1. Introduction

A critical factor for fire protection engineers is the ability to determine the heat release rate (HRR) based on the composition of combustibles in the fire source within an analytic space in a fire scenario. An et al. [1] analyzed the performance-based fire protection evaluation reports produced in the past five years in South Korea and reported the deviations across input variables according to the engineer in a fire simulation. The study showed that the deviation of HRR from the fire source in the designs applied to the same specific analytic space was as high as approximately 35%. Large deviations could occur in the same fire scenario when the HRR is calculated based on the subjective judgment of the engineer, especially in the presence of multiple fuels that cause charring and exhibit a complex process of thermal decomposition, such as wood, within a specific space. Based on the close association of the HRR from fire with the visibility that affects the escape time and the CO gas concentration and temperature at the respiratory limit calculated using the life-threatening factors via fire simulation, these variables may be the key factors to consider in evaluating the risk of fire for performance-based fire protection designs [1].

Figure 1 schematizes the effects of thermal thickness and charring of solid combustibles on the HRR. As can be seen, in the step of early growth of fire, thermally thick non-charring combustibles enter the combustion process, resulting in a rapid increase in HRR, followed by a phase of fire at a steady rate in the step of fully developed fire. In contrast, the HRR increases continuously for non-charring combustibles of intermediate thickness. For thermally thick charring combustibles (Figure 1(c)), an early rise in HRR is observed before the formation of a charring layer, and the HRR subsequently falls as the charring layer thickens. Of note is that thermally thick charring combustibles (Figure 1(d)), such as wood, display a sudden rise in HRR immediately at the onset of combustion, followed by
a phase of fire at a steady rate. However, as the combustion reaction continues with a decreased mass of combustibles and increased proximity between the surface of combustibles with thermal decomposition and the reverse side to reduce the thermal thickness, the rate of thermal decomposition is rapidly facilitated, resulting in the second heat release peak. In contrast, a sharp peak of HRR is observed for thermally thin combustibles as their entire surfaces simultaneously undergo thermal decomposition. As the figure shows, the HRRs of combustibles are closely correlated with the level of charring and thermal thickness.

Figure 1. Typical HRR curves for different characteristic burning behaviors[2].

As previously described, in a case of fire in a space that harbors multiple charring and non-charring solid combustibles, such as an office or residence, the HRRs of combustibles are also closely correlated with CO gas concentration, a well-known factor that threatens human life. This study thus aimed to determine the effects of thermal thickness and charring of solid combustibles on the heat release and CO emission from those combustibles to provide the data to researchers and engineers of relevant fields. Notably, as charring is a crucial property of wood in designing the fire source, the basic thermal decomposition and heat release characteristics of charring and non-charring combustibles were investigated in relation to the thermal thickness of solid combustibles. To this end, a series of experiments were performed using poly methyl methacrylate (PMMA) combustibles that do not produce charring upon combustion and using wood as a representative combustible that produces charring upon combustion. The results were comparatively analyzed to identify the basic characteristics of heat release and CO emission that vary according to thermal thickness and charring of solid combustibles.

2. Experimental Methods

In this study, the HRRs of PMMA and Douglas-fir wood were measured, following the oxygen consumption method and using the ISO 5660-1 cone calorimeter, as shown in Figure 2. The level of heat release $\dot{q}$ can be calculated using Eq. (1) with the data of the change in mass of combustibles ($\dot{m}_c$), measured in real time via a load cell immediately after ignition, the mass flow in the mixer, measured at the exhaust hood, and the concentration of combustion products[3].

$$\dot{q} = \Delta H_{L,O_1} \times \frac{\Phi}{1 + \Phi (a - 1)} \times \dot{m}_c \times \frac{MW_{O_1}}{MW_{air}} \times (1 - X_{H,O_1}^O - X_{CO}_O^O) \times X_{O_2}^O$$  

(1)
Here, $\Delta H_{O_2}$ is the thermal energy of oxygen emission per unit mass (kJ/kg), $\phi$ is the oxygen consumption index, $\dot{m}_e$ is the mass flow of exhaust gas (kg/s), and $\alpha$ is the expansion coefficient for combustion (1.105). $X_i$ is the volume ratio for the chemical species $i$, with the superscript 0 indicating the reference value in the atmosphere. $MW_i$ is the molecular mass of the chemical species $i$ (g/mol).

The instantaneous yield for CO was calculated using the volume ratio for CO ($X_{CO}$), measured at the duct, which can be expressed as Eq. (2):

$$y_{CO} = \frac{\dot{m}_e \times X_{CO} \times MW_{CO}}{MW_{air}}$$

In the case of Douglas-fir wood, the combustion experiment was preceded by dehydration at 104 ℃ in reference to the ASTM D4442-92[4] to minimize the effect of moisture content in the specimen. To perform the experiment, the radiative heat flow that reaches the surface of the specimen in the vertical direction to the cone heater was set to 50 kW/m² and to prevent the release from the holder that fixates the specimen because of the swelling in the process of thermal decomposition, a metal mesh was fixed to the upper part of the holder. The distance between the specimen and the cone heater was 25 mm, while the ventilation flow rate was set to 24 L/s. The onset of combustion followed the natural ignition by the transfer of radiative heat from the cone heater to the surface of the specimen, while the end of the experiment was determined based on the observation of fire extinction and a change in the mass of the specimen (See Figure 2).

![Figure 2](image)

**Figure 2.** Burning Douglas-fir and PMMA specimens using the ISO 5660-1 cone calorimeter.

### 3. Results and Discussion

The thermal thickness was determined for the Douglas-fir wood and PMMA specimens by calculating the thermal penetration depth $\delta_p$ in Eq. (3)[5].

$$\delta_p = \sqrt{\frac{k t_{iso}}{\rho c_p}}$$

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In Eq. (3), $A$ is the property coefficient that varies across different combustibles, which was set as 1.0 for Douglas-fir wood[5] and 1.13 for PMMA[6], while $k$ is the heat transfer coefficient, $\rho$ is the density and $c_p$ is specific heat. $t_{ig}$ is the time taken until ignition, following the input of the radiative heat flow of 50 kW/m$^2$ to the surface of the specimen using the ISO 5601 cone calorimeter. When $\delta_p$ as calculated using Eq. (3) exceeds the physical thickness of the specimen, the combustible is thermally thin, and a lower value of $\delta_p$ than the physical thickness indicates that the combustible is thermally thick. Table 1 summarizes the thermal properties and ignition time of the Douglas-fir wood and PMMA specimens for the calculation using Eq. (3).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Douglas-fir 29 mm</th>
<th>PMMA 5 mm</th>
<th>PMMA 10 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity, $k$ [W/m $\cdot$ °C]</td>
<td>0.109</td>
<td>0.336</td>
<td></td>
</tr>
<tr>
<td>Ignition Time, $t_{ig}$ [s]</td>
<td>12</td>
<td>132</td>
<td>126</td>
</tr>
<tr>
<td>Specific Heat, $c_p$ [kJ/kg $\cdot$ °C]</td>
<td>2.03</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>Density, $\rho$ [kg/m$^3$]</td>
<td>474.8</td>
<td>1180</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Thermal Properties and Ignition Time of Douglas-fir and PMMA[7,8]

Figures 3(a)-3(c) show the thermal thickness $\delta_p$ of the Douglas-fir wood and PMMA specimens, as calculated using Eq. (3). As the figures show, the calculated thermal penetration depth increased in the following order:

$$\delta_p, \text{Douglas-fir} < \delta_p, \text{PMMA 10 mm} < \delta_p, \text{PMMA 5 mm}.$$

Hence, Douglas-fir wood is thermally thick as the thermal penetration depth is below the physical thickness at 29 mm; for the same reason, PMMA of physical thickness at 10 mm is also thermally thick. In contrast, PMMA of physical thickness at 5 mm is thermally thin as the thermal penetration depth is above the physical thickness of combustibles.
Figures 4(a) and 4(b) show the HRRs compared between the PMMA and Douglas-fir combustibles. As the figures show, in the case of PMMA of physical thickness of 5 mm, the heat release occurs rapidly with the combustion approximately 120 s after the input of the radiative heat (50 kW/m²) from the cone heater. The maximum heat release is subsequently reached at a fast rate by approximately 250 s, followed by extinction. This result occurs because, for thermally thin combustibles without charring, the entire combustibles simultaneously undergo thermal decomposition, with the relatively high thermal penetration depth allowing a fast rate of thermal energy conduction to the upper and lower surfaces of the combustibles. In contrast, in the case of 10 mm-thick PMMA, the onset of combustion and maximum HRR were similar to the case of 5 mm-thick PMMA, but the increase in heat release continued until 500 s to reach the maximum heat release, followed by extinction. Hence, there had been a delay of approximately 250 s for the thermally thin (5 mm) PMMA combustibles to reach the maximum heat release as combustion with a low rate of thermal decomposition continued according to the thermal thickness, suggesting an effect of the thermal thickness on the slope, i.e. the time taken to reach the maximum heat release by the combustibles.

In the case of Douglas-fir wood as an example of thermally thick charring combustibles, the radiative heat (50 kW/m²) from the cone heater caused thermal decomposition on the surface of Douglas-fir wood, as shown in the figures. In addition, as the resulting flammable steam reached a point of natural ignition at approximately 12 s after the start of the experiment, the maximum heat release was achieved at a fast rate. While several heat release peaks were observed subsequently, a trend of gradual decrease in heat release was shown. Despite the extinction after approximately 2,300 s, smoldering combustion continued due to oxidation to allow heat release. In the case of thermally thick charring combustibles, the rapid heat transfer to the interior during the early stage of combustion leads to rapid heat release to reach the maximum heat release, but the thermal thickness and the formation of a charring layer prevent the thermal energy conduction to pure wood to cause a rapid fall in heat release. In addition, unlike non-charring PMMA combustibles, wood combustibles show the oxidation of the charring layer and the thermal decomposition of the wood component occurring simultaneously, possibly resulting in the n'th peak of heat release as thermal decomposition is re-facilitated by a crack in the charring layer or the secondary reaction of tar[2]. Lastly, insignificant low-temperature energy is released through the oxidation of the charring layer after the extinction, but the smoldering combustion ultimately leads to a state of ignition[6]. Hence, in contrast to non-charring combustibles, charring combustibles showed continuous release of a low level of heat even after the extinction due to the smoldering combustion caused by the oxidation of the charring layer.

![Figure 4](image_url)
known to cause fatalities among residents or firefighters[9]. As seen in the figures, the onset of flame combustion with the generation of the flame after the combustion reaction causes an increase in CO yield in addition to the HRR for non-charring combustibles such as PMMA. Further, with the extinction of the flame, CO yield shows a trend of gradual decrease. In addition, the maximum CO yield is approximately 0.0015 for thermally thin, 5 mm-thick PMMA combustibles but as high as approximately 0.003 for thermally thick, 10 mm-thick PMMA combustibles, showing an approximately 2-fold deviation. This is because, for thermally thin combustibles, the relatively high thermal penetration depth upon combustion leads to the thermal decomposition of entire combustibles at a relatively fast rate to rapidly increase the rate of thermal decomposition, but for thermally thick combustibles, despite the identical rapid heat release during the early stage of fire, a low rate of thermal decomposition continues according to the thermal thickness to reduce the amount of fuel, thus causing the deviation in the overall CO yield. Hence, despite the trend of increase in CO yield with an increase in the HRR, non-charring combustibles show a deviation in the overall CO yield due to the difference in the rate of reduction in the thermal decomposition of fuel caused by the difference in the thermal thickness and the consequent rate of thermal decomposition.

![Graph of HRR & CO Yield measured from the cone calorimetry experiment of PMMA 5 mm](image1)

![Graph of HRR & CO Yield measured from the cone calorimetry experiment of PMMA 10 mm](image2)

![Graph of HRR & CO Yield measured from the cone calorimetry experiment of Douglas-fir](image3)

Figure 5. Comparisons of HRR & CO Yield measured from cone calorimetry experiment of PMMA & Douglas-fir.
In contrast, wood combustibles with a charring layer, such as Douglas-fir, show a low level of CO yield during the early flame combustion phase with the generation of the flame, unlike non-charring combustibles such as PMMA. While a trend of increase in CO yield is obtained with the reduction in heat release and the flame, thermal thickness is further increased by the charring layer formed upon thermal decomposition. Notably, after approximately 2,300 s, a rapid fall in CO yield was observed with the onset of smoldering combustion. According to a previous study [2], the rate of reduction in fuel mass falls during smoldering combustion, while the CO yield significantly increases. Considering that the CO yield is generally expressed as the ratio of the time-averaged CO mass flow against the rate of reduction in fuel mass, the CO yield in smoldering combustion is considerably high compared to the early flame combustion. Hence, in contrast to non-charring combustibles, charring combustibles showed an increase in CO emission due to smoldering combustion caused by the oxidation of the charring layer despite the reduction in the fuel mass.

Compared to flame combustion with the generation of the flame, smoldering combustion displays a relatively lower rate of oxidation, ensuring that the reaction continues even at a low oxygen concentration, possibly increasing the probability of incomplete combustion reactions to increase the CO yield. Thus, for combustibles (such as wood) that exhibit charring during combustion, a method to differentiate the flame and smoldering combustion domains based on the CO yield is deemed reasonable [10].

4. Conclusions

In this study, ISO 5660-1 cone calorimetry experiments were performed on non-charring combustibles (PMMA) and charring combustibles (wood) to determine the basic characteristics of heat release and CO emission that vary according to the thermal thickness. The comparative analysis of the results led to the following conclusions.

For PMMA without a charring layer during combustion, the maximum HRRs were almost identical irrespective of the thermal thickness, while the time taken to reach the maximum heat release varied, indicating a deviation in the maximum CO emission across combustibles according to the thermal thickness. For Douglas-fir wood with a charring layer, a rapid fall in heat release was observed due to the charring layer developed as the heat release in the early combustion rapidly reached the maximum value. Furthermore, in contrast to non-charring PMMA combustibles, and despite the low CO yield in the early flame combustion with the generation of the flame, a notable trend of increase in CO yield was shown, as the heat release and flame were reduced due to further increases in the thermal thickness by the charring layer formed upon thermal decomposition. Based on the findings, a method to differentiate the flame and smoldering combustion domains based on the CO yield is deemed reasonable for combustibles such as wood that exhibit charring during combustion.

Author Contributions

MY Lee.; formal analysis, investigation, and writing—original draft preparation, SH Park.; writing—review and editing, All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

References


