

A HIGH-RESOLUTION TEM STUDY OF COMBUSTION-INDUCED CHANGES IN CARBON CRYSTALLINITY

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Recently, low oxidation reactivities and high-degrees of crystalline order have been observed in carbon samples extracted from power station fly ash [1,2], and in laboratory chars in the late stages of combustion [3,4]. Thermal deactivation at peak particle temperatures (1800 - 2400 K) and short times (< 1 sec) has been suggested as the likely explanation for the low reactivities at the end of the combustion process[2,4]. The general phenomenon of thermal annealing of carbons is well established [5,6], but there is little data in the literature directly relevant to the short times of interest here. Levendis and Flagan [7] have examined the crystal structure of partially-combusted polymer-derived carbons. Davis et al. [4] have used high-resolution transmission electron microscopy (HRTEM) to study the crystalline transformations of Illinois #6 coal chars during high temperature combustion and have correlated decreases in global oxidation reactivity with increases in the amount of recognizably ordered carbon. The present paper extends that work to a range of solid fuels in order to reveal the general features of combustion-induced char carbon crystalline transformations as a function of char precursor.

Experimental

Partially combusted char samples were prepared in a flame-supported, entrained-flow reactor by combustion in vitiated air streams at a nominal gas temperature of 1600 K. Char samples were collected at residence times of 47, 72, 95, and 117 msec, yielding a range of carbon conversions from 0% (at the end of devolatilization and beginning of char combustion) to a maximum value of 50 - 80%. Oxygen concentration was systematically varied from 12 to 20 mole-% to produce similar peak particle temperatures (1900 - 2000 K) and similar degrees of carbon conversion for each of the precursors. The char samples were ground, placed on a holey carbon grid, and examined in a Phillips Model CM30 microscope operating at 300 kV. Carbon structures were inspected at 2,000,000x magnification in the vicinity of particle edges.

Results

Table 1 summarizes the features observed in the HRTEM images and lists global oxidation reactivities for the same samples. The nature of the carbon crystalline transformations under combustion conditions is a pronounced function of the parent fuel, with the extent of order decreasing with increasing geologic age or oxygen content. The lowest rank materials (from biofuels) are disordered and maintain their disorder throughout combustion. The two high-volatile bituminous coals (Illinois #6 and Pittsburgh #8) undergo a transition from nearly amorphous to fully turbostratic during the char combustion stage. The development of turbostratic order in these two chars correlates with their loss of reactivity and early near-extinction, observed previously [4]. The high-rank Pocahontas char shows a high degree of order after only 47 msec of residence time, suggesting an ordering process in the fluid stage of carbonization.

For the lignite samples at 72 and 117 msec, large scale curved crystalline structures were observed as a minority phase embedded in a poorly organized carbon matrix. The circular regions may be two-dimensional crystalline rings or, more likely, two-dimensional projections of three dimensional nested shell structures. The concentric structures are typically found in clusters, concentrated in only a few of the regions examined. These same regions tend to contain dark patches associated with inorganic inclusions, suggesting that inorganic material plays a catalytic role in the nucleation or growth of the ordered phase.

Discussion

Both the timing and the extent of carbon crystalline order development during solid-fuel combustion is a pronounced function of the parent fuel. Under similar combustion conditions, the extent of order increases and reactivity decreases with increasing rank. The observed propensity of the high-volatile coal chars to pregraphitize *during* char combustion is consistent with the observation of global deactivation and early extinction for these chars [3,4]. Low-rank materials

Table 1
Summary of HRTEM Image Features for Chars
as a Function of Precursor and Combustion History

<i>Precursor</i>	<i>Combustion residence time</i>	<i>Degree of crystalline order</i>	<i>Degree of anisotropy</i>	<i>Combustion reactivity[†]</i>	<i>Comments</i>
Pocahontas #3 coal	0 ms	none	—	—	- raw coal
	47 ms	high	very high	—	- early ordering
	72 ms	high	very high	4.9	
	95 ms	high	very high	—	
	117 ms	high	very high	—	
Pittsburgh #8 coal	47 ms	low		—	
	72 ms	moderate	slight	8.2	
	117 ms	moderate-high	slight	< 8.2	
Illinois #6 coal	47 ms	low	—	—	- primarily curved singlets
	72 ms	low-moderate	none	10.2	
	117 ms	high	none	2.6	
Beulah lignite	47 ms	moderate	slight	—	
	72 ms	moderate	slight	> 28	- some large, curved crystalline structures
	117 ms	moderate	slight	—	
Southern Pine [9]	47 ms	low	none	—	
	72 ms	low	none	13.3	
	95 ms	low	none	—	
Switchgrass [9]	47 ms	low	none	—	
	72 ms	low	none	15.2	
	95 ms	low	none	—	
Residual carbon ^{††} Illinois #6		high	moderate	3.8	
Residual carbon ^{††} Daltex		high	moderate	2.2	

[†] global preexponential factors, g-carbon/s-cm²-atm^{0.5}. For some samples, time/conversion dependent reactivities are presented; for most, a single reactivity measurement was made in the early-to-intermediates stages.
^{††} extracted from the fly ash from commercial-scale coal combustors

maintain their disordered structures through high conversion, and this parallels the recent observation of late extinction events for lignites and biomass chars. Finally, the degree of crystalline order appears to show a strong correlation with global oxidation reactivity across the entire set of samples examined to date. The trends observed by HRTEM coincide with the trends in reactivity, both as a function of parent material (rank) and as a function of combustion history (time/carbon conversion). HRTEM analysis is providing extremely valuable insight into the high-temperature combustion and burnout behavior of a variety of solid fuels.

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