

# THERMAL DEGRADATION OF ORIENTAL BEECH WOOD IMPREGNATED WITH DIFFERENT INORGANIC SALTS

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## ABSTRACT

This study investigated the thermal properties of Oriental beech (*Fagus orientalis*) treated with  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{SO}_4$  salts and their mixtures (1:1; w/w) aqueous solutions at 3% concentrations. The effects of different inorganic salts fire retardants on the thermal degradation characteristics of wood samples were evaluated by thermogravimetric analysis (TGA). Based on the TGA curve for untreated beech wood, weight loss takes place at three distinct steps. The impregnation of inorganic salts resulted in higher char yields and additional thermal degradation steps were identified. The highest char yield (80%) was obtained from  $(\text{NH}_4)_2\text{HPO}_4$ - $\text{K}_2\text{HPO}_4$  mixture impregnated sample. Salt mixtures containing phosphates ( $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{K}_2\text{HPO}_4$ ) have remarkable effects on thermal stability of beech wood, whereas  $\text{NH}_4\text{Cl}$  salt lowered the decomposition temperatures and char yield.

**Keywords:** *Fagus orientalis*, thermal stability, thermogravimetric analysis, wood impregnation, wood protection.

## INTRODUCTION

Flame retardancy property of products had become mandatory for public security, especially in public transportation, aircraft and automobile parts, buildings, housing and even in baby blankets (Ohashi *et al.* 2017, Salman *et al.* 2014). Wood is an easily flammable material and its thermal stability can be improved by different techniques. The wood components (hemicellulose, cellulose and lignin) start to degrade when wood is subjected to heat. At around 200°C, acetic acid is released from hemicelluloses by hydrolysis and this acid acts as a catalyst for cleavage of cellulose chains. At lower temperatures, volatile compounds are generated from hemicellulose and cellulose carbohydrates. When the temperatures reach high levels, the levoglucosan is formed, which can be further decomposed into volatile and flammable products and lignin starts to decompose (Kartal *et al.* 2007). Flame retardant/wood preservative systems may be impregnated into wood by non-pressure dipping, diffusion and vacuum or pressure processes (Thevenon *et al.* 2009).

Impregnation is an economic and easy wood treatment technique in flame retardancy. Phosphoric acid, ammonium polyphosphate, ammonium sulfate, boric acid, borax and zinc borate are commonly used flame retardants (Ayrlmis 2007). Chemicals with acidic character like inorganic phosphates, increase the degradation rate of wood at lower temperatures, which causes the higher char yield. Roth *et al.* (2007) explained also flame retardant mechanism of ammonium polyphosphate (APP). It can both change the pyrolysis reactions and diminish the degradation temperatures (Roth *et al.* 2007). Boric acid, borax and their mixture were used with APP as a synergist for environmentally friendly and halogen-free flame retardants (FR) in wood-high density poly(ethylene) composites (Kurt *et al.* 2012). The same formulations were also used in the manufacture of wood polymer composites with polypropylene. APP and boron compounds retard flame by producing carbona-

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ceous foam which protects the material from temperature rise (Kurt and Mengeloglu 2011). Boron compounds, such as disodium octaborate tetrahydrate (DOT), boric acid and borax are odourless, colourless, non-corrosive, cheap and non-toxic chemicals (Mohareb *et al.* 2011). However, the leaching of boron compounds from wood has been one of the significant problems for over years. (Obanda *et al.* 2008). Different FR chemicals showed various degradation mechanisms. For example, both the phosphorus and nitrogen containing FR chemicals, the initial reaction is dephosphorylation by releasing acids resulting in enhanced dehydration. Hence, second stage occurs at lower temperatures and forms char. For nitrogen and halogens based FR, the halogen free radicals scavenge the other radicals and inhibit the formation of volatiles and so, retard the weight loss (Gao *et al.* 2006).

In this study, different phosphate, sulfate and chloride salts and their mixtures were impregnated into Oriental beech wood samples. The thermal degradation temperatures and char yields of different inorganic salts impregnated wood samples were determined by thermogravimetric analysis (TGA). Simply, TGA is a thermal characterization method in which the mass loss of sample is measured as a function of temperature.

## MATERIALS AND METHODS

### Materials

Wood samples obtained from sapwood of Oriental beech (*Fagus orientalis* L.) timber free of knots and excessive cross-grain was machined into narrow strips. The strips were carefully chosen for having the same annual ring and then cut into small pieces prior to milling. Wood flour was prepared by grinding the small wood pieces in a Wiley mill to pass a 50 mesh screens. Before treatment of ground particles, the samples were stored at 65% relative humidity and 20°C for two weeks. Diammonium hydrogen phosphate,  $(\text{NH}_4)_2\text{HPO}_4$ , (ACS Reagent, Merck), dipotassium hydrogen phosphate,  $\text{K}_2\text{HPO}_4$  (98%, Sigma Aldrich), ammonium chloride,  $\text{NH}_4\text{Cl}$ , (99,5% Sigma) and ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , (99%, Sigma Aldrich) were used without further purification.

### Impregnation method

Aqueous solutions of the wood preservatives having concentration of 3 % were prepared using distilled water for the impregnation procedure. The wood flour approximately 100 g was immersed in the solutions at 60°C for 2 h. The treated wood specimens were subsequently dried at 60°C until they had the unchangeable weight. The impregnation procedure of wood flour and wood specimens was similar as described by Jiang *et al.* (2010) and Yunchu *et al.* (2000). Then, wood specimens were moisture conditioned for two weeks at 20°C and 65% relative humidity.

### Thermal analysis

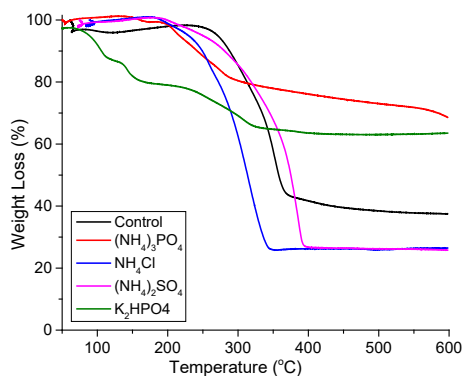
Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were performed under nitrogen atmosphere with heating rate of 10°C/min and a purge rate of 50 mL/min (Argon) using a LABSYS TG-DTA analyzer between room temperature to 600°C. For each individual experiment, 10 mg of sample was analyzed, and the weight loss of the sample was recorded continuously. Derivative TG (DTG) curves were obtained from TG curve as a function of time.

## RESULTS AND DISCUSSION

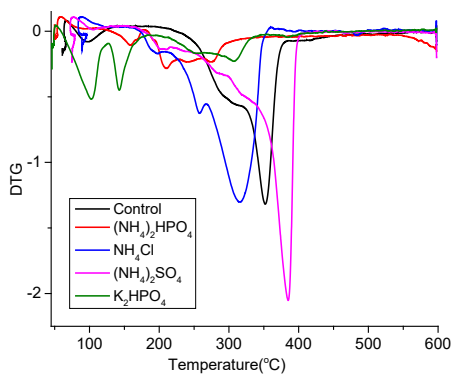
As highly combustible materials, wood and wood products have been treated with different chemicals in order to provide fire retardant properties. Various approaches have been used to make wood more resistant to fire such as chemical modification of wood, in situ deposition of polymers and the impregnation of insoluble inorganic compounds into wood. (Marney and Russell 2008) Among these techniques, the impregnation of different phosphate, sulphate, amine, amide and boron compounds is the most common, fast, economic and effective method (Keskin *et al.* 2009). Attempts have been made to formulate more environmentally friendly

chemicals against thermal degradation and fire retardancy.

The thermal stabilities and decomposition temperatures of treated and untreated beech wood (control) samples were investigated and their TGA/DTG thermograms were given in Figure 1 and Figure 2. The TGA data for all samples was also tabulated in Table 1.



**Figure 1:** TGA curves for beech wood and treated beech wood with different inorganic salts.



**Figure 2:** DTG curves for untreated and treated beech wood samples.

According to TGA thermogram of untreated beech wood, the weight loss takes place at three distinct steps with a maximum rate of weight loss at 351°C. The first loss of weight at 97°C is due to the evaporation of adsorbed water and dehydration of untreated wood sample. The onset of peak at around 200°C shows the starting point of decomposition of wood. Typically, wood has a larger shoulder region due to degradation of hemicelluloses before the degradation of cellulose (Beall and Eickner 1970, Jeske *et al.* 2012). Hemicellulose has an amorphous structure and degradation extends through the peak at 300°C (Figure 2). Then, the sharp decrease in weight can be seen at 351°C due to the splitting of cellulose macromolecules. At temperatures above 351°C, degradation of lignin starts and the residue consists primarily of charcoal from lignin decomposition (Slopiecka *et al.* 2011).

**Table 1:** TGA data of all treated samples and untreated beech wood.

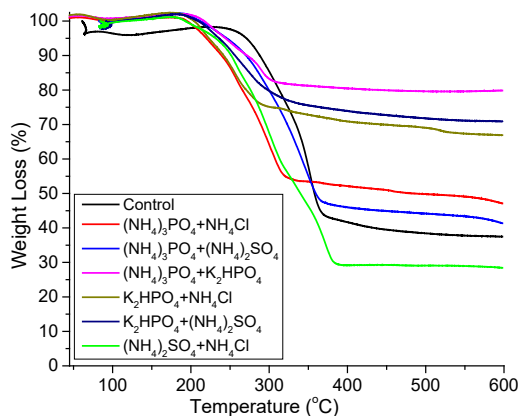
Sample	T <sub>i</sub> (°C)	T <sub>main</sub> (°C)	% Char yield
Control	291	351	38
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> *	211	275	69
(NH <sub>4</sub> )Cl	257	316	27
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	283	384	26
K <sub>2</sub> HPO <sub>4</sub>	256	306	64
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> +(NH <sub>4</sub> )Cl**	258	300	47
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> +(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	292	345	41
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> + K <sub>2</sub> HPO <sub>4</sub>	253	290	80
K <sub>2</sub> HPO <sub>4</sub> +(NH <sub>4</sub> )Cl	256	323	67
K <sub>2</sub> HPO <sub>4</sub> +(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	254	273	71
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> +NH <sub>4</sub> Cl	259	300	29

\*For one type salt, the aqueous solution salt concentration is 3% (w/w)

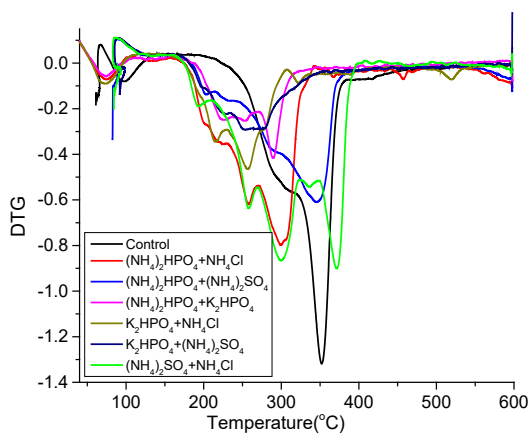
\*\*For two types of salts, the total salt concentration is 3%, e.g. 1,5% (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>+1,5%(NH<sub>4</sub>)Cl (w/w)

TGA of inorganic salt impregnated wood samples revealed that degradation took place between 200°C and 400°C. The % char yield is the solid residual mass percent at 600°C. For all treatments, the main peaks migrate to the lower temperatures, especially for hemicellulose degradation. For NH<sub>4</sub>Cl and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> salts the hemicellulose was degraded at 197°C and 206°C, respectively. Also, NH<sub>4</sub>Cl and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> salts treated samples showed less % char than that of untreated (control) sample. Similar observations were reported for ammonium sulfamate and NH<sub>4</sub>Cl treated wood samples. These salts can sublime completely below 400°C and especially for NH<sub>4</sub>Cl, the structural change (from  $\alpha$  to  $\beta$  form) takes place at 184°C (Browne and Tang 1962). Wood treated with one of the ammonium salts began to pyrolyze at much lower temperatures and was much more extensively volatilized than untreated wood at 250°C. Browne and Tang (1963) also explained this increased volatilization by effects of ammonium salts. All of the ammonium salts are possible sources of ammonia. For the phosphate salts (e.g. (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and K<sub>2</sub>HPO<sub>4</sub>) initial decomposition products appeared as a new peaks at 159°C and 143°C, respectively. Hence, the impregnation of inorganic salts changed the TGA curves and main decomposition temperatures were lowered (Table 1). This diminishment can be attributed to the filler effect. The inorganic salts were doped into the wood and they reduce the intermolecular interactions between the macromolecules of wood (hemicellulose and cellulose chains). The effect of inorganic salts on thermal behavior of wood samples was also explained by Müller-Hagedorn *et al.* (2003). Only (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-treated beech wood samples showed a bit higher T<sub>main</sub>=384°C degradation temperature (Table 1), but its char yield was lower than that of untreated wood sample. Elyounssi *et al.* (2012), declared that the peaks temperatures corresponds to cellulose and hemicellulose are both shifted and lowered in intensity. The main reason is that the decreasing the crystallinity. Hence, the chemicals added to wood reduce the interactions between the chains and the crystallinity. The highest % char yields were obtained from (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and K<sub>2</sub>HPO<sub>4</sub>-treated samples and phosphate containing salts had a char-forming catalytic effect on wood protection against fire. However, NH<sub>4</sub>Cl-impregnated wood lost more than 73% of its initial weight and NH<sub>4</sub>Cl salt is not effective in char formation (Table 1).

Mixtures of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub>, NH<sub>4</sub>Cl and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> salts (1:1; w/w) aqueous solutions at 3 % (w/w) concentration were prepared and then impregnated into wood samples. TGA and DTG thermograms of control and different salt mixtures impregnated samples were presented in Figure 3 and Figure 4, respectively. The chemical structures and physical properties of used salts are different and these variations can result in different fire protection mechanisms in wood. The general mechanism is to cool the flame (with the releasing of water) or to cause a lack of oxygen by releasing nitrogen / halogen or to inhibit oxygen diffusion by forming a carbonaceous protective layer on the burning wood (Roth *et al.* 2007, Su *et al.* 1998). Flame retardants can also act as diluent for combustible gases or reduce the pyrolysis temperature and form more char (Tomak *et al.* 2012).



**Figure 3:** TGA curves for beech wood and treated samples with different salt mixtures.



**Figure 4:** DTG curves for untreated and treated beech wood samples with salt mixtures.

Different mixtures impregnated wood samples degraded between 165-400°C (Figure 3). The formulation of  $(\text{NH}_4)_2\text{HPO}_4\text{-NH}_4\text{Cl}$  mixture reduce the initial ( $T_i$ ) and main ( $T_{\text{main}}$ ) degradation temperatures (258°C and 300°C) and also the weight of residue from this formulation was lower than the others. Similar result was obtained from  $(\text{NH}_4)_2\text{SO}_4\text{-NH}_4\text{Cl}$  mixture and both degradation temperatures (259°C and 300°C) and char yield (29%) were decreased. There was a new peak appeared in DTG curve at around 371°C corresponds to the decomposition of lignin parts of wood. Besides, with the addition of phosphate salts ( $(\text{NH}_4)_2\text{HPO}_4$  or  $\text{K}_2\text{HPO}_4$ ) into the formulation, the char yields were increased regardless of the type of phosphates (Table 1). The reason for this increment is the higher amount of carbonization reactions between phosphate and lignin. The highest char yield can be observed for  $(\text{NH}_4)_2\text{HPO}_4\text{-K}_2\text{HPO}_4$  mixture impregnation (80%). Again, the main wood degradation peaks were shifted to the lower temperatures due to the filler effect. Same phenomena was observed for the inorganic filler added poly(lactic acid) and the crystallinity and degradation temperatures decreased (Liu *et al.* 2014). Hence, the  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{K}_2\text{HPO}_4$  salts were found to be successful inorganic salts in fire retardancy. It seems to have been widely accepted that effective flame retardants lower the onset temperature of decomposition, lower the amount of volatile combustibles and promote the char formation (Yorulmaz 2006, Stimely and Blankenhorn 1985). At above 300°C cellulose depolymerization is very fast and anhydro-sugars,

randomly linked oligosaccharides and levoglucosan are formed (Shafizadeh 1982). Collard and Blin explained the char as an aromatic polycyclic structure. Intra- and intermolecular rearrangements lead to higher cross-linking and thermal stability of the residue (Collard and Blin 2014). Consequently, there is a potential synergy between the  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{K}_2\text{HPO}_4$  salts which resulted in increasing in char yield due to the interactions between the lignin derived product and promoting residue from cellulose and hemicellulose. Furthermore, the other combinations which were used in this study achieved a reasonable degree of fire retardancy.

## CONCLUSIONS

Formulation of environmentally friendly flame retardants for wood protection against fire is a very complex and challenging issue for researchers. Four different phosphate, sulphate and chloride containing salts and their mixtures were impregnated into the Oriental beech wood in this work. The thermal behaviors of impregnated wood samples were evaluated by TGA. The Oriental beech untreated wood started to degrade at around 200°C with a maximum at 291°C for hemicellulose and then continued to degradation of cellulose component at 350°C. The incorporation of inorganic salt changed the degradation mechanisms of woods by adding more steps and lowered the peak temperatures. The  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{K}_2\text{HPO}_4$  salts increased the char yield from 38% (control) to 69% and 64%, respectively. Their 1:1 (w/w %) mixture, improved the thermal stability of wood. Phosphates salts containing formulation showed the best performance in % char yield (80%) due to the higher amount of carbonization reactions between phosphate and lignin. However,  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{SO}_4$  salts did not contribute to achieve higher thermal stability of wood. Also, they created a significant reduction in char yield when compared with untreated wood.

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