Combustion Characteristics of Wood Panels Treated with Phosphorus-Nitrogen Additives

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The combustion characteristics were evaluated for wood samples either untreated or treated with a piperazine-N-N´-bis(methylenephosphonic acid) flame retardant. Combustion properties were investigated using a cone calorimeter (ISO 5660-1 2002). The time to ignition of samples treated with the chemical additive was delayed by 193%, 124%, and 61% for maple, ash, and cypress, respectively, compared with the untreated samples. Compared with the untreated sample, the PHRR value was reduced by 20% for t-ash and by 2.6% for cypress, whereas it was increased by 0.28% for t-maple. The time of PHRR for the treated sample was shifted to 1605 s (698%), 470 s (45%), and 340 s (32%) for cypress, ash, and maple, respectively, compared with the untreated samples. The reduced PHRR value and postponed time to PHRR indicated that combustion was suppressed by the thicker char layer. The mean CO yield of t-ash and t-cypress was increased by 2.9% and 27%, respectively, compared with the untreated sample, but t-maple was reduced by 46% compared with maple. The mean CO_2 yield of t-maple, t-ash, and t-cypress was decreased by 4%, 13%, and 37%, respectively, compared with the untreated sample. The combustion properties of treated wood were inhibited more than those of untreated wood.

Keywords: Flame retardant; Time to ignition; Peak heat release rate; Carbon monoxide; Carbon dioxide; Cone calorimeter

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INTRODUCTION

Wood is an important and widely used natural material because of its environmental and aesthetic aspects, physical and mechanical properties, and easy processing. It is used mainly as a construction material in the building industry. However, the flammability of wood has limited its wider applicability as a building material. Wood can be classified into hardwood and softwood according to its chemical composition. Hardwood and softwood have a similar percentage of cellulose, but hardwood has slightly more hemicellulose and less lignin than softwood (Janssens and Douglas 2004). These three components have very different thermal pyrolysis characteristics and are degraded thermally, producing ignitable gas above 300 °C; thus, wood catches fire easily and burns vigorously with a flame (Hirata *et al*. 1991). Therefore, flame retardancy in wooden materials has attracted increasing attention to comply with various safety requirements (JIS A 1321 1994; ISO 5660-1 2002; ASTM E84-09 2009; Lowden and Hull 2013).

Recent research has focused on intumescent flame retardants (IFR) (Chen and Wang 2010). Conventional IFR additives (*e.g.* ammonium polyphosphate, pentaerythritol, and melamine) are phosphorus–nitrogen additives that are effective in flame retardancy of polypropylene materials (Horacek and Grabner 1996; Horrocks 1996; Bourbigot *et al*. 2004; Chen and Jiao 2009) and wood plastic composites (Anna *et al*. 2003; Pandey *et al*. 2005; Zhang *et al*. 2005; Fu *et al*. 2010). The effects of fire retardant synergetic agents, such as zinc borate, montmorillonite, manganese dioxide, and stannic oxide, on the mechanical properties, thermal degradation, and flame retardant performance of wood flour/recycled polypropylene composites comprised of intumescent flame retardants have been studied (Ren *et al*. 2015).

Hyperbranched macromolecules and polymers with triazine ring structures have attracted considerable attention because of their high thermal stability, which is derived from the structural symmetry of the triazine rings (Blotny 2006; Nguyen *et al*. 2012). Some triazine-based macromolecules have been used as charring-foaming agents in intumescent flame retardant systems (Mahapatra and Karak 2007; Feng *et al.* 2012). Their good properties are attributed to the tertiary nitrogen in the triazine ring structures (Dai and Li 2010). Together, flame retardant and low molecular reactive oligomer resin synergistically improves wood properties, both for flame retardancy and dimensional stability (Jiang *et al*. 2015).

Growing environmental issues have gradually restricted the use of halogenated flame retardants (Beyer 2002; Fu *et al.* 2010). Predicting the behavior of commercial materials in fires by measuring their intrinsic flammability properties in small-scale apparatus is increasingly desirable for fire safety and material design. Phosphorous-based fire retardants in wood increase the dehydration reactions during thermal degradation to produce more char and less total (flammable and non-flammable) volatiles. Flame retardant (FR) chemicals include phosphorus, nitrogen, boron, silica, and synergistic combinations of these elements (Levan 1984; USFS 1999). The fire retardancy of wood involves a complex series of simultaneous chemical reactions, whose mechanisms depend on the particular fire retardant and the thermophysical environment (Hirata *et al.* 1991). The piperazine-N-N'-bis(methylenephosphonic acid) has hydrophilic OH groups and a hexagonal ring structure of carbon and nitrogen. If nitrogen and hydroxyl group are introduced to a phosphorous compound, a synergistic effect can be created. An excellent molecular structure of flame retardant can be provided having affinity with wood materials and thermal stability.

This study assessed the key combustion characteristics of wood materials treated with piperazine-N-N'-bis(methylenephosphonic acid), which has a symmetrical molecular structure, and provided basic information on the flame retardant design.

EXPERIMENTAL

Materials

Maple, ash, and cypress panels were obtained from a commercial supplier (3S-Trade Company, Seoul, South Korea) and cut to dimensions of 100 mm (L) × 100 mm (W). Piperazine-N,N'-bis(methylenephosphonic acid) (PIPEABP) was synthesized as described by Chung and Jin (2013).

Methods

Moisture contents

Samples without knots on the surface were selected for the experiments. Samples were incubated in an oven at 105 °C, and their weight was measured at 4-h intervals until no further weight change was observed. The moisture content was estimated to be in the range of 7.3 to 7.8% by mass based on the dry mass of the material using Eq. 1 (USFS 1999),

$$MC\ (\%) = \frac{W_m - W_d}{W_d} \times 100\% \tag{1}$$

where W_m is the initial weight of the specimen and W_d is the absolute dry weight after drying. This equation relates the equilibrium moisture content to the relative humidity and ambient temperature. Table 1 lists the moisture content and volume density of the test specimens.

Table 1. Properties of Wood Species Used in the Tests

Samples	Maple	Ash	Cypress	t-Maple	t-Ash	t-Cypress
Class	Hardwood	Hardwood	Softwood	Hardwood	Hardwood	Softwood
Volume Density (kg/m^3)	608.5±0.8	539.6±2.8	438.9±2.9	657.8±0.9	594.4±2.4	472.0±2.5
Moisture Content (%)	7.4±0.0	7.3±0.0	7.8±0.0	7.4±0.0	7.3±0.0	7.8±0.0
Thickness (mm)	18.0±0.1	20.0±0.1	18.3±0.0	18.0±0.1	20.0±0.1	18.3±0.0

t: treated

Sample preparation

One side of the specimens was painted three times with a brush with distilled water or 50 wt.% PIPEABP solution at room temperature and then air-dried. The samples were pre-conditioned in an oven at 55 °C for 23 h before the tests until the mass had stabilized.

Flammability tests by cone calorimeter

Combustion tests were performed using a dual cone calorimeter (Fire Testing Technology Ltd, East Grinstead, UK) at a heat flux of 25 kW/m^2 according to the ISO-5660-1 method (2002). The 100 mm (L) × 100 mm (W) specimens were tested in a horizontal orientation with a conical radiant electric heater located above the specimen. The unexposed surfaces of the test specimen were wrapped in aluminum foil, and the specimen was placed on a piece of low-density refractory fiber blanket within the holder. The back of the sample was insulated with low-conductivity high density ceramic plate material to reduce the heat losses to the sample holder. The retainer frame for the test specimen was used without a wire grid. The electric spark igniter was inserted above the test specimen until the time for the sustained ignition of the test specimen was observed and recorded. Before the test, the heat of the cone heater was set within ± 2%, and the oxygen concentration of the oxygen analyzer was calibrated to 20.95 ± 0.01%. The exhaust flow was set to 0.024 ± 0.002 m^3/s. The combustion test was terminated after 30 min from when the fire started burning.

The experimental data of three experiments were averaged. The following fire properties of the materials were determined: average heat release rate (HRRav, kW/m^2) (within 1800 s); peak heat release rate (PHRR, kW/m^2); total heat release rate (THRR, MJ/m^2); time to ignition (TTI, s); and time to PHRR (s). The PHRR and HRRav values corresponded to the acceleration of thermal degradation of the materials, which is related to the spread of fire. The total heat release rate (THRR) indicated the total heat capacity during the process of material combustion. Overall, a longer time to initiate a fire (T_{ig}) and lower consequent heat release information (PHRR, HRRav, and THRR) are the criteria of good fire performance.

RESULTS AND DISCUSSION

Time to Ignition (TTI) and Heat Release Rate (HRR)

The heat release rate (HRR) and total heat release rate (THRR) are important parameters used to assess the development, intensity, and degree of fire spreading (Almeras *et al*. 2003; Kiliaris and Papaspyrides 2010).

Properties of wood species after the tests are shown in Table 2. The time to ignition (TTI) of combustion of the specimen from exposure to the heat source before the beginning of a continuous flame was measured. The ignition of wood occurs when there is sufficient oxygen in the air and heat. Table 3 lists the time to ignition (TTI) of the wood panels. The TTI of maple was the longest among the base panels, which was caused by the combustion inhibiting effect due to the high volume density. The TTI of t-maple was the longest among the treated panels, and it was caused by the combustion inhibiting effect due to the high volume density. All the chemically treated wood samples showed a combustion inhibiting effect, as the TTI was delayed by 193%, 124%, and 61% for maple, ash, and cypress, respectively, compared with the base samples. The combustion inhibiting effect was greater when the volume density was higher.

Table 2. Properties of Wood Species after the Tests

Samples	Maple	Ash	Cypress	t-Maple	t-Ash	t-Cypress
Mass Lost (g)	84.8±2.8	91.3±1.9	64.8±2.7	73.0±2.7	86.8±0.3	49.2±2.2
Residual Mass (g)	24.1±2.1	17.7±1.3	15.5±1.2	44.7±2.5	33.3±2.1	37.2±1.4
Residual Char (wt.%)	22.1±2.8	16.2±3.3	19.3±2.3	38.0±2.6	27.7±1.3	43.0±1.9

t: treated

Ash samples showed the highest the peak heat release rate of 244.46 kW/m^2; lower values were obtained for maple (184.14 kW/m^2) and cypress (112.91 kW/m^2). The PHRR value increased with increasing mass loss. The main reasons for the higher PHRR value of ash were the low char formation, high mass loss, and burning of large amounts at the same time. Compared with ash, cypress had considerable char formation as well as low volume density and low mass loss.

The peak heat release rate of t-ash trees was the highest of the treated samples at 195.38 kW/m^2; lower values were obtained for t-maple (184.65 kW/m^2) and t-cypress (104.22 kW/m^2). The PHRR value increased with increasing mass loss and increasing char layer thickness on the wood surface according to the progress of combustion, which resulted in lower HRR values. The PHRR value of the treated sample was reduced by 20% for ash and 2.6% for cypress. In contrast, the PHRR values for t-maple were increased by 0.28% compared to the base samples. The residual char of the treated samples compared with the base sample was increased by 70.6%, 71.0%, and 122.8% for ash, maple, and cypress, respectively. Low mass loss was obtained with high char formation. The PHRR of ash was reduced by 20%, showing that PIPEABP exerted considerable influence.

Table 3. Combustion Properties of Untreated or PIPEABP-Treated Wood Panels

Samples	Maple	Ash	Cypress	t-Maple	t-Ash	t-Cypress
TTI (s)	299±5	148±5	172±6	876±7	355±7	352±7
[a]MLR $_{mean}$ (g/s)	0.053 ±0.001	0.052 ±0.001	0.038 ±0.001	0.074 ±0.001	0.05 ±0.001	0.0315 ±0.001
[b]PHRR (kW/m^2)	184.14 ±4.26	244.46 ±7.21	112.91 ±5.69	184.65 ±7.21	195.38 ±6.25	104.22 ±6.36
PHRR time (s)	1050±10	1035±10	230±14	1390±14	1505±14	1835±14
[c]THRR (MJ/m^2)	129.7 ±6.5	113.9 ±5.7	112.1 ±6.5	94.4±2.5	98.2±6.6	46.5±4.9
[d]EHC $_{mean}$ (MJ/kg)	13.53 ±0.10	11.03 ±0.33	15.31 ±0.63	11.50 ±0.28	10.00 ±0.56	8.29 ±0.44
CO $_{mean}$ (kg/kg)	0.0265 ±0.0007	0.0205 ±0.0008	0.0324 ±0.0008	0.0142 ±0.0006	0.0211 ±0.0008	0.0411 ±0.0007
$CO_{2\ mean}$ (kg/kg)	1.10±0.01	1.05±0.01	1.14±0.00	1.06±0.01	0.91±0.01	0.72±0.01
CO/CO_2	0.0241	0.0195	0.0284	0.0134	0.0232	0.0571

[a]mass loss rate; [b]peak heat release rate; [c]total heat release rate; [d]mean effective heat of combustion

Figure 1 exhibits two peaks, PHRR 1 and PHRR 2, which have been previously reported (Bourbigot *et al*. 2004; Duquesne *et al*. 2008; Du *et al*. 2009). The first peak was attributed to the formation of carbonaceous char. The middle portion of the HRR was attributed to the combustion of the specimen through the thickness gradually after the initial char layer was formed by heating the end of the sample. The second peaks were attributed to the formation of volatile substances in the remaining parts of the specimen. The heat flux absorbed on the surface of the protection char gradually makes fine cracks, resulting in the collapse of the char structure. The end of the curve is non-flame combustion that appears after the volatile components are exhausted.

The time of PHRR for the treated sample was postponed to 1605 s (698%), 470 s (45%), and 340 s (32%) for cypress, ash, and maple, respectively, compared with the untreated sample. The inhibition of combustion was observed in decreasing order as follows: t-cypress, t-ash, and t-maple. A reduced PHRR value and postponed time to PHRR indicated that combustion was suppressed. All treated panels showed combustion suppression due to the thicker char layer. The total heat released rate (THRR) is a function of the sample surface and time. It is calculated by integrating with respect to a given time and is expressed as the heat release rate (Table 3).

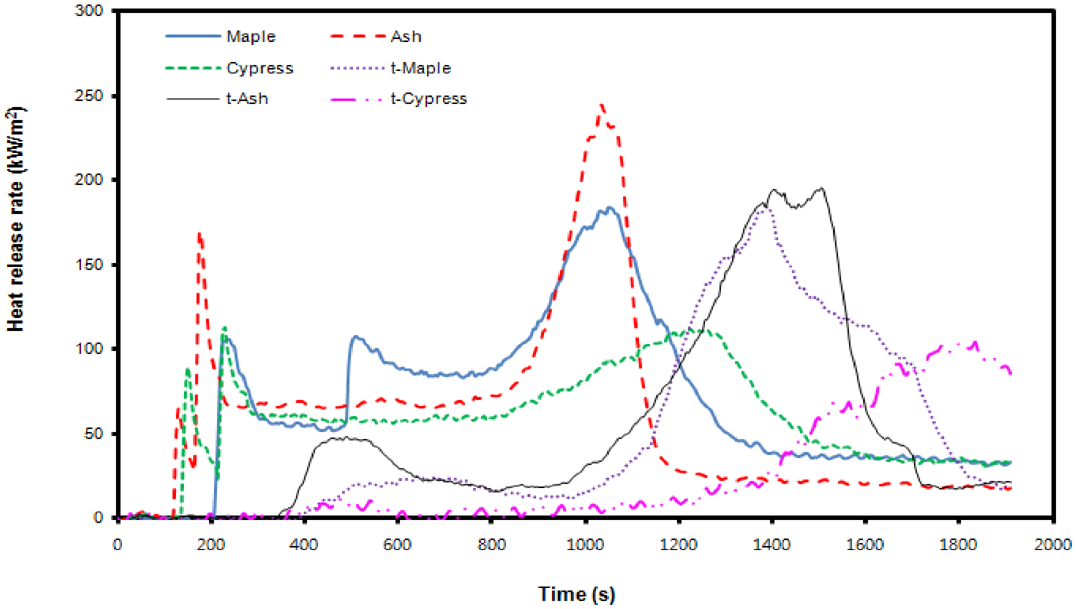


Fig. 1. Heat release rate curves of wood painted with 50 wt.% PIPEABP

The THRR of the hardwood was greater than that of the softwood, and it showed a high value with a high volume density. The THRR of the treated sample was reduced by 27.2%, 13.8%, and 58.5% for maple, ash, and cypress, respectively, as shown in Table 3 and Fig. 2.

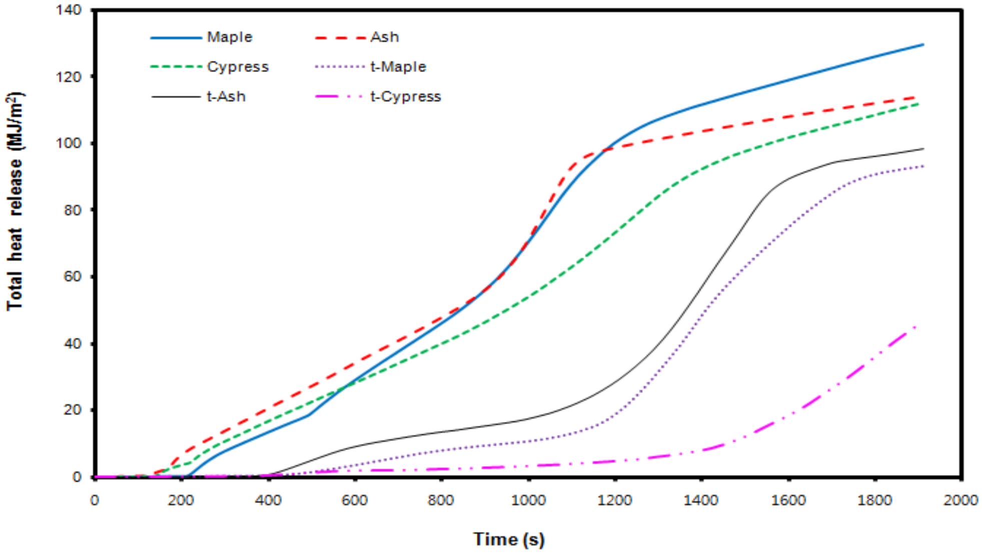
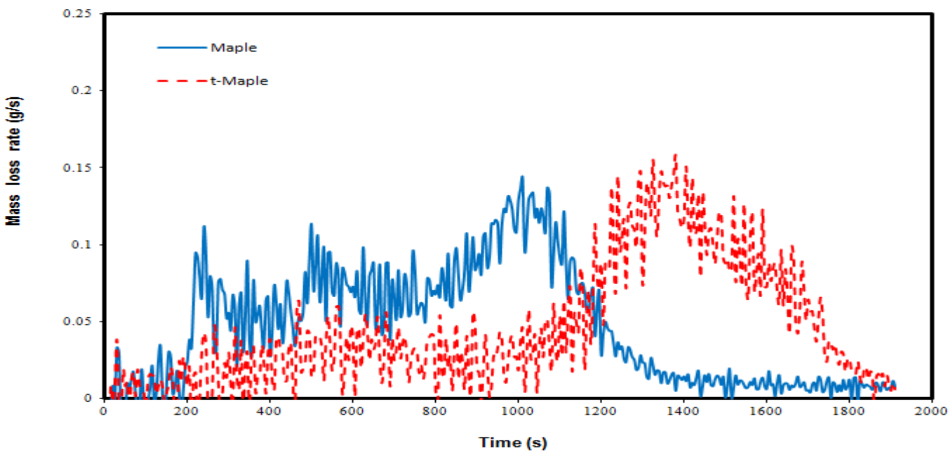


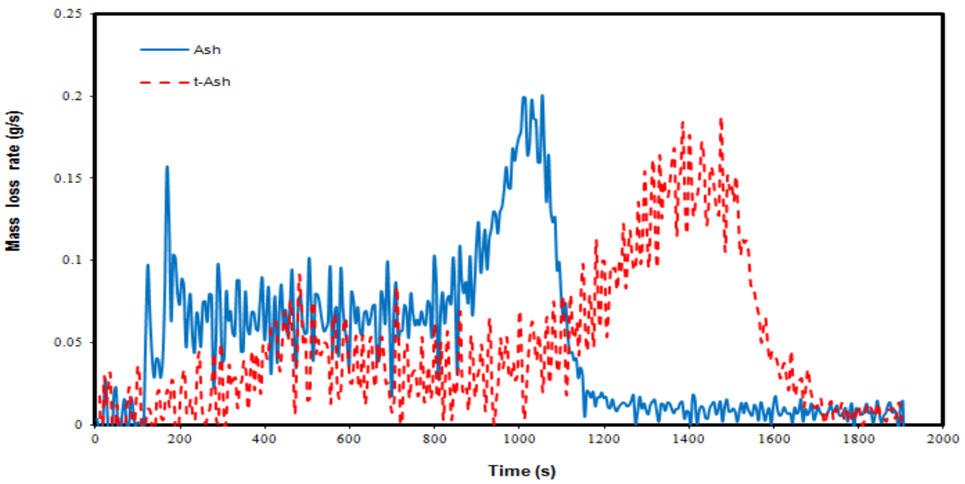
Fig. 2. Total heat release curves of wood painted with 50 wt.% PIPEABP

A low value was obtained when the residual char increased. A similar trend was observed with the PHRR values. The flame retardant containing phosphorus generates a PO radical that stabilizes the H or OH radical. The other is made of a glass surface due to the formation of HPO_3 *via* the thermal decomposition of phosphate. The formation of more char has a combustion-inhibiting effect by blocking oxygen in the air (Liodakis *et al*. 2006; Samyn *et al.* 2007). All treated samples showed lower THRR values than the base samples, suggesting that the flame retardant effects are due to the thicker char layer.

Mass Loss Rate (MLR)

The primary parameter responsible for the decreased HRR of the samples is the mass loss rate (MLR) during combustion. The MLR of cypress was noticeably lower than that of the other samples (Table 3 and Fig. 3).





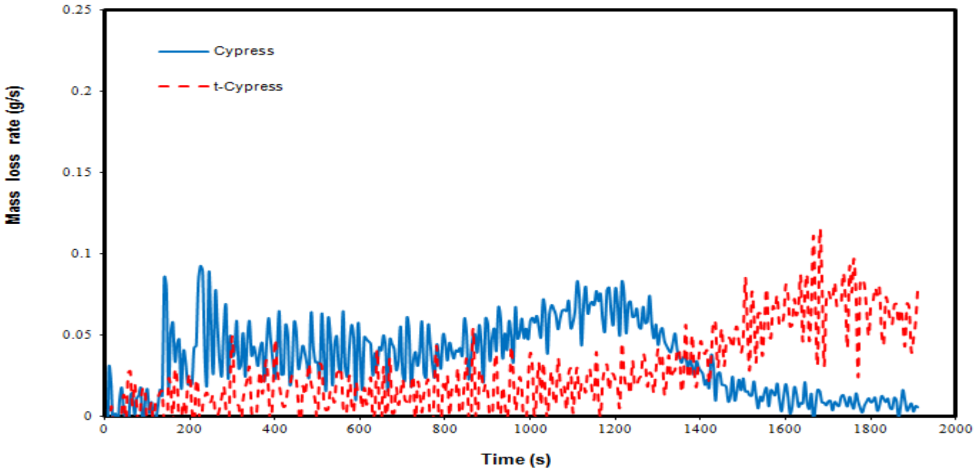


Fig. 3. Mass loss rate curves of wood painted with 50 wt% PIPEABP

Maple had the highest mass loss rate. The MLR value of the treated sample was increased 39.6% for maple and 7.7% for ash, but t-cypress showed a 17.1% lower MLR value than untreated cypress. The combustion-inhibiting effect of cypress was the best because it had the smallest MLR value. The t-cypress showed the lowest mass loss rate among the samples examined, indicating that the flame retardant improved the properties of char residue. These similarities suggested that the mechanism of the observed reduction in HRR and the MLR depends mainly on the condensed phase process instead of the gas phase process (Chen *et al*. 2013).

The effective heat of combustion (EHC) provides additional information. EHC is the HRR divided by the mass loss rate, as determined from the cone calorimeter test as a function of time. This constant value during the loss of effective mass is calculated as an average value, which corresponds mostly to the flame burning condition and thus to the combustion of volatiles from the material (Grexa and Lübke 2001). Lower EHC values reflect better fire performance characteristics. The EHC of the base samples was 15.31 MJ/kg, 13.53 MJ/kg, and 11.03 MJ/kg for cypress, maple, and ash, respectively. The EHC value of the treated samples was reduced by 45.9%, 15.0%, and 9.3% for cypress, maple, and ash, respectively, compared with the base sample. This data suggests that combustion was suppressed. t-Cypress showed the best result, and the treated samples had markedly lower EHC values than the base samples. The decreased values of all the samples was explained with formation of char due to glassy surface coating by HPO_3, and the blocking of oxygen in air; this effect inhibits combustion (Liodakis *et al.* 2006; Samyn *et al.* 2007).

CO and CO_2 Production

The concentration of CO released during the burning of a material is another key factor when estimating the fire hazard. As the CO emissions increase, the fire risk increases. The yield of CO and CO_2 is dependent on the combustion material (Hull and Paul 2007). Table 3 lists the CO yield (mass production of CO divided by mass loss) and CO_2 yield. The mean CO yield of wood treated with the phosphorus-nitrogen flame retardants was much higher than that of the untreated wood, except maple. The mean CO yield of t-ash and t-cypress was increased by 2.9%, and by 27%, respectively, compared with the base sample but reduced by 46% for t-maple compared with maple. The higher CO yield was attributed to the char layer, which shut off the oxygen to the burning surface and resulted in incomplete combustion. The treated samples showed increased CO generation during combustion and were determined to be somewhat toxic. The decreased CO yield of t-maple was due to the delayed CO production time during the experiment time. The mean CO_2 yield of the treated sample was decreased by 4%, 13%, and 37% for maple, ash, and cypress, respectively. The CO_2 yield of the treated wood was lower than that of the untreated wood. The decrease in CO_2 yield was attributed to the reduced amount of flammable gases. The decreased CO_2 yield was due to the hindered access of O_2 to wood due to the high concentration of CO_2 produced in advance and to the barrier of the char layer formed (Hurt and Calo 2001). The mean CO yield increased with the flame retardant, whereas the mean CO_2 yield decreased, providing a flame retardant quenching effect in the gaseous phase. The types and quantities of gas produced by combustion depend on a combination of factors including flammability of the fuels, the chemical composition, and the specific fire conditions (Shi *et al*. 2010).

Figure 4 shows the CO production rate. The main chemical components of wood include cellulose, hemicelluloses, and lignin, which have specific decomposition temperatures of 240 to 350 °C, 200 to 260 °C, and 280 to 500 °C, respectively (Janssens and Douglas 2004). The CO peak production rate for the base sample was 3.57×10^{-3} g/s at 1380 s, 2.86×10^{-3} g/s at 1580 s, and 2.30×10^{-3} g/s at 1190 s for maple, cypress, and ash, respectively. The CO peak production rate for t-maple, t-ash, and t-cypress was 3.62×10^{-3} g/s at 1910 s, 3.22×10^{-3} g/s at 1810 s, and 2.26×10^{-3} g/s at 1345 s, respectively. The maximum peak value of the treated sample was increased by 40% and 1.4% for ash and maple, respectively. The peak time of the treated samples was reached more slowly than those of the base samples. Maple did not achieve the maximum peak in the experimental conditions; delayed peak times indicating combustion inhibition. t-Cypress showed the lowest peak CO production rate, with a 21% decrease compared with cypress.

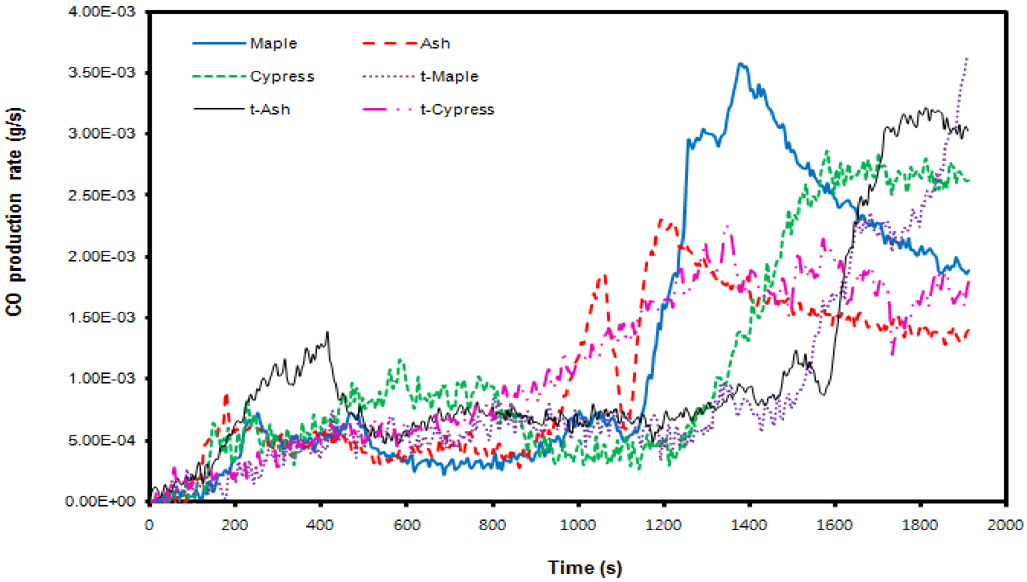


Fig. 4. CO production rate of wood painted with 50 wt.% PIPEABP

Figure 5 shows the CO_2 production rate as a function of time.

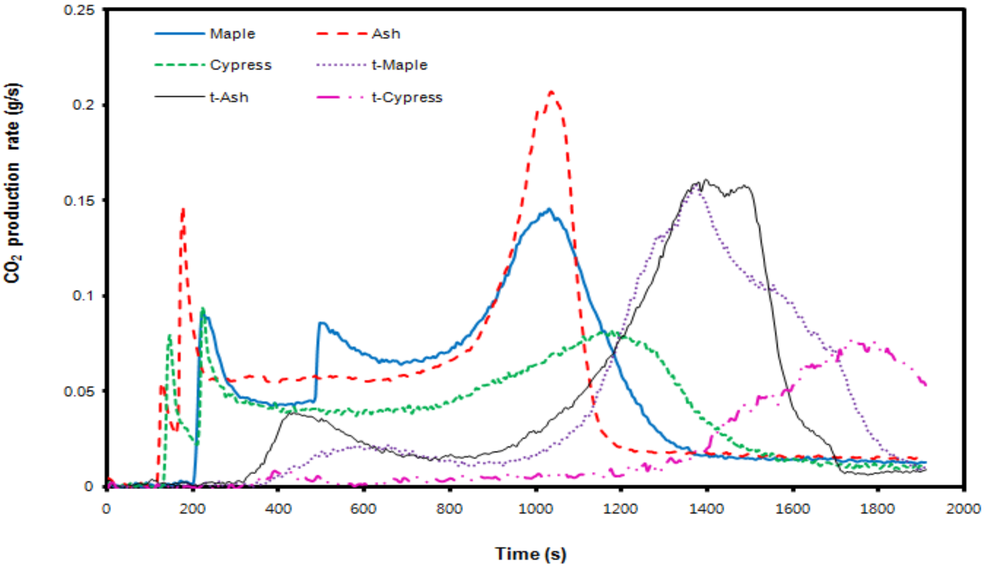


Fig. 5. CO_2 production rate of wood painted with 50 wt.% PIPEABP

The peak CO_2 production rate for the base sample was 0.207 g/s at 1035 s, 0.146 g/s at 1030 s, and 0.0936 g/s at 220 s for ash, maple, and cypress, respectively. The peak CO_2 production rate for the treated samples was 0.161 g/s at 1395 s, 0.156 g/s at 1380 s, and 0.0771 g/s at 1740 s for t-ash, t-maple, and t-cypress, respectively. Decreased CO_2 evolution was observed for the samples treated with the flame retardant systems. The peak CO_2 production rate of the treated sample was decreased by 18% for cypress and 22% for ash. The CO_2 production rate of t-maple, however, was increased by 8%. The maximum peaks occurring in secondary pyrolysis were attributed to the generation of more combustible gases during cellulose/lignin decomposition (Browne 1958). The maximum peak was delayed for all samples, which indicated a combustion inhibiting effect.

CONCLUSIONS

1. The TTI of treated samples was delayed. When the volume density of the treated samples was higher, the combustion inhibiting effect was greater.
2. The PHRR of the treated samples was reduced by 20% and 2.7% for ash and cypress, respectively, but increased by 0.28% for t-maple. The time of PHRR for the treated samples was postponed. A reduced PHRR value and postponed time to PHRR indicate the suppression of combustion by the thicker char layer.
3. The THRR of treated samples was reduced because more char was formed by PIPEABP. The formation of more char has a combustion inhibiting effect by blocking oxygen in the air. This result suggests that the flame retardant suppresses combustion through the production of a thicker char layer.
4. The reduced EHC values of treated samples reflected suppressed combustion. The t-cypress showed the best result. The decreased values of all the samples was explained with formation of char due to glassy surface coating by HPO_3 and the blocking of oxygen in air. This can be understood as a combustion inhibiting effect.

5. The mean CO yield of treated samples increased, whereas the mean CO_2 yield decreased, providing a flame retardant quenching effect in the gaseous phase.

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Article submitted: Dec. 15, 2015; Peer review completed: Feb. 27, 2016; Revised version received and accepted: March 17, 2016; Published: March 29, 2016.
DOI: 10.15376/biores.11.2.4319-4331