Assessing the fire behavior of woods modified by N-methylol crosslinking, thermal treatment, and acetylation

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Summary
Wood products are often treated by different techniques to improve their longevity when used as building materials. Most of the time, the goal is to increase their resistance to weathering effects, deformations in material dimensions or biotic decomposition. These wood treatment techniques have a significant impact on pyrolysis and burning behavior. The general effects of three different common wood treatments on flame retardancy were investigated by comparing treated woods with their untreated counterparts and with other kinds of wood. While the acetylation of beech leads to a slightly increased fire hazard, the thermal treatment of wood and crosslinking of cellulose microfibrils dimethyloldihydroxy-ethyleneurea show a limited flame retarding effect. Switching to woods with a higher lignin content, and thus higher char yield, however, results in a more pronounced improvement in flame retardancy performance. This article delivers a comprehensive and balanced assessment of the general impact of different wood modifications on the fire behavior. Further, it is a valuable benchmark for assessing the flame retardancy effect of other wood modifications.

KEYWORDS
acetylation, cone calorimeter, DMDHEU, heat of combustion, thermal treatment, wood modification

1 | INTRODUCTION

The role of wood in construction applications has been significant for centuries due to its low costs and availability, and is currently experiencing a revival because wood is sustainable. However, despite its good mechanical properties, the vulnerability of wood to weathering effects, microorganisms, and fire shows its limitations in usage. Nevertheless, the look of wood in outdoor and indoor building applications such as decking, cladding, façades, and flooring is much desired. Therefore, the task is to find the right treatments for wood products to make them more stable in everyday utilizations. Besides wood-inorganic composites, different approaches have been attempted for wood preservation, from chemical treatments, to coatings, to impregnations. Woods are also treated with dimethyloldihydroxy-ethyleneurea (DMDHEU) to make them more resistant to weathering effects, termite infestation, and fungal infections, and to improve dimensional stability. DMDHEU acts as a crosslinking agent between cellulose microfibrils and is able to displace water in that interspace. The technical properties of wood as a building material can also be improved through thermal treatment. Heating the wood up to 250°C in the absence of oxygen leads to the recrystallization of hemicellulose and the elimination of acetyl groups, the degradation of alpha-cellulose, and an increase in the lignin content of the wood. The reduced water absorbency
decreases swelling, shrinking, and tearing; resistance to rotting and fungal infestation is increased. A common way to desensitize wood and prolong its longevity is to treat it with acetic anhydride.\textsuperscript{4,20-25} This acetylation prevents the absorption and release of water in the free hydroxyl groups by esterification to acetyl groups. Rotting due to enzymatic reactions is averted as well, which leads to increased dimensional stability and durability.

Materials comprised of only wood have a relatively low fire risk,\textsuperscript{26-28} and their reaction to fire is well described in the literature.\textsuperscript{29,30} Although the reactive cellulose content of a wooden material promotes initial burning, the harder lignin takes more energy to pyrolyze and produce flammable fuel.\textsuperscript{31} Furthermore, the resulting char layer has an insulating effect on the underlying material, hindering continuous burning.\textsuperscript{32-34} Charring plays an important role in the fire protection of wood and wooden materials; in fact, one way to increase the fire resistance of wood is to intentionally char its surface, producing a protective layer.\textsuperscript{35} Other common ways of enhancing the flame-retardant properties of wood include treatment with coatings and impregnation with fire-retardant solutions. Also, tropical woods, DMDHEU-modified, and acetylated wood have been burned before in a few studies.\textsuperscript{36-38} It was proposed that effective DMDHEU-crosslinking could have a small positive effect.\textsuperscript{37} Also acetylation was believed to improve fire properties,\textsuperscript{38} although a larger char area was observed. However, these first attempts have not yet delivered a reliable assessment, particularly to compare the results in broader context.

There are many papers proposing, discussing, and developing different wood treatments,\textsuperscript{39} but there is a lack of reliable assessment of the fire behavior. This publication aims to clarify the effects in principle of thermal treatment, DMDHEU-crosslinking, and the acetylation of woods on their fire behavior. Furthermore, a comparison between treated woods and woods from different trees is made in order to assess whether the wood treatment or the change to another kind of wood is more effective in terms of thermal properties and burning performance. The distinct treatments were not varied or optimized but modified wood materials were used just as they are commercially offered to get a representative but general assessment.

\section{Experimental}

\subsection{Materials}

In order to evaluate the fire properties and burning behavior of different kinds of woods and treated woods, seven different materials were investigated. European Beech (\textit{Fagus sylvatica}) was used as a reference for the commercially treated beech products Belmadur beech and Thermo beech. Belmadur beech is beech wood treated with DMDHEU in order to establish crosslinks between cellulose microfibrils. Thermo beech is created by thermally treating beech at 250°C in an anaerobic atmosphere for at least 24 hour. Furthermore, beech, Monterey pine (\textit{Pinus radiata}), Meranti and Scots pine (\textit{Pinus sylvestris L.}) were compared to each other. \textit{Pinus radiata} is simultaneously used as a reference for Accoya, which is commercial acetic anhydride-treated \textit{Pinus radiata}. Modified hardwoods and softwoods as well as the tropical Meranti were chosen reflecting what is nowadays proposed as durable wood materials. The treatment processes were not varied, but typical and representative materials were chosen to get a general assessment. Nevertheless, changing the process parameters influences the results significantly, but not the general assessment.

The equilibrium density of the specimens at 23°C and 50% relative humidity was 0.753 g/cm\textsuperscript{3} for beech, 0.825 g/cm\textsuperscript{3} for Belmadur beech, 0.651 g/cm\textsuperscript{3} for Thermo beech, 0.558 g/cm\textsuperscript{3} for \textit{Pinus radiata}, 0.644 g/cm\textsuperscript{3} for Meranti, 0.629 g/cm\textsuperscript{3} for \textit{Pinus sylvestris L.}, and 0.547 g/cm\textsuperscript{3} for Accoya. All samples were cut to obtain 100 x 100 x 10 mm plates for cone calorimeter experiments (Figure 1). Sapwood was used, and the cut was radial for beech, tangential for Belmadur beech, Thermo beech, \textit{Pinus radiata}, Meranti, and \textit{Pinus sylvestris L.}, whereas the cut was transverse for Accoya. The repeatability of the fire performance was very good, the uncertainty of the cone calorimeter results was below 3\% to 7\%. Thus, the specimens were representative and well comparable, although strictly speaking for the Accoya a minor influence of the transverse cut was not explicitly ruled out. Wood dust of the respective specimens was used for thermogravimetric analysis, pyrolysis combustion flow calorimetry, and bomb calorimeter experiments. Beech, Belmadur beech, Thermo beech, and \textit{Pinus radiata} were provided by the Burckhardt Institute (University Göttingen, Germany), Accoya was supplied by Enno Roggemann GmbH & Co. KG (Bremen, Germany) and Meranti was provided by Küpfer Anders Holz GmbH & Co. KG (Berlin, Germany).

\subsection{Methods}

Thermogravimetric analysis was realized with a TG 209 F1 Iris (Netzsch Instruments, Selb, Germany). Pyrolysis under nitrogen was conducted at a heating rate of 10 K/min on 5 mg of powder from each material.

The C 5000 Control Calorimetry System (IKA, Germany) was used for bomb calorimeter experiments. Calorific values of the average of five measurements according to DIN 51900-3 were determined under adiabatic conditions. Portions of 0.4 g of a powdered sample were mixed with the same amount of spike to control the burn rate and ensure complete combustion.

Heat release capacity (HRC) measurements on the milligram scale were conducted on a pyrolysis combustion flow calorimeter (PCFC) apparatus (FTT, UK) according to method A stipulated in ASTM D 7309. Specimens were measured as powder in portions of 5.00 ± 0.05 mg. The pyrolyzer temperature gradient ranged from 150°C to 750°C at a heating rate of 1 K/s, and the combustor was set to a temperature of 900°C. Results were determined after performing a Gaussian fit to the heat release rate (HRR) curve. The results obtained from the PCFC, such as HRR and total heat release (THR), are presented and discussed per mass specimen, and thus in W/g and kJ/g, respectively. All PCFC measurements were performed in duplicate.

Fire behavior under forced flaming conditions was investigated with a dual cone calorimeter (FTT, UK) at a heat flux of 50 kW/m\textsuperscript{2}.
and a distance of 25 mm from the cone heater to the sample surface. The specimens were conditioned for 7 days at 23°C and 50% relative humidity before fire testing. Each specimen was taken out of the climatic chamber just before measuring. The samples were wrapped in aluminum foil and placed on the sample holder in a steel frame, resulting in a surface area of 88.4 cm². End of test criterion for the cone calorimeter measurements was determined to be the achievement of a steady HRR after the disappearance of visible flames. The measures obtained with the cone calorimeter, such as HRR and total heat evolved (THE) = total heat released (THR) at the end of test, are presented and discussed per unit area, thus in kW/m² and MJ/m², respectively.

3 | RESULTS AND DISCUSSION

3.1 | Thermogravimetric analysis

Differences in pyrolysis behavior became visible in thermogravimetric analysis (Figure 2 and Table 1). When beech and Pinus radiata were compared with their treated counterparts Belmadur beech, Thermo beech, and Accoya, respectively, significant differences were observed. Except for Thermo beech and Accoya, every wood material exhibited a main decomposition step and a shoulder on the lower temperature flank of the mass loss rate (derivative thermogravimetry, DTG; Figure 3). While the main peak is attributed to the decomposition of cellulose, the shoulder indicates decomposition of the amorphous hemicellulose content in the samples. During the thermal treatment of beech, hemicellulose sugars like xylan are partly decomposed, and the degradation products undergo condensation or crosslinking reactions. The shoulder of hemicellulose vanishes (Figure 3), because the corresponding mass loss is shifted to higher temperatures. Further, the decomposition range is narrowed resulting in an enhanced single peak at higher temperatures in the mass loss rate. Treating Pinus radiata with acetic anhydride results in esterification mainly with the hemicellulose part, also leading to a narrower but higher peak without a shoulder visible in the DTG. The temperature at a mass loss of 5% was 195°C for beech and 239°C for Pinus radiata. This temperature increased to 275°C for Thermo beech and 279°C for Accoya. The untreated woods exhibited a reduced T5% because of the release of water. For Belmadur beech, beech treated with DMDHEU, water release occurred, while thermally treated beech had a decreased ability to absorb water, and thus showed no water release in TG. In Accoya, the free hydroxyl groups of the wood constituents are acetylated, which significantly reduces the ability of the wood to absorb humidity and results in lower water content. Furthermore, it increased the temperature at maximum decomposition rate T_max by 8°C compared to Pinus radiata. Belmadur beech exhibits a 7 wt% increase in the amount of residue. For Thermo beech, the higher decomposition temperature compared to beech, as well as the increased residue formation, are explained by the chemical changes due to thermal treatment, such as the emission of volatile organic compounds and the structural changes in hemicellulose and lignin. The decrease in cellulose and hemicellulose results in an increase of the relative content of lignin. The release of combustible volatiles is delayed, just as the time to ignition. The char yield due to the lignin is enhanced.
All investigated untreated wood samples exhibited water loss, associated with the first mass loss step. The temperature at maximum decomposition rate $T_{\text{max}}$ was different for each wood. Beech exhibited a decomposition temperature of 352°C, Pinus radiata and Pinus sylvestris L. had their highest decomposition rates at 363°C and 369°C, respectively, and Meranti decomposed at 366°C. The residue of beech at 800°C was the lowest with only 13 wt%. Pinus radiata and Pinus sylvestris L. yielded residue of 15 and 16 wt%, respectively, and the residue of Meranti was the highest of all tested woods at 21 wt%. The char yield of lignin is reported to outperform cellulose by a factor three. Thus, the residue amounts correlated well with the lignin contents of the woods, which were around 23% for beech, between 26% and 30% for pines and about 33% for Meranti wood.

### Table 1

| Material                  | $T_{5\%}$ (°C) | $T_{\text{max}}$ (°C) | Mass 800°C (wt%) |
|---------------------------|----------------|----------------------|-----------------|
| Beech                     | 195 ± 16       | 352 ± 1              | 13 ± 3          |
| Belmadur beech            | 192 ± 33       | 348 ± 1              | 20 ± 1          |
| Thermo beech              | 275 ± 6        | 363 ± 1              | 20 ± 1          |
| *Pinus radiata*           | 222 ± 16       | 363 ± 2              | 15 ± 2          |
| Accoya                    | 279 ± 1        | 371 ± 1              | 14 ± 0          |
| Meranti                   | 230 ± 9        | 366 ± 3              | 21 ± 1          |
| *Pinus sylvestris L.*     | 218 ± 11       | 369 ± 1              | 16 ± 1          |

3.2 Heat of combustion of volatiles and char residue

Heats of complete combustion (HOC) of all investigated wood materials were investigated by means of the bomb calorimeter. HOC values are shown in Table 2. Beech and Belmadur beech exhibited the lowest HOC values, whereas the treated soft woods Thermo beech and Accoya had the highest HOC. The thermal treatment of beech led to a significantly lower water content and thus an increased energy release per weight during complete combustion. The acetylation of beech entails the increase of combustible carbonyl groups, which led to a higher heat of combustion. *Pinus radiata* and *Pinus sylvestris L.* showed a similar HOC, while the HOC of Meranti slightly increased to...
more than 19 MJ/kg. This higher value is attributed to the higher lignin content of Meranti considering the higher HOC of lignin compared to cellulose.3

The PCFC was used to assess the HRR/HRC and THR of the treated and untreated wood samples per specimen mass. This PCFC investigation of a few milligrams of each wood allows for conclusions about their material-specific fire behavior potential. Measuring residue yields enables the calculation of the heat produced solely by combustion of the volatiles (HOCvol) during anaerobic pyrolysis in the PCFC. Comparing the THR obtained from PCFC measurements (pyrolysis with subsequent total oxidation of the volatiles) to the HOC values from bomb calorimeter measurements (total oxidation of the whole material), the remaining energy in the residue was determined to equal (HOC_{bomb} - THR). Consequently, the THR = heat released/specimen mass is also always smaller than the HOCvol = heat release/mass loss measured in the PCFC. As the effective heat of combustion of carbonaceous char is around two times the effective heat of combustion of wood, encouraging charring is a very promising way to reduce the fire risks of burning wood.

It is apparent from Figure 4 and Table 2 that the HRR of Belmadur beech did not differ significantly from the HRR of untreated beech; the HRC decreased from 147 to 134 W/g and the THR was reduced to 8.7 from 10.1 kJ/g. Due to the treatment of beech with DMDHEU, the crosslinked structure is a better precursor for char formation, which explains the increased residue, the lower HRC, and the lower HOC_{vol} in the PCFC. The energy stored in the char (HOC_{bomb} - THR) thus increased from 44.2% to 50.3%. The treated wood products Thermo beech and Accoya exhibited higher peaks than the untreated woods beech and Pinus radiata (Figure 4). The effect of the vanishing shoulder and increase in peak maximum was discussed above for the mass loss rate obtained from the thermogravimetry (Figure 3). Indeed, all HRR curves of the PCFC corresponded extremely well with the mass loss rate curves from thermogravimetry. However, thermal treatment and crosslinking increased the precursor structures for charring, such as crosslinks and lignin content, and thus allowed for higher energy storage in the char (50.7% of HOC_{bomb} compared to 44.2% in untreated beech). In Accoya, the acetyl groups that were added to block the free hydroxyl groups served as additional fuel, contributing to the heat of combustion of the volatiles and thus to the HRC. The fact that the HOC of the char residue is constant at around 39% for both untreated Pinus radiata and treated

**TABLE 2** Bomb calorimeter results, pyrolysis combustion flow calorimeter results, and calculated amount of energy stored in the char residue

| Material       | HOC_{bomb} (MJ/kg) | HRC (W/g) | THR (kJ/g) | T_{max} (°C) | Residue (%) | HOC_{vol} (kJ/g) | HOC_{bomb} - THR (MJ/kg) | HOC_{bomb} - THR (%) |
|----------------|---------------------|-----------|------------|--------------|-------------|------------------|--------------------------|------------------------|
| Beech          | 18.1 ± 0.1          | 147 ± 4   | 10.1 ± 0.0 | 359.7 ± 1.1  | 15.2 ± 1.2  | 12.0 ± 0.2       | 8.0                      | 44.2                   |
| Belmadur beech | 17.5 ± 0.1          | 134 ± 3   | 8.7 ± 0.3  | 354.4 ± 1.4  | 19.6 ± 0.5  | 10.8 ± 0.4       | 8.8                      | 50.3                   |
| Thermo beech   | 20.1 ± 0.1          | 195 ± 2   | 9.9 ± 0.4  | 369.8 ± 0.1  | 19.5 ± 0.3  | 12.3 ± 0.6       | 10.2                     | 50.7                   |
| Pinus radiata  | 18.4 ± 0.2          | 143 ± 2   | 11.2 ± 0.1 | 372.4 ± 0.6  | 13.7 ± 0.1  | 13.0 ± 0.1       | 7.2                      | 39.1                   |
| Accoya         | 19.8 ± 0.1          | 213 ± 1   | 12.1 ± 0.7 | 371.4 ± 0.2  | 14.3 ± 0.1  | 14.2 ± 0.8       | 7.7                      | 38.9                   |
| Meranti        | 19.1 ± 0.1          | 145 ± 5   | 9.9 ± 0.3  | 374.5 ± 1.0  | 18.3 ± 0.1  | 12.1 ± 0.4       | 9.2                      | 48.2                   |
| Pinus sylvestris L | 18.4 ± 0.1     | 152 ± 3   | 11.6 ± 0.2 | 375.7 ± 2.4  | 12.1 ± 0.2  | 13.2 ± 0.2       | 6.8                      | 37.0                   |

Abbreviations: HOC, heats of complete combustion; HRC, heat release capacity.

**FIGURE 4** HRR curves derived from PCFC measurements for comparison of (A) treated and untreated woods and (B) different kinds of untreated wood. HRR, heat release rate; PCFC, pyrolysis combustion flow calorimeter

Accoya suggests that the acetyl groups introduced by the treatment only contribute to the HOC of the volatiles and do not increase energy storage in the char.

Comparison between the HRR of different untreated woods showed a similar HRC for all specimens (Figure 4B). The start of pyrolysis and the temperature at maximum HRR was shifted. Pinus radiata,
Pinus silvestris L., and Meranti wood had a similar $T_{\text{max}}$ at 372°C, 376°C, and 375°C, respectively, while the $T_{\text{max}}$ of beech was lower at 360°C. The THR of Meranti wood was the lowest at 9.9 kJ/g. The increased HOC$_{\text{bomb}}$ of Meranti compared to beech results in increased energy storage in the char (48.2% compared to 44.2%). This is associated with its higher lignin content. The pine woods Pinus radiata and Pinus silvestris L. exhibit higher HOC$_{\text{vol}}$ and lower energy storage in the char than beech, amounting to 39.1% and 37.0%, respectively.

Comparing the HRR curves derived from PCFC measurements with the derivative mass loss from TG shows high accordance. Apart from narrower peaks in the PCFC due to a higher heating rate of the pyrolyzer, the heights of the HRR as well as the appearance of a water release peak and shoulders prior to the main decomposition step are in very good conformity with derivative TG. The values for residue formation during PCFC measurements are in good accordance with the residue values obtained from TG measurements for the treated woods. However, the untreated woods exhibit higher deviations in amounts of residue between the two methods. Pinus radiata, Meranti, and Pinus silvestris L. all show decreased residue formation in the PCFC.

### 3.3 Forced flaming combustion

The burning behavior of treated and untreated woods under forced flaming conditions was observed and evaluated in the cone calorimeter. The results are displayed in Table 3. All investigated wood samples exhibited an HRR consisting of two maxima, a first peak HRR (PHRR$_1$) as a result of the rapid initial increase in HRR, and a second peak HRR (PHRR$_2$) toward the end of burning (Figure 5). The PHRR$_1$ occurred due to the initial release of volatiles before the creation of a char layer, which then acted as a heat and fuel barrier for the underlying material, thus causing a decrease in HRR. The PHRR$_2$ was the result of the char layer cracking and breaking under the constant heat impact, which led to a second pyrolysis front going through the specimen and thus a second heat release regime. The PHRR$_2$ is not only considered as a measure for fire growth in this case, but much more, as a value describing the quality and stability of the formed char residue. Further, a lower PHRR$_1$ also hints at an improvement in the quality of the char as a protective layer, be it due to a treatment method or due to a change in the kind of wood.

**Table 3** Results from measurements under forced flaming conditions in the cone calorimeter; maximum of the average rate of heat emission (MARHE)

|            | $t_{\text{ig}}$ (s) | PHRR$_1$ (kW/m$^2$) | PHRR$_2$ (kW/m$^2$) | THE (MJ/m$^2$) | TML (wt%) | TML (g) | THE/TML (MJ/g) | TSR (m$^3$/m$^2$) | MARHE (kW/m$^2$) |
|------------|---------------------|----------------------|----------------------|----------------|-----------|---------|----------------|----------------|-----------------|
| Beech      | 32 ± 2              | 201                  | 548 ± 21             | 72.6 ± 0.5     | 78.5      | 59.1    | 1.2            | 144             | 212.2           |
| Belmadur beech | 34 ± 1            | 219                  | 556 ± 34             | 62.1 ± 0.2     | 71.4      | 59.6    | 1.0            | 57              | 175.0           |
| Thermo beech | 26 ± 1            | 223                  | 354 ± 24             | 64.6 ± 1.7     | 72.7      | 47.3    | 1.4            | 266             | 180.5           |
| Pinus radiata | 27 ± 2             | 187                  | 354 ± 19             | 57.9 ± 1.1     | 79.7      | 44.5    | 1.3            | 316             | 161.2           |
| Accoya     | 22 ± 2              | 274                  | 392 ± 9              | 66.9 ± 0.8     | 75.9      | 41.5    | 1.6            | 152             | 225.2           |
| Meranti    | 33 ± 2              | 229                  | 224 ± 12             | 59.1 ± 2.1     | 73.7      | 47.4    | 1.2            | 374             | 115.5           |
| Pinus silvestris L. | 24 ± 1     | 193                  | 279 ± 8              | 70.0 ± 1.2     | 80.0      | 50.3    | 1.4            | 328             | 155.1           |

Abbreviations: TML, total mass loss; PHRR, peak heat release rate; THE, total heat evolved; TSR, total smoke released.

**Figure 5** Heat release rate curves from cone calorimeter measurements to compare (A) treated woods and their untreated counterparts and (B) different untreated woods.
was strongly increased due to the improved charring. After the effect of the protective barrier was lost, the HRR increased strongly and PHRR2 was even higher than that of untreated beech. The residue pictures (Figure 6) of the Belmadur beech sample show more stable char formation, but with many more small cracks. This increased number of cracks enabled the pyrolysis gases to fuel the flame and led to an increased heat impact on the underlying material. The effective heat of combustion derived from cone calorimeter experiments, displayed here as the ratio between the THE and the total mass loss, is obtained during the flaming period and allows for a statement about the fire growth of the material. For Belmadur beech, the effective heat of combustion is greatly reduced due to DMDHEU treatment, which led to increased carbonization and thus energy storage in the residue. Compared to beech, Thermo beech exhibited a time to ignition reduced by 6 seconds and an increased PHRR of the first peak (PHRR1) of about 22 kW/m². Both phenomena resulted from the reduced water content of Thermo beech, leading to a higher and earlier HRR as well as a slightly increased effective heat of combustion. The minimum to which the HRR relapsed after the initial peak was lower than that of beech, indicating a marginally improved protective char layer formation. The second peak was greatly decreased from 548 to 354 kW/m². However, the time to PHRR2 was the same for both samples. This showed that the thermal treatment had a significant effect on the flame retardancy behavior of beech.

In comparison to Pinus radiata, the treated Accoya showed an earlier time to ignition, reduced by 5 seconds, and a PHRR1 increased by 87 kW/m². Due to the additional acetyl groups, which were released at the early burning stage, \( t_w \) was lowered and the HRR was accelerated, leading to the observed increase. The acetyl groups, which were released in the form of highly flammable acetic acid, also contributed to the increased effective heat of combustion. These increased fire hazards also led to less effective protective char and a shortened overall burning time, notably due to the shift in time of PHRR2 to 250 seconds, as opposed to around 330 seconds for the untreated wood.

Figure 5B shows the HRR curves of the investigated untreated woods, in which beech exhibited the highest PHRR. The lower HRR curves of Pinus radiata, Pinus silvestris L. and Meranti indicated less intensive combustion. The height and the length of the plateau, which occurred between PHRR1 and PHRR2 illustrated the effectiveness of the protective char layer. For beech, this steady burning plateau was relatively high, with only 20 to 30 kW/m² less than the PHRR1. After the plateau, the HRR increased very rapidly up to PHRR2. In comparison, the HRR curve of Pinus silvestris L. exhibited a much lower and longer steady burning plateau, and the HRR increased in a slower fashion to a PHRR2, which was around 280 kW/m² lower than that of beech. For Meranti, the steady burning plateau and the PHRR2 were decreased even more, with PHRR2 being lower than PHRR1. Meranti had the best protective char layer effect of all tested materials, which is associated with the highest lignin content of all tested materials. This can be seen in the residue photograph of Meranti (Figure 6C), which shows a very compact char structure with only a relatively small number of cracks.

Compared to the untreated beech, the CO production (Figure 7) of the treated woods Belmadur beech and Thermo beech is slightly increased in the first step prior to the char layer formation. At the steady burning phase, CO production by beech and Thermo beech stays at a low level, while Belmadur beech exhibits a slight increase. For Accoya, the duration of the steady burning
phase is shortened and PHRR$_2$ is reached earlier than for the other materials. However, the CO production is proportional to the HRR of the materials, with beech releasing the highest amount of CO. After flameout, CO production falls back to a minimum and begins to increase as the afterglow phase starts. In this afterglow phase, beech and Belmadur beech exhibit a significant rise in CO release as compared to the other investigated materials, due to more intense thermo-oxidation.

Smoke production is a crucial factor when investigating the burning process of wood materials. Figure 7 also shows the total smoke released (TSR) for the investigated materials. The smoke release is divided into two steps for all materials. Compared to beech, Belmadur beech shows slightly increased smoke release in the first step; however, the release of smoke in the second step increases only marginally. The TSR of Belmadur beech is significantly lower than that of untreated beech. Due to the crosslinked structure, the production of soot particles that result in visible smoke is intensified. Thermo beech exhibits a much stronger release of smoke during both steps. Accoya, the acetylated Pinus radiata, shows a constantly increasing release of smoke, in contrast to the other tested materials. This is mainly due to the fact that the burning time is shortened and no real steady burning plateau is formed. However, the TSR of Accoya is greatly reduced compared to Pinus radiata, because of more complete combustion as a result of acetylation.

When compared with other untreated woods, beech showed the lowest TSR. Meranti, which showed the best flame retardancy performance, exhibits the highest TSR due to incomplete combustion, and thus increased formation of soot particles during burning. The TSR of Pinus radiata and Pinus silvestris L. are only slightly lower.

To assess and compare the differences in fire load and fire growth between treated and untreated woods and different kinds of woods, respectively, Petrella plots are shown in Figure 8. As there were no significant changes in PHRR$_1$, the parameter PHRR$_2$/$t_{ig}$ was chosen to assess the fire growth in Figure 8A. It is also a valuable parameter to investigate the effectiveness of the protective char layer, since it incorporates the period for which the protective barrier maintains its effect until PHRR$_2$ is reached. In Figure 8B, the maximum of the average rate of heat emission (MARHE) value is used to assess fire growth. The ARHE averages the HRR to a curve with only one maximum instead of multiple maxima. The maximum of that curve includes both typical PHHRs of the HRR of burning wood in the cone calorimeter.

All woods, treated and untreated, are compared to beech as a reference, except for Accoya, whose reference is the untreated Pinus radiata.
radiata. It is apparent that treatment with acetic anhydride to achieve acetylation of the hydroxyl groups in wood significantly increases fire load as well as fire growth. Thermal treatment and crosslinking with DMDHEU result in a moderate reduction of both fire load and fire growth. However, switching from beech to another wood may have a stronger impact on fire load and fire growth reduction, with Meranti being the most effective.

4 | CONCLUSIONS

The comparison of treated and untreated wood reveals and assesses the impact of the treatment methods, acetylation, thermal treatment, and treatment with DMDHEU, on their fire retardancy performance. While protecting the wood or wood product from other influences and improving their general lifetime, the treatments investigated here may lead to an overlooked change in burning performance. The crosslinking of cellulose microfibrils with DMDHEU in beech enables a stronger charring mechanism than the untreated beech. This leads to enhanced fuel storage and thus to a decreased fire load. However, this treatment method is not able to decrease PHRR. While thermal treatment of beech reduces its water content, decreases the organic volatiles, increases crosslinking, and thus it slightly increases the relative lignin content and thus the char yield, and reduces the fire load. The associated reduction in fire load results in a decrease in HRR and fire growth to some extent. Acetylation does not improve thermal stability and flame retardancy behavior, because acetyl groups are introduced, adding to the combustible volatiles and increasing the effective heat of combustion of the pyrolysis products. This enhances the burning speed of woods treated with acetic anhydride. Comparison with kinds of wood other than the respective untreated counterparts shows an improvement in flame retardancy when woods with higher lignin content and thus higher char yield are used. Meranti shows the best flame retardancy performance, while having the highest lignin content of all the materials investigated.

The fire performance of only one typical representative of each wood treatment was investigated; the variation of the parameters of the treatments was not addressed, the resulting variation of the performance not investigated. Further, only a limited number of different woods were investigated. Nevertheless, the main conclusion is underlined that switching the kind of wood is generally in the same order of magnitude and more effective than the treating methods acetylation, thermal treatment, and treatment with DMDHEU, in terms of flame retardancy performance.

ACKNOWLEDGEMENTS

The authors would like to thank our material suppliers for providing us with the required specimens, namely the Burckhardt Institute University Göttingen, Enno Roggemann GmbH, and Klöpperholz GmbH. The authors received no specific funding for this work.

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How to cite this article: Rabe S, Klack P, Bahr H, Schartel B. Assessing the fire behavior of woods modified by N-methylol crosslinking, thermal treatment, and acetylation. Fire and Materials. 2020;44:530–539. https://doi.org/10.1002/fam.2809