STRUCTURE-BASED PREDICTIVE MODEL FOR COAL CHAR COMBUSTION

**Quarterly Technical Progress Report
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EXECUTIVE SUMMARY

During the second quarter of this project, progress was made on both major technical tasks. Three parallel efforts were initiated on the modeling of carbon structural evolution. Structural ordering during carbonization was studied by a numerical simulation scheme proposed by Alan Kerstein involving molecular weight growth and rotational mobility. Work was also initiated to adapt a model of carbonaceous mesophase formation, originally developed under parallel NSF funding, to the prediction of coke texture. 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. Boston University has initiated molecular dynamics simulations of carbonization processes and Ohio State has begun theoretical treatment of surface reactions. Experimental work has also begun on model compound studies at Brown and on pilot-scale combustion systems with widely varying flame types at OSU. The work on mobility / growth models shows great promise and is discussed in detail in the body of the report.

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

A variety of activities are underway at Brown, OSU, and Boston University, and significant progress was made this period on both major technical tasks (Tasks 2 and 3). Brief summaries of the individual activities are listed in this section, and one selected topic (mobility / growth models) is presented in full technical detail in the section thereafter.

Brief Summary of Activities

Development of structural models

Efforts in Task 2 focused on developing new model formulations capable of describing dynamic structural evolution in carbons. As discussed in the project plan, this activity addresses a major scientific hurdle in the overall project, and requires, in the early phases, the development and assessment of competing approaches. This quarter, two modeling approaches were considered for describing order development in carbonizing systems in general, and in coal in particular.

Mobility / Growth model. The first approach involves numerical simulations based on a class of algorithms proposed to the project team by Alan Kerstein at Sandia National Laboratories. A set of simulations were completed this quarter that treat the competition between molecular weight growth and layer mobility that is ultimately responsible for the degree and nature of order in carbon materials. The first generation algorithm is very similar to that proposed by Kerstein, which treats the mobility / growth competition in the simplest possible manner using hard lines in two dimensions. While lacking a number of features necessary to accurately describe complete carbonization processes, this first generation model captures the essence of the carbonization problem for a broad spectrum of precursors, and careful analysis of the simple model is a necessary scientific step in the development of more comprehensive descriptions. The first set of simulations and their significance to carbonization is presented in detail in a later section.

Mesophase thermodynamic model. The Brown team also embarked on a second, quite different modeling approach designed to predict the extent of structural order in coals that pass through a fluid phase upon carbonization. The cokes that result from the pyrolysis of softening coals can be isotropic or anisotropic under visible light, and the nature and length scale of anisotropy varies greatly. The anisotropic regions possess a high degree of orientational order on the nanoscale and are believed in large part responsible for the lower surface areas and lower reactivities of higher rank bituminous coals. The modeling approach being pursued makes use of a thermodynamic model of the liquid crystal phase transitions in carbonizing melts recently developed under the parallel NSF CAREER grant of R. Hurt. In its current form the model of mesophase thermodynamics is directly applicable to pitches, but can be adapted to coal processing for the prediction of structure in bituminous coal chars if the pool of non-covalently-linked aromatic clusters can be specified. During the next period, the model of mesophase thermodynamics will be used in conjunction with Advanced Fuel Research's FG-DVC model (which predicts the molecular weight distribution of metaplast during pyrolysis) in an attempt to make the first *predictions* of the amount of mesophase and ultimate anisotropy in cokes of various rank.

Boston University task

Work at BU this period focused on the use of molecular dynamics (MD) to understand the mesophase formation process that is key to predicting order in higher rank coals and in pitch used as a precursor for a variety of carbon materials. Simplified MD simulations were carried out with square well potential interactions to reveal the basic properties of the phase transition. Early results indicate that the system of aromatic clusters exists in an amorphous phase with pentagonal symmetry at low temperatures, but when heated, it transforms into an anisotropic liquid crystal phase with square symmetry.

Ohio State University tasks

Progress was made on the Task 2 activities at OSU in the subtask on surface chemistry led by Professor Chris Hadad. This work will be described in the upcoming quarterly report. Task 3 activities at OSU led by Professor Robert Essenhight focused on the refurbishing, start-up, and testing of the furnace facilities at OSU, as envisioned in the project plan. Initial results have also been obtained on the microscopic examination of chars extracted from the OSU reactor facilities. This work will also be discussed in detail in the following quarterly report.

Coal selection

Also in Task 2, a suite of coals were selected for study by the project team, and as a source for selection of a coal subset for study in parallel projects at Brigham Young University and Advanced Fuel Research. The coal list is attached as Appendix A.

IEA Workshop

The IEA Workshop on Emerging Issues in Coal Combustion was attended by many members of the project team: PIs Essenhight, Calo, Hurt and consultant Eric Suuberg. Following the workshop, a technical meeting was held between Hurt, Calo and Sandia researchers Nancy Yang, Melissa Lunden, and Chris Shaddix. Progress in the Sandia project on mineral effects was discussed, in particular the exciting new information on the possibility of mineral incorporation into the ultrafine carbon structure during combustion [Lunden et al., 1997]. EDS analysis of TEM images suggests a mineral component in many images that do not contain discrete mineral particles visible by TEM. The incorporation of mineral matter into the ultrafine structure of chars could be an important new char deactivation mechanism. More work is needed to verify this result and understand the implications.

In order to most efficient progress on this topic, an active collaboration between the two groups was proposed. The collaborative work would involve sample preparation and simple reactivity characterization at Brown, followed by microscopic study at Sandia and high temperature flow reactor studies at Sandia on selected samples. Initial work will focus on pure carbon materials (phenol-formaldehyde resin chars) doped with specific, pure, inorganic compounds. Progress on the samples preparation and characterization is described in the section below.

Sample preparation/characterization for HRTEM studies at Brown and Sandia

Complementary to the development of structure-based models of char reactivity, experimental work at Brown University is being conducted to investigate carbon lattice dynamics which will ultimately be used for model validation purposes. In particular, a model char produced from a phenol-formaldehyde resin is being used for this purpose. As a result of previous work in our laboratory for other coal-related applications using this material [Suuberg et al., 1989], we have developed significant experience with respect to its synthesis, subsequent carbonization to char, and reactivity measurements. The basic approach is to study the real-time ordering behavior of model char samples with hot-stage, high resolution TEM (HRTEM) fringe imaging. Such fringe images, only obtained by *ex situ* analysis, already constitute the type of data upon which the modeling effort is partially based. This quarter, progress was made on sample preparation and characterization for this effort (involving undoped samples) and for the Sandia collaboration (involving doped samples).

Progress: undoped samples. Phenol formaldehyde resin was produced by reaction of phenol and formaldehyde in a molar ratio of 1:4.33, using NH_4OH as a catalyst. The resin was separated from the reaction mixture, and then cured in vacuo for 2h @ 60°C and 12h @ 120°C, followed by 2h @ 300°C in ultrahigh purity helium. The prepared resin was ground and sieved into 250-149 μm and 149-75 μm size ranges. The resin was then pyrolyzed at 1100K for 1h in helium, with an attendant mass loss of about 43.5%. The surface area of this material by single point nitrogen BET was determined to be 162 m^2/g . This material is then ground further and dispersed on electron microscope grids. Although some room temperature HRTEM work has already been conducted, a suitable grid type is currently being sought for the “hot-stage” work.

Doped Samples. The general outline of the work with these samples was established at a meeting at Sandia National Laboratories in April, 1997, and was recently discussed in more detail at a meeting with Nancy Yang of Sandia at Brown University in early June, 1997. The same phenol formaldehyde resin char sample described above, was gasified in 1 atm of pure oxygen at 673K to 19% burn-off. A 77K nitrogen adsorption isotherm indicated that this particular char sample exhibited a very narrow pore size distribution with a maximum at about 5Å and with most pores being < 20Å. Since this microporous distribution is not optimum for doping, it has been decided to activate the material further to shift the pore size distribution to larger pore sizes. The material has now been burned-off to ~30%, and the pore size distribution will be determined shortly.

Once a sample with an acceptable pore size distribution is prepared, a portion will be doped with iron using 1.5M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Following rinsing to pH neutral with deionized water, the sample will be dried in a vacuum oven, and then heated to 1573K in He for 1h. The resultant sample will be called PRCFeH. Another portion of the resin char will be heat-treated at 1573K for one hour (PRCH) and part of this sample will then be doped with Fe as before (PRCHFe). Doping of the material both before and after heat-treatment will be done to ascertain whether the same dispersion and iron forms are achieved via both methods. Pore size distributions, BET surface areas and reactivities will then be determined for these samples.

Ordering Behavior of ^{13}C -Labeled Resin Char Samples. In addition to the preceding samples, some of the same phenol-formaldehyde resin was synthesized using ^{13}C -formaldehyde. Since the labeled carbons are concentrated in the methylene bridges in the polymer, and there is evidence that these decompose first during pyrolysis, it is hypothesized that a larger proportion of the labeled carbon would reside in the amorphous carbon material than in the aromatic rings which are primarily formed from the unlabeled phenol. The evolution of labeled and unlabeled carbon as CO and CO_2 was monitored during gasification and post-gasification thermal desorption experiments in order to investigate this hypothesis.

It was found that the evolution patterns of CO upon post-reaction TPD are consistent with the early burn-off of amorphous carbon regions where ^{13}C originating from methylene bridges in the resin had concentrated, followed by attack of more crystalline aromatic regions. The unusually large amount of mass loss upon post-reaction TPD from these chars has been attributed to a well developed microporosity arising from a highly crosslinked resin [Antxustegi and Calo, 1997]. The idea of using labeled resin char for the electron microscopy studies is being considered as a means of accounting for the influence of amorphous carbon (which cannot be observed with HRTEM) on char reactivity.

Detailed Technical Discussion: Mobility / Growth Models of Carbonization

An important near-term goal in this project is the development of a modeling framework capable of describing the observed rank dependence of char structure and reactivity. Only after we are capable of describing the known rank dependence with a *mechanistic* model, can we begin to address rank anomalies (unusual coals). As we consider the carbonization of coals of varying rank, the most pronounced feature is the transition solid-state carbonization for low rank coals, producing disordered, reactive, optically isotropic chars, to fluid phase carbonization for high rank coals, producing less reactive, ordered, optically anisotropic cokes. (Note that optically isotropic cokes represent an intermediate case in this rank sequence).

The predominate cause of these differences is believed to be differences in layer mobility in critical phases of carbonization. The higher degree of crosslinking occurring early in low rank coals reduces layer mobility and hinders the alignment favored by Van der Waals forces between aromatic clusters. Although most low rank materials do not visibly soften during carbonization, nor form optically anisotropic regions, high resolution TEM clearly shows the presence of local crystalline order in many chars occurring over length scales below those accessible to the optical microscope. This local order suggests that the aromatic clusters have some mobility, but not enough to readily allow cooperative effects between layers over large length scales. For this project we seek a simple formulation with a variable layer mobility that has the potential to describe the range of char structures seen in coals of widely varying rank. To our knowledge there is no such model formation in the literature or under development.

Because the tools are not available to treat this problem, it is a major scientific hurdle for the project team. In January 1997, during a trip to Sandia National Laboratories, R. Hurt met with Alan Kerstein who suggested a simple formation that captures the competition between layer mobility and growth. Kerstein wrote a sample code based on growth and motion of 2-D lines and

performed a selected simulation that generated images showing a random dispersion of distinct ordered regions, reminiscent of the polycrystalline nature of heat treated low-rank coal chars. Based on this promising result, Brown graduate student Yin Hu wrote his own version of the Kerstein algorithm and carried out a systematic study of the effect of layer mobility. A dimensional analysis of the algorithm was also carried out, allowing efficient coverage of the parameter space and aiding physical interpretation of the results.

The simulation begins with 500 points randomly placed in a square, two-dimensional simulation box. An orientation is assigned randomly to each point and growth occurs by elongation along the orientational vector. The lines also translate and rotate at fixed translational and angular velocities specified at the start of the simulation. In the specific algorithm used, small growth steps alternate with small translation/rotation steps until the structure freezes into a gel and no more motion or growth is possible. The actual simulation algorithm is listed in Table 1 and an example structural time sequence is shown in Fig. 1.

Table 1
Mobility / Growth Algorithm
for Hard Lines in Two Dimensions

-
1. Define a square simulation box of unit length and place n points (here 500) at coordinates (x_i, y_i) where x_i, y_i are random numbers between 0 and 1.
 2. Choose a random angle θ_i for each point defining the initial growth direction
 3. Select each line in turn and perform the following steps:
 - a) increase its length by L on both sides .
 - b) if (a) causes interparticle overlap, choose one side only and grow by L
 - c) if (b) causes interparticle overlap, choose other side only and grow by L
 - d) generate two random numbers between 0 and 1, r_1, r_2 , and move the particle to $(x_o + 0.1 \cdot (r_1 - 0.5), y_o + 0.1 \cdot (r_2 - 0.5))$
 - e) if (d) causes interparticle overlap, do not move
 - f) generate a random number between 0 and 1, r_3 , and rotate through angle $(r_3 - 0.5) \cdot 0.5$ radians
 - g) if (f) causes interparticle overlap, do not rotate
 4. Repeat until no more motions or growth events possible (gel point)
-

At early times the lines interact infrequently, their rotations are largely unhindered, and disorder prevails (see first panel in Fig. 1). As growth proceeds the lines begin to interact frequently, and adopt a variety of ordered or disordered arrangements depending on the simulation parameters. A number of parameters must be specified to run the simulation but the dimensional analysis presented in a later section shows that for sufficiently small step size the model results depend on only two dimensionless parameters, one describing the ratio of orientational mobility to growth and one of lesser importance describing the ratio of translational to orientational mobility.

time step: 50

time step: 210

time step: 1200
(frozen state)

Figure 1. Growth / mobility simulations: time sequence showing the structural evolution predicted for moderate mobility, $M^* = 833$. Note the short range order in the frozen state image (time step = 1200).

Simulations were carried out for a variety of mobilities. Interpretation of the simulation results requires a way to quantify order in the line structures, and a way to interpret the independent variables input to the simulations. The next section treats these issues before the main simulation results are presented.

The Nematic order parameter

The extent of orientational order in a set of lines whose ends are indistinguishable is measured by the nematic order parameter in two dimensions:

$$S = \frac{1}{n} \sum_{i=1}^n [\cos^2 \theta_i] - \frac{1}{2} \quad (1)$$

where n is the number of layers and θ_i is the angle between any given layer and the vector of preferred orientation, the "director". This director itself can be found from the set of unit vectors defining the orientation of the layers by solution of the eigenvalue problem:

$$Q d = \lambda d \quad (2)$$

where d is the director and Q is the order tensor:

$$Q = \frac{1}{N} \begin{bmatrix} \sum x_i^2 - 1/2 & \sum x_i y_i \\ \sum y_i x_i & \sum y_i^2 - 1/2 \end{bmatrix} \quad (3)$$

For an infinite set of layers, S has a value of zero for random lines (complete disorder) and a value of one for a set of lines all parallel to the director (perfect order). We have recently discovered this definition to be inadequate for small sample sets, as even sets of randomly chosen lines have mean order parameters systematically greater than zero. In particular it can be shown that for sets of random line pairs, $n = 2$, the expected value of the order parameter is not zero but $2/\pi$. The effect arises when the director is not known *a priori*, but must be determined from the given set of lines. The choice of the director from the small set of lines biases the result in favor of order, an effect that decreases rapidly as sample size increases. We have numerically determined the function that represents the expected value of the order parameter for n random lines, $f_{ran}(n)$ and have defined a new order parameter, valid for small sample sets as:

$$S_n = \frac{S - f_{ran}(n)}{1 - f_{ran}(n)} \quad (4)$$

This definition is particularly useful when calculating length-dependent order parameters, which for small length scales necessarily involve small sample sizes. The length dependent order parameter is a useful tool for describing short-range polycrystalline order such as is found in lower rank coal chars.

Dimensional analysis

Consider the dynamic arrangement of growing layers with a number density ρ and constant rotational velocity R , and translational velocity V . The layers grow at a rate G and the resulting structure is characterized by an order parameter S . The physical problem is defined by specification of the first four parameters with the fifth, the order parameter representing the result. The variables are listed in Table 2.

Table 2
Parameters and Units in the Mobility / Growth Model

	the number density of lines,	length ⁻²
G	the growth rate,	length / time
R	the angular velocity,	radians / time
V	the translational velocity,	length / time
S	nematic order parameter,	dimensionless

The appearance of five parameters involving two fundamental units (length and time) indicates the necessity for three dimensionless groups. We choose the order parameter itself for one, as well as a dimensionless mobility, defined as

$$M^* = G^{1/2} / R \quad (5)$$

representing the relative rates of rotation and growth, and a translation / rotation ratio:

$$V^* = V^{1/2} / R \quad (6)$$

The problem can now be formulated as:

$$S = f(M^*, V^*) \quad (7)$$

and the simulation results plotted as S vs. M^* with V^* as a parameter. We expect M^* to be the key parameter representing the competition between growth and orientation, so the initial simulations have been done with a constant value of V^* (4.5) implying a constant ratio of translational to angular velocity. Preliminary simulations with other values of V^* suggest that this variable has only a secondary influence on the structure. Additional results include a dimensionless mean layer length, $L^* = L_{\text{mean}}^{1/2}$, and length-dependent order parameters defining the characteristic scale of order.

As an example of how to relate the simulation parameters to the dimensionless variables, consider Eq. 5 for M^* . G is specified in the simulation as

$$G = L / \tau \quad (8)$$

where τ is the time step and L the growth increment expressed as a fraction of the simulation box length, L_{box} . The number density is given by:

$$(N / L_{\text{box}}^2)^{1/2} \quad (9)$$

and the rotation rate:

$$R = R / \tau \quad (10)$$

where R is the rotational increment in radians. Combining eqs. 5 with 8-10 yields a simple expression for M^* for any simulation:

$$M^* = (L / L_{\text{box}}) N^{1/2} / R \quad (11)$$

Note that if we express the growth increment as a fraction of the box length, that neither the box length nor the time step must be specified in physical units to perform the simulation. For the simulations carried out here, R is 0.5 radians, $N = 500$ and L / L_{box} is treated as the independent variable. The results are expressed as S vs. M^* . In a similar way we get $V^* = (V / L_{\text{box}}) N^{1/2} / R$ for the simulations, and since each of these parameters is held constant, $V^* = 4.5$ in all simulations.

Figures 1 and 2 present time sequences for two values of M^* , while Figure 3 shows the final frozen states for three values of M^* . A high mobility, $M^* = 5 \cdot 10^4$, yields an ordered phase (Fig. 2), moderate mobility, $M^* = 833$, yields short range order (randomly ordered crystallites), and no mobility, $M^* = 0$ yields the random structure seen in the topmost frozen state in Fig. 3.

Order parameters for the frozen states are plotted as a function of M^* in Figs. 4 and 5. Figure 4 shows a clear transition from order to disorder in a critical range of the dimensionless mobility from 10^2 to 10^3 . Figure 5 shows the mean layer length and nematic order parameter together — they behave in a similar way, with the length approaching infinity as long-range order develops. Note that the mean layer length shows noticeable increases in the region $-5 < \log_{10} M^* < 0$, reflecting the development of short range order, while the overall order parameter remains essentially zero.

time step: 5000

time step: 65,000
(frozen state)

Figure 2. Growth / mobility simulations: time sequence showing the structural evolution predicted for high mobility, $M^* = 5 \cdot 10^4$. Note the overall anisotropy in the late time image.

$M^* = 0$

$M^* = 833$

$M^* = 50,000$

Figure 3. Growth / mobility simulations: Comparison of equilibrium structures from simulations with widely varying mobility.

Figure 4. Summary of growth / mobility simulation results: nematic order parameter as a function of dimensionless mobility, M^* . Simulations a, b, and c produce the final structures seen in Fig. 3 in the bottom, middle, and top panel respectively.

Figure 5. Summary of growth / mobility simulation results: nematic order parameter and mean layer length as a function of dimensionless mobility, M^* .

Physical interpretations of the growth / mobility simulations

This section discusses the simulation results of Figs. 1 - 5 in terms of sol-gel transitions, lyotropic liquid crystal phase transitions, and coal carbonization. If the lines are regarded as solid needles growing in a fluid continuum, the simulation describes the transition from a sol, a colloidal system with fluid properties in which solids are suspended in a continuous liquid matrix, to a gel, a two phase mixture with liquid dispersed in a continuous solid network that imparts rigidity or elasticity to the mixture. When the layers grow to a size that ensures their frequent interaction, their effective mobility is reduced and a gel is formed. The simulations end with the formation of a perfectly rigid solid matrix that allows no further growth.

Because the solid elements are anisometric (much larger in one dimension than the other) the system can develop orientational order before the gel point. The orientationally ordered phase can be regarded as a liquid crystal which grows further to gel into an ordered (anisotropic) solid. When the solid elements are far apart, they rotate freely and show no tendency toward orientational order. When they are brought into frequent close proximity, repulsive interactions favor orientational order which better accommodates close packing. In the absence of growth, this order/disorder transition occurs as concentration increases and the system is referred to as a lyotropic[†] liquid crystal. The Onsager model [Onsager, 1949, De Gennes, 1993] treats assemblies of hard rods in three dimensions and gives an analytical solution for the volume fraction at which a first order phase transition to the liquid crystal occurs. The absolute predictions of the Onsager model cannot be compared to our simulations (which are based on 2D hard lines) but it is clear that repulsive interactions alone are capable of producing ordered phases.

Now consider the simulation results of Figs. 1 - 5. When growth is slow, a near equilibrium state is achieved at each growth step and the liquid crystalline phase is formed abruptly at a threshold value of the line density (L / A). At higher growth rates, the transition is passed quickly and the system reaches the gel point before the equilibrium, ordered phase forms. In this sense the simulations describe a kinetically limited phase transition.

Interpretation as compression. As an interesting aside, the growth process can be interpreted with equal validity as a compression process that increases the number density, ρ , at constant line size. In this interpretation, the dimensional value of L_{box} varies to maintain constant line length, and the three panels in Fig. 1 correspond to increasing "magnification". Viewed in this way the model describes a phase transition as specific volume decreases (ρ increases). The equilibrium state at

[†] Lyotropic transitions are those brought about by an increase in concentration; thermotropic transitions are those brought about by a decrease in temperature. Thermotropic phase transitions only occur for soft intermolecular potentials (incorporating finite values of the potential energy of interaction). The simulations here are based on hard lines, in which the potential is zero (no overlap) or infinite (overlap), and thus do not show thermotropic transitions. Temperature plays no role in simulations based on hard potentials. The mesophase formation process in carbonization has both a lyotropic and thermotropic nature. Mesophase formation is initiated by an increase in concentration of high molecular weight mesogens through chemical growth processes and the evaporative loss of

lower molecular weight material. At the same time the mesophase process has been shown to be reversible upon rapid increases in temperature, demonstrating its thermotropic nature and the role played by intermolecular forces.

high density is the ordered phase, but if the compression occurs quickly the ordered phase does not have time to form and a glassy phase results. Thus the simulation describes a kinetically limited phase transition.

Quantitatively, the critical density for the order / disorder phase transition at equilibrium would be predicted by the Onsager model adapted for lines in two dimensions. The kinetic results determined in Figure 4 predict the existence of a critical compression rate above which equilibrium is not achieved and a glassy state is established. That transition range is given in terms of M^* in Fig. 4, which can be converted to a critical compression rate:

$$M^* = R / (G N^{1/2}) = R / [(G/L_{\text{box}}) N^{1/2}] = R / [(1/L_{\text{box}})(dL_{\text{box}}/dt) N^{1/2}] \quad (12)$$

where N is the initial number density, and (G/L_{box}) , the growth rate in sec^{-1} , can be replaced by a compression rate, $(1/L_{\text{box}})(dL_{\text{box}}/dt)$ in sec^{-1} , the rate at which the box size decreases.

Application to carbonization

Our compelling interest in the mobility / growth simulations stems from their ability to mimic the solid structures found in chars from coals of varying rank. For example, Fig. 6 shows results of an optical microscope study on a range of bituminous coal chars, presented as anisotropic content vs parent coal rank. As rank decreases (carbon increases) an abrupt transition is observed from predominantly anisotropic to isotropic structures. Other studies clearly show that this trend continues to lower rank materials not studied by Patrick et al. [1973]. This transition is perhaps the most important feature of the rank trend in coal char structure. The low rank chars that are isotropic in the optical microscope, are revealed by HRTEM to possess short range order of a greater or lesser degree depending on the severity of heat treatment conditions.

The transition shown in Fig. 6 is believed to be due in large part to variations in the number and stability of crosslinks in the solid coal network. The mobility / growth simulations, while lacking in many details at this point, reproduce the essential features of the rank dependence remarkably well. They show: (1) a relatively abrupt transition to long-range order at a critical mobility threshold, (2) short range order at moderate mobility and, (3) a transition to complete disorder as mobility approaches zero. The key to the long term success of the growth / mobility approach will be the development of techniques to assign mobilities as a function of coal properties and processing conditions. The next section makes initial estimates of mobility for certain idealized cases.

Mobility estimates. Mobilities can be estimated in a number of simple cases as shown in Fig. 7. If there is no liquid medium implied between the growing layers, they are gas molecules with mobilities that can be estimated from their mean angular velocities. The angular velocities can be

Figure 6. Anisotropic content of bituminous coal chars determined by optical microscopy and plotted vs. the rank of the parent coal. Data of Patrick et al.[1973]. Chars prepared at 1000 °C. This data shows an abrupt order/disorder transition similar to Figs. 3 and 4.

estimated from rotational kinetic energies ($1/2kT$ for one degree of rotational freedom) the rod half length, R , and the mass as:

$$= (3 k T / M \cdot R^2)^{1/2} \quad (13)$$

Assuming 2 nm layers, a molecular weight of 1000, and a temperature of 400 C, a mean rotational velocity of 10^{11} rad/sec is estimated. Considering slow carbonization at 400 C (1 nm layer growth / hr), and a layer packing density of 1 nm^{-2} , M^* is estimated to be $\sim 10^{14}$, a high value that assures the development of order during growth (see Fig. 7).

Typical liquid phase mobilities can be estimated through calculation of mean diffusional velocities. Diffusion coefficients can be estimated from the Stokes-Einstein equation:

$$D = kT / 4 \pi \eta R \quad (14)$$

where η is the viscosity of the medium and R is the molecular size of the diffusing species.

A characteristic velocity for use in the simulations can then be computed as $V \sim D / L$ where L is the characteristic length scale between neighboring layers. L is taken as 1 nm and is equivalent to $1/\sqrt{2}$. The order-of-magnitude estimate of V is then used in equation 6 to find the rotation rate, R (note that V^* is 4.5 in all simulations and η is 1 nm^{-2}). For a given growth rate, G , M^* can then be computed by equation 5.

This procedure was used to estimate liquid mobilities for three cases: (1) a 1 nm solute in a low viscosity liquid medium (1 cP) assuming slow growth, (2) a 1 nm solute in a typical coal-derived metaplast at 700 K for slow growth and (3) rapid growth. Coal liquid viscosities at 700 K were estimated to be 300 Poise using the correlations developed by Solomon et al.[1992]:

$$\eta_{\text{liq}} = C e^{(E/RT)} \quad (15)$$

with $C = 7.5 \cdot 10^{-31}$ and $E = 100 \text{ kcal/mol}$. Note that the viscosities in Eq. 15 are for the liquid fraction only — coal melts are typically modeled as two phase mixtures (solid/liquid) in attempts to predict the overall viscosities measured by plastometry. Here we are interested in the viscosity of the fluid portion alone and Eq. 15 is appropriate.

The results in Fig. 7 show that liquid-like mobilities are high enough under all conditions to ensure the development of an ordered phase. Even rapid carbonization (1 nm/sec) involving viscous liquid mixtures (300 Poise) should lead to the development of anisotropic structures. This prediction is consistent with the observation that optically anisotropic chars do form during rapid pyrolysis, indicating mesophase formation on subsecond time scales. In our simulations and in real carbonizing systems, the ordering process, if it occurs in a liquid-like medium, is too rapid to be resolved in most experiments or to be suppressed by rapid reaction. This agreement is an important validation of these simple simulations.

As temperature is decreased, however, the viscosity of coal melts increases sharply, and at some point a glass transition is expected. The glass transition has been specifically studied for pitches [Rand, 1987, Ehrburger et al., 1991], whose rheological properties are important in their applications as binders. A typical viscosity for a glass transition is 10^{12} Poise and the corresponding M^* in Fig. 7 indicates disorder. Somewhere between 300 Poise and the glass transition lies a threshold viscosity that defines the order/disorder transition. A promising interpretation of the data in Fig. 6 is that partial crosslinking increases the melt viscosity as rank decreases, until the threshold viscosity is reached that prevents mesophase formation.

More work is needed to understand the relationship between mobility, liquid viscosity, and softening behavior (as indicated by particle morphological features such as vesicles and rounded edges). It is not yet clear whether the mobility / growth simulations can explain the existence of isotropic cokes (material that fuses but does not order), or of solid phase ordering (materials that order but do not fuse). (The latter phenomenon has only been observed for model compounds.) The key to the practical application of this class of models will be development of techniques for

assigning mobilities based on coal properties and processing conditions. Certainly this class of model is promising and will be pursued further.

Figure 7. Summary of growth / mobility simulation results: nematic order parameter as a function of dimensionless mobility, M^* . Plot includes estimates of dimensionless mobility based on rotational kinetic energies (for gases) or the Stokes-Einstein equation (for liquids). The diffusion coefficients calculated by the Stokes-Einstein equation are used to obtain effective velocities of the growing units as $v \sim D / L$ where L is the characteristic length scale between growth centers. L is taken as 1 nm and is equivalent to $1 / \sqrt{2}$. The viscosities for metaplast are those for the liquid phase (only) of carbonizing coals as used by Solomon et al., 1992.

Relation among the competing techniques.

This report considers the science of ordering phenomena and makes a first attempt to apply the concepts to coal carbonization. A number of competing techniques were discussed. For nonbonded aromatic clusters, the transition to orientational alignment can be regarded as a liquid crystal phase transition and can be treated by a number of methods. Parallel efforts are underway to understand this transition using classical thermodynamics (at Brown), and molecular dynamics (at BU). This work is directly related to pitches, which have low oxygen concentrations and low crosslink densities, and can perhaps be applied to coals if the clusters can be artificially divided into a liquid and a solid fraction using network statistics and the model applied only to the liquid fraction. This approach is promising but needs to be more closely evaluated.

Simulations provide more information than macroscopic thermodynamics, but are difficult to generalize to crosslinked networks. In the presence of crosslinks, large compound structures occur whose spatial motion becomes difficult to describe. Full simulations of spatial arrangements in partially linked reacting networks are not practical at this time. For this reason, it is attractive to lump the effect of crosslinking into a mobility parameter that can be used directly in the simpler mobility / growth simulations. This approach will also be pursued, with emphasis on the enhancement of the simple platform to better reflect real carbonization processes, including the effects of layer volume, finite pools of growth material, constant pressure simulations (NPT ensemble), addition of intermolecular attractive forces, etc. It will be important in this effort to add only those features necessary to usefully describe carbonization.

PLANS FOR NEXT PERIOD

Work will continue on all the activities discussed above. The mobility / growth models will be improved in several ways: (1) by quantifying the length-dependent order in the existing images, (2) by addition of finite volume to the basic structural units to produce structures more closely resembling HRTEM fringe images, (3) by considering finite pools of growth material, such as are present in coal. More work will be done to related mobility to coal properties and softening behavior, and to examine the important special cases of isotropic cokes.

A major effort next quarter will be devoted to the prediction of char structures based on mesophase thermodynamics coupled to the cluster size statistics in AFR's FG-DVC model. This is a promising approach for dealing with the complex depolymerization / repolymerization in coal pyrolysis that provides the pool of aromatic material for early order development. Upcoming reports will present the technical progress at BU (molecular dynamics simulations) and OSU (on reaction mechanisms and combustion system experimentation) in much more detail.

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APPENDIX A

1. Final list of selected coals / coal types
2. Copy of letter with original tentative selection explaining rationale

Table A1
Coal Selection for DOE Initiate on
Structure-Based Models of Char Combustion

Coal Name	Rank	Source
<i>Group I</i>		
Pittsburgh seam	hvb	Penn. State, DECS-23
Guasare	hvb	New England Power
Blind Canyon	hvb	Penn. State, DECS-17
<i>Group II</i>		
Pocahontas #3	lvb	Penn. State, DECS-13
Southern Hemisphere high-inertinite coal	hvb	to be determined
<i>Group III</i>		
Hiawatha	hvb	Penn. State, DECS-5
high-ash Chinese coal	--	to be determined
<i>Group IV</i>		
Rosebud	hvb	Penn. State, DECS-10
Illinois #6	hvb	Penn. State, DECS-2
<i>Group V</i>		
bituminous steam coals from eastern U.S. (1 or 2)	hvb	as available at start of for OSU test program

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May 9, 1997

Phil Goldberg
U.S. DOE
Federal Energy Technology Center
PO Box 10940, MS 922-342C
Pittsburgh, PA 15236-0940

Dear Phil,

Please find attached a suggested list of coals for the char combustion project, along with a list of the DEC's Series coals in the Penn State sample bank. This latter list presents the coals sorted by daf carbon content and was used to help make the selection. I have forwarded the list to Bob Essenhigh and hope to gather input from both of you before we proceed. Let me briefly explain the reasons for the tentative selection.

The first three coals on the list are similar in elemental composition, but very different in at least some of their behaviors. Blind Canyon is adjacent to Pitt #8, but has a maximum fluidity of 5 compared to 30000 for the Pittsburgh coal. These are different classes of coals but with similar elemental composition — a difficult case for crude models based on statistical relationships. In the same group is the South American coal Guasare, which has a terrible reputation in full-scale boilers regarding LOI. The cause of the poor performance is not understood, or is at least in hot dispute. I have a small sample of Guasare (a part of which I passed on to Sandia) and this sample has an elemental composition almost identical to Pitt. 8. Again, a big problem for conventional methods.

The second set of two coals are both low reactivity materials, but very different in their nature and properties. The southern hemisphere coal (to be chosen based on availability) will be very high in inertinite and a typical coal for which LOI problems are anticipated. Pocahontas is a high-rank, low-reactivity coal (which by the way of compensation is very soft and easy to grind), that has been burned at NEP and also in PowerGens 1 MW facility. Both groups report that it burns reasonably well, despite its low reactivity in drop tubes, and we cannot predict this with the EPRI LOI predictor. It is a mystery that is worthy of our collective attention.

Thirdly, I suggest the Hiawatha coal. Although it may be similar to the Blind Canyon coal, it is a known outlier in the Sandia set of 10 coals (it has an anomalously high reactivity for its rank). Many chinese coals have high ash contents and are rumored to cause problems with LOI predictions and if we could obtain one it would be an important addition. Fourth, I suggest the Rosebud and Illinois coals as a pair. Rosebud has an unusually low hydrogen content (if you plot this list it stands out in striking fashion) and does not swell, but finds itself adjacent to the well-studied Illinois #6 coal with respect to daf carbon.

Lastly, to round off this group of oddballs, I suggest we burn some traditional eastern U.S. bituminous steam coals (one or two), and that Bob (Essenhigh) dictate which ones he can obtain in large quantities. He can send us smaller samples from his batches and we will add them to the Penn State coals. Let me know your reaction to this. Thank you very much.

Sincerely,

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

Project start date: 9/30/96

182 Hope Street,
Providence, RI 02912

Project completion date: 9/30/99

Number	Task / Subtask	Activity	Project Duration		Comments / notes / performer
			1998	1999	
1.	general	selection of test coals	complete		Brown / OSU
2.	2.1	development of dynamic structural models			
2a.		<i>nonbonded</i>			BU / Brown
2b.		<i>graphene layers</i>			BU / Brown
		<i>linked networks</i>			
2c.		<i>model synthesis</i>			Brown
3.	2.	in-situ, hot-stage fringe imaging			Brown
4.	2.2	computational chemistry of surface oxidation			OSU
5.	3	experiments in contrasting flame types			OSU
6.	3	analyses of char samples from part 5.			OSU
7.	2.1	establishment of secondary correlations:			
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	May, 1997	
2	First successful simulation of structural ordering in nonbonded graphene layers	Sept., 1997		
3	Completed set of simulations of growth and hindered motion based on self-avoiding lines	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		
6	First set of thermochemical computations complete for model organic structures	Dec. 1997		
7	Shakedown / testing of OSU furnace facilities complete	Oct. 1997		
8	First set of char generation experiments complete on OSU furnaces	Apr. 1998		
9	First set of char samples characterized -- major differences in flame types identified	Sept. 1998		
10	Structure-based prediction concept developed for fluidity and char macromorphology	Sept. 1998		
11	Reactivity / structure link assessed for mineral-free model carbon	Sept. 1998		

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

Project title: Structure-based models for char combustion

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