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Technical Note

Flammability and Acetic Acid Emissions from Acetylated Wood under Well-Ventilated Burning Conditions

Laura E. Hasburgh and Samuel L. Zelinka *

US Forest Service, Forest Products Laboratory, Madison, WI 53726, USA; laura.e.hasburgh@usda.gov
* Correspondence: samuel.l.zelinka@usda.gov; Tel.: +1-608-231-9277

Abstract: Acetylation is a type of commercial wood modification used to enhance the durability of wood. Despite its adoption, especially in outdoor environments, there are mixed data on how acetylation affects the combustion of wood. This paper evaluates the differences in acetylated and untreated wood using a cone calorimeter in combination with Fourier Transform Infrared Spectroscopy (FTIR) to look for acetic acid vapors in the combustion gases. Two thicknesses of acetylated pine boards were tested and compared against an untreated board from the same genus. No differences were observed between the peak heat release between the acetylated and untreated boards. Likewise, there were no trends in the time to ignition between the acetylated wood and the control group. Differences were observed however in the chemical composition of the combustion products. An increase in acetic acid in the products of combustion was observed for the acetylated samples that corresponded with the peak heat release of the sample.

Keywords: modified wood; acetylation; fire performance

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1. Introduction

Acetylation is a non-toxic method of wood modification used to enhance wood properties, especially resistance to fungal decay. Wood is reacted with acetic anhydride (or in some cases ketene gas) and a 1:1 displacement reaction occurs where hydroxyl groups in the wood cell walls are replaced with acetyl groups [1]. Fuchs [2] was the first to acetylate wood in 1928; however, the commercialization of acetylated wood was not attempted until the 1960s [3]. The first successful commercialization of acetylated wood was developed in 2003 in the Netherlands by Accys Chemicals [4] who now produce 60,466 m^3 of acetylated wood per year [5].

It is generally accepted that acetylated wood treated to an uptake of 15%−20% weight percent gain (WPG) is decay-resistant [6–9]. However, the mechanisms by which acetylation protects wood from fungi are still under debate [10–12] and it is possible that wood treated to 20% WPG is not decay-resistant, but instead the kinetics are retarded or delayed enough that decay is not a practical concern [10,13–15]. In addition to improving the resistance of wood to fungal decay, acetylation also changes the physical properties of wood. Since acetyl groups are larger than the hydroxyl groups they replace, the acetylation reaction permanently bulks the wood. This irreversible swelling means that wood is more dimensionally stable, i.e., it swells less in the presence of moisture and shrinks less when the moisture is removed [16,17].

While acetylation has been extensively studied, very little is known about how acetylation affects the flammability or fire resistance of wood members. When exposed to high temperatures, wood undergoes pyrolysis, a series of thermochemical reactions that change the physical and chemical properties of wood [18]. These pyrolysis reactions lead to the formation of char, an insulating carbonaceous layer that helps to protect the underlying wood from further pyrolysis and char [19]. Reasonably, one would expect that the replacement of hydroxyl groups with acetyl groups within the wood may affect pyrolysis. For example,

acetyl groups may be cleaved from the polymeric chains during pyrolysis forming acetic acid; in this case, this endothermic process may retard the combustion kinetics compared to untreated wood. On the other hand, the liberated acetic acid in the volatiles is flammable and the combustion of this volatile may cause the wood to experience more rapid burning.

Even though acetylated wood has clear chemical differences from untreated wood, relatively little is known about its flammability. Only four previous studies have examined the interaction of acetylated wood with fire [20–23]. Importantly, the literature on how acetylation affects the flammability of wood is inconsistent; two of these studies found that acetylated wood was less flammable than untreated wood and the other two studies came to the opposite conclusion. The inconsistent findings could be due to the different reaction-to-fire tests used, the initial wood species that was acetylated, and/or the comparative control materials.

Two researchers utilized ISO 11925-3 to study the flammability of acetylated wood [24]. In these tests, a burner was placed on the wood surface for one minute and then removed. The fire performance is evaluated by measuring the time of flaming combustion, glowing combustion, and the charred area. Mohebby et al. [21] examined acetylated wood and noted that at higher levels of acetylation, the time of flaming combustion decreased and the time of glowing combustion increased. Similar results were observed by Papadopoulos et al. [22] for orientated strand board (OSB) made with acetylated chips. Both studies claimed that since the time of flaming combustion decreased as the level of acetylation increased, acetylation decreases flammability. However, it should be noted that the amount of glowing combustion increased with acetylation and, therefore, the total combustion time (flaming + glowing) remained about the same for all samples tested.

In contrast, Morozovs and Buksans used a radiant panel flooring test (ISO 9239-1) [25] and the cone calorimeter (ISO 5660-1) [26] to examine the flammability of acetylated wood [20]. They observed that acetylated wood had increased flame spread when compared to an untreated control in the radiant panel test. While the heat release rate was not significantly different between the treatments, the acetylated wood had a longer time to flameout. Rabe et al. [23] also used the cone calorimeter to evaluate the flammability of acetylated wood. They found that acetylation did not improve the thermal stability or flammability of wood, but rather resulted in a shorter time to ignition and an accelerated heat release rate. They noted that the acetyl groups inherent in the acetylation process act as combustible volatiles, increasing the effective heat of combustion of the pyrolysis products that resulted in the observed increases in burning speed.

One commonality across the literature was that large amounts of "blue smoke" were produced in the combustion of acetylated wood, although Morozovs and Buksans found that acetylated wood had a lower total smoke release in the cone calorimeter test. The blue smoke was attributed to acetic acid released in the pyrolysis of acetylated wood.

The release of acetic acid during the pyrolysis process likely affects the flammability of acetylated wood. While blue smoke was observed in several tests, Rabe et al. concluded that the acetic acid produced during pyrolysis was rapidly consumed by the fire and contributed to the more rapid consumption of the acetylated wood compared to the controls. Despite its presumed importance in the combustion of the modified wood, evolved acetic acid has not been measured during any of the previous fire tests on acetylated wood.

In this paper, we examine the flammability of acetylated wood using a cone calorimeter. Furthermore, we use Fourier Transform Infrared Spectroscopy (FTIR) to observe the products of combustion during flammability testing; specifically looking at acetic acid to see if there is any correlation between acetic acid in the products of combustion and differences in the heat release rate signatures of the different materials.

2. Materials and Methods

Three different sample types were tested: two types of acetylated wood and one control. All samples were developed with pine (*Pinus* spp.) and had a surface area of 100 mm by 100 mm. The term species in this article in some contexts is used to refer

to commercial groups that include multiple species, such as the Southern pine group. The control samples were cut from Southern pine dimension lumber produced in the United States with a grade stamp of "select structural" The Southern pine group is a commercial species group which contains four species that cannot be separated through wood anatomy [27]. The control samples were 37 mm thick. The first acetylated sample, hereafter referred to as Ac1, was obtained from a commercial supplier and was radiata pine. The thickness of the Ac1 sample was 53 mm. The second acetylated wood sample, Ac2, was also radiata pine but obtained from a second distributor with a sample thickness of 19 mm. Both Ac1 and Ac2 were acetylated by the same commercial acetylation process and were sold as the same tradename. Each sample group was tested in triplicate (n = 3).

The flammability of the acetylated and control groups was tested using a cone calorimeter (FTT iCone Mini, East Grinstead, West Sussex, UK) according to ASTM E1354 [28]. All cone calorimeter tests were conducted in the horizontal orientation and at a constant heat flux exposure of 35 kW m^{-2}. This heat flux is commonly used for exploratory testing. A standard holder frame was used for each test which allowed an exposed surface of 88.4 cm^2 for each specimen. The sides and bottom of the sample were wrapped in aluminum foil and the foil-wrapped samples were placed on a ceramic fiber blanket in the holder. A spark ignitor provided the piloted ignition source. Prior to testing, the samples were conditioned for six months in a 21 °C/50% relative humidity chamber. The tests were terminated two minutes past either the end flaming combustion or when the specimen had been consumed, whichever was longer. To terminate the tests, the heat flux source was blocked, the specimens removed, and water was applied. The heat release rate (HRR) was calculated using the oxygen consumption method [29] by measuring the amounts of O_2, CO, and CO_2 in the products of combustion and the mass loss of the specimen was also measured. Key flammability parameters were tabulated for all samples including the heat release rate, total heat release, time to ignition, mass loss rate, total smoke release, and effective heat of combustion. However, differences in sample thicknesses between the groups will affect the duration of the tests, features of the heat release rate curves, and cumulative properties such as the total heat release between samples. Therefore, because of the differences in thickness, the analysis was restricted to the initial peak heat release rate and time to ignition between samples.

In addition to the O_2, CO, and CO_2 used to calculate the heat release rate, the composition of the combustion gases was monitored using Fourier Transform Infrared Spectroscopy (FTIR) (Protea atmosFIR AFS-A-15, Middlewich, UK) which was coupled with the cone calorimeter. This FTIR utilizes a multi-pass gas cell interferometer operating at 180 °C, with a path length of 4.2 m and spectral resolution of 4 cm^{-1}. This set up allows for the simultaneous identification and quantification of 35 gaseous compounds including CH_3COOH (acetic acid). The acetic acid data were calculated at a frequency of 0.25 Hz from the spectra. The acetic acid signal contained an appreciable amount of noise and, to better see the signal, the acetic acid data were smoothed by using a moving average filter over 22 points (or approximately 1.5 min) via the "smooth" function in MATLAB (Natick, MA, USA).

3. Results and Discussion

The initial peak heat release rate (PHRR) and time to ignition (Tig) for the various groups are presented in Figure 1. Since the sample thicknesses varied across groups, it was not possible to compare other metrics such as the total heat release and information related to the second heat release rate peak. The graphs present the data from each replicate with the solid lines representing the range of measured values.

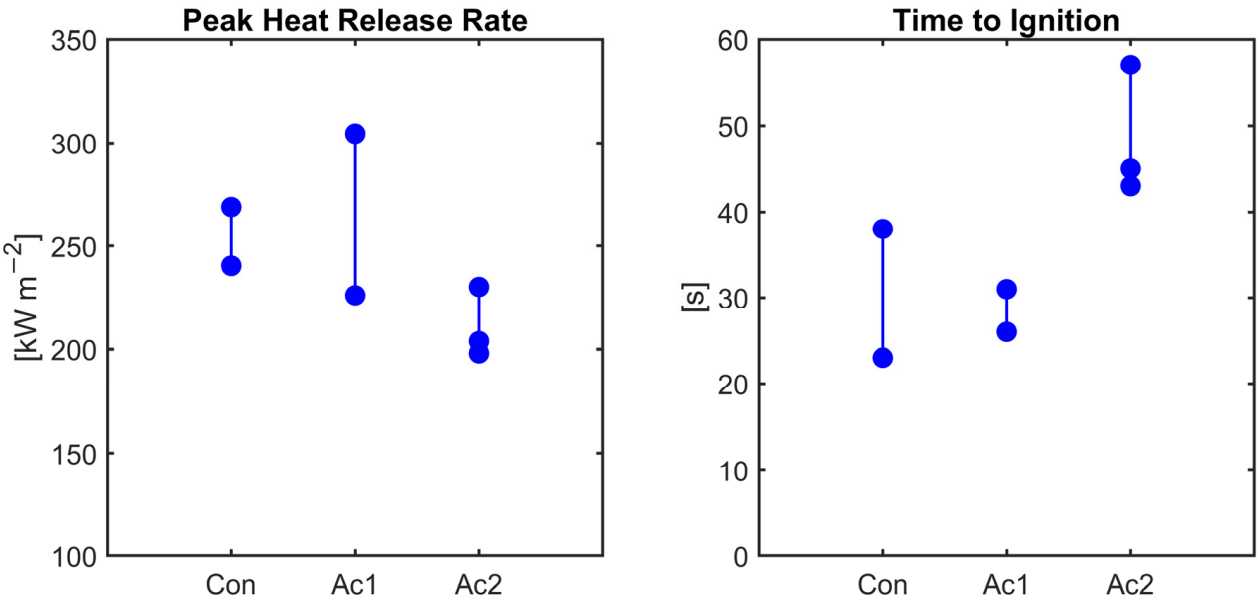

Figure 1. Initial peak heat release rate and time to ignition for the three sample groups tested. Abbreviations: Con = control; Ac1 = acetylated group; 1 Ac2 = acetylated group 2.

No obvious trends can be observed in either the PHRR or Tig data between the acetylated wood and the control samples. The PHRR of the replicates for the Ac2 group were lower than those for the control group; however, the Ac1 group had measured values both above and below those measured for the control group. The heat release rate depends upon several material properties including density, heat of combustion, and thermal conductivity. Variations in the sample density between the groups may have contributed to the lower PHRR observed for the Ac2 group. All replicates of the Ac2 group had a longer Tig than either the control or Ac1 group; however, the measured Tig for the Ac1 group fell between the highest and lowest Tig measured for control specimens.

While further testing is needed to determine the statistical significance between these treatments, acetylation does not appear to cause a large shift in these measurements of flammability in either direction.

A more complete picture of the flammability and acetylation can be obtained from Figure 2 which plots the average heat release rate of all replicates as a function of time. The bottom half of Figure 2 contains the amount of acetic acid measured in the combustion gases from the cone calorimeter during the tests. The HRR curves for each sample group exhibited features standard for wood-based materials with a sharp PHRR. This sharp initial peak is accredited to the ignition and rapid exothermic reaction for uncharred surface material [30–32]. After this peak, the HRR reduces once char forms and eventually leads to a second peak. The second peak reflects the thermal wave reaching the unexposed side of the specimen and can be affected by many variables including the density, heat flux, material thickness, and backing product [33].

The HRR curves are very similar across the control group and both groups of acetylated wood. The largest differences occur in the placement and magnitude of the second peak in the heat release rate curve. The second heat release rate peak is sensitive to factors such as the thickness and type of insulating substrate but is largely attributed to specimen burn-through [33]. Therefore, it is not surprising that the Ac2 group, which was the thinnest sample, had the earliest and most pronounced second peak.

Although the HRR curves across all three groups are similar and exhibit the typical two-peak behavior, differences can be seen in the acetic acid detected by the FTIR. Both the Ac1 and Ac2 groups exhibit a peak of acetic acid emissions that is slightly offset from the initial peak in the heat release rate curve. In examining the acetic acid concentration as a function of time, it is important to mention that the data in Figure 2 contain time averaging

of the data to smooth out the high amount of noise in the data. Therefore, some of the observed shift in the acetic acid peak from the heat release peak may be a result of the smoothing routines applied to the acetic acid data. Both Ac1 and Ac2 exhibit peaks above 1 part per million (ppm) before tapering off throughout the test. In contrast, the acetic acid in the combustion gases of the control group exhibited minor fluctuations around and under 0.5 ppm.

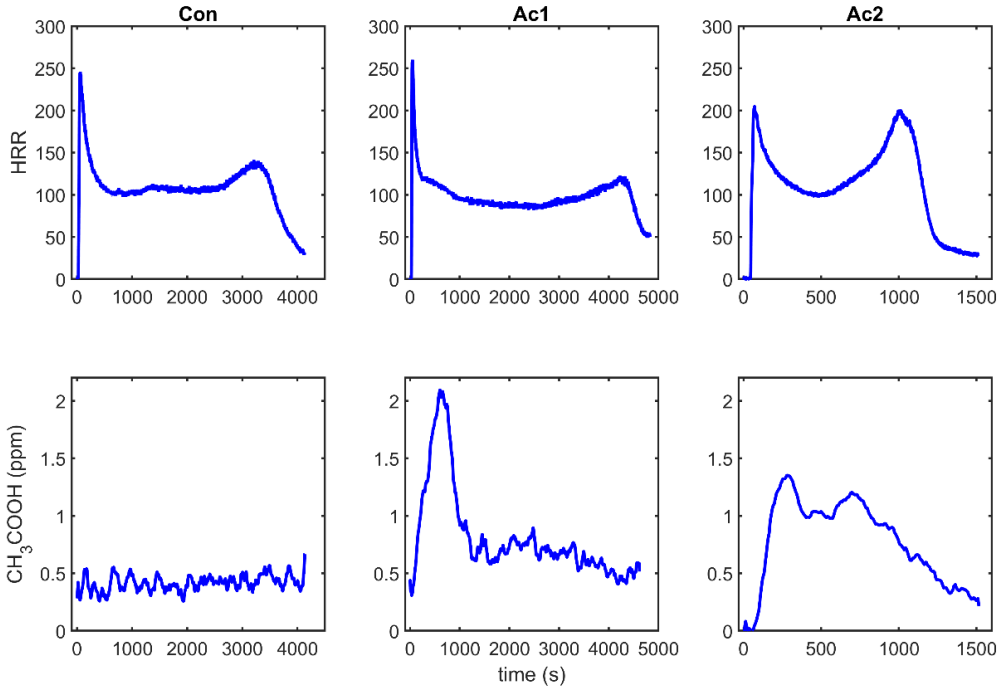

Figure 2. Heat release rate (HRR) curves for acetylated and control wood (**top**). Acetic acid concentrations measured in the combustion gases with FTIR (**bottom**). Note differences in scale on x axis.

The FTIR data In Figure 2 clearly indicate differences in the amount of acetic acid liberated from the acetylated and control wood during combustion. Acetic acid is clearly present in the combustion gases of acetylated wood. In general, the amount of acetic acid measured in the experiment was related to the heat release rate. This measurement of evolved acetic acid was consistent with previous observations of the flammability of acetylated wood. However, previous work had suggested that this release of acetic acid may reduce the flammability of the wood by absorbing energy, whereas other work had suggested that the acetic acid may increase the flammability by adding additional volatiles to be consumed in the fire. Although acetic acid could be measured in the cone calorimeter combustion gases of acetylated wood in these experiments, the release of acetic acid appears to not have a large effect on the flammability of the acetylated wood.

Compared to the broader literature on the flammability of wood, fewer studies have been published on the levels of various chemical species in the products of combustion. FTIR is commonly used in conjunction with thermogravimetric analysis to look at gases released during thermal decomposition, although it should be noted that the exposure conditions vary greatly between TGA and the cone calorimeter [34]. Limited work has been conducted analyzing the products of combustion using a cone calorimeter for wood and wood-based materials [35–37]. These experiments used solvent absorption to look for specific toxic gases in the products of combustion, namely hydrogen cyanide. Previously, acetic acid was identified as one of the condensates in wood smoke under smoldering conditions [38]. However, the current work shows that even under well-ventilated conditions within the cone calorimeter, acetic acid is evolved from acetylated wood.

The results from these experiments suggest that acetylation does not have a large impact on the flammability of wood. However, cone calorimeter experiments are conducted in a highly ventilated environment where the sample has ample access to oxygen. While acetylation does not appear to greatly impact the flammability of wood in cone calorimeter tests, it may be that acetylation has a greater impact on smoldering combustion and differences may be observed in a less oxygen-rich environment.

4. Conclusions

The goal of this work was to examine the flammability of acetylated wood and further examine the relationships between the release of acetic acid from acetylated wood during combustion and changes in the heat release rate.

The results showed that the heat release rate curves were similar between the acetylated and untreated wood. From a practical standpoint, these results suggest that the flammability of acetylated and untreated wood are similar. FTIR revealed acetic acid emissions during combustion for acetylated wood; however, these emissions did not correspond with a distinctive feature of the heat release rate curve. In all cases, the total amount of acetic acid in the smoke was small, a maximum of 2 parts per million.

The cone calorimeter utilized in the present study produces well-ventilated burning conditions. Future work will include evaluating the acetylated wood in a controlled atmosphere cone calorimeter to determine the toxicity of fire effluents in an under-ventilated condition more properly.

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