COMPARISON OF BIOMASS AND COAL CHAR REACTIVITIES

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ABSTRACT

Char combustion is typically the rate limiting step during the combustion of solid fuels. The magnitude and variation of char reactivity during combustion are, therefore, of primary concern when comparing solid fuels such as coal and biomass. In an effort to evaluate biomass' potential as a sustainable and renewable energy source, the change in reactivities with the extent of burnout of both biomass and coal chars were compared using Sandia's Captive Particle Imaging (CPI) apparatus. This paper summarizes the experimental approach used to examine biomass and coal char reactivities and extinction behaviors and presents results from CPI experiments.

The reactivity as a function of extent of burnout for six types of char particles, two high-rank coal chars, two low-rank coal chars, and two biomass chars, was investigated using the CPI apparatus. Results indicate that both of the high-rank coal chars have relatively low reactivities when compared with the higher reactivities measured for the low-rank coal and the biomass chars. In addition, extinction behavior of the chars support related investigations that suggest carbonaceous structural ordering is an important consideration in understanding particle reactivity as a function of extent of burnout. High-rank coal chars were found to have highly ordered carbon structures, where as, both low-rank coal and biomass chars were found to have highly disordered carbon structures.

INTRODUCTION

Char combustion is typically the rate limiting step during the combustion of solid fuels. Incomplete combustion of solid fuels in utility boilers has long been an important concern for power generation facilities [Hottel and Stewart, 1940]. The result of incomplete combustion is a high level of unburned carbon in a boiler's flyash. This, in turn, causes a number of deleterious effects, including, a significant decrease in combustion efficiency, an adverse effect on heat transfer and electrostatic precipitator operation, and a greater difficulty marketing the flyash for recycling (i.e., for carbon contents greater than 3 to 6 percent). Determining the relative level of unburned carbon from burning coal and biomass fuels in boilers motivates this investigation.

This paper concentrates on biomass chars produced from the pyrolysis of two biomass feedstocks—a soft wood, Southern Pine; and an herbaceous material, switchgrass. The biomass chars were formed by pyrolyzing pine and switchgrass particles in a vortex reactor at 625 °C, described elsewhere [Diebold and Scahill, 1988]. Previous work on biomass chars has focused on (1) structural and compositional changes [Wornat *et al.*, 1995] and (2) quantitative measurements of global reactivity at early and intermediate levels of combustion under pulverized-fuel conditions [Wornat *et al.*, 1994]. This paper focuses on the reactivity of chars during the late stages of combustion, which is critical to unburned carbon in flyash.

In practice, the level of unburned carbon in the flyash is related to the fuel's rank. Coal rank is a measure of volatile matter contained in the coal and is generally considered an indicator of its geologic

age. Our earlier work [Hurt, 1993; Hurt and Davis, 1994; Davis *et al.*, 1995] indicates that the carbonaceous structure of young materials (biomass and low-rank coal chars) is less susceptible to the structural ordering process that bituminous and high-rank coals can undergo. The more amorphous nature of the younger materials during the latter stages of combustion should maintain their initially high level of reactivity throughout the entire combustion process, insuring lower levels of unburned carbon in the flyash.

Bituminous and high-rank coals produce high levels of unburned carbon, whereas, low-rank coals produce lower levels of unburned carbon. Biomass, with a very high volatile matter content, high oxygen content, and a correspondingly low heating value, is thermochemically similar in many respects to a low-rank coal. Given the thermochemical similarity of low-rank coals and biomass chars, we expect both fuels to exhibit comparable reactivities and to produce similarly low levels of unburned carbon. This paper presents an investigation of char reactivity as a function of burnout for biomass chars and compares them to our observations for coal chars of various ranks.

A relationship exists between a char's reactivity and extinction behavior and its temperature-time profile [Hurt, 1993]. Temperature-time profiles of chars provide the relative magnitude of reactivities for different chars, where as, normalized temperature-time profiles of chars are best suited to illustrate and compare the extinction behavior of different chars. Because maximum temperatures and extinction times vary greatly for different types of chars, temperatures and times were normalized to allow for a comparison of extinction behaviors for various types of chars.

EXPERIMENTAL METHODS

The high-temperature reactor in Sandia's Coal Combustion Laboratory (CCL) was used to measure the temperature-time profiles during combustion of two high-rank coal chars (Illinois #6 and Pocahontas #3), two low-rank coal chars (Beulah and Dietz), and two biomass chars (pine and switchgrass). Data were obtained with the Captive Particle Imaging (CPI) diagnostic system that has been discussed in previous reports [Hurt and Davis, 1994]. Figure 1 presents a schematic of the CPI. The system provides optical access for high-resolution video imaging of complete particle combustion for individual 100 μm to 200 μm char particles in a well-controlled combustion environment. Particles are placed on an alumina fiber bed supported by fine platinum wires. The particles are oxidized in a laminar flow of vitiated air with 6 mole-% excess oxygen at a temperature of approximately 1600 K. The particle is positioned along the reactor centerline at the focal point of a long-focal-length microscope. During the positioning process a water-cooled coil surrounding the particle holder provides local cooling and therefore prevents premature reaction of the particle. This microscope is connected to a video system capable of simultaneously imaging both reflected light and near infrared (IR) emission from the reacting particles. The IR images can be used for determination of radiance temperatures. Radiance temperature is defined as the temperature of a hypothetical black body emitting the same radiative power as the real object (particle) in the wavelength range of interest (here 700 to 1000 nm). For particles that have undergone low to intermediate extents of burnout, emissivities are approximately 0.8 [Baxter *et al.*, 1988] and true particle temperatures will be approximately 20 K greater than the reported radiance temperatures.

For the temperature-time profiles, the radiance temperatures are normalized to their corresponding maximum temperatures (i.e., normalized temperature equals the actual temperature divided by the maximum temperature). The temporal data are normalized by the time at which near-extinction (in the case of the higher rank coals) or extinction (in the case of lower rank coals and biomass chars) of the combustion process occurs. These extinction (and near-extinction) times correspond to the inflection point in the temperature-time profile that occurs after the peak temperature.

Using the CPI, normalized temperature-time profiles of several coal chars and solid biomass-derived fuels were determined for at least 20 particles of each type. Figures 2, 3, and 4 present the normalized temperature-time profiles for bituminous and high-rank coal chars (Illinois #6 and Pocahontas #3), low-rank coal chars (Beulah and Dietz), and biomass chars (pine and switchgrass), respectively. The figures show that for all the chars the particle temperature increases to a maximum and decreases to the reactor temperature, nominally 1400 to 1500 K. Table 1 summarizes the overall reactivity for various char particles [Wornat *et al.*, 1994].

RESULTS AND DISCUSSION

The general shape of a temperature-time profile is an indicator of a char's reactivity as a function of extent of burnout. A gradual decrease in temperature occurring after a char's peak temperature indicates that the reactivity of that char is decreasing with the extent of burnout, as shown for bituminous and high-rank coals in Figure 2. Chars that remain at or near their peak temperature for a

significant period during combustion then display a sudden decrease in temperature at the end of oxidation are believed to have relatively high reactivities that do not decrease with extent of burnout. Figures 3 and 4 show examples of chars with high reactivities that do not decrease with extent of burnout. These results show that the time or conversion dependence of reactivity for low-rank coal chars and biomass chars are very similar, the reactivities for both types of chars are relatively high, and the reactivities do not decrease with extent of burnout.

In addition to the information regarding extinction behavior, the CPI technique allows one to qualitatively compare the magnitude of the global reactivities of the various chars. Peak temperatures and burnout times obtained from these experiments suggest global reactivities qualitatively similar to the earlier quantitative work of past work [Wornat *et al.*, 1994]. The relative overall reactivities of chars are in the following order.

lignite chars > biomass chars > high-volatile bituminous coal chars

Table 1 lists the quantitative results obtained in the CCL over the past several years. The slightly higher reactivities of the biomass chars under CPI conditions may be a result of the somewhat lower temperatures used for the CPI compared to the CCL.

CONCLUSIONS

Based on our previous work on carbon reactivity and ordering of the carbon structure during coal and char combustion [Davis *et al.*, 1995], the current results for the biomass chars are not surprising. High-rank coals are observed to undergo a significant decline in reactivity with increasing burnout. This is a consequence of carbon structural ordering in the char during exposure to the high-temperature combustion environment. Highly ordered carbon structures offer fewer active sites for heterogeneous surface oxidation, which, therefore, decreases the reactivity of the carbon particle. In our related work on biomass chars [Wornat *et al.*, 1995], short-range ordering of the biomass char carbon is observed in carbon-rich portions of the chars. However, the high levels of oxygen content in biomass fuels favors cross-linking of the carbon chains that inhibits further carbon ordering during combustion This persistence of disorder in the carbon structure during biomass char oxidation is also observed for the high-oxygen-content chars of low-rank coals. We believe that the disorder in the carbon structure is responsible for the high reactivities found in both the low-rank-coal and biomass chars throughout their combustion lifetime. A consequence of this high char reactivity is that the particle temperature remains high for these chars through the entire burnout. In summary, the combustion behavior of biomass chars was found to be similar to that of low-rank coals—high reactivity with no evidence of a decrease with extent of burnout.

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Table 1. Overall Reactivities of Various Chars

Fuel Name	*Fuel Type*	*Rate*† *(g of C/cm²·sec)*
Southern Pine Char[1]	woody	0.0037
Switchgrass Char[1]	herbaceous	0.0041
Beulah[2]	lignite	0.0065
Lower Wilcox[2]	lignite	0.0056
Smith-Roland[2]	subbituminous	0.0065
Dietz[2]	subbituminous	0.0061
Hiawatha[2]	high-volatile bituminous	0.0059
Blue #1[2]	high-volatile bituminous	0.0045
Illinois #6[2]	high-volatile bituminous	0.0033
Pittsburgh #8[2]	high-volatile bituminous	0.0024
Lower Kittaning[2]	low-volatile bituminous	0.0021
Pocahontas[2]	low-volatile bituminous	0.0012

† rates are calculated from global kinetic parameters at gas conditions of 1500K & 6 mole-% O_2, the value 0.0065 is the diffusion-limited maximum for these conditions

1 Wornat, Hurt, and Yang (1994)

2 Hurt and Mitchell (1992)

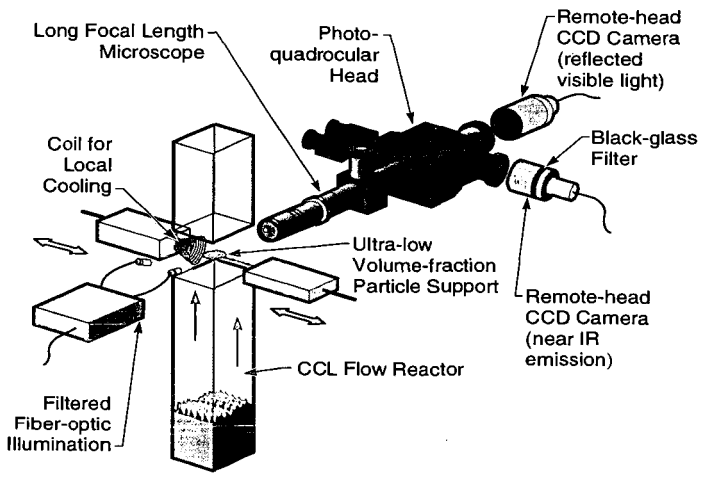

Figure 1. Schematic of the Captive Particle Imaging System

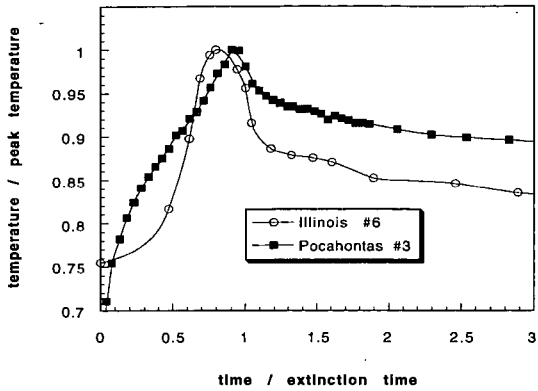

Figure 2. Normalized Temperature versus Normalized Time for Bituminous and High-Rank Coals

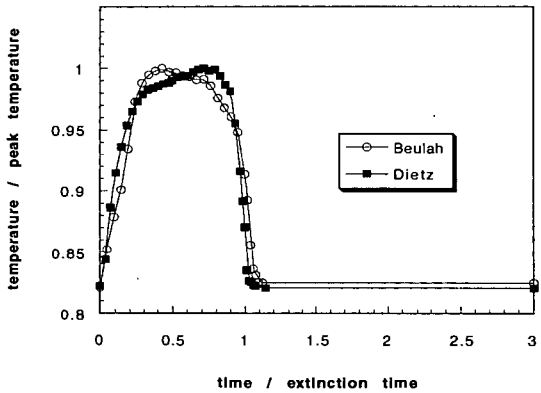

Figure 3. Normalized Temperature versus Normalized Time for Low-Rank Coals

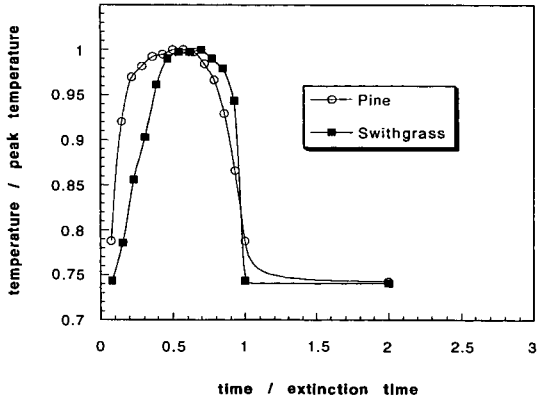

Figure 4. Normalized Temperature versus Normalized Time for Biomass Chars