STRUCTURE-BASED PREDICTIVE MODEL FOR COAL CHAR COMBUSTION

**Quarterly Technical Progress Report
October 1 - December 31, 1996**

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TABLE OF CONTENTS

EXECUTIVE SUMMARY	4
PROJECT DESCRIPTION.....	5
PROGRESS THIS PERIOD	7
MILESTONE PLAN... ..	8
MILESTONE LOG	10
APPENDIX A Meeting Agenda	12
APPENDIX B Excerpts from Project Planning Document	13

EXECUTIVE SUMMARY

The first quarter of this project was used to carry out a detailed planning process to coordinate the various aspects of this collaborative effort. A workshop was held at Brown University on December 4, 1996, attended by all project participants and key visitors, in which presentations were given by the principal investigators on their respective subtasks. The planning process culminated in the completion of a comprehensive document submitted to DOE / FETC under separate cover. Following the planning exercise, research work was initiated and will be continued in the second project quarter.

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

The project was initiated this quarter and effort was focused on a detailed planning process. The major goal of this first project quarter, as specified in the Cooperative Agreement, was the completion and submission of a planning document that details the logical plan of attack and clearly delineates the role of the three groups involved in the collaboration.

As a first step in a coordinated planning process, a workshop was held at Brown University on December 4, 1996, attended by all project participants (Brown, OSU, BU), DOE representatives, and representative from Sandia National Laboratories (SNL) and Science Applications International Corp. (SAIC). The meeting agenda is attached as Appendix A. Presentations were given by the principal investigators (Hurt, Calo, Essenhig, Hadad) on their respective subtasks and by Mellissa Lunden from Sandia on a parallel project addressing the role of mineral matter on burnout. The Boston University group also demonstrated molecular simulation tools and discussed how they may be applied to carbonization processes.

The formal presentations were followed by an open discussion period, in which a consensus was sought on the best pathways and strategies for achieving the overall project goals. The participants left the meeting with assignments to develop their individual task and subtask plans, to be synthesized at Brown into a single project planning document.

The collaborative planning document has been submitted to DOE / FETC (under separate cover), and consists of 62 pages, a logic flow chart for structure-based models prediction, a milestone chart, and milestone log. Appendix B contains excerpts from the planning document that describes the task structure and the overall approach.

Following completion of the planning process substantive research work began. An initial experiment was carried out at Brown to test the feasibility of *in situ* hot-stage fringe imaging for direct visualization of carbon lattice dynamics. Simulations of order development in limited-mobility networks were also initiated. Results of these activities will be described in latter quarterly reports.

In addition, students and post-doctoral personnel were recruited, and several working subgroup meetings were held between the Brown and BU groups. A new member was also added to the advisory board.

APPENDIX A

Meeting Agenda

for the

First Project Planning Meeting
on the new DOE Initiative: "Structure-Based Models of Char Combustion"

December 4, 1996

Location: Room 631, Barus & Holley Bldg (Home of Engineering and Physics)
Brown University Campus

8:45 - 9:00 Refreshments

9:00 - 9:15 Opening comments

9:15 - 9:45 Project Overview, Task Structure - Robert Hurt

9:45 - 10:15 Experiments at Brown - Joseph Calo

10:15 - 10:45 Modelling Activities at Boston U. and Brown - Robert Hurt

10:45 - 11:00 Break and/or Discussion

11:00 - 11:30 Experiments and Modelling at Ohio State - Robert Essenhigh

11:30 - 12:00 Molecular Modelling at Ohio State - Chris Hadad

12:00 - 1:30 Lunch at Brown Faculty Club

1:30 - 3:00 Open Discussion - All participants

3:00

Departure

APPENDIX B

Excerpts from Planning Document (Section on Technical Approach)

Overview and Logic Diagram

The flow of logic in the proposed structure-based model is depicted in Fig. 1. The ultimate goal is a fundamental predictive framework linking coal and environment properties to high temperature char combustion behavior. The numbered steps in squares represent critical links in this predictive chain where research is needed to establish the scientific basis for tools. These are the steps that are emphasized in this proposal. The numbered steps in circles represent less critical links where adequate tools already exist, or where there are significant research efforts underway in other projects or at other institutions. Fig. 1 also depicts the current semi-empirical methods that make this link in only two steps, the first being estimation of high-temperature char reactivity through rank-dependent correlations (lowest dashed line), followed by application of semi-empirical models of surface kinetics coupled with classical descriptions of transport processes involving single particles (step 10).

In contrast, the proposed prediction logic begins with the use of network pyrolysis models (such as those already developed by Advanced Fuel Research, Stanford Research Institute, or Sandia/ACERC) to relate simple coal properties to the aromatic cluster population liberated by bond breaking during pyrolysis [Zhao, et al., 1994, Niksa, 1995, Fletcher, 1996]. In a separate step, this cluster population is input into a spatial framework and its evolution into ordered structures (crystallites) is modeled by Monte Carlo (MC) or molecular dynamic (MD) approaches. An example spatial framework for representing structural order uses Voronoi diagrams, as described subsequently.

Development of this portion of the model will make use of the proposed collaboration with Professor Eugene Stanley at Boston University and will also leverage work on generic mesoscale algorithms for flame carbons to be initiated soon at Brown under NSF CAREER program funding. Excerpts from this project proposal outlining the general mesoscale approach to carbons are reproduced in Appendix A. The predicted char microstructures can be directly compared to HRTEM images for heat treated coal chars currently under study in an ongoing University Coal Research Project at Brown (step 4). The direct link from simple, readily-available coal properties (elemental analysis) to char microstructures, and the ability to validate the link through comparison with HRTEM fringe images is one of the unique aspects of this approach.

Additional work will be carried out to derive numerical fluidity indices from the mesoscale simulations (step 3), that can be used as a rational correlating parameter for char particle macroporosity (step 5). Also, heat treatment and reaction studies on mineral-free carbons will be used to establish a quantitative link to elements of the microstructure observed in the HRTEM fringe images (layer diameters, curvatures, and stacking heights). In parallel, fundamental work on surface kinetics will proceed, based on specification of the environment (step 1), with possible inputs related to char microstructure. Separate work will be carried out to relate char microstructures to intrinsic carbon reactivities (step 6). Microstructures influence reactivity by

Logic Diagram for a Structure-Based Predictive Model of Coal Char Combustion

KEY:

critical links emphasized in this project

other links (where there are existing tools or significant efforts within other projects)

influencing the number and type of carbon active sites as well as the micropore structure that provides access to these sites.

The role of mineral matter is critical to the understanding and prediction of late stage burnout behavior. Minerals can catalyze char oxidation and, at high temperatures, can present transport barriers that decrease combustion rates. Mineral matter has also been observed to hinder fragmentation in the late stages of combustion. Recently, ash inhibition in the late stages of combustion has been shown to be a critical phenomenon delaying final burnout in laboratory entrained flow reactor studies. The various physical and chemical mechanisms by which ash can affect combustion, especially in the late stages, are currently under investigation in a parallel preproject at Sandia National Laboratories. The present collaborative project at Brown, OSU, and BU will not directly address mineral issues, but will maintain a close tie to the Sandia group and incorporate their insights and submodels into new predictive tools for char combustion.

Finally, steps 8,9, and 10 have been the subject of extensive research and the important scientific principles are relatively well established. These steps do not currently represent the critical barriers to coal-general prediction. Detailed descriptions of the technical approach in each task follow.

Task 1. Project Management

The objective of this task is to coordinate the effort of the three universities, including reporting, documentation, data transfer, and meeting coordination. Brown University shall have overall responsibility for project management. Project management and reporting activities will include (1) preparing and submitting all reports and forms required for the performance of this Cooperative Agreement, as identified in the Financial Assistance Reporting Checklist; (2) coordinating, managing, and integrating the subcontractor efforts and results, (3) integrating and delivering to DOE the final work output of all tasks, this included delivery of models, data, the Final Report and other items specified in Section IV, Deliverables; and (4) planning and conducting project review meetings.

SAMPLE SELECTION

The intermediate goal of the early phases of the project is to lay the scientific foundation for predicting the evolution of char structures and their implications. Some of the experimental work will employ well-characterized model carbons. In task 3, and in all the tasks in the latter phases of the project, experimental work will be carried out on whole coal chars. One of the most sensitive tests for predictive ability in a model is the comparison of predicted results with observations on coals whose combustion behavior is atypical of their rank. A project currently underway at Brown is assessing the predictive capability of current rank-based char combustion models based on comparisons with a set of international coals of diverse rank and petrology. Coals that show rank-anomalous behavior in this study will provide ideal test cases for the more fundamental approach proposed here for the next-generation models. In the early phases of this project, these coals will be identified and chosen for special emphasis. An ongoing goal of the project will be to find model-based routes linking char combustion behavior to some measurable property or properties of these parent coal.

Task 2. Development of Structure-Based Models

OBJECTIVE

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.

BACKGROUND

A better fundamental understanding of the char formation and maturation process and its influence on reactivity and burnout is critical to improved design and operation of coal fired boilers. Current models of char oxidation have a rigorous theoretical basis for the descriptions of *transport processes*, but are not sufficiently fundamental in their description of the solid phase or surfaces to allow prediction of reaction rates or burnout times without coal-specific kinetic data. The mechanistic relation between char structure and reactivity is what is missing at this time. Qualitatively the relation between the two, including the influence of such critical factors as heat treatment, has long been recognized, with a history of many decades [Suuberg, 1991, Essenhigh, 1981]. Linking the two characteristics in a quantitatively useful manner, however, is still an unsolved problem.

Recent work has highlighted the critical role of char microstructure in determining combustion and burn-out behavior. In recent combustion experiments involving a variety of parent coals and combustion conditions, char reactivity is reported to correlate well with the degree of crystalline order in HRTEM fringe images [Hurt and Yang, 1995]. This work strongly suggests a fundamental structure-based approach to describing char combustion — that is explicitly based on *mesoscale* entities in coal chars (i.e. structures with length scales between the atomic and macroscopic). In chars these can be defined to be small graphene layers of size comparable to typical aromatic clusters in coal (2 - 5 rings). A brief review of structural models for coal, and to some extent its carbonization products, is found in Appendix D.

New models of the solid phase must also be coupled with fundamental surface kinetic expressions in order to describe complete reaction processes. Fundamental work is needed to develop and validate advanced kinetic expressions for the broad range of gas environments and char structures that arise in pressurized combustion systems, in the reducing zones of deeply staged systems, and in reducing regions within single coal particles. The surface chemistry of char combustion is currently described by empirical or phenomenological models. It is planned here to pursue *mechanistic* approaches that can provide insight into the relationship between carbon structures and surface reactions, and have the long-term potential to yield more widely applicable kinetic expressions. Modern computational chemistry will be employed to address conformational, thermochemical and even kinetic issues for a variety of chemical questions relevant to carbon oxidation. Of special interest to this proposal is the relationships between carbon structure and surface reaction mechanisms.

The project team believes that further long-term progress towards a generally applicable predictive tool will require a new approach based on the detailed description of char chemistry and crystalline structure at the mesoscale level. There have been significant efforts to describe coal structure and pyrolysis chemistry using, variously, empirical correlations, statistical and phenomenological models, and molecular and mesoscale approaches. Network pyrolysis models, in particular have shown substantial success in relating coal properties to pyrolysis behavior [e.g. Zhao, et al., 1995, Niksa, 1995]. There have not, however, been comparable efforts, as we note above, to describe char structure and char combustion behavior by analogous approaches. Accordingly, the goal of this project is to lay the foundations for these new approaches, and to develop first-generation comprehensive, structure-based models of char combustion combined with predictive capability based on coal properties.

This task is broken into two subtasks, one dealing with dynamic models of structural evolution, the other with fundamental computation related to surface oxygen attack. The technical approaches are presented in separate sections below.

APPROACH:

Subtask 2.1 Mesoscale models of char structural evolution

The overall approach is to develop dynamic structural models along with auxiliary correlations that relate the structures to reactivity and other char properties. The major scientific hurdle is the development of the dynamic structural models that describe motion and growth in assemblies of graphene layers.

Traditional macroscale approaches for describing carbons are inadequate in many respects. On the atomic scale carbons are quite complex, and our current understanding is insufficient to formulate atomistic models of complete structures. Atomistic calculations and considerations can answer certain questions or provide inputs into macroscopic models, but will not lead to comprehensive structural models in the foreseeable future. An alternative is the explicit description of carbon structure on the mesoscale — dimensions lying between the atomic scale and the macroscopic scale. Mesoscale approaches are finding increasing use in materials science, and are particularly appropriate for carbons for several reasons. First, graphitic carbon is one of the most anisotropic materials known, with strong bonding within graphitic planes and weak forces between planes. Consequently, carbon structure can be approximated as an assembly of small graphene layers that are subject to relatively weak interactions with one another, but are internally stable under most conditions of interest here. In the following discussion, the small graphene layers are referred to as basic structural units (BSUs) and they are of mesoscale dimension.

The basic mesoscale model framework is described below and depicted in Fig. 2. In this framework:

1. Carbon solids can be represented as assemblies of small graphene layers (BSUs) whose orientation and configuration depend on simple rules of interaction describing the interplay of repulsive forces, weak attractive forces (Van der Waals forces) and strong chemical linkages (covalent bonds) at the layer edges.

2. The BSUs themselves are immutable. The carbon-carbon bond in graphite is one of the strongest bonds in nature and can be regarded as stable under almost all of the conditions of interest here.
3. Unconstrained layers undergo thermal motions, allowing them to reorient to lower overall energy states.
4. Lattice structure can be idealized as collections of layers, either centered on points in a discrete grid and oriented along one of a finite number of discrete angles, or able to translate and rotate in continuum space. Two dimensional and three dimensional simulations will be evaluated.

Figure 2. A portion of a simulation grid for the first-generation mesoscale model of combustion-generated carbon solids.

There are three steps required to develop any model implied by Fig. 2: (1) development of pair potentials describing the nonbonded interactions between neighboring layers, (2) description of the thermal motions of unconstrained layers, and (3) determination of the effect of crosslinking on layer mobility and the establishment of crosslink formation and destruction kinetics.

The first step is being pursued in the parallel NSF CAREER project (R. Hurt, Brown). Computationally efficient pair potentials for individual graphene layers have been developed and validated against published potentials for high molecular weight PAH generated with CACHE and other molecular modeling packages. The second step can be dealt with by Monte Carlo or molecular dynamics approaches, while the incorporation of crosslinks will require new concepts and algorithms.

A phased approach will be taken, in which competing techniques will be pursued and evaluated in parallel, followed by the synthesis to a single unifying model in the latter stages of the project. One important limiting case is the description of dynamic structural rearrangements in assemblies

of nonbonded (noncrosslinked) graphene layers. Examination of this case allows the project to focus on techniques for describing motion (and later growth and motion) without the complication of crosslinkages that lead to compound objects or even continuous linked networks. By eliminating crosslinks, this first model formulation becomes quite relevant to the technological problem of carbonaceous mesophase formation in pitch pyrolysis.

Carbonaceous mesophase

Pitches have low concentrations of the divalent atoms oxygen and sulfur, which, in many coals serve as crosslinking agents. Without the high concentration of crosslinks, pitches containing highly mobile PAH constituents and lead to highly ordered cokes that are suitable for production of synthetic graphite. The key to understanding ordering phenomena in pitches (and in coals in the nonbonded limiting case) is the treatment of the liquid crystalline intermediate in melts, the celebrated carbonaceous mesophase. This mesophase contains high molecular weight PAH aligned with their basal planes perpendicular to a common vector, the liquid crystalline director. The size of the liquid crystal domains determine the size of the ordered, optically anisotropic regions in the solidified coke and can be thousands of times the size of the primary mesoscale unit (the unit graphene layer).

In this project, the mesophase formation problem will be attacked in a quantitative fashion using some combination of molecular dynamics or Monte Carlo simulations. Very useful insights into this problem have recently been generated by a classical thermodynamic approach to modeling nonbonded PAH phase transitions within the NSF CAREER project. Fig. 3 illustrates the conditions allowing formation of carbonaceous mesophase in a model binary system (one containing two PAH constituents of differing molecular weight). Insights from these phase diagrams will be used to guide the detailed simulations in the nonbonded case. A near term goal in this part of the project is the first successful computer simulation of carbonaceous mesophase.

Growth in linked networks with hindered motions

The modeling of structural arrangement in partially crosslinked networks is a difficult problem that requires new algorithms. The spatial connectivity of networks has been extensively studied due to important applications in pyrolysis, fragmentation, and porous media phenomena. Likewise, rearrangements of *unlinked* layers can be dealt with by some of the techniques described in the previous section. The combined problem, however, is much more difficult to treat explicitly.

When crosslinks are added to the Monte Carlo or molecular dynamics simulations described above, the simulations become intractable. One must deal with the translational and rotational degrees of freedom for compound objects, and, as the network becomes more extensively linked, cluster sizes grow to encompass large numbers of basic structural units. This in turn forces simulations to carry enormous numbers of units for proper statistical representation of structure. For these reasons, the modeling of linked networks through simple addition of crosslinks to existing MC / MD formulations does not appear practical at present.

Alan Kerstein at Sandia National Laboratories has recently proposed a simple model of growth and motion that will be explored as an alternative basis for describing linked networks. This model is based on points placed randomly in two-dimensional space, each point assigned a random orientation. The points grow along their assigned orientations at a specified rate, forming lines, while also undergoing random translations and rotations. The lines are self avoiding and eventually grow into a immobile glass-like final state. The model is defined by a single dimensionless parameter that defines the relative rates of motion and growth. The random motions coupled with self avoidance give rise to structural order, but rapid growth can freeze the structure before order is achieved.

For carbonizing systems we can associate the increases in line length with the polymerization reactions that produce molecular weight growth, and associate the translation and rotation with the thermal motions of the graphene layers hindered, in an average sense, by presence of crosslinks. The proposed formulation is perhaps the simplest construct that involves competition between motion and growth of anisometric objects. Early results from this approach have given glassy state images that resemble HRTEM fringe images in essential features. A number of other features will need to be eventually incorporated in such a model before realistic carbon structures are produced, but the existing 2-D self avoiding line model will be pursued as a starting platform for modeling network systems.

Unified model

Finally, as stated above, the insights and algorithms generated in the parallel efforts above will be unified into a single model in the latter stages of the project. One possible form for this model would be the Kerstein self-avoiding line formulation amended to include volumetric effects, Van der Waals interactions, and a time-dependent mobility parameter. That parameter can be adjusted continually to reflect the effects of crosslink destruction and reformation. Other concepts for the unified model will also be considered.

Structure / property relations

Another important aspect of the overall problem is the development of structure / property correlations. One example technique to be evaluated for quantifying the spatial structure of chars involves Voronoi diagrams and is described below.

Voronoi diagrams and related constructions have become increasingly popular for a number of applications concerned with the description of both random and ordered structures (Okabe *et al.*, 1992), as well as the evolution of such structures as determined by molecular dynamics (Hsu and Rahman, 1979; Capeet *et al.*, 1981; Watanabe and Tsumuraya, 1987; Shih *et al.*, 1994); and Monte Carlo (Allen and Tildesley, 1987) calculations.

The principle of the Voronoi construction is straightforward. Given a finite set of distinct, isolated points in a continuous space, all locations in that space are associated with the closest member of that set. This construction partitions the space into a set of non-arbitrary, space-filling set of polyhedra (known variously as Voronoi polyhedra or Wigner-Seitz cells or Dirichlet regions or domains; Brostow *et al.*, 1978). Each such polyhedron defines a “domain” which is bounded by

plane faces which perpendicularly bisect lines joining the centers of the original points. Consequently, all points inside each domain are associated with a particular point in a unique fashion (Gellatly and Finley, 1982). The resultant set of polyhedra are unique and rigorously define the structure.

The Voronoi construction provides a convenient means of analyzing the structure. One common approach is to compare the resultant construction to one obtained from a Poisson distribution of points representing a structure with complete spatial randomness (CSR). The most obvious characteristics for comparison are the numbers of sides (or alternatively, vertices) of the resultant polygons, and their perimeters and areas. These can all be used as metrics to generate statistics that define the structure and its evolution in terms of frequency distributions, either differential or integral.

From the preceding brief description, Voronoi-type constructions ($V(S) \in \mathbb{R}^2$), represent a natural approach to the analysis of the two-dimensional HRTEM fringe images of graphene layers in chars. The results of pixel-level digitization of these electron micrographs using image analysis techniques will be used to define one set of Voronoi points. This might be done in the following fashion. First an image length scale is chosen to represent the mesoscale “basic structural unit” (BSU) of graphene fragments, which are estimated to be on the order of three or so aromatic units. In order to represent layers of more than one BSU, each structural unit can be weighted by the number of BSUs of which it is comprised. The *location* of this point must reflect the structure of the graphene fragment in terms of some measure or measures, such as its centroid, radius of gyration, etc. Consequently, all Voronoi points will be assigned a weight and location reflecting the size/conformation of the corresponding graphene fragment. Also, since the electron micrograph represents a two-phase system (i.e., graphene layers and interlayer space/voids), another set of Voronoi points must be defined such that the resultant polyhedra are related to the voids or porosity of the sample. Evolution of the char structure will naturally cause the evolution of both sets of Voronoi points and polyhedra due to processes such as coalescence, alignment of BSUs, etc.

Secondly, we will attempt to establish a link between microstructural parameters on the one hand, and reactivity and char macromorphology (swelling) on the other. This subtask will attempt to relate the reactivity of mineral free model chars to structural indices derived from the fringe images. This subtask overlaps with a University Coal Research Project underway at Brown University. The chars in this part of the study will be ground finely to minimize the role of char macromorphology and macropore transport. By eliminating catalytic and macrotransport effects in this way, the best quantitative link can be made between microstructure (which determines microporous surface area, accessibility, and carbon active sites) and reactivity. Also, a bulk fluidity index will be defined from the simulation parameters and used to correlate measured bulk char porosities and/or measured viscosities.

Supporting experiments

An experimental effort is also planned at Brown in direct support of the model development. The experimental program has two parts. First *in situ* hot-stage HRTEM fringe imaging will be explored for obtaining direct visual information on the nature of carbon crystalline transformations.

The existing HRTEM database was derived exclusively from post-combustion analysis, in which the heterogeneous coal char structure is "sampled" to obtain semi-quantitative results on crystal structure changes. This project will explore the use of a 1300 °C hot stage available on the Brown high-resolution TEM to continuously track changes in selected microscopic regions in real time to obtain unique insights into the dynamic mechanisms of crystal growth in coal chars. To our knowledge, this technique has never before been carried out on amorphous carbons, and it is quite possible that the direct real-time visual information will significantly change our picture of structure development in chars.

Subtask 2.2 Computational investigations of char oxidation pathways

The problem of coal and char combustion is far too complex in its full form to be treated rigorously with atomistic computational methods. We therefore propose to study the reaction channels for O₂ attack on model compounds, such as PAHs (naphthalene, anthracene, and pyrene) or model graphitic structures.

Specific computational goals for this project include understanding the oxygen addition process and subsequent cleavage of a graphitic "coal char" surface. To understand this process, we need to consider a carbon-rich graphitic material and the attachment of oxygen in a variety of orientations, positions, etc. These would include C-C edge and C-C bridge attacks by O₂ and then the further rearrangements and cyclizations for ring cleavage. Since *accurate* calculations on large graphitic materials are very difficult, we propose to proceed to graphitic materials by first calibrating appropriate theoretical methods on small aromatic systems and then proceed towards larger aromatic systems.

One important property that will be investigated initially will be bond dissociation energies for C-H bond cleavage on small aromatic rings, such as benzene, furan, thiophene, pyrrole.

Figure 4 Small aromatic molecules to be considered in early thermochemical calculations

There is some experimental data available for a few aromatic systems, and furthermore, these model systems will provide information pertinent to coal char combustion. Besides bond dissociation energies, we intend to examine the O₂ chemistry with these systems, and this will include oxygen addition to the ring, dioxirane formation and subsequent aromatic ring cleavage. For all of these processes, we will examine the entire potential energy surface to probe minima as well as maxima (transition states) for oxidation of the ring. These calculations will be done at very reliable levels of theory, including Complete Basis Set (CBS) and Gaussian (G1 and G2)

theoretical methods. These methods have been shown to be very accurate in reproducing bond dissociation energies, atomization energies, electron affinities and other properties to within 2 kcal·mol⁻¹ accuracy. In addition, we hope to probe the ability of Density Functional Theory (DFT) to analyze these systems. DFT has the advantage of being computationally inexpensive and thereby applicable to larger systems. We hope to calibrate a variety of DFT methods in comparison to the well applied and calibrated CBS and Gaussian methods.

We will also examine small H-poor aromatics, such as benzyne (C₆H₄) and its O₂ chemistry as this will be an important model for understanding H-poor (C-rich) coal chars and their combustion. It will be vitally important to calibrate the DFT methods for exploring these H-poor aromatics as these intermediates may push the DFT methods to their limits. Success with these species will be very important to understand the unsaturated, H-poor coal chars.

While these systems are “small” on the graphitic scale, we will obtain some vital information. With confidence on the appropriate pathways to consider, we intend to proceed to larger “carbon” systems. We will proceed to naphthalene, anthracene, phenanthrene and consider the attack of O₂ to the bridgehead regions of these aromatics.

Figure 5 Larger aromatic structures for second phase calculations

We will once again use the insight gained from the smaller model systems to examine the “important” edge interaction processes and the subsequent ring cleavage from O₂ addition to these polyaromatic hydrocarbons. At least naphthalene is small enough for further calibration of the DFT methods with higher level calculations. This will be particularly important for the bridgehead attack process that can not be examined with the single ring aromatics. We intend to explore the effect of nitrogen, oxygen and sulfur on the chemistry of the aromatic ring by performing calculations on benzofurans, indoles, and so on.

We will then proceed further to larger polyaromatic hydrocarbons (PAHs), such as pyrene, coronene, and so on. These PAHs are more appropriate to begin discussing an amorphous coal char, but they are “large” from a computational view-point. The size of these systems will make it prohibitively expensive to do CBS and Gaussian calculations, but with calibrated DFT methods, we hope to probe these systems as well. Once again, we will examine the O₂ addition process and cleavages resulting in coal char combustion. We will proceed to larger H-poor PAHs as well.

pyrene

coronene

Figure 6 Large aromatic structures typical of carbonizing melts

Task 3. Experiments in Practical Combustion Systems

OBJECTIVE

The overall objective of this work is to determine the dependence of coal/char reactivity on coal rank, coal type, and combustion environment through experiments in practical flames. A second objective is to understand whether the reactivity differences are governed by changes in physical properties and/or changes in intrinsic chemical reactivity.

BACKGROUND

To maintain a sharp focus on practical coal combustion systems, the modeling work proposed above will be accompanied by experimental investigations tracking char structure and properties in practical combustion systems with widely contrasting flame types. To illustrate the importance of flame type, consider coal particles entering a boiler. Depending on the precise burner design, the particle heating rate can range from under 10,000 °C per second to over 100,000 °C per second (and up to one million deg/sec in special-design High Intensity coal combustors). The difference in heating rates is then known to affect the quantity of volatiles evolved but also, and more significantly, the quality and structure of the char formed, and thus the reactivity.

Heating rate strongly affects the char formed since the thermoplastic properties of the coal, allowing such behavior as swelling, are substantially determined in the temperature range for pyrolysis and, as heating rate increases, the time available for the thermoplastic behavior is reduced. In consequence of the change in thermoplastic behavior, at the higher heating rates, and the differences in VM release, the flame-generated structure is generally more open so that a greater fraction of the char particle combustion will be internal, typically leading to high reactivities and short burnout times. There is also the question whether the microparticles or crystallites exposed by this behavior may not be more fully graphitized and thus less inherently reactive, again with the potential for increasing carbon loss. This, clearly, affects the combustion efficiency, with a small additional influence on the boiler thermal efficiency.

A closely related factor is the effect of staging which is increasingly being used for NO_x control but also affects the carbon in the ash. With staging, the char formed is then modified due to low oxygen concentrations in the fuel-rich regions of primary firing. With reduced oxygen, the potential for cross-linking is reduced; the char formed can be more dense with lower internal porosity so that the particles are more likely to burn in the shrinking-core mode than in the Thiele mode. Reaction time can then be longer, and the known practical result is that unburned carbon leaving the boiler increases, frequently to the point that the captured ash is then unmarketable. All these factors emphasize the close connection between practical problems such as carbon loss in the ash and the intrinsic char reactivity at the molecular or mesoscale level.

Based on the above considerations, our approach includes a task in which analyses are performed on char samples extracted from practical, but well-characterized combustion systems. These experiments will serve to document and quantify the importance of thermal history effects on char structure and reactivity in real coal flames. Experiments will be carried out in two combustion facilities at OSU designed to produce different char particle heating rates, and peak temperatures: the one-dimensional flame and the high intensity combustor. Heating rates in the 1D flame system are approximately 10⁴ K/s, while the high intensity combustor achieves 10⁵ K/s. Chars will be analyzed for physical and chemical properties and the differences related to their flame histories. The results of this task will also provide an assessment of the current theory that the high intensity combustor at OSU yields high carbon conversions due in part to the limited opportunities for thermal annealing in this firing configuration.

In the final phase of the project, the fundamental advancements in the various critical areas discussed above will be examined in a unified way and the net result assessed. The cumulative results will serve to identify the optimal predictive scheme and the pathway to the generation of concrete practical tools based on the same fundamental principles.

APPROACH

In this Task, furnace experiments will be carried out with the general objectives of: generating char samples (under fuel rich conditions) for characterization; and generating phenomenological kinetic data (under combustion conditions) for comparative evaluation of reactivity. Experiments will be carried out in two combustion facilities at OSU designed to produce different char particles heating rates, T-t histories, and peak temperatures. These are: a 1-D (plug-flow) furnace [Howard and Essenhigh, 1967]; and a High Intensity Combustor [HIC] [Farzan and Essenhigh, 1982]. Heating rates in the two furnaces are, respectively: about 10⁴ K/s, and 10⁶ K/s. Peak temperatures in the HIC can be modified by water injection as diluent but the high heating rates are still obtained. These two heat treatment rates generate chars of substantially different reaction characteristics. Equipment that is also available for supplementary experiments including a copy of the jet mix reactor first described by Goldberg [Goldberg and Essenhigh, 1979]. This permits extraction of chars developed just in the primary mixing region in a well-defined reacting volume. Descriptions of the furnaces/reactors appear in the facilities section.

The furnaces can be operated in the following modes:

Air Rich: combustion mode with no staging. Objective is to follow burn-out. Measurements are designed to determine the *in situ* kinetics of the formed char.

Fuel Rich: char forming mode with no staging (first stage of either combustion or gasification). Objective is to create chars for analysis with continued heat treatment in the POC gases following the combustion zone.

HIC Fuel-Rich with delayed staging: Objective is to provide some degree of thermal treatment after formation followed by determination of kinetics to compare the kinetic behavior without and with a degree of heat treatment in the second stage burn-out.

Jet mix reactor: char forming mode in well-defined volume: no staging.

Samples removed for char property evaluation will be examined physically by one or more of the following methods (this depends on the size of each individual char sample): particle size distribution (PSD); internal surface area (BET); char structure properties by FTIR/Raman and/or imaging Raman using equipment in the OSU Center for Materials Research. They will also be examined chemically for: VM and ash determination for degree of pyrolysis at OSU; and low-temperature reactivity (selected samples) at Brown.

To execute this segment of the project, the following sub-tasks will be carried out with the first five subtasks executed substantially in parallel.

Subtasks

- Tune up existing furnaces and equipment: furnace #1: instrumentation [probes, meters, and analyzers (TC's, CO₂, O₂, CO)];
- Repeat Subtask 1 on Furnace #2
- Review / train student operators on furnace operation and performance
- Training on analytical equipment (moisture, VM, ash, BET, PSD)
- Training on Center for Materials analytical equipment (FTIR, Raman)
- Plan preliminary matrix of survey experiments (variables: furnace #1/2; coal type; (coal grind); firing rate; stoichiometry; staged/unstaged; combustion/char-formation: Execute preliminary matrix
- Plan complete matrix of experiments : Execute matrix

Operational rate will be one run every 4 to 6 weeks: this includes furnace and system preparation; execution of experimental runs (generally 6 to 10 hour run); samples analysis and characterization; data reduction and evaluation; furnace and equipment maintenance. Total expected in preliminary matrix: 6 to 8; Total expected in main matrix: 20 to 30, or as time and facilities permit and/or other developments require.

Analyses

The objective of the experimental work summarized above is to develop the experimental data base needed as a target for testing analytical flame models. The analytical flame models contain (phenomenological) kinetic model assumptions. The key objective of the analytical modeling -- given a demonstration of validity -- is then to provide a means of reducing the experimental results to kinetic parameters (activation energies and related frequency factors) corresponding to the kinetic assumptions. The phenomenologically-based kinetic parameters thus obtained then provide targets for comparison with predictions of the corresponding parameters from the mechanistic models. Repeating this procedure for a range of coals of different rank then, in principle, provides a basis for establishing the true role of coal rank in determining the reactivity of the flame-formed char. This procedure assumes the validity of the model assumptions, but tests or challenges the assumptions as the work proceeds. This is the experimentum crucis approach since if the model is incorrect, the model evaluation will fail, but providing at the same time identification of the source of failure that conceptually can provide the basis for model revision.

Projected Data Base.

The data base will be constructed out of the experimental measurements, mostly on the furnaces, but including the jet-mix reactor. In the furnace experiments, in a single run, the procedure is as follows. At steady state, the independent measurements are: input feed rate of the selected coal, particle size distribution (PSD) by Microtrac, and air rate. This includes coal type and coal analysis (proximate and ultimate).

For the analytical model testing, the primary measurements of dependent behavior are made at a number of different horizons in the flame. These include: gas analyses (CO , CO_2 , O_2), solid samples, and gas and wall temperatures. The gas analyses are used to get the local combustion efficiency at that horizon. The solid samples are analyzed for VM, and ash; this provides an additional determination of the burn-off (combustion efficiency) for cross-comparison with the gas analyses. The solid samples are also analyzed to the extent possible (determined by sample size) for PSD. The gas temperatures are measured by suction pyrometer. A two-color pyrometer is used to get the particle(s) temperature. This typically is a random variation about a mean value where the fluctuations have been identified as due to the random variation in local PSD in the particle cloud crossing the pyrometer view [Shaw and Essenhigh; Combustion and Flame: 86: 333-346 (1991)]. These measurements permit construction of burn-off and temperature profiles along the flame.

For this project, the further measurements to be made on the extracted solid samples are: physical measurements to determine physical structure, including porosity and internal surface by BET; and reactivity measurements for comparison with flame reactivities determined as set out below. The target here is to see to what extent there is continuing alteration of the carbon structure, as part of or independent of the reaction process (e.g., internal porosity development by reaction or thermal annealing as heat treatment). For the reactivity measurements, selected samples will also be examined by a standard TGA procedure. Absolute reactivity determinations by TGA are known to be open to alternative evaluations. However, in this instance, the procedure will be used for comparison of reactivity under the same testing conditions, of samples obtained in flames under very different operating conditions.

Data Analysis and Evaluation.

The principal method of evaluating the data is by comparison with predictions from relevant flame models. For the two primary furnaces [the Plug-Flow and the High Intensity] the theoretical bases are given in the two previous papers (and citations therein): Xieu, Masuda, Cogoli, and Essenhigh; Proc. 18th Symp. pp. 1461-1468 (1982) and Farzan and Essenhigh; Proc. 19th Symp. pp. 1105 - 1111 (1982). For the Jet mix reactor the source used is Choi, Rahamian, and Essenhigh, Proc. 21st Symp. pp. 293-302 (1986) and citations.

In the plug-flow [1-D] furnace, the analytical basis is a combined radiation-kinetics model. In a thin element of the flame, radiation is emitted from the particles (gas radiation is minor to trivial by comparison), dependent on their particle size and size-dependent temperature. The thin element is also absorbing radiation from other segments of the flame, upstream and downstream. The solution method is iterative, involving variation between iterations of the burn-off rate, dependent on temperature, size and oxygen concentration, and variation of oxygen concentration, dependent on burn-off. The model requires inclusion of a distribution of particle sizes in the input feed (obtained from the PSD experimental analysis), and it requires independence of the gas and particle temperatures. CPU time has varied from 5 to 15 hours depending on the details included. The model includes initial pyrolysis for the particles on entering and through heat-up. The outcome is prediction of profiles of: temperature with distance through the flame; combustion efficiency; particle size changes; and gas analyses. The kinetic inputs to the model include: the adsorption and desorption activation energies and frequency factors, and the second Thiele internal burning parameter defined previously [Essenhigh,; Proc. 22nd Symp. pp. 89-96 (1989)].

The prior work using this model has used selected and partially-adjusted kinetic parameter values. What will be targeted for the proposed work will be extension of this procedure to a wider range of operating conditions (feed rate, stoichiometry, PSD), with the objective of determining: (i) the best-fit values of the needed kinetic parameter values; (ii) the sensitivity of that determination required for best-fit; (iii) the dependence of the parameter values on the firing conditions; (iv) the dependence of the parameter values on coal type. This will also create the needed data-base as the critical target for the mechanistic predictive modeling of the kinetic constants.

In the High-Intensity furnace, the method of operation is to introduce the coal and air under very intense (back)mixing conditions so that the volatiles are released and reacted in 10 to 20 msec. Downstream of the mixing section the flow reverts to plug-flow, with continuing reaction to final burnout of the char formed in the mixing section. In this lower section, the same procedures are used as in the 1-D furnace, of obtaining solid samples, gas analyses, and temperatures. The results obtained from this have shown that the reactivity of the char is so high that the combustion is at the diffusion limit. The device can be used in two different modes to take advantage of this.

In the first mode it can be used to compare different coals under the diffusion limit conditions. If there is no swelling (due to the very high heating rate), then the differences between coal type should then be due only to the initial PSD and to the Q-factor for volatile release. If the chars formed have different reactivities, this is not expected to show up in the burn-out behavior and kinetics, unless the char is unusually low reactivity.

In the second mode of operation, the procedure will be to stage the combustion, with the char formed in the high mixing section under reducing conditions. The remaining air is then introduced downstream, and the point of introduction can be changed to allow heat treatment for determinable periods of time. This allows for measurement of reactivity in the final burnout section, after different periods of heat treatment. The temperature of the final burnout is also reduced so that the reaction is in the kinetic regime. This procedure has already been examined and shown to be feasible. The limited results available have shown that the reactivity decreases as the result of the delayed secondary air introduction. What is needed is fully quantitative determinations for precisely defined conditions for a suite of coals. The precise suite of experiments can not be specified at this time; it will have to be developed on the basis of the data base of results as these develop.

A parallel and critically important component of this segment of the proposed work will be extraction and analysis of char samples under different conditions of firing and of heat treatment time between the primary zone and the secondary air introduction. The particular focus of the analyses will be determination of the physical and reactivity properties, and particularly of changes in those properties with heat treatment time.