected to take most of the summer (next quarter). Accordingly, in the current work, the ME 581 student activities were limited to the basic actions of firing the furnace and obtaining solid samples. This involved: checking the coal feeder, the air lines, the feed pick-up point and vacuum control, the wall TC data-logger, the furnace draft control, and assembling the water-cooled solid sampling probe with the necessary filter to capture the samples, and with a line to the vacuum pump. These units were available but had been disconnected and required re-assembly.

These defined activities were substantially completed in the period of time reported, with some problems identified. Getting to the point that the furnace could be fired took two to three weeks. Some difficulties were initially experienced with the coal feed into the pick up point due to imbalance of the pressure in the plexiglass box. After rectification, stable flames were obtained in the furnace and, after assembling the coal sampling equipment, the samples identified were obtained. Towards the end of the Quarter, further difficulties were experienced with the coal pick up that now have to be resolved; the feeder is feeding faster than the pick-up can take the coal. At this time the problem is thought to be plugging of the feed line from the feeder to the top of the cone; alternatively, it may be wear in the jet pick-up point. This problem is now being addressed. Other problems that have been identified include: logging difficulties with the data-logger that is used both for the (slow) wall TC data and for the (fast) 2-color data. Immediately, the problem has been side-stepped by using a direct reading zero-voltmeter and converting to temperatures by tables. This is another problem now being addressed.

For the gas analyses, the O₂ and CO₂ analyzers have been separately checked out and are on-line though it was not possible to include them in the reporting period measurements for lack of time and experience on the part of the student operators.

Results

Results are limited at this time to: getting the furnace substantially on-line; and obtaining char samples with some initial analyses.

The SEM photographs are more visually than analytically informative at this time. They show, in some cases, the typical rounding of the local surfaces of the char particles at high magnification, but also a general 'granulation' of multitudes of particles at low magnification. There are also highly ordered broken spheres that are most probably from molten minerals. A question to be considered is how much attention should be given to detailed analysis of the non-organic accessible constituents.

The NMR results reported by Dr. Hadad may be more informative, particularly if more complete sample solution is possible. Notably, as he reports, the results show significant levels of hydrogen (and of different kinds) in the solvent samples.

Discussion

The most significant result may be the reported level of hydrogen in the samples. This relates to the question of the structure of coal and to its behavior on heating. For purposes of discussion, without representing this as yet established fact, a working model for coal constitution is the Two-Component Hypothesis which represents coal as consisting of two primary components, essentially an (X-ray) ordered component and an (X-ray) amorphous component. The ordered component is identified as consisting essentially of condensed aromatic rings in layers, with about half the double bonds between carbons saturated with hydrogen. The number of rings per layer is about four up to roughly 90% carbon; it then increases rapidly (interpreted as condensation of the ordered component). The amorphous component is identified as the main source of hydrocarbon volatiles that are also identified as "easily evolved" during pyrolysis. This model is derived partly from and is consistent with the known behavior of coal in pyrolysis where the initial components are hydrocarbon gases (notably methane) together with condensable vapors and tars, and the final gaseous component is mainly hydrogen. Removal of the condensable components from the volatiles leaves a mixture of light gases with, typically, about 50% H₂ and 30 to 35% CH₄ as the main constituents, these being the principal components of coal (city) gas.

The release of the light gases, vapors, and tars is relatively fast. Release of the hydrogen is relatively slower, requiring temperatures (in coking ovens) in excess of 600°C. The kinetics of release of Component I from the coal, and of the hydrogen from Component II (left after the Component I release) are substantially different. It is known on the "long term" (10 minutes) heating basis during standard BSS/ASTM volatile analysis, that there is hydrogen (and nitrogen) left in the coke button so that the total volatiles are under-reported in standard BSS/ASTM-V_m analysis by about 2%. For the hydrogen, this on a DMMF weight basis is about 1% with the balance mostly carbon, but on an elemental basis this would approximate as C₈H which is also one of the bounds found for carbon formed in sooting flames, of C₈H to C₁₂H. The implication could be that an important fraction of the hydrogen remains in the char after pyrolysis, possibly persisting right through the flame. The further implication is that this may result in a more reactive char structure depending on the quantity of hydrogen remaining. There are a substantial number of pyrolysis models

now available, notably those of Howard, of Niksa, and of Solomon. It is not evident, however, that these models show any hydrogen (or nitrogen) residue in the char residue during flame heating times. This is something to be examined.

Future Work

The principal task for the next quarter is completion of the re-commissioning of the furnace, the ancillary equipment, and the instrumentation. In addition, it will be necessary to move the furnace (about 10 ft.) during this period to accommodate removal of the existing Combustion Laboratory chimney stack and construction of a replacement. This may involve a complete rebuild of the furnace; this has yet to be determined.

The principal problems identified at this time to be addressed are: the choking of the feed line from the feeder to the cone; and the problem of the data logger (required both for the wall temperatures and for the 2-color pyrometer). The O₂ and CO₂ analyzers are on-line; a new CO analyzer is required, however, and this must be purchased; also the sampling probes and filter system require some re-building. The MicroTrac II particle size analyzer is operating. The BET analyzer and the suction pyrometer require checking for operability.

The target of the experimental work will be to obtain char samples simultaneously with flame profiles (temperature, gas analyses, etc) in flames of different stoichiometry, firing rates, and coal type. The need for the flame profile data is to provide the particle history through the flame to the sampling points. The focus of the tests on the chars will be to determine changes in reactivity (e.g., by TGA), structure, and/or composition. With regard to this last, the H/C ratio may be critical, and this possibility is to be addressed.

U.S. DEPARTMENT OF ENERGY

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

Project start date: 9/30/96

Project completion date: 9/30/99

[illegible]

U.S. DEPARTMENT OF ENERGY

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
			1999												
			1998												
			1998												
1.	general	selection of test coals	complete												Brown / OSU
2.	2.1	development of dynamic structural models													
2a.		<i>nonbonded graphene layers</i>													BU / Brown
2b.		<i>linked networks</i>													BU / Brown
2c.		<i>model synthesis</i>													Brown
3.	2.	<i>in-situ, hot-stage fringe imaging</i>													Brown
4.	2.2	<i>computational chemistry of surface oxidation</i>													OSU
5.	3	<i>experiments in contrasting flame types</i>													OSU
6.	3	<i>analyses of char samples from part 5.</i>													OSU
7.	2.1	<i>establishment of secondary correlations:</i>													
7a.		<i>structure / reactivity</i>													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		near completion
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		in progress
6	First set of thermochemical computations complete for model organic structures	Dec. 1997		near completion
7	Shakedown / testing of OSU furnace facilities complete	Oct. 1997		near completion
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	Auxilliary correlations complete	Dec. 1998		