STRUCTURE-BASED PREDICTIVE MODEL FOR COAL CHAR COMBUSTION

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EXECUTIVE SUMMARY

Progress was made this period on a number of separate experimental and modelling activities. At Brown, the models of carbon nanostructure evolution were expanded to consider high-rank materials with initial anisotropy. The report presents detailed results of Monte Carlo simulations with non-zero initial layer length and with statistically oriented initial states. The expanded simulations are now capable of describing the development of nanostructure during carbonization of most coals. Work next quarter will address the remaining challenge of isotropic coke-forming coals. Experiments at Brown yielded important data on the "memory loss" phenomenon in carbon annealing, and on the effect of mineral matter on high-temperature reactivity. The experimental aspects of the Brown work will be discussed in detail in the next report.

At Ohio State, ongoing theoretical work has provided evidence for the accurate treatment of the reactivity of graphitic surfaces by density functional theoretical methods. In particular, the "hybrid" B3LYP method has been shown to provide quantitative information on the stability of the corresponding radicals that arise from hydrogen atom abstraction from monocyclic aromatic rings. In this most recent quarter, efforts have focused on understanding the specific sites of hydrogen atom abstraction of model PAHs (i.e. the preference for bond dissociation and the beginning of reactivity), the bond dissociation energies of larger PAHs, and the mechanism of oxidative decomposition of monocyclic rings. In the experimental task at Ohio State, the laboratory retrofits reached near completion and experimental work began on the small jet stirred reactor. This experimental work will be described in more detail in upcoming reports.

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

Progress was made this period on a number of separate experimental and modelling activities. At Brown, the modelling effort targeted at carbon nanostructure evolution was expanded to consider high-rank materials with initial anisotropy. Monte Carlo simulations were carried out with non-zero initial layer length and with statistically oriented initial states. The expanded simulations are now capable of describing most of the nanostructural features of carbonization for coals of various rank. Work next quarter will address the remaining challenge of isotropic coke-forming coals.

Experiments at Brown yielded important data on the "memory loss" phenomenon in carbon annealing, first reported by Seneca et al [1996]. Heat treatment is shown to reduce reactivity (as widely observed), but the reactivity differences *diminish* as the samples are progressively oxidized. For three of four coals studied this quarter, the reactivities of 900 °C and 1300 °C treated chars are *similar* after they have been oxidized to 90% conversion. This appears to be a common but not universal behavior of chars. Work is proceeding to explain the origin of the memory loss.

A separate experimental study was also initiated on the effect of mineral matter on high-temperature reactivity. The CBK model includes a description of mineral inhibition in the late stages of combustion, a model feature that was necessary to explain experimental burnout profiles at high conversion. To validate and/or improve this model, data is needed that directly addresses the mineral effects, distinct from other phenomena that may occur at high conversion. Acid demineralization has been employed in the past, but it is difficult to ensure that this harsh treatment has not also affected the chemistry and reactivity of the carbonaceous matrix. Experiments were performed this quarter in which ash particles were doped into coal chars at varying levels, and the high temperature combustion behavior studied in an entrained flow reactor. This "reverse" approach does not alter the carbon matrix and should clearly indicate what ash concentrations are needed to influence high-temperature combustion rates. The first set of experiments on the entrained flow reactor showed a strong inhibitory effect of ash. Work is continuing and will be described in more detail in later progress reports. Finally, a series of *in situ* hot stage high-resolution TEM studies were also carried out on pure and inorganic doped model chars made from phenol-formaldehyde resin. The experimental aspects of the Brown work will be discussed in more detail in the next report.

At Ohio State, recent theoretical work has provided evidence for the accurate treatment of the reactivity of graphitic surfaces by density functional theoretical methods. In particular, we have shown that the "hybrid" B3LYP method can be used to provide quantitative information on the stability of the corresponding radicals that arise from hydrogen atom abstraction from monocyclic aromatic rings. The eventual goal is to examine the potential energy surface and mechanism of reactivity on a coal char surface so as to understand the kinetic issues involved. In this most recent quarter, efforts have focused on understanding the specific sites of hydrogen atom abstraction of model PAHs (i.e. the preference for bond dissociation and the beginning of reactivity), the bond dissociation energies of larger PAHs, and the mechanism of oxidative decomposition of monocyclic rings.

In the experimental task at Ohio State, the laboratory retrofits reached near completion and experimental work began on the small jet stirred reactor. It has been successfully fired numerous times with a stable, sustained coal flame and sample acquisition is expected within weeks. This work will be described in more detail in upcoming reports.

DETAILED DISCUSSIONS OF PROGRESS

Section 1: Modelling of Carbon Nanostructures

Many carbon properties depend on nanostructure — the spatial arrangement of the graphene layers that are the basic building blocks of the material [Oberlin, 1990]. For organic precursors poor in oxygen and stable sulfur, nanostructural ordering occurs through phase transitions in the molten stage of carbonization, and there have been several attempts to model these transitions with liquid crystal theory [Shishido et al., 1997, Hurt and Hu, 1998]. Nanostructural ordering in coals is more complex, as they have high concentrations of oxygen and sulfur, which act as crosslinking agents that can hinder the liquid crystal transitions. In earlier reports, we have presented simple mathematical formulations capable of describing the development of orientational order among graphene layers for a variety of organic precursors and carbonization conditions, coals from across the rank spectrum. Two techniques are being explored: Monte Carlo simulations of order / disorder transitions, and a macroscopic thermodynamic model of liquid crystal phase transitions coupled to a network pyrolysis model for prediction of the liquid pyrolysis intermediates. In this report we present further progress on the Monte Carlo simulations, an effort carried out in collaboration with Alan Kerstein at Sandia National Laboratories.

Model description

The procedure used in the Monte Carlo simulations is as follows. Points are chosen at random in a two-dimensional simulation space and allowed to grow into lines at a fixed rate, G , with growth at both ends. The lines (which represent layers) are also allowed to translate and rotate with mean linear and angular velocities, V and R , respectively. Random numbers are generated at each time step to determine the actual change in position and orientation for a proposed motion event. Overlap between the lines is forbidden, and thus both growth and motion are carried out in a given time step only if the required space is available. Results from these simulations have been presented as structural images in earlier reports. At high layer mobility, mutual avoidance causes the layers to align during the later stages of growth leading to an ordered phase. At lower mobility the alignment is hindered and the layers adopt a final state with short range order only, reminiscent of distinct crystallites with random orientation in isotropic carbon materials. The order in the final state can be characterized by a 2D order parameter,

$$S = 2\langle \cos\theta \rangle^2 - 1$$

which ranges from 0 for random layer orientational (or for crystallites oriented at random) to a value of 1 for perfect long-range alignment. Nondimensionalization of the model inputs and outputs reveals that the simulations are defined by two dimensionless input parameters,

$$S = f(M^*, T^*)$$

$$M^* \equiv R / (G \rho^{1/2})$$

$$T^* \equiv V \rho^{1/2} / R$$

of which M^* , a dimensionless orientational mobility / growth ratio, is the more important.

The results of the simple simulations are summarized in Fig. 1.1 in the curve labeled "initial isotropy branch". In a critical range of mobility-to-growth ratio, M^* , the process undergoes a transition from short range order to long range order. We believe this is analogous to the transition from nongraphitizing carbons to graphitizing carbons as the concentration of crosslinking agents decreases and thus layer mobility increases. For example, one can interpret Fig. 1.1 in terms of the coal rank spectrum, with the lower left branch of the solid curve representing low rank coals and the upper right branch the high rank bituminous coals that exhibit coke texture. The solid curve cannot describe anthracites, however, which exhibit low mobility (are nonsoftening), but form graphitizing carbon in some cases.

Figure 1.1 Simple simulations of coal char order development from initially random states (isotropic parent materials) and initial ordered states (anisotropic parent materials). Long-range nematic order parameter is plotted as a function of the dimensionless mobility / growth ratio, M^* . Each of these simulations begins with layers of zero length.

In an attempt to represent anthracites, additional simulations were carried out, in which the layers have a preferred initial direction (nonzero S_0), giving rise to the curve labeled "initial anisotropy branch" in Fig. 1.1. At very low mobility, the initial orientational order in the coal is preserved intact in the char ($S = S_0$). At higher mobility, the initial order is lost, leading to isotropic final chars (see the deep trough in the initial anisotropy branch of Fig. 1.1). This deep trough does not correspond to any known natural carbonaceous substance. To accurately simulate order development in high-rank materials, an additional factor must be added to the simple simulations to eliminate the trough.

It was found that anthracitic order can be adequately represented by simulations in which the layers have a preferred initial direction (nonzero S_0) and nonzero initial length. Indeed, TEM and XRD studies of raw anthracites indicate that significant graphene layer development has occurred during coalification. These simulations lead to the dashed curve in Fig. 1.2. The anthracitic branch shows an gradual increase in order from the initial state as mobility increases. The low mobility

Figure 1.2 Simple simulations of coal char order development from initially random states (isotropic parent materials) and initial ordered states (anisotropic parent materials). The anisotropic starting materials are also given non-zero initial length. Long-range nematic order parameter is plotted as a function of the dimensionless mobility / growth ratio, M^* . The incorporation of initial length and initial anisotropy is sufficient to explain the major features of anthracitic order, and the interpretation in terms of the coal rank spectrum is indicated on the diagram.

materials are thus predicted to have a moderate degree of orientational order — much more than the low rank chars but less than the mobile, high-rank bituminous cokes. Overall, by incorporating initial anisotropy and initial length, these simple simulations reproduce most features of the coal rank spectrum, and the various curve branches are labeled in Fig. 1.2 correspondingly.

It is also found that these simple simulations exhibit a *time-dependent* behavior that parallels observations. Fig. 1.3 shows time dependent simulation results for three cases representing important classes of coals. The simulations show that: (1) the low rank coals are nearly isotropic and remain so during carbonization, (2) the high rank bituminous coals lose their initial anisotropy, but regain it during the latter stages of carbonization, (3) some anthracites retain and slightly enhance their anisotropy during carbonization.

Measurements of optical birefractance (a indicator of the degree of orientational order) as a function of precursor and carbonization conditions show trends very similar to those in the simulations. Figure 1.4 show measurements of optical birefractance as a function of carbonization temperature for three coals of various rank [Murchison, D., 1978]. These results are given as a function of temperature, rather than time, but are indicative of the solid structures observed during the various stages of carbonization, as they might occur during non-isothermal heat treatment. The lowest rank coal is isotropic it its initially state and remains essentially so during carbonization. The low

Figure 1.3. Time evolution of the long-range nematic order parameter in three simulations representing important classes of coals.

volatile coal shows measurable anisotropy in its initial state, but loses this anisotropy at 400 °C, and then regains it above 400 °C. The final degree of order is very high in the sample carbonized at temperatures above 400 °C. The anthracite in raw form shows significant anisotropy, which is unaltered up to 600 °C and then slightly enhanced by higher temperature heat treatment. Despite the high degree of initial order, the anthracite does not develop the same degree of order as the low volatile bituminous coal. This is consistent with the observation that some anthracites are graphitizing carbons, while others are not. Comparing Figs. 1.3 and 1.4, it is seen that the simple hard-line simulations mimic the major trends seen in bireflectance studies.

Figure 1.4. Measurements of optical bireflectance as a function of carbonization temperature for three important classes of coals from Murchison [1978].

The first version of the numerical model proposed by Kerstein [Hurt et al., 1997] was attractive for its simplicity, being defined primarily by a single dimensionless parameter, M^* , representing the mobility to growth ratio for planar aromatic clusters. In this report we have extended its applicability to a range of coals (anthracites, low-volatile bituminous, and low rank) by the incorporation of initial anisotropy and initial length as additional parameters. The remaining challenge is to find the minimum modification necessary to correctly predict the behavior of some high-volatile bituminous coals which are highly mobile (of low viscosity) but produce isotropic cokes. Work next quarter will focus on this challenge. Overall, this modelling approach, while obviously neglecting many features of carbonization, is quite promising as a first step in the quantitative description of the formation mechanisms of carbon nanostructures.

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Section 2: Computational Chemistry

In our recent quarterly reports, we have provided evidence for the accurate treatment of the reactivity of graphitic surfaces by density functional theoretical methods[1]. In particular, 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 from hydrogen atom abstraction from monocyclic aromatic rings. Our eventual goal is to examine the potential energy surface and mechanism of reactivity on a coal char surface so as to understand the kinetic issues involved. Our approach has been to model these coal char surfaces by using polycyclic aromatic hydrocarbons (PAHs), and this report will provide more information towards this goal. In this most recent quarter, we have focused our efforts on understanding the specific sites of hydrogen atom abstraction of model PAHs (i.e. the preference for bond dissociation and the beginning of reactivity), the bond dissociation energies of larger PAHs, and the mechanism of oxidative decomposition of monocyclic rings.

Thus far, we have expended significant effort on calibrating different electron correlation methods such as Møller-Plesset (MP) perturbation theory[3] and density functional theory[1] for studying problems in PAHs. The density functional methods will be most useful as the “hybrid” B3LYP functional has shown success in predicting *accurate* chemical phenomena and at a *reasonable cost* for large systems.[4] As noted earlier, these types of calculations suggest tremendous promise for treating PAHs.[5]

Our previous reports have shown that the B3LYP method provides more accurate results when compared to experiment[6] for PAH bond dissociation energies (BDEs) than Complete Basis Set (CBS),[7] Gaussian-2 (G2),[8] and G2MP2 [9] methods and the latter have been shown to be very accurate (less than 2 kcal/mol) for a host of chemical properties. We have provided previous information on the performance of the different methods to calculate BDEs of monocyclic PAHs (Scheme I). We have spent considerable effort recently at understanding the preferences for low BDE in these systems. In particular, we have noted the following trends. The BDEs are relatively similar (about 112 kcal-mol⁻¹) between all of the monocyclic aromatic compounds, and only the H-atom abstraction processes from the azabenzenes (nitrogen-containing aromatics) have a significantly lower BDE than for benzene. There seems to be something very special about the energy for H-atom abstraction when a nitrogen is in a 6-membered ring.

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

The average BDE for 5-membered rings ($117.1 \text{ kcal}\cdot\text{mol}^{-1}$) is higher than that for 6-membered rings ($108.3 \text{ kcal}\cdot\text{mol}^{-1}$). Comparing between positions in the same molecule, there is no special preference (less than $1 \text{ kcal}\cdot\text{mol}^{-1}$) for hydrogen atom abstraction in furan and pyrrole. However, in thiophene there is roughly a $3 \text{ kcal}\cdot\text{mol}^{-1}$ preference for abstraction of a H-atom from C-3

Figure 2.1. Dependence of the C-H BDE on the excess spin density at the position of abstraction.

compared to C-2. This preference for C-3 over C-2 is opposite to that in furan and may be related to the different lone pairs on the heteroatom in the different systems. We have noted that the C-X-C bond angle is significantly different for X=O and N (107-110°) than when X=S (~91°).

We have analyzed how much of the excess radical spin density resides on the location where the hydrogen atom was abstracted. From a simple delocalization argument, the lower BDE will be expected when the unpaired spin can be spread out over more atomic centers rather than localized on only one atomic center. We have plotted in Figure 2.1 the dependence of the C-H bond dissociation energy vs the excess spin density on the position of abstraction. The spin density was evaluated via Bader's Theory of Atoms in Molecules[10] which should be quantitatively accurate. There is a strong correlation between the two items, and the correlation is independent of being a 5 or 6 membered ring or having a first (C, N, or O) or second row (S) substituent. Thus, the ability to stabilize the excess radical spin density seems to dictate a low bond dissociation energy.

In pyridine, the C-H bond dissociation energies are significantly lower than that for benzene. In addition, for pyridine there is approximately a 5 kcal-mol⁻¹ preference for abstraction of the hydrogen attached at C-2 (immediately adjacent to the nitrogen). Once again, we consider that there is a strong effect of the adjacent nitrogen lone pair and there is a large amount of spin density on the nitrogen center. The geometrical effect has been noted previously.[6]

Figure 2.2. Relationship of the C-H BDE to bond angle changes after radical formation.

We have also examined the geometric changes that occur after hydrogen atom abstraction and they are consistent with a significant sp-type hybridization at the center of H-atom abstraction. Figure 2.2 shows that there is a rough correlation between the increase in geometric bond angle (C-X-C, where X is the center of H-atom abstraction) and the BDE for the 6-membered rings. The 5-membered rings show much less of a correlation. The latter effect may be due to the extra strain involved in placing an sp-hybridized atom in a 5-membered ring vs a 6-membered ring.

Since we have shown that the B3LYP level (and other DFT methods) can be well applied to calculating accurate energies for these aromatic systems, we have begun an exploration of some larger PAHs. In Figure 2.3, we have listed BDEs for some larger PAHs as DH° values at 298 K. We noted previously in calculations on naphthalene and anthracene (Scheme II) that HF values are significantly different than that at the B3LYP level. As a result, we have examined the other large PAHs with the B3LYP method only.

As can be seen from Figure 2.3, the C-H BDEs are relatively insensitive to ring types when the C-H bond is not adjacent to a heteroatom. In such cases, the C-H BDE ranges from 110.9 to 113.8 kcal-mol⁻¹ and they are very similar to that of benzene. All of the naphthalene and anthracene BDE values are relatively insensitive to position, with a deviation of only 0.3 kcal-mol⁻¹. Many of the other molecules reveal the same trends. When the C-H bond is adjacent to a heteroatom, there are significant differences for the C-H BDE. However, for the fused 5 membered rings (benzofuran, indole, benzothiophene and benzoxazole), the C-H BDE is higher than that for a C-H bond in benzene. The quinoline system has a low C-H BDE (104.5 kcal-mol⁻¹) for the C-H bond adjacent to nitrogen. This is similar to that observed for pyridine and the other azabenzenes.

We have continued to explore the potential energy surfaces for oxidative decomposition of aromatic radicals with oxygen. We are particularly interested in the intermediates involved in the combustion process and 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.[11] They have also published calculations in the past few years on intermediates of relevance to the oxidation of benzene.[12] Their results 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.

Previously, we reported preliminary potential energy surfaces for the O₂ chemistry of radicals derived from benzene and furan (at the C-2 position only). We have continued with these projects and have also added pyridine to our study. We are particularly interested in the mode of decomposition of these radical intermediates so as to provide the bottle-necks for oxidation on a coal char surface.

Figure 2.3. Bond dissociation energies for polycyclic aromatic hydrocarbons.

Scheme II. Aromatic systems and the numbered location (see Figure 2.3) for hydrogen atom loss.

The potential energy surfaces are provided as Figure 2.4 (phenyl radical), Figure 2.5 (furan at C-2), Figure 2.6 (furan at C-3) and Figure 2.7 (pyridine at C-2). In our calculated mechanisms, we have chosen to explore intermediates in the oxidation of these radicals according to a mechanism proposed by Barry Carpenter[13] using semi-empirical MO theory. Figure 2.4 demonstrates the thermodynamic energy changes for the phenyl radical with O_2 system to proceed from one intermediate to another with eventual CO_2 production. Indeed, the initial adduct formation with O_2 is exothermic by about $45 \text{ kcal}\cdot\text{mol}^{-1}$ and most steps thereafter are significantly exothermic or slightly endothermic. This value is very similar to that reported for the adduct of O_2 with the vinyl radical (from H-atom abstraction on ethylene)[11]. These results would suggest that the overall rate of benzene oxidation might be limited by the initial formation of the phenyl radical and the stabilization of the O_2 adduct. Indeed, Morokuma, Lin and coworkers have shown that the reaction of vinyl radical with O_2 is dominated by the stabilization of the adduct.

Furan and pyridine present additional problems as there are more than one unique site of H-atom abstraction. We have proceeded to examine the oxidation of furan (see Scheme I) at the B3LYP/6-31G(d) level (see Figures 2.5 and 2.6). The surfaces look very similar to that for phenyl radical. The initial adduct with O_2 is exothermic by about $49 \text{ kcal}\cdot\text{mol}^{-1}$. Opening of the 5-membered ring to a 6-membered ring with a carbonate functionality is very favorable. We have found two different avenues for CO_2 formation as well as routes for CO generation.

Pyridine (Figure 2.7) shows many of the same trends. The initial addition of O₂ is very exothermic (−43 kcal·mol^{−1}) and similar structural modifications follow that initial exothermic reaction. We have determined pathways for the evolution of CO, CO₂ and HCN as products. Due to the large initial exothermic addition of O₂, we expect that the oxidation of pyridine will be limited to initial formation of the pyridyl radical. We are continuing on our search for intermediates for the other positions of pyridine. Previously we also presented preliminary results on the radical formation step with these simple aromatic compounds. We have found that the potential energy surfaces for H-atom abstraction by H, OH, O (³P), and O₂ are actually quite complicated, and we will present more information in our next quarterly report.

For the near future, we will continue to explore the hydrogen atom abstraction step for monocyclic and larger PAHs. We will also continue to probe the O₂ mechanism for oxidation of benzene and other PAHs that was recently postulated by Carpenter. We have extended this study to pyridine, and we will also examine the chemistry of thiophene. 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 as provided by Professor Essenhight. Such an experimental characterization may provide tremendous insight into the reactivity of the coal chars.

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OXIDATION OF PHENYL RADICAL

B3LYP (this work)

HF (this work)

PM3 (Carpenter)

Figure 2.4. Mechanism of oxidation for the phenyl radical.

Figure 2.5. Mechanism of oxidation for the 2-furanyl radical.

OXIDATION OF 3-FURANYL RADICAL B3LYP/6-31G*

Figure 2.6. Mechanism of oxidation for the 3-furanyl radical.

Figure 2.7. Mechanism of oxidation for the 2-pyridyl radical.

Section 3: Combustion Experiments in Contrasting Flame Types

Reconstruction of the laboratory installations at Ohio State is nearly complete. The small jet stirred reactor is now coming back into commission, and first samples are now being obtained. The construction of the new chimney two tower furnaces is nearly completed. The main stack has been installed, and installation of a secondary flue to vent the exhaust from the tower furnaces is under way. The reconstruction has required complete dismantling and relocation of all services and supply equipment (coal feeder, etc.) going to the tower furnaces, with relocation of the two furnaces on the other side of the laboratory. As identified above and detailed below, the jet mix-reactor has been recommissioned and a stable coal flame has been attained. The solid sampling probes are essentially in working order; but, require slight modifications, in progress. Particle size analyses have been completed for each of the coals currently on site using the MicroTrac PSD equipment. Additionally, the theoretical developments reported as a Poster Paper at the Penn State Carbon Conference meeting in July have been reformulated into a paper and submitted to the Twenty-Seventh International Combustion Symposium.

Tasks in progress or completed

A. Furnaces

1. 1-D (Tower) Furnace

The plug-flow tower furnace has been repositioned. To complete the re-installation, construction of a duct to the new chimney is required and is now under way. As soon as that task is completed, the furnace will be brought on line to start collection of samples under different firing conditions.

2. Large High Intensity Reactor

The large high intensity reactor, which shares a flue with the plug flow furnace, has also been successfully repositioned. Likewise, completion of installation requires connection to the new chimney duct. This reactor requires a rebuild of the coal injection assembly. The hot face insulation brick required for reconstruction is on site and the reassembly is under way.

3. Jet Mix Reactor

Following a complete overhaul, the jet mix reactor is operational. It has been successfully fired numerous times with a stable, sustained coal flame. We anticipate samples to be available for distribution, analysis and testing within the next few weeks, contingent on the sampling method, as explained below.

B. Ancillary Equipment

1. Coal Spring Feeder (Jet Mix Reactor)

A bolt was recently discovered lodged in the spring of the feeder. The resulting damage necessitates a new spring which is to be installed as soon as a suitable

replacement can be located. This unanticipated problem set back the development of the program. Currently, a smaller version of the same type of feeder has been installed; this required alterations and maintenance but the reactor has now been successfully operated after installation of the new spring feeder.

2. Coal Feeder (Tower Furnaces)

The coal feeder used in conjunction with the tower furnaces is in process of being reinstalled; it is also receiving some routine maintenance. The front control panel requires a new potentiometer which is to be replaced.

3. Solid Sampling Probes

The solid sampling probes are being brought back into operation. This was given second priority to the relocation of the furnaces and recommissioning of the jet mix reactor. Sampling volume rates were found to be inconsistent with requirements for this application. Part of the problem was the need to replace a malfunctioning vacuum pump. This is also needed to properly match the suction air flow rate to the velocity of the exhaust as closely as possible. It is anticipated that a correction to the motor size will alleviate the problem. The sampling procedure is the only obstacle which must be overcome to secure the samples.

4. Flow Meters

Operation of the two tower furnaces still requires reinstallation of the air flow meters and supply lines, both for primary air that will provide the coal pick-up, and for secondary air for staging. These have been retained as an assembled sub-unit; but, will now require a reposition and reconnection to the air supplies and to the furnaces.

5. Temperature Measurement

Temperature measurement requires measurement of wall temperatures by thermocouples in the walls, and gas and/or particle temperatures in the flame. The wall thermocouples are in position and only require reconnection to the data collection and recalibration. The in-flame temperatures will be made by suction pyrometer (for gas temperatures) and by two-color for particle temperatures. Recommissioning of these instruments will be started shortly.

6. Gas Analysis

Gas analyzers include CO₂, O₂, NO_x, and SO_x. The CO₂ analyzer is on-line, the O₂, NO_x, and SO_x are being recommissioned. The replacement CO analyzer has yet to be purchased. Quotes on the price of this analyzer are being investigated.

7. Particle Size Analysis

Particle sizes analyses have been performed on all of the coals currently on site using the L&N MicroTrac PSD. A summary of the relevant findings will accompany each sample submitted.

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

[illegible]

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