

## CHARRING MATERIAL PROPERTIES

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#### ABSTRACT

There are various methodologies available<sup>1,2,3</sup> for the determination of flammability properties of non-charring polymeric materials. This paper presents a demonstration, validation and extension of a distinct methodology, for obtaining the flammability properties of charring materials. Australian radiata pine was used for the study wherein ignition and pyrolysis characteristics were obtained using a cone calorimeter. The deduced properties were applied for the prediction of ignition and pyrolysis histories of wood. These predictions were compared with data obtained from the cone calorimeter at different imposed heat fluxes and wood thicknesses and a close agreement was observed between the theoretical and experimental results.

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#### INTRODUCTION

Ignition and pyrolysis of timber materials is of intense interest in fire safety research because of their extensive use as building and construction materials. In building fires, thermal radiation from flames and from sources such as hot walls or ceilings is the primary source of external heating of the timber products and the ignition can take place either spontaneously or in majority of cases it occurs as a piloted ignition due to the presence of burning materials.

There are several models available that describe heat transfer through solid wood slabs during ignition and pyrolysis<sup>1,2</sup> but these models involve complex transport phenomenon occurring inside the wood material to describe the ignition and pyrolysis characteristics. In this paper, a simple methodology for obtaining flammability properties in polymeric materials<sup>3</sup> has been extended to charring materials. The methodology has been applied to determining the flammability properties for untreated Australian radiata pine.

The experiments were conducted using a Cone Calorimeter<sup>4</sup>, which is a bench scale instrument and is widely used to study fire properties of various materials under controlled conditions. Ignition times were measured at five different incident heat fluxes: 15, 20, 25, 30, 40 and 50 kW/m<sup>2</sup>. Pyrolysis experiments were conducted at two imposed heat fluxes: 30 and 50 kW/m<sup>2</sup>. The following properties can be obtained from such experiments:

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Conductivity of unpyrolysed material,  $k$

Thermal capacity of unpyrolysed material,  $c$

Density of unpyrolysed material,  $\rho$

Ignition temperature,  $T_{ign}$

Latent heat of pyrolysis,  $L$

Density of char,  $\rho_c$

Char conductivity,  $k_c$

Heat of combustion of timber,  $\Delta H_c$

In the present work, the product  $k_c$  was determined from present experiments whereas the value of specific heat of the unpyrolysed wood,  $c$ , was taken from literature. It was shown earlier that these properties are sufficient to characterise the ignition and pyrolysis and burning properties of charring materials<sup>5</sup>. The properties obtained from the experiments are not exact material properties as many of them change, for example, with temperature. Instead, they may be considered as equivalent properties in the sense that they are sufficient to reproduce the ignition and pyrolysis behaviour of the charring material<sup>3,5</sup>.

## EXPERIMENTAL DATA

Experiments were conducted at the University of Newcastle using a cone calorimeter<sup>4</sup>, which is an internationally recognised testing apparatus (Figure 1). For the ignition experiments, only time to piloted ignition for each sample was obtained. Ignition times were measured in the presence of a spark igniter which was held 13 mm above the surface of the sample. During the pyrolysis experiments, the measured data included the time to piloted ignition, mass loss, oxygen depletion rate and yield of combustion products including CO and CO<sub>2</sub>. Heat release rate and heat of combustion were calculated from the oxygen depletion and mass loss data. The dimensions of the samples were 100 mm x 100 mm x 19 mm and the samples were conditioned in a constant temperature and humidity environment (23°C, 50% humidity) until stable. Heat release rate (HRR) is an important parameter in the study of flammability properties of materials and is determined based on oxygen depletion, and utilising the fact that heat release per unit mass of oxygen consumed is approximately independent of the type of fuel.



**Figure 1:** Cone Calorimeter.

## RESULTS AND DISCUSSION

### Properties obtained from ignition data

Ignition times are plotted in Figures 2 and 3 assuming thermally thin conditions and thermally thick conditions respectively<sup>6</sup>.

For thermally thin conditions the inverse of ignition time should be proportional to the imposed heat flux. Figure 2 shows that this is not true for the present case. A simple extrapolation towards the x-axis would show that the critical heat flux (below which ignition cannot occur) is 18 kW/m<sup>2</sup>. This plot was made to show that if only data for high heat fluxes (over 30 kW/m<sup>2</sup> in Figure 2) is used, it is possible to assume that the material is thermally thin and that the critical heat flux is over 25 kW/m<sup>2</sup> which of course would be totally wrong.

For the thermally thick conditions<sup>6</sup>, ignition time is given by:

$$\frac{1}{\sqrt{t_{ign}}} = \frac{2}{\sqrt{\pi}} \cdot \frac{\dot{q}_o'' - a\dot{q}_{cr}''}{\sqrt{k\rho c(T_{ign} - T_o)}} \quad (1)$$

where  $k$ ,  $\rho$ ,  $c$  are physical and thermal properties of the material,  $T_{ign}$ , is the so-called ignition temperature and  $T_o$  is the initial sample temperature. The ignition temperature can be estimated from the critical heat flux (discussion following) from a surface re-radiation balance:

$$T_{ign} = \left(\frac{\dot{q}_{cr}''}{\sigma}\right)^{1/4} \quad (2)$$

where  $\sigma$  is the Stefan-Boltzmann radiation constant. For the last relation, all heat losses are considered to arise from the exposed surface and are expressed as radiation heat losses which are dominant in the present case because the ignition temperature is estimated to be 751 K (shown later).

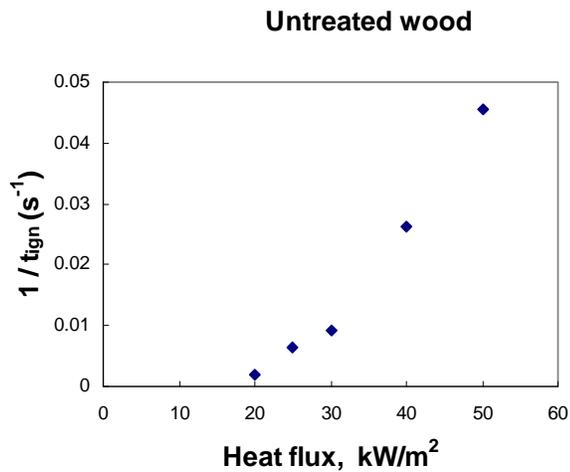


Figure 2: Ignition times plotted assuming thermally thin conditions (19 mm thickness).

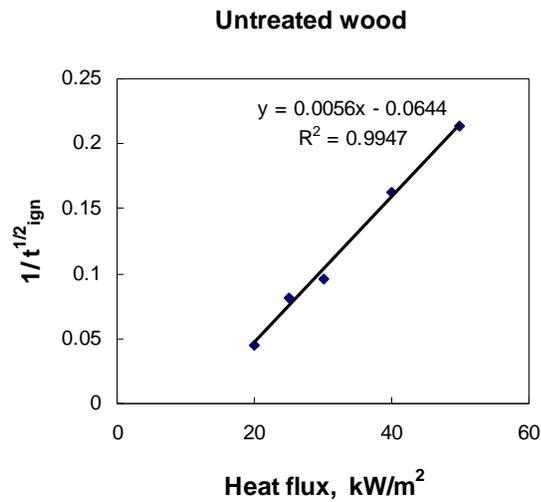


Figure 3: Ignition times plotted assuming thermally thick conditions (19 mm thickness).

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The intercept of the straight line in Figure 3 is a fraction,  $a$ , of the critical heat flux  $\dot{q}_{cr}''$ . The critical heat flux is the maximum imposed heat flux below which ignition cannot occur. The critical heat flux can easily be estimated from the experiments that lie between 15 and 20 kW/m<sup>2</sup> since ignition occurred at 20 but not at 15 kW/m<sup>2</sup> irradiance. The intercept of the straight line with the x-axis in Figure 3 is 11.6 kW/m<sup>2</sup>, as indicated from the linear fit. Note that this intercept is significantly below the critical heat flux range determined from the ignition tests. For well-insulated samples, the intercept is 64% of the critical heat flux<sup>3,6</sup>. Thus the critical heat flux is estimated to be 18 kW/m<sup>2</sup> (11.6/0.64) for untreated radiata pine timber. This agrees with the value obtained from extrapolation of ignition times in Figure 3.

The inverse of the slope in Figure 3, together with Equation 1, gives  $a$ , thermal response parameter of the sample:

$$\sqrt{k\rho c}(T_{ign} - T_o) = 201 \text{ kW.s}^{(1/2)}/\text{m}^2 \quad (3)$$

The analysis can now proceed to determine the thermal parameters for radiata pine. The density,  $\rho$ , was measured to be 526 kg/m<sup>3</sup>, whereas the density of the char,  $\rho_c$ , was estimated to be 50 kg/m<sup>3</sup> by weighing the samples after the end of combustion experiments in the cone. Density of char was estimated by using the initial sample volume, because contraction of the sample was not visibly significant. The ignition temperature was calculated to be 751 K, as described earlier.

Using these values and Equation 3 the product  $k_c$  can be determined.

At this point, lacking more information, the thermal capacity of radiata pine was assumed to be that of a low density timber:  $c = 1950 \text{ kJ/kg}$ <sup>(5)</sup> (this value can be further optimised for prediction by using the pyrolysis tests, if needed). It is then possible to calculate the conductivity of the unpyrolysed material:  $k = 0.19 \text{ W/m.K}$ . This value is consistent with conductivity values of cellulose board and particle board reported earlier<sup>6</sup>.

### Properties obtained from the pyrolysis data

Pyrolysis and burning tests were conducted in duplicate at two imposed heat fluxes: 30 and 50 kW/m<sup>2</sup>. Heat release rates and mass loss rates are shown in Figures 4a, 4b and 5a, 5b respectively. The heat release rate for one of the tests at 30 kW/m<sup>2</sup> is missing because the data was corrupted.

Prior to analysing these data, it is important to notice that the heat flux to the surface increases as ignition occurs. It would have been desirable to have conducted the experiments under a nitrogen atmosphere as suggested in<sup>3,5</sup>. Nevertheless, the analysis can proceed by estimating that the additional contribution to the heat flux by the flame is approximately 10 kW/m<sup>2</sup><sup>(7)</sup>.

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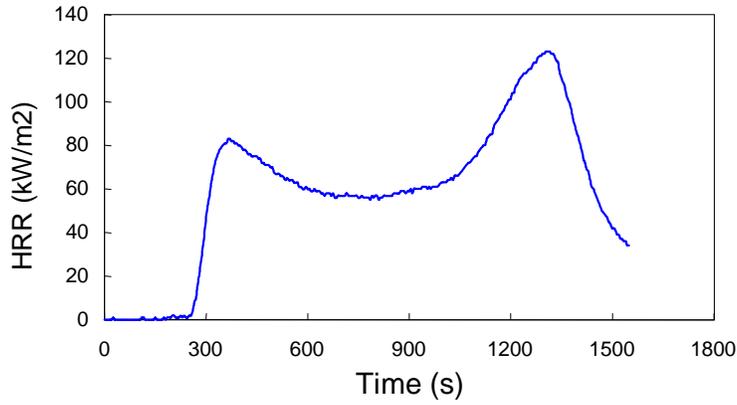
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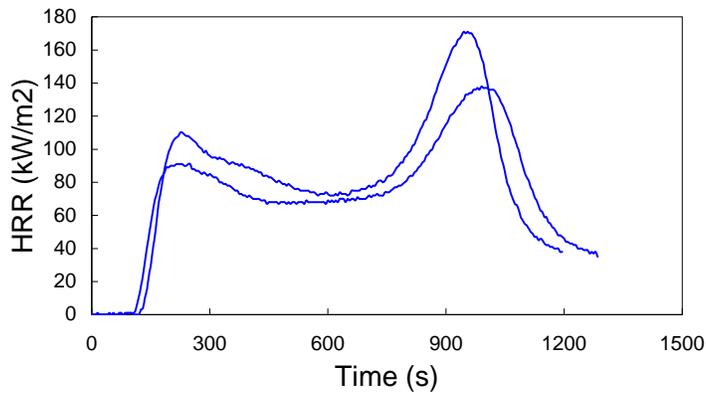
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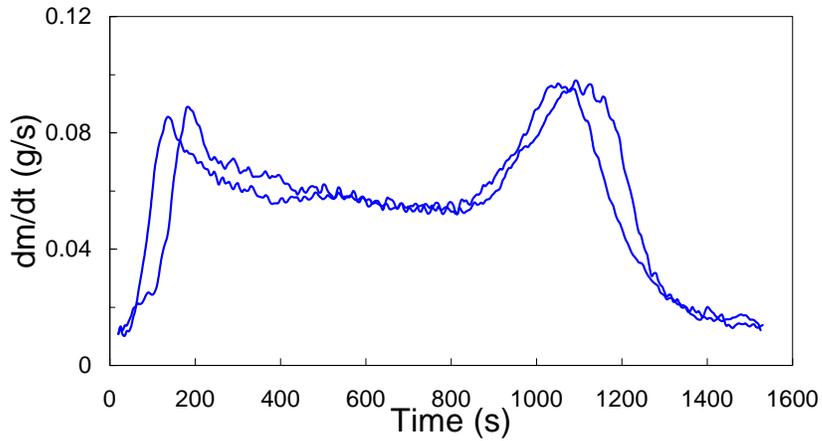
Figure 4a: Heat release rates at 30 kW/m<sup>2</sup> (exposed area 0.009 m<sup>2</sup>).



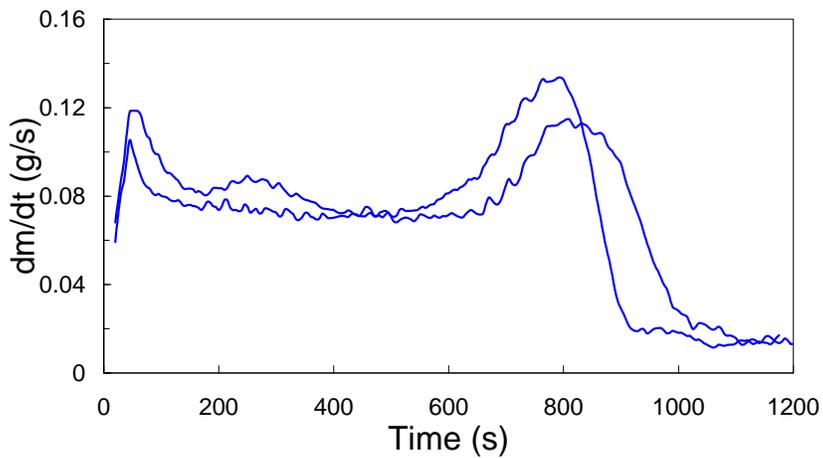
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Figure 4b: Heat release rates at 50 kW/m<sup>2</sup> (exposed area 0.009 m<sup>2</sup>).



**Figure 5a:** Mass loss rates at 30 kW/m<sup>2</sup> (exposed area 0.009 m<sup>2</sup>).



**Figure 5b:** Mass loss rates at 50 kW/m<sup>2</sup> (exposed area 0.009 m<sup>2</sup>).

To obtain the charring properties, the same charring model and methodology were used as described in<sup>5</sup>. The pyrolysis model is a thermal pyrolysis model and the sought after properties are the char conductivity  $k_c$  and the latent heat of pyrolysis  $L$ . The thermal capacity of char has been shown not to be an important parameter<sup>5</sup>.

The model was run using the following heat flux history:

$$\dot{q}_o'' = 30 \text{ kW/m}^2 \quad \text{for } t \leq t_{ign}$$

$$\dot{q}_o'' = 40 \text{ kW/m}^2 \quad \text{for } t > t_{ign}$$

or

$$\dot{q}_o'' = 50 \text{ kW/m}^2 \quad \text{for } t \leq t_{ign}$$

$$\dot{q}_o'' = 60 \text{ kW/m}^2 \quad \text{for } t > t_{ign}$$

By varying  $k_c$  and  $L$  systematically<sup>5</sup>, the values that best fit the mass pyrolysis rate can be found from the histories for the two pyrolysis/burning tests shown in Figure 5. The procedure is simple; since all properties of the unpyrolysed material and the pyrolysis temperature are known, the only variables to be determined are the char conductivity  $k_c$  and the (latent) heat of pyrolysis. The heat of pyrolysis can be expressed as fraction of the sensible heat.

The values  $k_c$  and  $L$  are calculated to be 0.70 W/ m.K and 750 kJ/kg respectively. Predicted ignition times compare well with the experiments at 30 and 50 kW/m<sup>2</sup> as shown in Table 1.

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**Table 1:** Predicted compared to experimental piloted ignition times.

Heat flux, kW/m <sup>2</sup>	Untreated radiata thickness, mm	Experimental Ignition time, s	Predicted Ignition time, s
15	19	No ignition	No ignition
20	19	484	1258
25	19	153	328
30	19	132	128
45	25	30	22
50	19	22	18

The disagreement is greater for the lower heat fluxes near the critical heat flux where ignition and burning are weak. The predicted values are larger than the experimental values possibly due to the sample holder being heated from the sides, thus assisting the external heat flux from the top to induce ignition. To avoid this effect the holder should be insulated from the sample.

Comparison of predicted mass pyrolysis rates with the experimental results is shown in Figures 6 and 7 for 30 and 50 kW/m<sup>2</sup> respectively. The agreement is good except at the beginning of pyrolysis because it was assumed that a sudden change of heat flux was imposed to the surface by 10 kW/m<sup>2</sup> just after ignition starts.

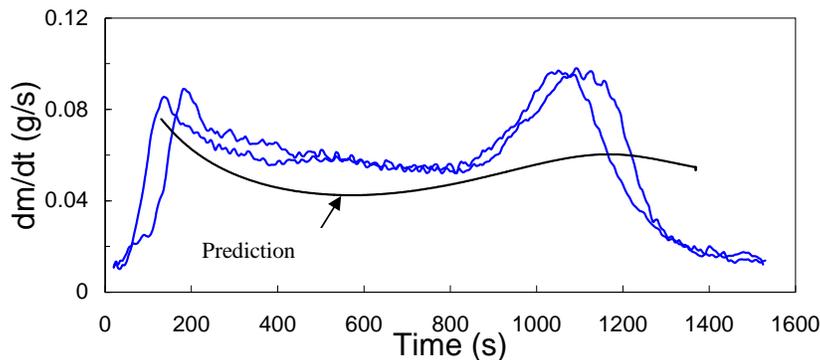
As a final validation of the present methodology, the estimated property values were used to calculate mass pyrolysis rates for radiata pine of thickness 25 mm tested at 45 kW/m<sup>2</sup> in earlier research that were not part of this project. The agreement with this experiment shown in Figure 8 provides a validation for the properties obtained using the present methodology.

Finally, from the heat release rate histories and mass loss histories in Figures 4 and 5 (where the exposed surface area is 0.009 m<sup>2</sup>) the effective heat of combustion of radiata pine can be estimated to be 9000 kJ/kg by using respectively the maximum values of these histories. The instantaneous values from the cone were not used because the mass loss rate history has significant fluctuations due to (a) noise and (b) the derivative of the directly measured mass loss. Instead, the data was using a 15 s moving average as shown in Figures 4 and 5. The maximum for heat release rate and mass loss rate occurred at nearly the same time following ignition as shown in Figures 4 and 5. Note that in Figure 4 the time is plotted from the beginning of the test including the delay in the oxygen measurements whereas time in Figure 5 is plotted starting from the ignition as recorded visually and confirmed from the mass loss history.

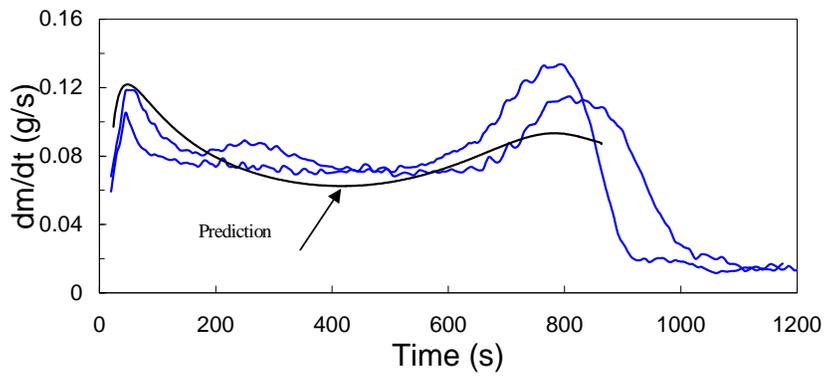
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The value for heat of combustion (9,000 kJ/kg) was checked at different times and also at different heat fluxes (Figures 4 and 5). Only near the second maximum in the mass loss rate history is the effective heat release rate higher (up to 11,000 kJ/kg).

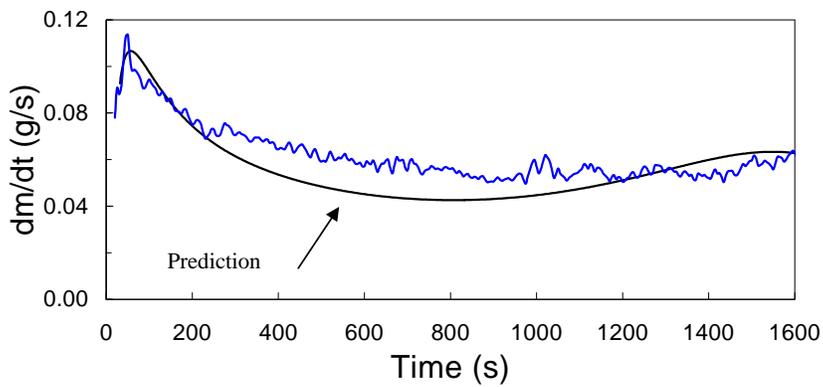
The present authors favor using the maximum values of heat release rate and mass loss rate (appropriately smoothed) to estimate the effective heat of combustion. Local maximum values of these quantities should occur at the same time because the heat of combustion is not expected to change during this period. A fixed delay time for oxygen measurements relative to mass loss measurements cannot be trusted (in the cone calorimeter). It was found that delay times varied from test to test. The standard report from the cone calorimeter's manufacturer software can often be wrong if the same delay time is used without checking carefully with the mass loss and heat release histories outputs.



**Figure 6:** Prediction of mass pyrolysis rates for 30 kW/m<sup>2</sup> (19 mm thickness, exposed area 0.009 m<sup>2</sup>).



**Figure 7:** Prediction of mass pyrolysis rates for 50 kW/m<sup>2</sup> (19 mm thickness, exposed area 0.009 m<sup>2</sup>).



**Figure 8:** Prediction of mass pyrolysis rates for 45 kW/m<sup>2</sup> (25 mm thickness, exposed area 0.009 m<sup>2</sup>).

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A methodology developed for the study of flammability characteristics of polymeric materials has been extended and validated to obtain flammability properties of charring materials. A good agreement was obtained between the theoretical predictions and the results obtained from experiments conducted in a cone calorimeter for radiata pine, an Australian type of wood. The property values calculated from a combined theoretical and experimental analysis compare well with the typical values for radiata pine obtained from the literature. The methodology has been validated using experimental results reported earlier and further validation of the methodology using different timber species is suggested as future research.

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## REFERENCES

1. Moghtaderi, B., Novozhilov, V., and Fletcher, D.F., "Transport Phenomena During Piloted Ignition of Wood", *International Journal of Transport Phenomena*, Vol. 1, 1999, pp. 79-96.
2. Janssens, M., "A Thermal Model for Piloted Ignition of Wood Including Variable Thermophysical Properties", *Proceedings of the Third International Symposium on Fire Safety Science*, 1991, pp. 167-176.
3. Delichatsios, M. A. and Craig Brescianini, "Methodology and Validation for Material Flammability Properties" submitted for publication to *Comb. and Flame*, 2001.
4. Cone Calorimeter, ISO 5660 Standard. 2000.
5. Chen, Y., Motevalli, V., and Delichatsios, M.A., "Material Pyrolysis Properties, Part II: Methodology for the Derivation of Pyrolysis Properties for Charring Materials" *Combustion Science and Technology*, 104, 101-425, 1995.
6. Delichatsios, M.A., "Ignition Times for Thermally thick and Intermediate Conditions in Flat and Cylindrical Geometries" *Sixth International Symposium Fire Safety Science*, p. 233. IAFSS, 1999.
7. Ritcie, S.J., Steckler, K.D., Hamins, A., Cleary, T.G., Yang, J.C., and Kashiwagi, T., "The Effect of Sample Size on the Heat Release Rate of Charring Materials" *Fifth International Symposium Fire Safety Science*, p. 177, IAFSS, 1997.