

# THERMAL ANNEALING OF CHARs FROM DIVERSE ORGANIC PRECURSORS UNDER COMBUSTION-LIKE CONDITIONS

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## Introduction

Prediction of char oxidation rates and burnout levels in solid fuel combustion processes requires quantitative information on the reactivity of flame-formed chars. Char reactivity is influenced by precursor, degree of heat treatment, degree of oxidation, and the initial formation conditions including heating rate and gas environment. Extensive studies have documented the strong dependence of char reactivity on heat treatment history, but there have been relatively few studies focusing on the short times of relevance to combustion processes [1,2]. This paper presents measurements of reactivity loss in coal and alternate fuel chars as a function of heat treatment under combustion-like conditions.

## Experimental

An all-graphite transient heat treatment device has been developed which can achieve temperatures from 700 - 3000 K, maximum heating rates of  $2 \cdot 10^3$  K/s, and hold times at peak temperature from 2 - 120 seconds in inert environments. The device was used to measure the degree of deactivation of chars from a diverse set of organic precursors, including many practical solid fuels, with emphasis on short time experiments (2 - 4 sec) simulating the thermal treatment received under combustion conditions. Experiment results are reported for coals ranging in rank from lignite to anthracite, a biomass fuel (*pinus radiata*), a fluid petroleum coke, and a model char

The heat-treated char samples were then subjected to nonisothermal TGA analysis for measurement of their intrinsic oxidation reactivity. The TGA experiments used 2 - 10 mg samples heated at  $7^\circ$  C/min in a flowing stream of 21-% oxygen in nitrogen. Additional TGA experiments were carried out on a commercial graphite powder, and on a set of carbon-containing fly ash samples from commercial power stations. For comparative purposes, the reaction rates are reported as standard preexponential factors,  $k_0$ , assuming a common activation energy for oxidation of 35 kcal/mol.

## Results

The main results of this study are summarized on Fig. 3. The left-hand panel shows reactivities of chars prepared by 2 second heat treatment as a function of the peak heat

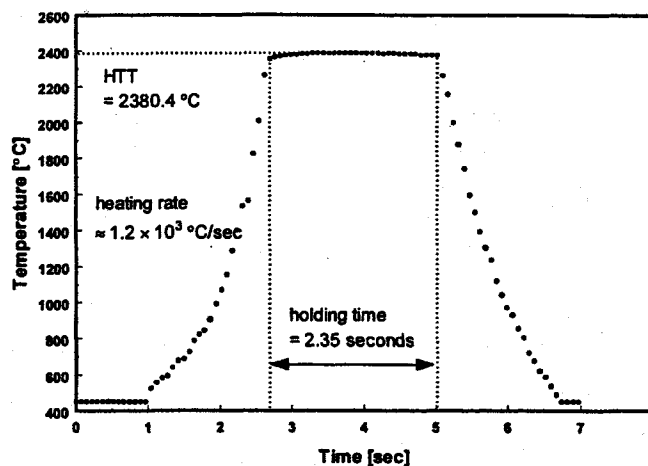


Figure 1. Typical temperature history achieved by the transient heat treatment device.

treatment temperature. The right hand panel shows the reactivity of as-received graphite powder and typical behavior for as-received carbon-containing fly ash samples. The reactivities on this plot, measured under similar conditions and normalized as standard preexponential factors,  $k_0$ , vary by almost six orders of magnitude, dependent on precursor and thermal history.

The oxidation reactivity of the low-temperature chars (prepared at  $700^\circ$  C) varies by over 3 orders of magnitude from lignite to anthracite. These precursor differences are reduced by heat treatment — the reactivity range is approximately 1.5 orders of magnitude after exposure to  $2400^\circ$  C for two seconds. The extent of thermal deactivation between  $700^\circ$  C and  $2400^\circ$  C for a given precursor ranges from 1.5 orders of magnitude for lignite, to 4.5 orders of magnitude for Pocahontas 1vb coal, to 4.5 orders of magnitude for lignite. Overall, the extent of deactivation at high temperature shows a strong rank dependence (the low-rank, high-reactivity chars undergo more deactivation), but there are significant fuel-to-fuel differences superimposed on the overall rank trend.

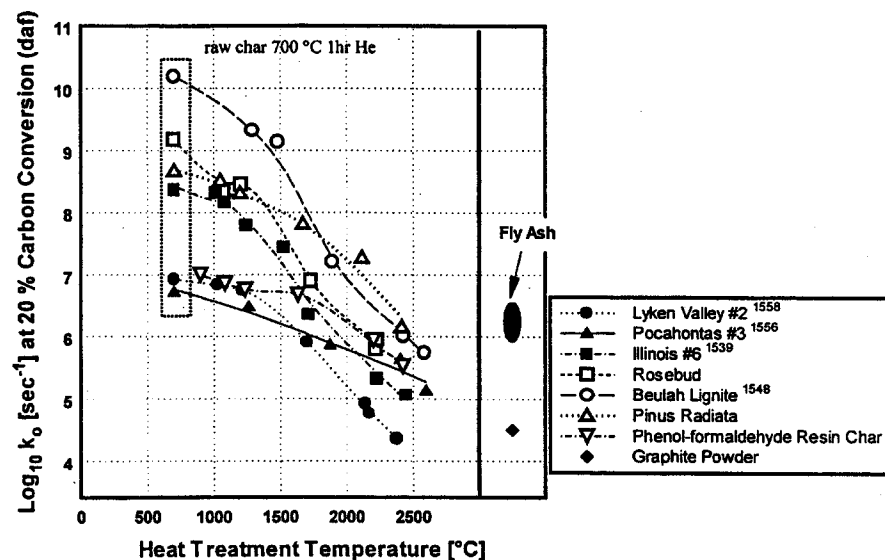


Figure 2. Results of short-residence-time (2 sec) heat treatment experiments: oxidation reactivities by TGA as a function of peak temperature and precursor. The right-hand panel gives for comparison the reactivities of graphite and of unburned carbon in a variety of commercial ash samples. Coal rank: Lykens valley: anthracite; Pocahontas: low-vol. bituminous, Illinois #6: high vol. bituminous; Rosebud: subbituminous; Beulah: lignite.

An example of fuel-to-fuel variation is the high annealing propensity of the anthracite, compared to Pocahontas, despite similar initial reactivities. HRTEM fringe images were obtained for the anthracite and Pocahontas chars. The low-temperature Pocahontas char shows long range layer alignment with significant "meandering" [4], i.e. random variation in orientation about the mean orientation vector (or "director"). This basic carbon nanostructure does not change significantly with further heat treatment. (A perfection of this meandering structure is often observed in carbons above about 1700 C [5], but apparently the residence times in this study (2 sec) were too short to allow for this transformation in Pocahontas.) The anthracite, on the other hand, shows significant structural rearrangement during similar heat treatment. The low-temperature char shows less order, and the high temperature char contains many regions with a near-perfect graphitic lattice. The relative disorder in the low-temperature anthracite char is not unexpected, as there is insufficient mobility in these materials for concerted rearrangements at such low temperatures (700 °C). At higher temperatures, however, a perfection of the crystalline order becomes possible for some anthracites, and highly ordered carbon results.

The commercial graphite powder has the lowest reactivity, although its value is approached by the anthracite char heated at 2400 K to 2 seconds. The carbon found in commercial fly ash samples (which originates from high-volatile bituminous and subbituminous coals) has a

reactivity comparable to the laboratory chars from high-volatile bituminous and subbituminous coals prepared at 1600 - 2000 °C. This value is close to peak particle temperatures in boilers, suggesting that thermal treatment plays an important role in establishing their reactivities.

## References

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