

THE BEHAVIOR OF CHARRING SOLIDS UNDER FIRE-LEVEL HEAT FLUXES

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It has recently been argued in the fire research community that the ability to quantitatively describe flame spread over combustible solids has reached the point at which our understanding of the complexity of the solid phase processes is limiting. Often the processes occurring in the solid are modeled by simple thermal diffusion in a solid (with ill-defined thermal properties) together with a crude empirical decomposition rate law. A critically important parameter- release rate of combustibles into the vapor phase- often becomes little more than an adjustable parameter, as decomposition rates, products of pyrolysis and solids thermal properties under relevant conditions are only approximately known. This is particularly so in the practically important case of charring solids such as wood and other cellulose. As a result, it is difficult to claim that a truly critical testing of combustion models for bulk, charring solids has ever been possible. This communication addresses some issues related to this problem.

Before attempting to model the behavior of more complex charring solids, we felt it important to better understand the solid phase behavior of one of the "simplest" charring solids- cellulose. What differentiated this study from many others on the same material were the careful attempts made to obtain kinetic and transport properties in experiments separate from those that simulate fire behavior, but with the latter experiments always being guided by the conditions found in fire situations. We further believe that the fire community would be well-served by focusing on "standard" easily-prepared materials of the kind studied here, so that there would be an ability to compare results between laboratories, as well as providing fire modelers a more reliable property data base than currently exists.

To simulate wood or other bulk cellulosic building materials, high purity alpha cellulose powder (Whatman CF-11) was dry-pressed in an ordinary laboratory press into pellets whose bulk densities bracketed those of real woods (0.4-1.0 g/cc). The intent here was *not* to simulate the full complexity of wood, but rather to obtain detailed data on a model charring material that is very wood-like in its behavior. The densities were reproducible from sample-to-sample to about 5%. An advantage of these samples is that they are relatively pure (0.009% ash) and contain none of the heterogeneity of real wood (i.e. no hemicellulose or lignin). This is important insofar as establishing the kinetics of pyrolysis is greatly simplified when potentially catalytic impurities are absent, and when there are not several distinct organic phases present. This allowed comparison with the large amount of data in the literature on cellulose decomposition, and also offered the possibility of reliable experimentation, on several scales, using several analytical techniques, to establish key properties.

The results of experiments on simulated woods and real woods are shown in Figure 1. The experiments were simulated fire experiments in which samples of 3.8 cm diameter and 1 cm thickness were irradiated on their front faces by a quartz lamp delivering 40 kW/m². The irradiation was chosen to simulate a fire level heat flux, but in this case the experiment was performed under inert gas, to avoid the further complexities introduced by actual combustion. Clearly the results show the ability to simulate

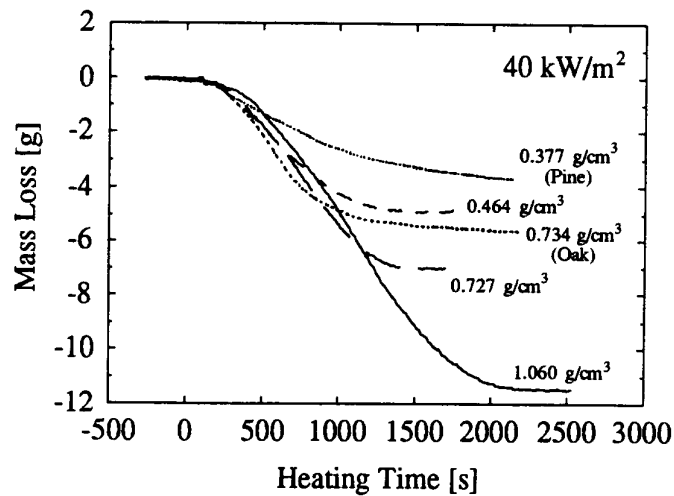


Figure 1. Mass loss as a function of time under simulated fire conditions for three different density cellulose samples and for two wood samples.

wood behavior, as far as combustibles release rates are concerned. The relatively constant pyrolysis front propagation velocity, implied by the nearly linear decrease in mass with time, is a consequence of the constant heat flux surface condition. A relatively constant temperature gradient between surface and pyrolysis front is maintained.

Attempts to model the observed simulated fire behavior led to a further battery of characterizations of the cellulose powder, bulk cellulose and char samples by TGA, DSC, and other thermal analysis techniques. These tests led to several unexpected conclusions, including the following:

- *The kinetics of cellulose decomposition will probably not be fit by a simple single reaction rate law, in a fire spread situation. There is a shift in the apparent decomposition kinetics at near 600 K which is of importance in the range of heating rates of relevance to such problems.*
- *The surface absorptivity of a sample is a strong function of wavelength. It was found that in a relevant range of wavelengths, char absorptivity is far lower than had been earlier thought. (0.7-0.85).*
- *The values of char heat capacity are not well modeled by temperature-independent values. Also, values for cellulose and graphite are poor estimates for char properties.*
- *Thermal conductivity and diffusivity used in many previous modeling attempts have been at variance with the properties determined here.*
- *The heat of pyrolysis is a strong function of combustible volatiles yield, which is itself a strong function of mass transfer/heating rate conditions.*

This study has highlighted the critical importance of independent measurement of key solids thermal properties and chemical decomposition kinetics in developing quantitative descriptions of fire spread phenomena on charring materials. Many current models of the solids decomposition process can correctly predict key trends, but accurate quantitative prediction of combustibles release rates requires that much more careful attention be paid to solids properties than has historically been the case.