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# Effects of Heat Treatment on Thermal Decomposition and Combustion Performance of *Larix* spp. Wood

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*Larix* spp., a wood species of low dimensional stability, was heat-treated in nitrogen at 180 to 210 °C for 6 h. Changes in the thermal decomposition and combustion behaviors of the wood after heat treatment were investigated by TGA, SEM, FTIR, and cone calorimetry. TGA confirmed the loss of hemicellulose from heat-treated *Larix* spp. Small cracks in the cell wall and loss of resin from the vessels of heat-treated wood were observed by SEM. Hemicellulose degradation within the heat-treated samples was indicated by decreased intensities of typical O-H and C=O stretching vibration peaks in the FTIR spectra. The HRR and MLR curves of treated wood were much lower than those of the untreated ones, which is preferable for fire safety. However, the time to ignition of treated samples decreased from 22 to 13 s and the total smoke production increased by 4.76 and 43.3% for 180- and 210 °C-treated samples, respectively, a detrimental effect on fire safety. To determine the influence of heat treatment on the combustion behavior of *Larix* spp., the fire safety properties of heat-treated wood (such as wood structure building, furniture, and floors) must be studied further.

## INTRODUCTION

Wood is a sustainable natural resource widely used as a building material and for flooring, furniture, and interior decoration due to its intrinsic properties and relatively low price. However, wood has some negative characteristics that may need to be improved. For instance, some applications may require higher biological durability and better dimensional stability.

Heat treatment research began in the 1920s, when the swelling and shrinkage properties of heat-treated wood were evaluated. The durability of heat-treated wood was investigated in the 1940s using different shielding gases. In recent years, heat treatment processes have been achieved through process conditions variations such as the duration and temperature of the treatment, the type of heating atmosphere, the pressure, and the catalysts used. Heat treatment processes have provided the basis for growth of prosperous companies in European countries including Thermo-Wood in Finland (Shi *et al.* 2007), PLATO-Wood in Holland (Tjeerdsma *et al.* 1998), Ratification in France (Candelier *et al.* 2013), and Oil Heat Treatment in Germany (Tjeerdsma and Militz 2005). Heat treatment improves the dimensional stability, aesthetic appearance, hygroscopicity, durability, and weather resistance (Huang *et al.* 2012; Yildiz *et al.* 2006; 2011) of wood and is an environmentally friendly process (Heigenmosera *et al.* 2013; Kamdem *et al.* 2002). The main components of the wood are modified by high-temperature treatments, in particular,

pyrolysis of amorphous polysaccharide (hemicelluloses) and the condensation and crosslinking reactions of lignin (Kasemsiri *et al.* 2012; Korkut *et al.* 2008; Rowell *et al.* 2009) take place.

Heat-treated wood is still sensitive to flames (Delichatsios *et al.* 2003; Ondrej *et al.* 2001). However, it is widely used as an indoor and outdoor structural material and for decorations. Heat treatment releases low molecular weight, volatile compounds from wood and degrades polysaccharides and lignin, which are related to the thermal pyrolysis, flammability, and smoke release properties of the wood. The fire safety of heat-treated wood has rarely been studied.

The main purpose of this study was to investigate the effect of heat treatment on wood's pyrolysis behavior and flammability performance *via* parameters such as the ignition time, heat release rate, mass loss rate, and smoke emission. Thermogravimetric analysis, SEM, FTIR, and CONE calorimetry were used.

## EXPERIMENTAL

### Wood Sample Preparation and Heat Treatments

Twelve-year-old *Larix* spp. was purchased from the Harbin timber market. *Larix* spp. is a softwood species planted heavily across northern and eastern China. It has wide adaptability, a long growing season, and high growth rates.

Wood blocks measuring 100 x 100 x 8 mm in the longitudinal, radial, and tangential directions according to ISO 5660-1, respectively, were cut and oven-dried at 103 °C (for approximately 48 h) before heat treatment. Twelve fine (free from defects) samples were randomly selected to be oven-dried. Four samples were left without heat treatment, while the remaining 8 samples were heat-treated. The blocks to be subjected to heat treatment were enclosed in an oven under a nitrogen atmosphere at 180, 190, or 210 °C for 6 h and treated by a thermal process used in furniture and structural wood factories. The temperature was controlled with an accuracy of ±1 °C. Next, each specimen was conditioned at a temperature of 30±1 °C and a relative humidity of 65±1% until testing. The whole blocks were ground and sieved to obtain particles between 0.2 and 0.3 mm in diameter for TGA (Thermogravimetric analysis) and FTIR analysis.

### Analytical Instruments

To investigate the decomposition behavior of the heat-treated wood in this study, a Perkin Elmer Pro-6 TGA system (State of Connecticut, USA) with a nitrogen atmosphere was used. The system was heated from the ambient temperature to 800 °C at a heating rate of 10 °C/min with a nitrogen flow 25 mL/min for all pyrolysis experiments with 2 replications. The mass loss rate of each sample was recorded by the TGA system.

Four blocks of dimensions 8×8×2 mm cut from heat-treated blocks were sputter-coated (BAL-TEC SCD 005) with a gold layer for 140 s and were mounted on standard aluminum stubs with a conductive paste. The samples were scanned using an FEI Quanta 200 Scanning Electron Microscope (Hillsboro, Oregon 97124 USA) at an accelerating voltage of 10 kV. The temperature was approximately 20 °C and the column vacuum was 0.83 mm Hg (absolute).

After grinding, samples were dried at 105 °C for 24 h before pellet preparation. The samples were analyzed by FTIR (Magna-IR 560 E.S.P, Nicolet Company, USA) at a resolution of 4 cm$^{-1}$ for 40 scans.

Fire safety tests were performed with a cone calorimeter (FTT Company, UK) according to ISO 5660[-1] (cone calorimeter) at a heat flux of 50 kW/m$^2$, corresponding to a temperature of 760 °C. The four samples that were prepared and heat-treated before (100 x 100 x 8 mm) were fixed to a horizontal sample retainer and were protected by a stainless steel mesh to prevent sample bending or extension during testing.

## RESULTS AND DISCUSSION

### Thermal Decomposition by TGA

Thermogravimetric analysis results for untreated and heat-treated wood in a pure nitrogen atmosphere are presented in Fig. 1 and more detailed data are listed in Table 1. Figure 1 shows the thermal degradation behaviors of the wood flour used in this study. A peak in the first stage was observed with the gasification of moisture in the wood (Fujii *et al.* 2011; Almeida *et al.* 2008), which is a familiar feature of other lignocellulosic materials (Das *et al.* 2000). With increasing intensity of the heat treatment, the mass loss in this stage gradually decreased, which is in line with the results of the moisture study of heat-treated wood.
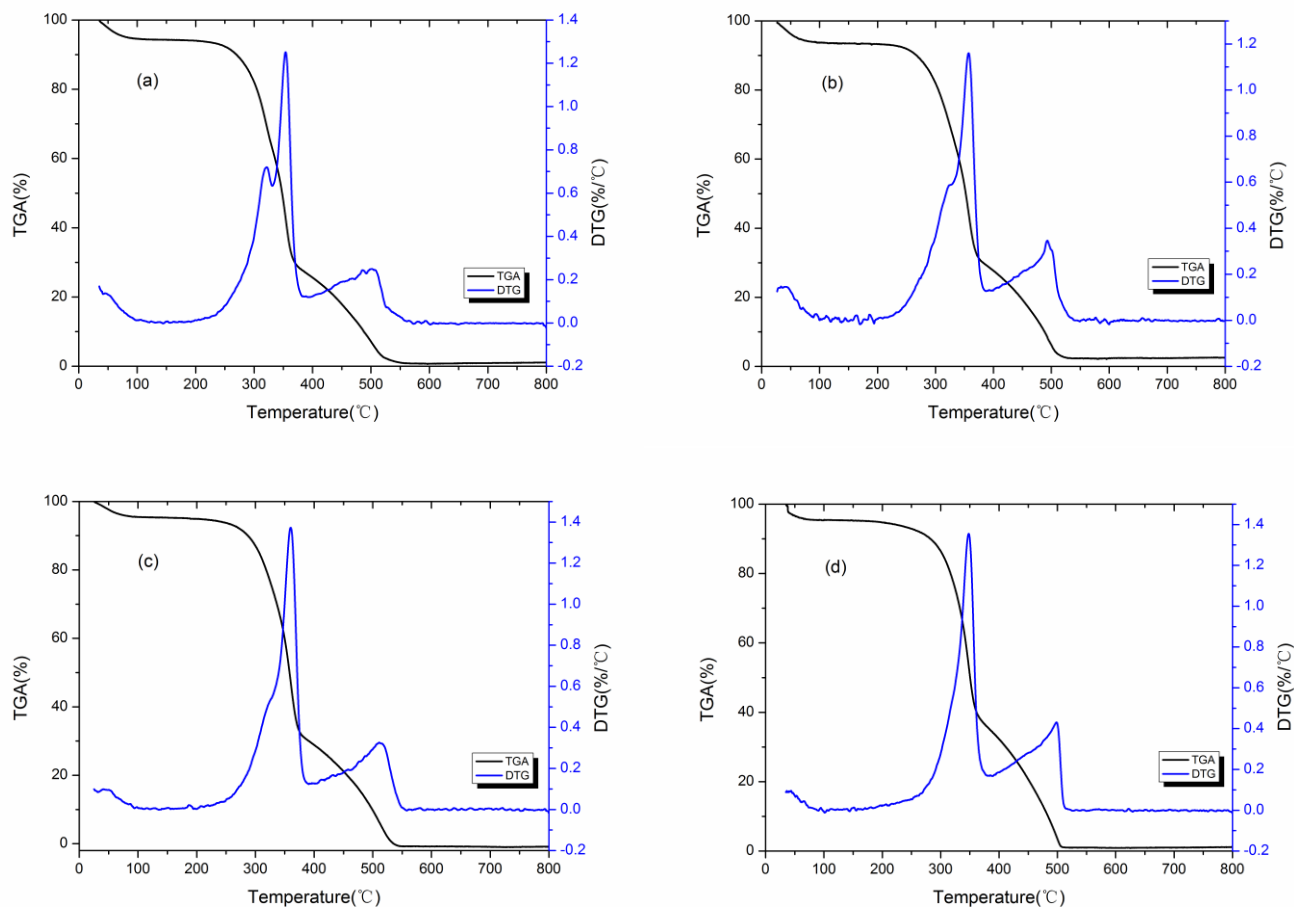


**Fig. 1.** TGA curves of heat-treated and untreated wood: a) untreated wood; b) heat-treated wood at 180 °C; c) heat-treated wood at 190 °C; and d) heat-treated wood at 210 °C

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**Table 1.** Thermogravimetric Analysis Data under a Pure Nitrogen Atmosphere

| Sample | First Stage | | Second Stage | | | Third Stage | | | Residue at 700°C (%) |
|---|---|---|---|---|---|---|---|---|---|
| | Temperature Range (°C) | Mass loss (%) | Temp range (°C) | $T_{max}$ (°C) | Mass loss (%) | Temp range (%) | $T_{max}$ (°C) | Mass loss (%) | |
| Untreated wood | Ambient to 110 | 5.56 | 197.3 to 394 | 353.8 | 67.7 | 394 to 558 | 506.1 | 25.46 | 0.932 |
| Heat-treated at 180 °C | Ambient to 98.5 | 6.26 | 184.2 to 399 | 357.2 | 65.56 | 399 to 535 | 493.2 | 25.51 | 2.408 |
| Heat-treated at 190 °C | Ambient to 99 | 2.55 | 183.2 to 390 | 359.9 | 64.99 | 390 to 549 | 511.1 | 30.82 | 1.095 |
| Heat-treated at 210 °C | Ambient to 81 | 2.55 | 184.8 to 381 | 348 | 59.4 | 381 to 514 | 514 | 34.558 | 3.022 |

The pyrolysis temperatures of hemicellulose (200 to 300 °C), cellulose (300 to 400 °C), and lignin (200 to 900 °C) are well-known. In the second stage (from 180 to 390 °C), the maximum mass loss rate appeared at a temperature of about 350 °C (see Table 1), corresponding mainly to the pyrolysis of amorphous hemicellulose and cellulose into char residues and the evaporation of the products ($CO_2$, CO, $CH_4$, $CH_3OH$, and $CH_3COOH$) (Becidan *et al.* 2007; Varhegyi *et al.* 1997).

The mass loss of untreated wood was 67.7% after the second main stage, larger than that of the heat-treated samples. This was attributed to the main decomposition process. However, the samples treated at 180, 190, and 210 °C did not have similar peaks at 320 °C in their respective TGA curves. This demonstrated that the heat treatments intensively degraded hemicellulose (Hosoya *et al.* 2007). The pyrolysis of cellulose began in the same stage as hemicellulose degradation (Yang *et al.* 2007; Zhang *et al.* 2012; Patwardhan *et al.* 2010). The highest decomposition intensity and the total degradation of cellulose appeared between 180 and 399 °C with a maximum rate at approximately 350 °C for all samples.

In the third stage, a similar peak, corresponding to lignin degradation, was observed for all samples (Eseltine *et al.* 2013). Lignin is one of the components of wood with the best heat-resisting ability (Garcia *et al.* 2008; Hosoya *et al.* 2006). According to the comparison of samples obtained in TGA experiments, heat-treated wood had greater mass loss in the third stage, which was partly caused by a higher ratio of lignin in the heat-treated wood. During the pyrolysis process, the breakage of 1-4 glycosidic bonds shortened cellulose chains, but sinistral glucose decomposed later (Hosoya *et al.* 2007; Gua *et al.* 2013). The degradation activation energy needed for hemicellulose was much less than that for well-crystallized cellulose (Raveendran *et al.* 1996). Within the range of 180 to 550 °C, the wood weight loss rate was about 90%, indicating that the major components of the wood were pyrolyzed and only a small amount of residual cellulose remained. Because of the strong chemical stability of the propyl-benzene derivatives in lignin, its thermal decomposition took place over a relatively higher temperature and with slower reaction compared with cellulose and hemicellulose.

## SEM Observations

SEM observations of cross-sections of wood samples show the anatomical structures of untreated *Larix* spp. (Fig. 2a), wood heat-treated at 190 °C (Fig. 2b), and wood heat-treated at 210 °C (Fig. 2c). Similar to the untreated *Larix* spp., the heat-treated wood maintained a stable cellular structure, while the high-temperature treatment caused some damage to the cell walls of the *Larix* spp. sample, as highlighted in Fig. 2. Most of the cell wall in the heat-treated samples had some deformations such as tracheid collapse and cracks. Comparing Figs. 2(a), (b), and (c), it is clear that the early wood tracheids of wood heat-treated at 190 °C remained intact, while the late wood tracheids gained several small cracks. The damage was much clearer in samples heat-treated at 210 °C. In the untreated sample, the resin canal of untreated *Larix* spp. was blocked by extractives. In the sample heat-treated at 190 °C, the extractives leaked partially out of the canal, forming a cavity. As shown in Fig. 2, the extractives of the canal in the sample heat-treated at 210 °C were completely evaporated.
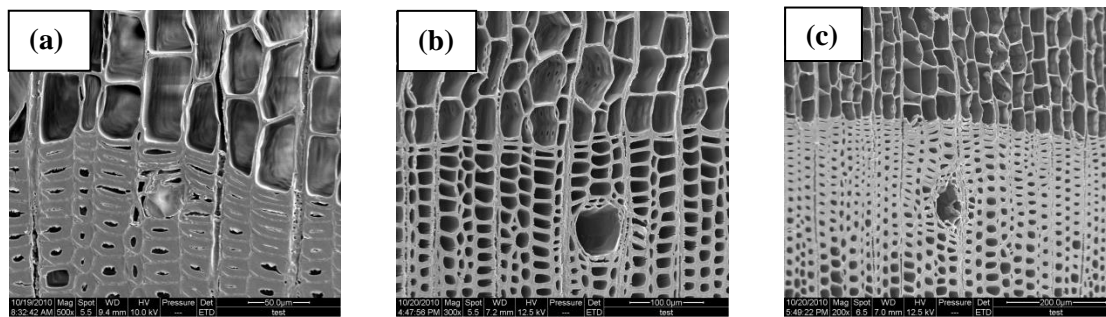


**Fig. 2.** Scanning electron micrographs of wood samples: a) untreated wood; b) heat-treated wood at 190 °C; and c) heat-treated wood at 210 °C

The findings from the SEM micrographs are supported by the TGA of the heat-treated samples previously discussed. The modification of the wood cell wall appeared to be as a result of the degradation of hemicellulose and the leakage of extractives due to the high-temperature treatment (Nuopponen *et al*. 2004). These observations demonstrate that the cell wall structure became increasingly loose and fragile with increasing treatment temperature (Duygu and Sudeshna 2012; Priadi and Hiziroglu 2013; Li *et al*. 2013). As with the observations made *via* TGA, it is apparent that the hemicellulose in heat-treated wood was hydrolyzed, causing cracks in the cell wall (Priadi and Hiziroglu 2013). The loss of cell wall substances of heat-treated *Larix* spp. can also be confirmed from this finding.

## FTIR Analysis

The results of the FTIR analysis of untreated and heat-treated *Larix* spp. wood samples are presented in Fig. 3 in order to investigate the structural and chemical component changes of the samples following heat treatment. The differences in the spectra of untreated and heat-treated wood were taken into consideration.

The characteristic bands of FTIR absorption in the region of 500 to 4000 cm$^{-1}$ for both untreated and heat-treated wood are listed in Table 2. In general, due to the composition changes of thermally-modified wood, the FTIR peaks can change (Hakkou *et al*. 2005; Colom *et al*. 2003; Şen *et al*. 2012). In Fig. 3, the peak at 3335 cm$^{-1}$ corresponds to O-H stretching vibrations; this peak's intensity gradually decreased with increasing treatment temperature, making the heat-treated wood less hydrophilic (Huang

*et al.* 2012). The reduction of the abundant hydroxyl groups present in hemicellulose from the FTIR spectra indicates the degradation of hemicellulose in heat treated-wood. This loss of hemicellulose from the cell wall is believed to have caused the cracks observed in the SEM images already shown. The peak between 1700 and 1750 cm$^{-1}$ corresponds to C=O groups and is due to the conjugated ketone and carboxylic acid groups in lignin and hemicellulose (Evans *et al.* 1991). The intensity of this peak decreased, which provides information about the chemical reactions taking place during heat-treatment. This could be due to the cleavage of acetyl side chains or the decomposition and evaporation of fatty acid esters, of which the ester and carboxyl groups are the most abundant functional groups of hemicellulose. With the exception of the sample treated at 180 °C, the peak at 1716 cm$^{-1}$ corresponds to pyrolysis byproducts (Singh *et al.* 2013) such as carboxylic acids. These acids can accelerate hemicellulose degradation by catalyzing hydrolysis (Alén *et al.* 2002). The peaks at 1592 and 1504 cm$^{-1}$ correspond to the carbon skeleton vibration of benzene rings in lignin (González *et al.* 2009). The intensity of these peaks increased with heat treatment, likely because of hemicellulose degradation and the increasing proportion of lignin. The decrease in intensity of the carbonyl band at 1264 cm$^{-1}$ was slight. The intensity of the peak decreased markedly only when the treatment temperature exceeded 200 °C. This demonstrated the cleavage of acetyl groups in the hemicelluloses which is in accordance with the results of the TGA study previously discussed. The peak at 895 cm$^{-1}$, corresponding to anti-symmetric, out-of-phase stretching of cellulose, started to diminish due to the depolymerization of hemicellulose (Risto *et al.* 2000).
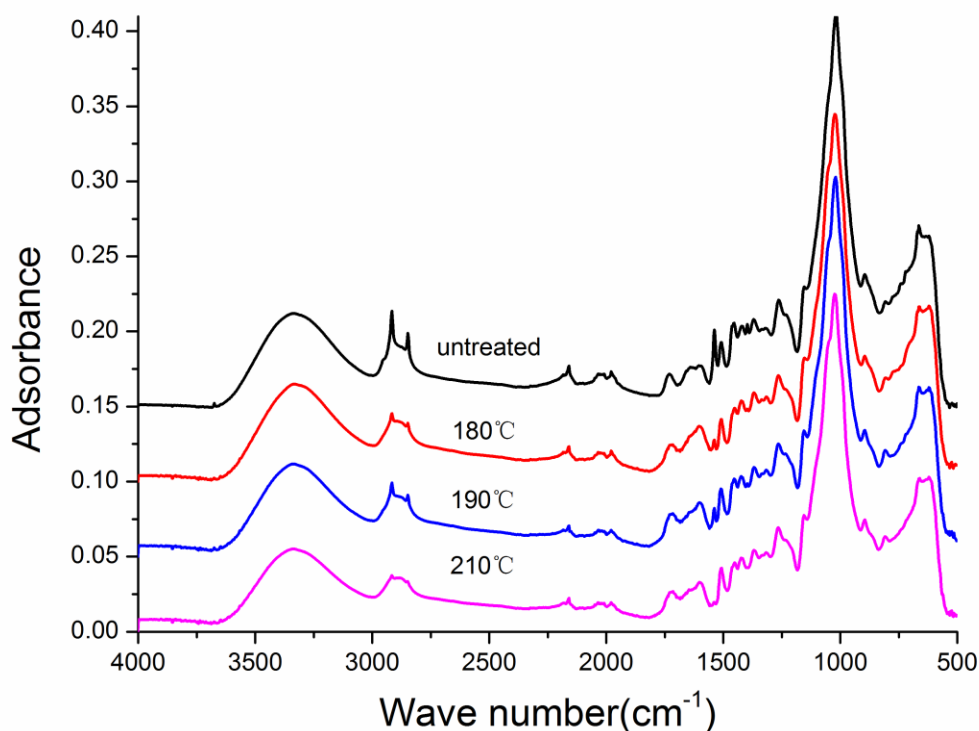


**Fig. 3.** Fourier transform infrared (FTIR) spectra of one untreated and three heat-treated wood samples

**Table 2.** Characteristic Bands of FTIR Absorption in the Region 500 to 4000 cm$^{-1}$ for Untreated and Heat-Treated Wood

| Wavenumber (cm$^{-1}$) | | | | Functionality | Vibration type |
|---|---|---|---|---|---|
| Untreated | 180 (°C) | 190 (°C) | 210 (°C) | | |
| 3335 | 3334 | 3335 | 3335 | O-H of alcohols, phenols, and acids | O-H stretching vibrations |
| 2848 to 2916 | 2848 to 2916 | 2848 to 2916 | 2849 to 2916 | CH$_2$, CH-, and CH$_3$ | C-H stretching vibrations |
| 1716 | 1715 | 1715 | 1716 | C=O of esters, ketones, aldehydes, and acids | C=O stretching |
| 1603 | 1602 | 1601 | 1601 | Aromatic ring (syringyl lignin) | Benzene ring stretching vibrations |
| 1509 | 1509 | 1510 | 1509 | Aromatic ring (guaiacyl lignin) | Benzene ring stretching vibrations |
| 1455 | 1452 | 1453 | 1451 | C-H (lignin, glycan) and Aromatic carbon skeleton | C-H bending vibrations |
| 1421 | 1423 | 1423 | 1423 | C-H and Aromatic ring | Benzene skeletal combined with C-H deformations |
| 1370 | 1368 | 1368 | 1368 | C-H (cellulose and hemicellulose) | C-H bending vibrations |
| 1318 | 1315 | 1316 | 1316 | O-H (cellulose and hemicellulose) | Bending vibrations in the plane |
| 1263 | 1264 | 1264 | 1265 | CO-OR (hemicellulose acyloxy); Aromatic ring ether (lignin) | CO-OR stretching vibrations |
| 1018 | 1022 | 1021 | 1023 | C-O-C | C-O deformation |
| 895 | 895 | 896 | 896 | Anti-symmetric out-of-phase stretching in pyranose ring | stretching in pyranose ring |

## Combustion Performance Test

The Cone Calorimeter was expected to effectively evaluate fire performance properties such as fire degradation, smoke emission, and heat release (Scudamore *et al.* 1991) of the tested materials.

The TTI (time to ignition), HRR (heat release rate), and THR (total heat release) are important parameters for evaluating the combustion of biomaterials, whereas the MLR (mass loss rate), SPR (smoke production rate), and TSP (total smoke production) can reveal the extent of mass loss and smoke expression during combustion. The representative MLR, HRR, SPR, and TSP versus time curves describe the combustion and smoke emission behaviors of heat-treated wood, as shown in Figs. 3, 4, 5, and 6 and Table 3.

**Table 3.** Influence of Heat Treatment on Wood Combustion

| Heat Treatment Temperature (°C) | Heat Release Rate | | | | | THR (mJ/m$^2$) | av-SEA | TTI |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | pk-HRR | | av-HRR | | | | | |
| | 1st | 2nd | q"60 | q"180 | q"300 | | | |
| Untreated | 169.6 | 247.6 | 122.9 | 102.8 | 132.4 | 49.5 | 60.5 | 24.0 |
| 180 | 175.3 | 219.8 | 121.4 | 107.6 | 131.6 | 49.0 | 68.0 | 19.0 |
| 190 | 136.1 | 150.2 | 126.6 | 96.2 | 115.7 | 42.0 | 57.5 | 22.0 |
| 210 | 139.2 | 144.2 | 104.2 | 90.2 | 102.5 | 36.8 | 86.9 | 13.0 |
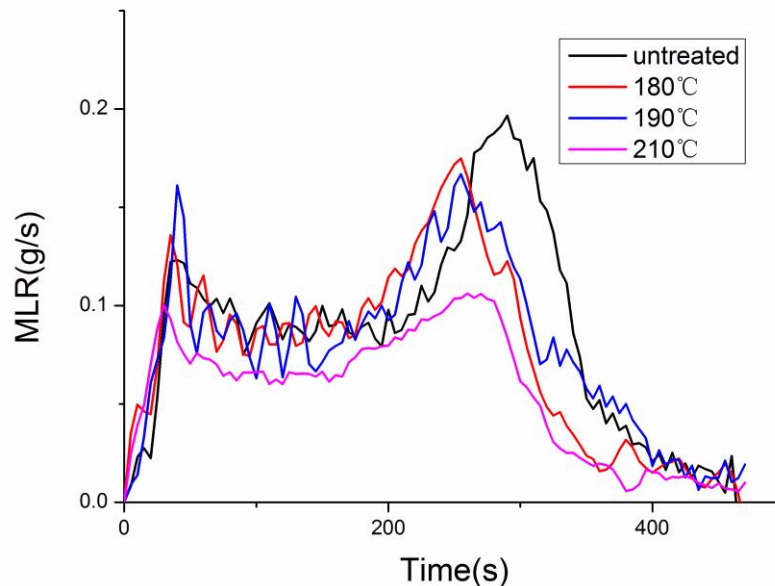


**Fig. 4.** Mass loss rate (MLR) curves for untreated and heat-treated samples

*Mass loss rate (MLR)*

The thermal decomposition behavior of the mass loss rate reflects the combustion process and is related to the heat release rate and smoke production. The heat treatment was a mild pyrolysis that did not change the tendency of the MLR curves. According to Table 3 and Fig. 4, *Larix* spp. pyrolysis reaction processes can be divided into two stages under a radiation intensity of 50 kW/m$^2$.

The first stage of the MLR curves was mostly due to the elimination of moisture from the wood. From Fig. 4, it can be seen that heat-treated wood contained less moisture than untreated wood, which is in agreement with the research regarding the moisture content of heat-treated wood. The second stage of the thermal decomposition process mostly involved the combustion of major wood components, including cellulose, hemicellulose, and lignin.

The results of MLR analysis demonstrated that the heat-treatment significantly influenced the thermal decomposition behavior of the wood. At the beginning of the

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burning process, the MLR curves were only slightly different, but in the second stage, the peak MLR of all heat-treated wood samples appeared earlier and the peak values were lower than in the untreated wood. The second-stage peaks of 180-, 190-, and 210 °C-treated wood were reduced by 11, 15, and 46%, respectively, compared to those of the untreated wood. This suggests that the extractives of the heat-treated samples were partly released, that the hemicellulose was degraded, and that the char residue content increased during heat treatment (Hosoya *et al.* 2008; Patwardhan *et al.* 2011). The MLR of the sample heat-treated at 210 °C was reduced in both stages under a radiation intensity of 50 kW/m$^2$, which demonstrated that the hemicellulose was fully degraded, the extractives were evaporated, and the moisture content was reduced (Yildiz *et al.* 2006). This is in agreement with the results of FTIR analysis and TGA. The condensation and crosslinking reactions of lignin during heat treatment promoted char residue formation, facilitating earlier carbonation during combustion. Earlier-appearing and lower peak MLR values indicated that the heat treatment was favorable for the wood's fire safety.

*Heat release rate (HRR)*

The HRR is one of the major parameters measured in a Cone calorimeter. It is considered to be the most important parameter used to assess a material's burning behavior (Fang *et al.* 2013).
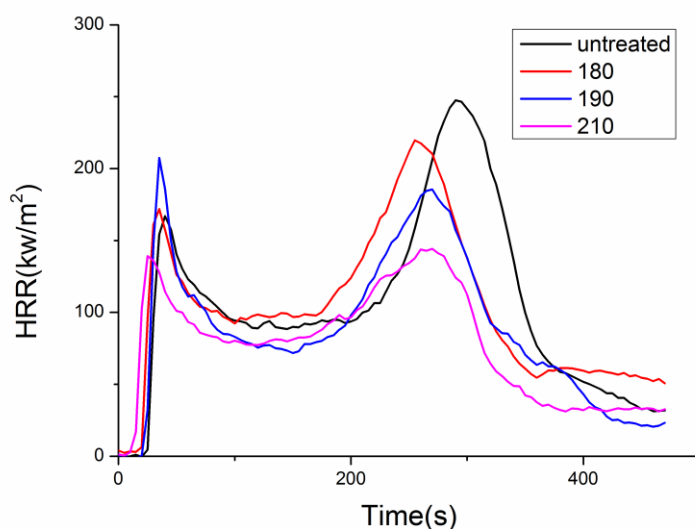


**Fig. 5.** Heat release rate (HRR) curves for untreated and heat-treated samples

From Table 3, the TTI of the heat-treated samples was dramatically reduced, from 24 to 13 s, which caused combustion to occur earlier than in untreated wood. From Table 3 and Fig. 5, although the TTI appeared in a shorter time, the HRR of the heat-treated wood was significantly reduced during the combustion process. The 300-s average HRR (av-HRR) and peak HRR (pk-HRR) values of heat-treated wood were about 23 and 42% lower than those of untreated wood, respectively. A lower pk-HRR is preferable to reduce the intensity of fires and has a positive impact on the combustion behavior of heat-treated wood. As shown in Fig. 5, at the end of burning, the HRR curves of the heat-treated samples gradually decreased and tended to smooth out, which made the exothermic peaks simultaneously lower and wider. The wood charred early, suppressing HRR in the first stage. In the second stage, char-surface rupture occurred. Moisture in

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untreated samples can absorb heat and reduce the surface temperature, which limited the first exothermic peak and caused the longer TTI. Because the moisture content in heat-treated wood was lower and the cell walls were cracked, it was easier for moisture to be evaporated. Meanwhile, heat-treated wood produced volatile fatty acids that leaked to the wood surface, which acted as an effective fuel. From Table 3, heat-treated wood has a lower THR, which is consistent with the results of TGA. This suggests that heat-treating wood lowers its heat release rate. Due to the shorter TTI, it cannot be asserted that heat treatment was favorable with regard to the flame retardant performance of the wood.

*Smoke production*

In wood architecture, smoke production is the most important factor in wood safety research, even more so than heat release (Lee *et al.* 2011). Figure 6 shows the smoke production behavior of both heat-treated and untreated wood samples. The total smoke production curves are shown in Fig. 7.
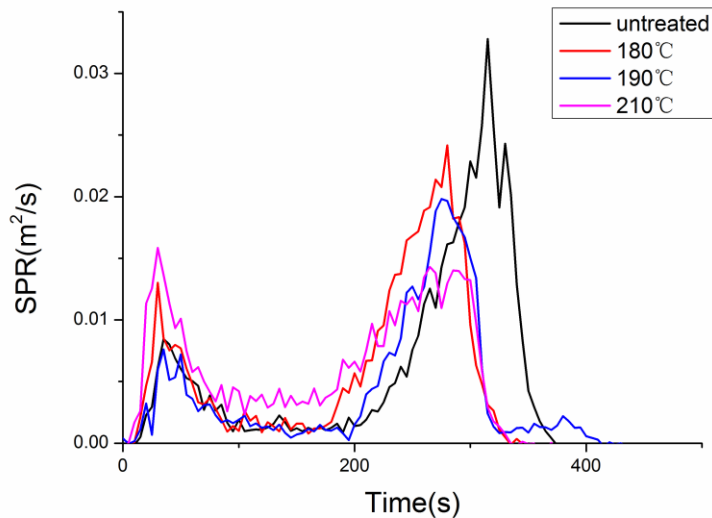


**Fig. 6.** Smoke production rate (SPR) curves for untreated and heat-treated samples
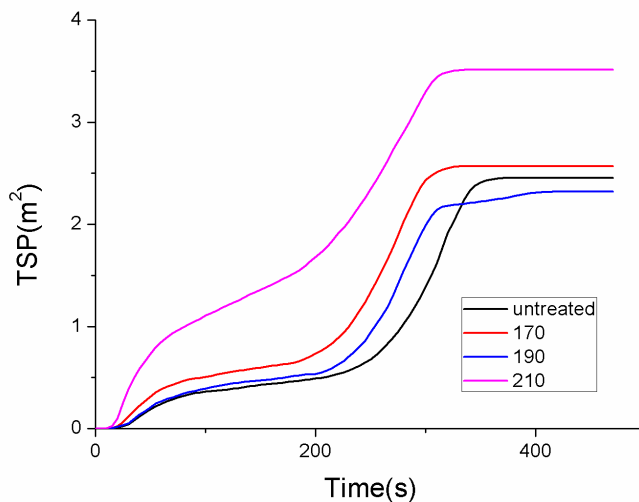


**Fig. 7.** Total smoke production (TSP) curves for untreated and heat-treated samples

From Table 3 and Fig. 7, it was observed that heat treatment increased the average specific extinction area (av-SEA) and smoke production rate of wood. Compared to untreated wood, TSP values for 180 °C, 190 °C, and 210 °C-treated wood were significantly changed by 4.76, -5.5, and 43.3%, respectively. Based on these data, heat treatment generally had a negative effect on the smoke release properties of the treated wood.

Figure 6 shows the smoke release behavior of the samples. The smoke release process can be divided into 3 stages: (1) the non-flaming mode, (2) the flaming mode, and (3) the after-glowing mode. Figure 6 clearly shows that the smoke emission of the 210 °C-treated wood was larger than that of untreated wood in the first and second stages. Heat treatment reduced the equilibrium moisture content of the wood, thus increasing the surface heating rate and shortening the TTI (Table 3). However, heat treatment caused cracks in the pit membrane and the cell walls of the wood, which made it more porous (Figs. 2 and 3). Porous materials are more likely to carbonize, and the incomplete combustion during this period was due to the combustion of smoke (Senneca 2007). This result is of great significance regarding the safe use of heat-treated wood for indoor and outdoor applications and should be studied further.

## CONCLUSIONS

1. The thermal decomposition, combustion properties, and smoke emission behavior of heat-treated wood were investigated. The heat treatment changed the chemical composition of wood, especially hemicellulose.

2. Tiny cracks in the cell walls and leakage of resin provided evidence that the degradation of the wood cell wall microstructure was a result of the heat treatment.

3. Due to the degradation of hemicellulose, the intensity of hydroxyl and carbonyl peaks in the FTIR spectra of heat-treated wood decreased, indicating weaker hydrophilicity and better dimensional stability in the treated wood.

4. Heat treatment showed positive effects on the fire safety of wood, weakening the intensity of its combustion and also reducing the ignition time of *Larix* spp. The smoke production of the heat-treated samples increased dramatically. The modification of the combustion behavior caused by the heat treatment should be further investigated.

## ACKNOWLEDGMENTS

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