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Chemical mechanism of fire retardance of boric acid on wood

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Abstract It is commonly accepted that the fire retardant mechanism of boric acid is a physical mechanism achieved by the formation of a coating or protective layer on the wood surface at high temperature. Although a char-forming catalytic mechanism has been proposed by some researchers, little direct experimental support has been provided for such a chemical mechanism. In this paper, new experimental results using thermal analysis, cone calorimetry (CONE), and gas chromatography–Fourier transform infrared spectroscopy (GC–FTIR) analysis are presented and the fire retardant mechanism of boric acid on wood is discussed. Basswood was treated with boric acid, guanylurea phosphate (GUP), and GUP–boric acid. Treated wood was then analyzed by thermogravimetry (TG/DTG), differential thermal analysis (DTA), CONE, and GC–FTIR analysis. Thermogravimetry showed that the weight loss of basswood treated with boric acid was about three times that of untreated or GUP-treated wood at 165°C, a temperature at which GUP is stable. The DTA curve showed that boric acid treated basswood has an exothermal peak at 420°C, indicating the exothermal polymerization reaction of charring. CONE results showed that boric acid and GUP had a considerable synergistic fire retardant effect on wood. The GC–FTIR spectra indicated that compounds generated by boric acid treated wood are different than those generated by untreated wood. We conclude that boric acid catalyzes the dehydration and other oxygen-eliminating reactions of wood at a relatively low temperature (approximately 100–300°C) and may catalyze the isomerization of the newly formed polymeric materials by forming aromatic structures. This contributes partly to the effects of boric acid on promoting the charring and fire retardation of wood. The mechanism of the strong fire retardant synergism

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between boric acid and GUP is due to the different fire retardant mechanisms of boric acid and GUP and the different activation temperatures of these two chemicals.

Introduction

Boron compounds are the basic components of many fire retardants for wood and other cellulosic materials and have a long history of widespread use (Lyons 1970). Borax tends to reduce flame spread, but it can promote smoldering or glowing. On the other hand, boric acid suppresses glowing but has little effect on flame spread. Consequently, borax and boric acid are generally used together (LeVan 1984). Using thermogravimetric analysis (TGA), Oberley (1983) found a synergistic effect between boric acid and guanylurea phosphate (GUP). Although several theories on the fire retardant mechanism of boron compounds on wood substrates were proposed decades ago (Browne 1958), it is now commonly accepted that the primary mechanism is the formation of a coating or protective layer on the wood surface at high temperature (Kandola and Horrocks 1996). LeVan and Tran (1990) mentioned the char-forming catalytic effect of borax and boric acid, but no supporting data for the mechanism were provided. In our previous research (Li and Wang 2000; Wang et al. 1999, 2000), we found that boric acid treated wood and wood treated with a combination of boric acid and GUP pyrolyzed at a much lower temperature than did untreated wood, and that the boron–phosphorous synergism was observed over a wide temperature range. These findings support the importance of the chemical mechanisms of boric acid on wood pyrolysis and fire retardance. In this paper, we determine the chemical fire retardant mechanism of boric acid on wood by thermal analysis, cone calorimetry (CONE), and GC–FTIR analysis.

Materials and methods

Wood treatment

Wood blocks (100 mm longitudinal×100 mm radial×10 mm tangential) were cut from clear air-dried basswood (*Tilia amuresis* Rupr.). Basswood was selected because it can be uniformly treated with chemicals and contains the proper amount of the fatty acid used as the internal standard for GC analysis. Twenty-eight blocks were sorted into four weight-matched groups of seven blocks each. One group of blocks was treated with distilled water and used as a control. The other groups were treated with aqueous solutions of boric acid,

Table 1 Treatment groups

Treatment	Chemical	Group
Boric acid	BA	BZ
GUP	GUP	GZ
GUP–boric acid	FRW	FZ
Untreated	-	UZ

GUP, and a mixture of GUP and boric acid (Wang et al. 1997; Wang 2000). The GUP–boric acid mixture (FRW) was 70% GUP and 30% boric acid by weight. The treatment groups are designated in Table 1.

The treating conditions were the same for all groups. The wood blocks were placed in a treating cylinder and subjected to a vacuum of 50 kPa for 10 min. After the introduction (in vacuum) of the treating solution, pressure was increased to 0.50 MPa and maintained for 10 min. The cylinder was emptied of solution and a final vacuum of 80 kPa was maintained for 10 min. The blocks were then kiln-dried at 70°C to constant weight. Weight deviations were less than 2% after drying. Final chemical retentions were $3.49 \pm 0.01\%$ for BZ, $7.77 \pm 0.02\%$ for GZ, and $7.48 \pm 0.02\%$ for FZ. The retentions were based on the total weight of the treated wood specimens and determined by calculation from weight gain. The values of these retentions were within the range of linear relations between the chemical retention of treated wood and its fire retardancy. Four specimens were randomly selected for the control group and for each treated group. Three blocks were then randomly designated for the cone test; the remaining block was used for thermal and GC–FTIR analysis.

Samples for cone test

Three blocks from each treatment group and the control group were conditioned at 23°C and 50% relative humidity to constant weight. The conditioned blocks were used as wood samples for the cone test.

Samples for thermal and GC–FTIR analysis

One wood block from each group was ground and sieved separately to supply two batches of wood powder. One batch of powder, approximately 40–60 mesh, was used for thermal analysis. The other batch, approximately 20–40 mesh, was used for GC–FTIR analysis. For comparison in thermal analysis, powdered batches of the three chemicals (boric acid, GUP, and FRW) were also ground to approximately 40–60 mesh. Prior to thermal or GC–FTIR analysis, wood and chemical samples were dried at 50°C to constant weight and stored in a desiccator.

Thermal analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out using a Perkin–Elmer TGA-7 thermogravimetric analyzer and a Perkin–Elmer 1700 differential thermal analyzer, respectively (Perkin–Elmer, Wellesley, MA). The TG and DTA curves were run under a dynamic nitrogen atmosphere flowing at 50 mL/min and at a scanning rate of 10.0°C/min.

GC–FTIR analysis

A 100-mg sample of 20–40 mesh powder was put into the bottom of a thin-walled U-shaped glass tube; one end of the tube was connected by a rubber tube to a high purity nitrogen gas tank, and the other end was bent to a 75° angle. After nitrogen gas was introduced at a flow rate of 30 mL/min for 5 min, the bottom of the tube was put into the heating hole of a heater with a constant temperature of either 300°C or 400°C; the bent end of the tube was inserted into ethyl ether solvent in a test tube and nitrogen gas was conducted continuously. The resulting volatile substance of each wood sample was dissolved in ethyl ether and the ether solution was used for GC–FTIR analysis.

Cone Calorimetry

The cone calorimetric tests (ISO 1993) were performed using a Standon Redcroft (FTT, East Grinstead, UK) cone calorimeter under a heat flux of 50 kW/m^2 corresponding to a temperature of 780°C which is the proper condition at which more information can be obtained (Wang 2000). The wood sample was oriented horizontally. The parameters of combustion were calculated from the basic data of the cone test using Microsoft Excel software.

Results and discussion

Thermogravimetry of fire-retardant chemicals

The results of thermogravimetric analysis are expressed by the TG curves and their derivatives (DTG). The TG and DTG curves of boric acid, GUP, and FRW are shown in Figs. 1, 2, and 3, respectively. By analyzing and comparing Figs. 1, 2, and 3, we noted that the peak number of the TG (and DTG) curve of FRW was equal to the sum of the corresponding peak number of boric acid and

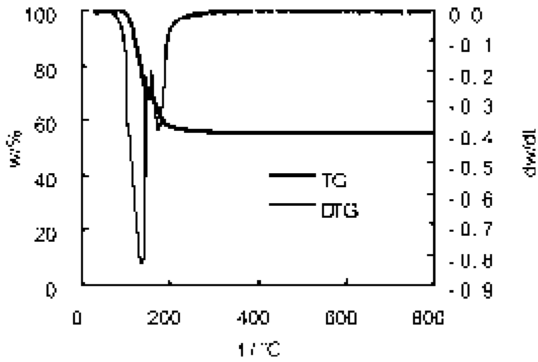


Fig. 1 Thermogravimetric (TG) curves and derivatives (DTG) of boric acid

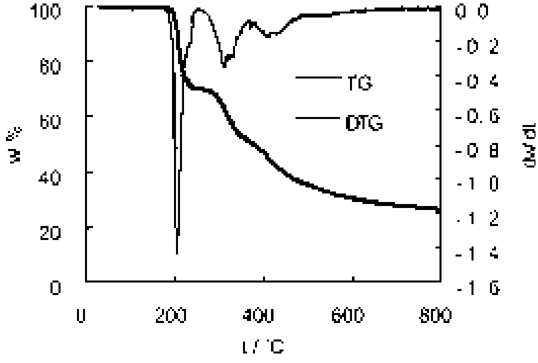


Fig. 2 Thermogravimetric analysis of GUP

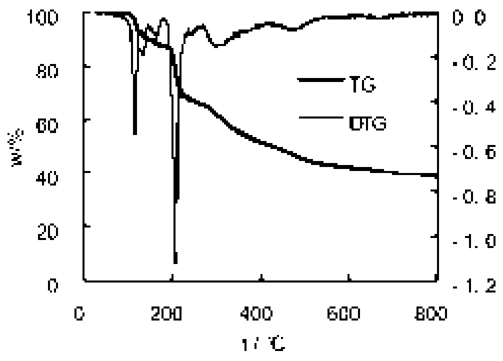


Fig. 3 Thermogravimetric analysis of FRW

GUP. The position (temperature) of the FRW peak was the same as the corresponding peak of boric acid or GUP. In other words, the TG or DTG curve of FRW was the linear combination of the corresponding curves of boric acid and GUP. Because each peak corresponds to a chemical reaction, the “linear combination” indicates that the decomposition of boric acid and GUP in FRW took place independently.

By comparing the measured weight loss with the calculated weight loss of a known decomposition reaction such as the thermal decomposition reaction of boric acid (Myers 1917), the decomposition temperature and products can be derived from the TG and DTG curves. The results are shown in Table 2. The decomposition temperatures in Table 2 are the temperatures at which the chemicals began to visibly decompose. The qualitative analysis of the thermal decomposition products of pure GUP indicated that GUP began to decompose at about 180°C with the gaseous release of NH_3 and CO_2. As the temperature rose to about 380°C, the resultant transparent sticky product was basically polyphosphoric acid.

Thermogravimetry of wood specimens

The TG and DTG curves of untreated (UZ) and treated (BZ, GZ, and FZ) wood samples are shown in Figs. 4, 5, 6, and 7, respectively. Figure 8 compares the TG curves of these samples.

Table 2 FRW products and components at different decomposition temperatures

	FRW decomposition products at various temperatures				
Sample	95°C	160°C	180°C	285°C	385°C
H_3BO_3	HBO_2, H_2O	B_2O_3, H_2O	–	–	–
GUP	–	–	guanidine polyphosphate, NH_3, CO_2	ammonium polyphosphate, $NCNH_2$	polyphosphoric acid, NH_3
FRW	HBO_2, H_2O	B_2O_3, H_2O	guanidine polyphosphate, NH_3, CO_2	ammonium polyphosphate, $NCNH_2$	polyphosphoric acid, NH_3

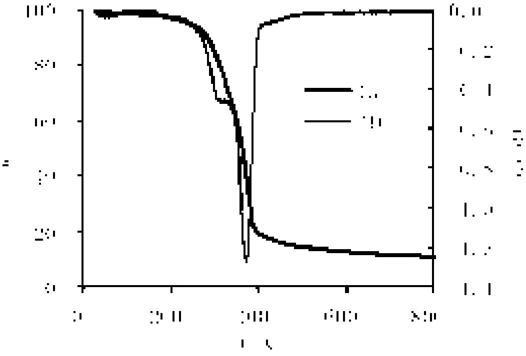


Fig. 4 Thermogravimetric analysis of untreated wood (UZ)

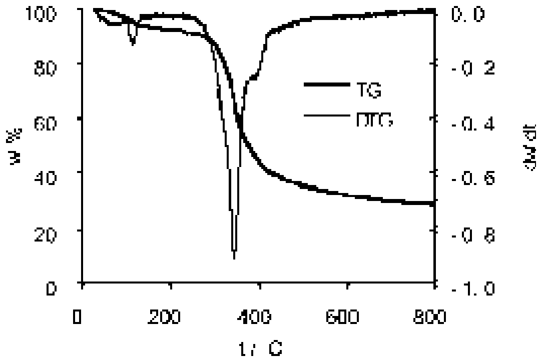


Fig. 5 Thermogravimetric analysis of boric acid treated wood

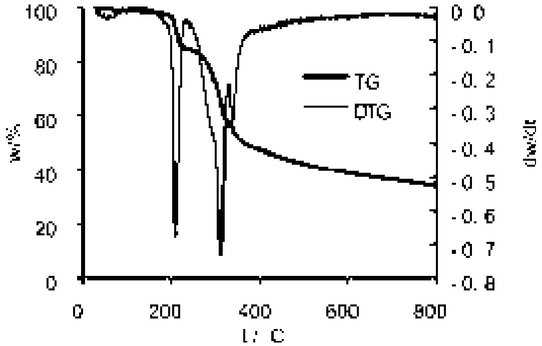


Fig. 6 Thermogravimetric analysis of GZ

Treatment of wood with boric acid, GUP, or FRW resulted in increased weight loss at lower temperatures and decreased weight loss at higher temperatures. The fire-retardant treatments of wood promote charring. To perform a detailed analysis of the influences of the chemicals on wood weight loss, the weight loss ratios of the wood samples at different temperatures were calculated (Table 3). Because the thermal conductivity of wood samples was lower than that of the pure chemical samples, the observational decomposition temperatures of the chemicals in the treated wood were usually 5°C higher than that of the corresponding pure chemicals. Accordingly, we used higher temperatures (plus 5°C) in Table 3 than the corresponding values in Table 2 for our comparison.

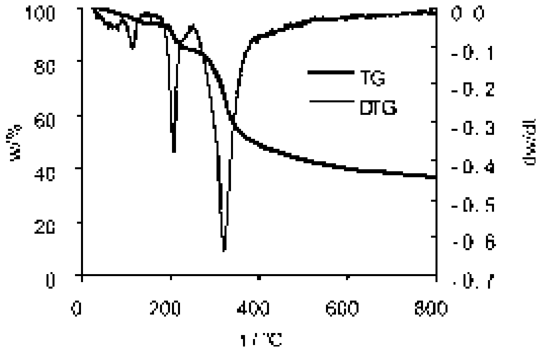


Fig. 7 Thermogravimetric analysis of FZ

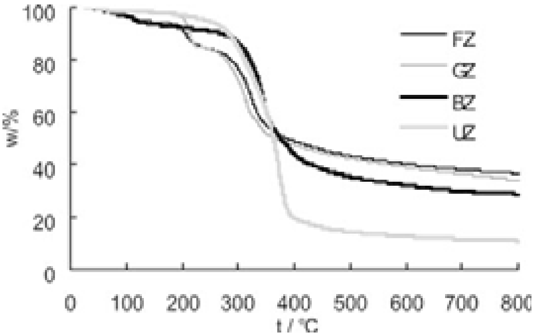


Fig. 8 Comparison of TG curves of UZ, boric acid treatment (BZ), GZ, and FZ

Table 3 indicates that the final weight loss of the wood samples occurred in the following order: UZ > BZ > GZ > FZ; that is, the charring order is FZ > GZ > BZ > UZ. The latter is just the fire retardance order of the corresponding chemicals. However, in the temperature range of approximately 100–180°C, after subtracting the weight loss of boric acid itself, the weight loss of boric acid treated wood (BZ) was substantially higher than that of untreated wood (UZ) and GUP-treated wood (GZ), indicating that boric acid promoted weight loss at lower temperatures. Because BZ wood lost considerably more weight at a temperature lower than 165°C, and because of the known fact that untreated wood loses only its absorbent water and that no significant chemical reactions take place in untreated wood at this low temperature, we can deduce that boric acid catalyzed the dehydration of the wood. Table 3 also shows that the weight loss of GUP-treated wood was similar to that of untreated wood in the temperature range 100–180°C because of the inactive property of GUP at this low temperature.

Table 3 Wood weight loss at different temperatures

	Ratio of weight loss (%) at various temperatures					
Sample	100°C	165°C	185°C	290°C	390°C	800°C
UZ	1.6	2.0	2.4	11.6	77.9	88.9
BZ	3.3	6.8	7.3	11.6	53.6	71.1
GZ	1.6	2.0	2.6	23.5	51.9	65.1
FZ	3.1	5.7	6.2	20.4	50.3	63.3

As shown in Fig. 8, the trends of the FZ, GZ, and BZ curves are different and intercross. The FZ curve is between BZ and GZ at lower temperatures, while the FZ curve is the highest in the higher temperature range. This may help to explain the nature of the synergistic effect of fire retardance between boric acid and GUP (Oberley 1983). Because no chemical reaction takes place between boric acid and GUP, and therefore no new chemicals are formed, the synergistic fire retardant effect arises from the differing fire retardant mechanisms and differing activation temperatures of boric acid and GUP.

Differential thermoanalysis of chemicals and wood specimens

The DTA curves of boric acid, GUP, and FRW are shown in Fig. 9. Figures 10, 11, and 12 compare the effect of treatment compared to the untreated controls.

Figure 9 indicates that the FRW curve is the linear sum of boric acid and GUP. This is consistent with the results of TG analysis. The endothermal peaks of boric acid and GUP in the DTA curves are relevant to the weight loss peaks in the corresponding TG curves. This indicates that some decomposition products of boric acid and GUP are volatile and resulted in gases (H_2O, CO_2, and NH_3) (Table 2).

The DTA curve of BZ has an exothermal peak at 425°C. This peak may be attributed to the catalytic effect of boron oxide on the charring of the polymeric products formed by condensation and polymerization of wood decomposition products. The structure of the charring residual, which is mainly charcoal, is aromatic, while that of its precursor substance is aliphatic. Therefore, the eventual aromatic structure must have resulted from the structural change from an aliphatic to an aromatic structure. This structural change is exothermal and can be catalyzed by Lewis acid at high temperature. There is a similar exothermal peak in the DTA curve of the FRW-treated wood, but at lower temperature. This phenomenon may be due to the co-catalysis of polyphosphoric acid (proton acid) and boron oxide (Lewis acid).

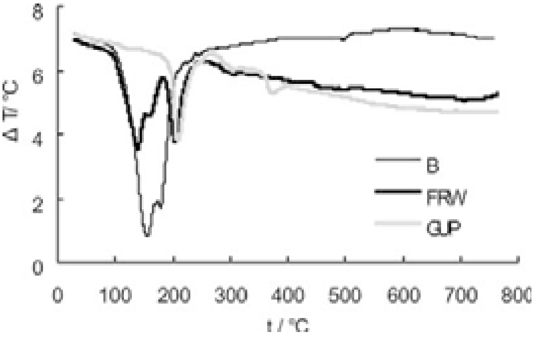


Fig. 9 Differential thermal analysis (DTA) of boric acid (B), GUP, and FRW

Fig. 10 DTA of boric acid (B), boric acid treated wood (BZ), and untreated wood

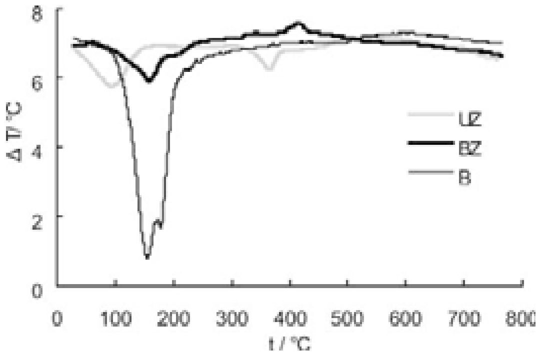


Fig. 11 DTA of GUP, GZ, and UZ

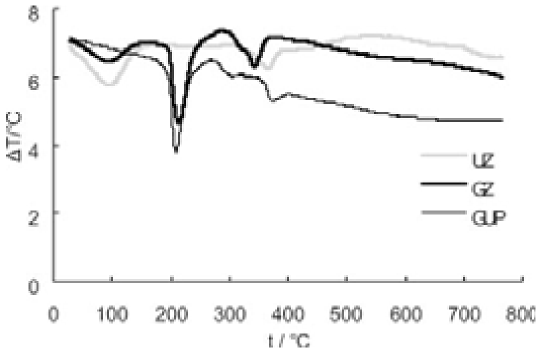
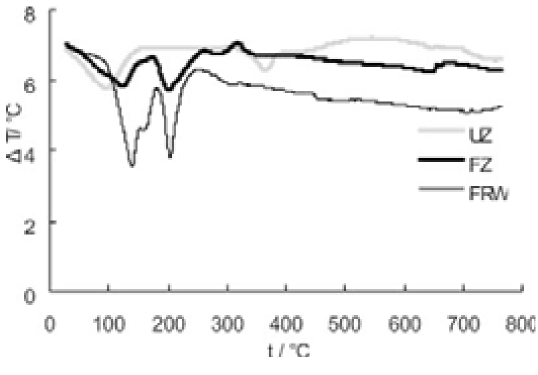


Fig. 12 DTA of FRW, FZ, and UZ



Cone calorimetry

The rates of heat release (RHR) for UZ, BZ, GZ, and FZ are shown in Fig. 13. Table 4 shows the peak RHR (pkRHR) values of the wood samples (earlier values = $pkRHR_1$, later values = $pkRHR_2$) and the percentage of difference for the corresponding peak RHR values (earlier values = $\triangle_1$, later values = $\triangle_2$) between treated and untreated specimens (i.e., untreated minus treated).

The fire retardant efficiency of FRW was much better than that of boric acid and GUP, as shown by the lower $pkRHR_1$ and $pkRHR_2$ values (Fig. 13 and Table 4). If we were to suppose that boric acid and GUP had additive fire retardant effects (i.e., boric acid or GUP had the same fire retardant effects when used separately or as a mixture), then the Δ value could be calculated from pkRHR and the chemical retention of the wood samples. The results are $\Delta_1(FZ) = 29.9\%$ and $\Delta_2(FZ) = 46.6\%$. The calculated Δ values of FRW are considerably lower than the determined experimental values (52% and 58%, respectively). Thus, it is clear that boric acid and GUP are not additive but synergistic in their effect on wood. Since the fire performance is linear with retention over the tested range of retention (Oberley 1983), the Δ values can be calculated as follows:

$$\begin{aligned}\Delta_1(\text{FZ,calculated}) &= [\Delta_1\text{BZ}(7.48\times30\%)/3.49 + \Delta_1\text{GZ}(7.48\times70\%)/7.77]\%\\ &= [15(7.48\times30\%)/3.49 + 30(7.48\times70\%)/7.77]\%\\ &= 29.9\%\end{aligned}$$

$$\begin{aligned}\Delta_2(\text{FZ,calculated}) &= [\Delta_2\text{BZ}(7.48\times30\%)/3.49 + \Delta_2\text{GZ}(7.48\times70\%)/7.77]\%\\ &= [25(7.48\times30\%)/3.49 + 45(7.48\times70\%)/7.77]\%\\ &= 46.4\%\end{aligned}$$

Carbon dioxide yield (Y_{CO2}) is shown in Figure 14. Y_{CO2} is the combustion parameter indicating the carbon dioxide yield per weight loss of wood sample. All treated woods, including wood treated with boric acid (BZ), had lower carbon dioxide yields during the flaming period of combustion. This indicates that both boric acid and GUP catalyzed dehydration and other oxygen-eliminating reactions of wood; these kinds of reactions release products that contain more oxygen and therefore result in lower heat of combustion.

Table 5 compares the determined CO_2 yields of untreated and treated basswood during the flaming period with the calculated values of CO_2 yields of related chemical reactions. During the flaming period, the CO_2 yields of all

Fig. 13 Rate of heat release (RHR) of UZ, BZ, GZ, and FZ

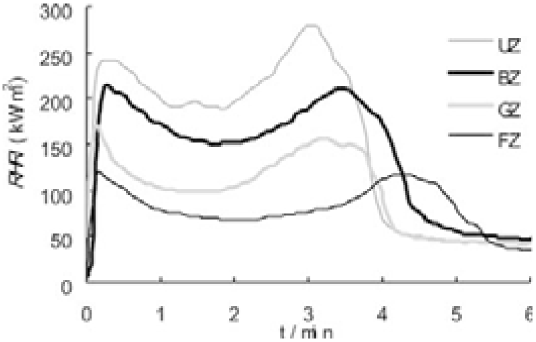


Table 4 Peak RHR (pkRHR) values of treated wood samples and difference from corresponding RHR values of untreated samples

Item	UZ	BZ	GZ	FZ
$pkRHR_1$ (kW/m^2)	242	206	169	116
$\triangle_1$ (%)	0	15	30	52
$pkRHR_2$ (kW/m^2)	279	209	153	117
$\triangle_2$ (%)	0	25	45	58

combustion samples were lower than those of the theoretical (calculated) CO_2 yields of polysaccharide, and therefore must be much lower than those of the CO_2 yields of lignin (expected to be 1.38 to 3.67; see Table 5). Wood treated with boric acid produced less carbon dioxide than did untreated wood; wood treated with GUP or FRW (fire retardants that are also dehydration catalysts) gave much less carbon dioxide. This indicates that dehydration takes place in the combustion of woods, including wood treated with boric acid, during the flaming period. Boric acid apparently catalyzes the dehydration of wood.

GC–FTIR analysis

GC spectra of wood specimens—For comparison, the GC spectra of the volatile substance of BZ and UZ pyrolysis under 300°C and 400°C are shown in Fig. 15. The peak at 17.7 min belongs to the fatty acid extract of basswood. By using this extract peak as internal standard (i.e., this peak has the same height for different specimens), we can compare the intensity (relative amount of the compound) of other peaks. There was a remarkable difference between BZ and UZ, especially at the lower temperature (300°C). Under the lower pyrolysis temperature, BZ produced a more volatile substance, indicating that boric acid

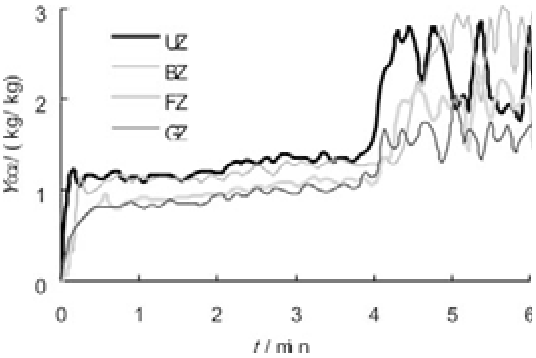


Fig. 14 Carbon dioxide yield (Y_{CO2}) of UZ, BZ, GZ, and FZ

Table 5 Basswood CO_2 yields during flaming and calculated CO_2 yields of typical oxidation reactions

Combustion time (min)	Y_{CO2} (kg/kg$_{wood}$)			
	UZ	BZ	GZ	FZ
0	0		0	0
0.06	0.96	0.33	0.34	0.08
0.50	1.13	1.05	0.80	0.84
1.00	1.15	1.12	0.84	0.90
2.00	1.18	1.11	0.95	0.93
3.50	1.32	1.31	1.01	1.10

Calculation of CO_2 yields typical oxidation reactions:

C → charcoal → CO_2 $Y_{CO2} = 44/12 = 3.67$

CHOH → degradation of polysaccharide → CO_2 $Y_{CO2} = 44/32 = 1.38$

Wood - OH → dehydration → H_2O $Y_{CO2} = 0$

catalyzed the decomposition of wood. Under higher temperature, wood underwent thermochemical reactions more easily and the products of pyrolysis from boric acid treated wood and untreated wood were more similar.

The GC spectra for FZ and GZ, which were tested at the same conditions as those for BZ, were different from each other and different from BZ and UZ. This indicated that boric acid influenced the pyrolysis of wood in a different way than did GUP.

GC–FTIR spectra of wood specimens—For BZ wood, under pyrolysis temperatures of 300°C and 400°C, the corresponding peaks of GC spectra (with the same retention time) had similar FTIR spectra. For example, the FTIR spectra of the 6.4-min peak at 300°C and the 6.5-min peak at 400°C for the BZ specimen are the same as those shown in Fig. 16. This experiment was repeated three times and the results were the same. The compound species of pyrolysis products are expected to be the same for BZ wood under different pyrolysis temperatures in the range from 300°C to 400°C. It is therefore adequate to analyze just one GC–FTIR spectrum of BZ wood.

Some spectra of the pyrolysis products of BZ basswood at pyrolysis temperature of 300°C are shown in Fig. 17. Most of these spectra belong to aliphatic carbonyl compounds, the dehydration and further reaction products of polysaccharide. Of the three main wood components, cellulose and especially hemicellulose are more susceptible to dehydration and pyrolysis at lower temperatures than lignin. Acids, such as the decomposition products of GUP and other phosphorus compounds, catalyze dehydration and may influence the direction of pyrolysis of the polysaccharides. Though boric acid is a weak acid, it has the ability to react with cis-1,2-diols (e.g., the mannose segment in hemicellulose) at a lower temperature (Fig. 18) (Böeseken and

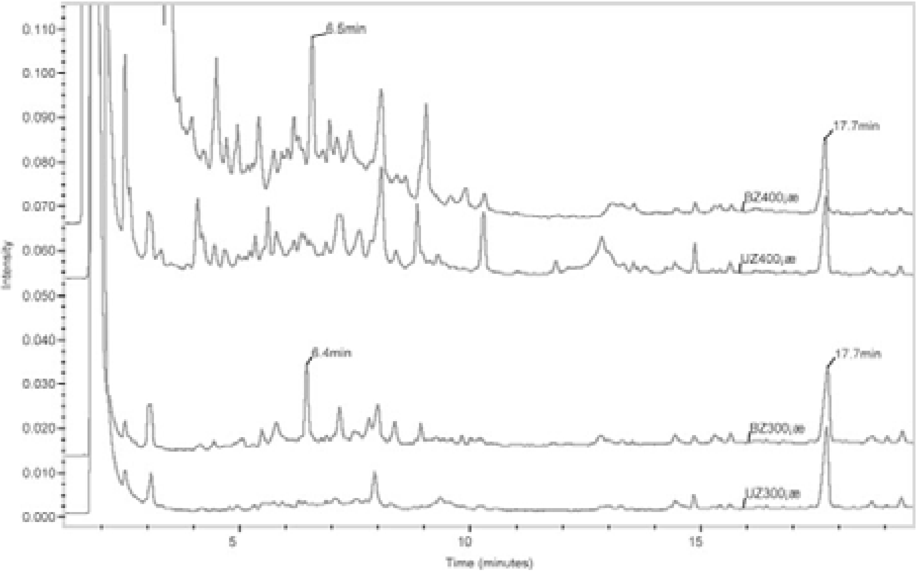


Fig. 15 Comparison of GC spectra of volatile substance of BZ and UZ pyrolysis at 300°C and 400°C

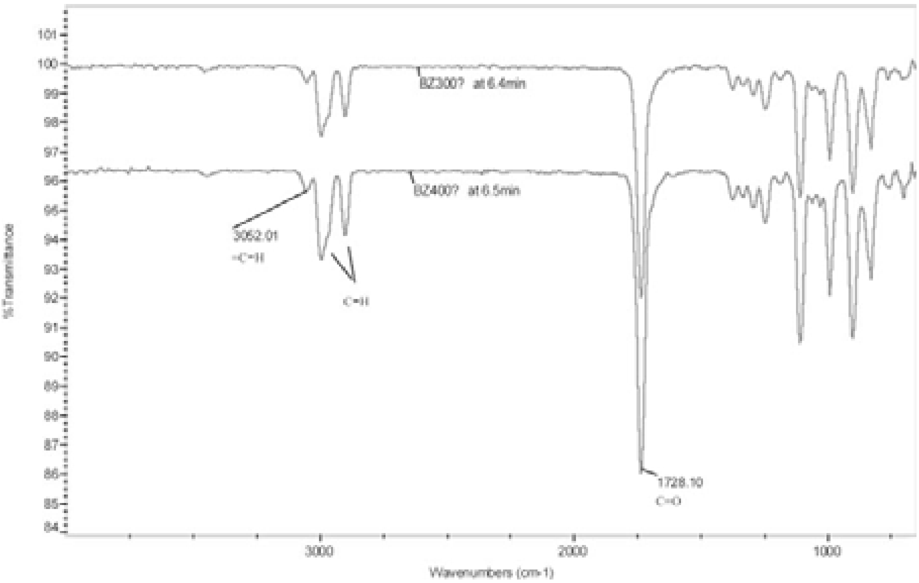


Fig. 16 Typical spectra of BZ pyrolysis product with 6.4-min retention time at different pyrolysis temperatures

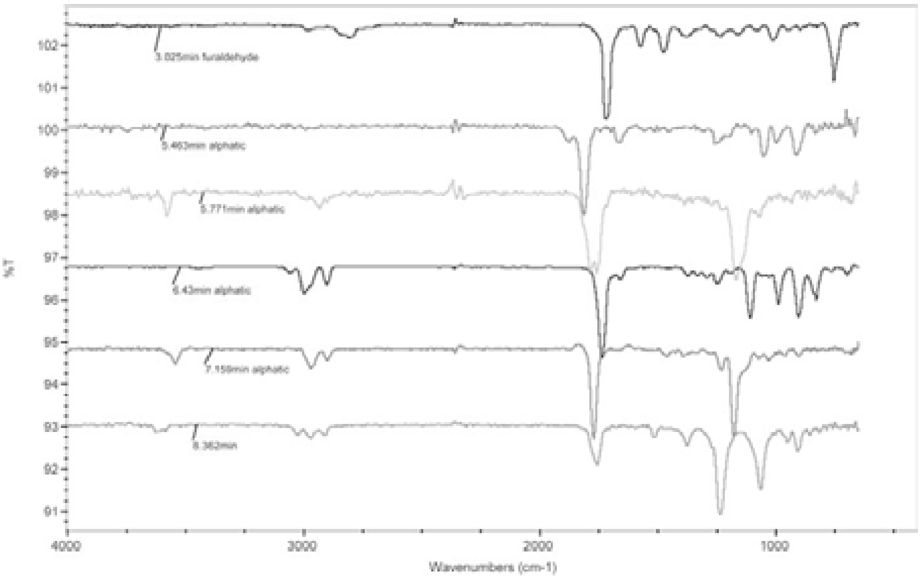


Fig. 17 GC-FTIR spectra of BZ pryolysis products at 300°C

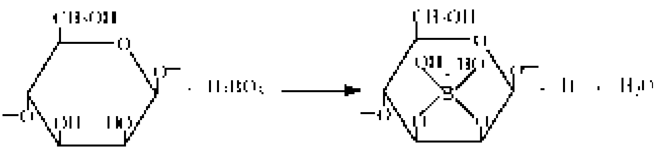


Fig. 18 Reaction of boric acid with polysaccharide (mannose segment)

Vermaas 1931). The resulting product, boric acid–polysaccharide complex (Matsumoto et al. 1999), is a stronger acid (Mukherjee and Ansuman 2002) and may act as an acid catalyst.

Conclusions

Boric acid catalyzes the dehydration and other oxygen-eliminating reactions of wood at a relatively low temperature (100–300°C). It may catalyze the isomerization of the newly formed polymeric materials to form aromatic structures. This contributes partly to the effects of boric acid for promoting charring and fire retardation of wood. The mechanism of the strong fire retardant synergism between boric acid and GUP is due to both the different fire retardant mechanisms of boric acid and GUP and the different activation temperatures of these chemicals.

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