TITLE: COAL CHAR CRYSTALLINE TRANSFORMATIONS DURING COMBUSTION AND THEIR IMPLICATIONS FOR CARBON BURNOUT

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ABSTRACT

Objective

Recent work has identified char carbon crystalline rearrangements as an important mechanism leading to thermal deactivation of chars in the flame zones of pulverized-coal-fired furnaces. The so-called thermal annealing of carbons is a well known phenomenon, but its key role in carbon burnout has only recently been appreciated, and there is a lack of quantitative data in this time/temperature range. Motivated by these recent developments, this UCR project is pursuing the following two objectives:

- to determine transient, high-temperature, thermal deactivation kinetics as a function of parent coal and temperature history.
- to characterize the effect of this thermal treatment on carbon crystalline structure through high-resolution transmission electron microscopy (HRTEM) and specialized, quantitative image analysis.

Accomplishments to Date

Crystal structure analysis

- Hardware and software have been developed and tested for the specialized analysis of HRTEM fringe images.
- An image analysis algorithm has been developed with the following basic steps: digitization, noise reduction.(spatial filtering), fringe identification, characterization of fringe geometries, and interpretation. Weaknesses in the state-of-the-art have been identified in each of these areas and new sub-algorithms have been formulated and tested.
- A number of new tools have been developed for interpretation of the fringe statistics, including measurement algorithms for fringe length, tortuosity, and orientation. New indices were developed for the quantification of orientational order (both type and degree) in carbons. An important new finding was made — that there exists long-range statistical order in the crystal structure of most chars, even those that pass through a fluid phase.

- The tools described above have been applied to a large series of HRTEM images (> 30) taken on coal chars generated during high temperature combustion. The time resolved data reveals the nature of the char crystalline transformations occurring during pyrolysis and combustion. Crystal structures are seen to differ greatly between different precursors. In some cases, the basic crystal structure is formed early (during pyrolysis) while in others there are significant transformations during combustion. Significant and important rank trends are seen in the data. High-resolution TEM fringe imaging is proving to be a useful new diagnostic for understanding fuel chemistry transformations during combustion and heat treatment.

Thermal deactivation kinetics

- Initial data on the thermal deactivation propensity of lithotypes and the accompanying crystalline rearrangements were obtained through collaboration with Imperial College and Sandia National Laboratories, leading to a joint paper at the 26th Combustion Symposium.

- A transient heat treatment apparatus was designed and built that is capable of higher temperatures and lower impurity levels than existing devices. The device is based on a thin graphite rod held at the ends by large brass electrodes connected to a DC power supply. An axial trough is made near the center of the rod to hold the powdered carbon samples kept in place by a high-porosity carbon fiber blanket. The device was proven to be capable of melting molybdenum, indicating a peak temperature above 2500 C.

- Transient heat treatment experiments were conducted on a low rank (Beulah lignite) and high rank coal char (Pocahontas #3). Samples were heat treated for 4 seconds at a series of temperatures from 700 C to 2400 C and their oxidation reactivities measured subsequently under controlled conditions. The data shows significant deactivation (despite the short times) and a convergence of reactivity at temperatures above about 2200 C. More data is being acquired before mechanistic interpretations are attempted.

Significance to Fossil Energy Programs

Thermal char deactivation is believed to be an important factor influencing carbon burnout in current pulverized coal-fired boilers. A better understanding of the phenomenon could improve predictive capabilities for carbon burnout and also improve furnace design methodologies. Char deactivation is also an important concern in many next generation combustion systems, especially those that employ deep staging for NO_x control. Thermal char deactivation should be especially important in entrained flow gasifiers used in combined cycle power generation. These systems exhibit high peak temperatures in the oxidizing zone, followed by lower temperatures and slower kinetics in the gasification zone, making the ultimate carbon burnout especially sensitive to late stage char reactivity.

Plans for the Coming Year

- to complete the data base on thermal deactivation kinetics at high temperatures and short times for a range of coal chars
- to develop new mathematical formulations for describing thermal deactivation under combustion conditions, suitable for inclusion in numerical models of combustion and carbon burnout.
- to prepare the final report

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Journal Articles (peer reviewed)

- Beeley, T., Crelling, J., Gibbins, J., Hurt, R., Lunden, M., Man, C., Williamson, J., Yang, N., "Transient High-Temperature Thermal Deactivation of Monomaceral-Rich Coal Chars" accepted for publication in the *Proceedings of the 26th International Symposium on Combustion*, January, 1996.

- Hurt, R.H., *Structure, Properties, and Reactivity of Solid Fuels*, Invited Topical Review Paper for the Twenty-Seventh International Symposium on Combustion, The Combustion Institute, Pittsburgh, 1998.

- two additional articles representing the major work performed in this contract are under preparation. One article focuses on HRTEM analysis of crystal structures and one on thermal annealing kinetics.

Conference Presentations

- Hurt, R. H., Yang, N. Y. C., "A High-Resolution TEM Study of Combustion-Induced Changes in Carbon Crystallinity," presented at the 22nd Biennial Conference on Carbon, San Diego, California, 1995.

- Hurt, R.H., "Prediction of Carbon Burnout in Practical Combustors: The Role of Fuel Science" invited lecture given at the 1996 Annual Technical Conference on the Clean and Efficient Combustion of Fossil Fuels and Waste Materials, Advanced Combustion Engineering Research Center, University of Utah, March, 1996.

- Robert Hurt, Eric Suuberg, Yu-Ming Gao, Peter Calvert, "Unburned Carbon in Ash: Formation, Properties, and Behavior in Construction Applications," presented at the EPRI Conference on the Impact of Coal Quality on Power Plants, Kansas City, 1997.

Students Supported under this Grant

- Hong-Shig Shim graduate student in chemistry

- Alicia Burnett undergraduate student in chemical engineering (prepared Sc.B. honors thesis on this topic)