

RESISTANCE OF SPRUCE WOOD (*Picea abies* L.) TREATED WITH A FLAME RETARDANTS AFTER THE RADIANT HEAT EXPOSURE

Iveta Čabalová – Martin Zachar – Michal Bélik – Žaneta Balážová

ABSTRACT

The aim of the paper was to determine the resistance of spruce wood (*Picea abies* L.) treated with a flame retardant after exposure to radiant heating. The treatment was performed with a typical flame retardant HR prof and an aluminium coating used to protect metal objects at high temperatures – Striebrenka, an atypical retardant not commonly used in wood protection. The samples treated with retardants as well as untreated (control) ones were heat-loaded by radiant heating using a radiation panel for 30 min. Changes in the basic chemical composition, especially the content of extractive substances, holocellulose, cellulose, hemicelluloses and lignin in two layers removed below the charred layer (layer 1 - thickness up to 20 mm. and layer 2 - thickness from 20 to 40 mm) and thickness of the charred layer were evaluated. During the thermal loading of the control sample, we observed the temperature of 300°C in time of 860 seconds on thermocouples (M 1.0). The average thickness of the charred layer was 15.41 mm. The limit temperature of 300°C was not reached on any thermocouple (M 2.0 – M 5.0) in all samples. The average thickness of the charred layer of the sample treated with HR prof was 14.9 mm and with Striebrenka 15.18 mm. Following the results, it can be stated that the chemical composition of the timber was changed as a result of the chemical treatment of wood by radiant heating. However, the largest changes were recorded in the sample not coated with any retardants at all. A decrease in the saccharides component of wood, especially hemicelluloses (from 13.57 to 20.25%) was observed in the case of this sample. When comparing the chemical changes of samples treated with flame retardants, it can be seen that the HR prof retarder was more effective in terms of saccharides and the Striebrenka retardant in terms of lignin protection. In contrast, during the thermal degradation of treated samples, a decrease in lignin (from 7.66 to 8.10%, HR prof retardant) and holocellulose (from 5.83 to 8.3%, Striebrenka retardant) content compared to the original sample was observed.

Key words: spruce wood, radiant heating, flame retardant, extractives, lignin, cellulose, hemicelluloses.

INTRODUCTION

Due to the properties of spruce wood and its availability, it is widely employed tree species in constructions (e.g. solid timber floors, windows, doors, furniture, toys, telegraph and other poles, structural material for trusses and ceilings). It is one of most often-used tree species in Slovakia represented by 22.5 % (ZELENÁ SPRÁVA 2019). However, the wood is a

combustible material and the process of its heat treatment results in degradation. Degree of degradation depends on time and type of heat loading (OČKAJOVÁ *et al.* 2020). Flame retardants or protective coatings improving its fire resistance are used to protect the wood. The nature of these products is chemical or physical. When applying to wood, stability of heat treated wood increases significantly. There are chemical and physical flame retardants, however, the difference is evident. While chemical flame retardants are focused on reducing the flame spread covering the material with a foam or producing the inert gasses into the fire, the physical retardants are able to absorb or to deflect heat released by fire. The fact that physical retardants are especially produced of solid material covering wood, thus the microclimate resulted in biodegradation of material is not created can be considered a disadvantage (ZAIKOV, LOMAKIN 2002).

During the process of heat treatment, firstly, the wood is dried, i.e. the redundant moisture evaporates, later, the significant chemical changes occur (KAČÍKOVÁ *et al.* 2013, KUČEROVÁ *et al.* 2016, KAČÍK *et al.* 2017, GAŠPARÍK *et al.* 2018, LUPTÁKOVÁ *et al.* 2018, GAFF *et al.* 2019a, b). At a temperature higher than 250°C, carbonization process starts and CO₂ and other pyrolysis products are emitted.

When the temperature is increasing, the main chemical components of wood, especially cellulose and hemicelluloses are affected by pyrolysis and oxidation reactions and inflammable gases are products resulting from their decomposition.

Polysaccharides are substances supporting combustion most. During the thermochemical reactions, lignin, which is thermally more stable, contributes to coal formation, in a similar way to hemicelluloses or cellulose (NUOPPONEN *et al.* 2005). Flammable gasses formation useful in protecting wood from thermochemical reactions is stopped when the product formation such as coal increases. Moreover, the development of the reactions is slowed. In our other paper we followed the thermal loading of untreated spruce wood by radiant heating and the results show the both lignin and extractives content increased in light and dark brown layer but extractive content in charred layer decreased. Cellulose content (determined by Seifert method) in each layer increased because of its carbonization and crosslinking but total content of saccharides dropped, the most in the charred layer. The strength of spruce wood is decreased by thermal loading and cellulose depolymerisation (ČABALOVÁ *et al.* 2013). A large part of lignin is resistant to the effect of thermal exposure. Its degradation starts at lower temperature, similar to polysaccharides, but the carbonization results in a product resistant to the heat and flammable only with difficulty. During slow heating and at the presence of atmospheric pressure, there are conditions suitable for condensation reactions. The amount of volatile products is relatively low in comparison to the extract of solid component, coal. Phenols are the most important products forming during the thermolysis. Radicals with different structures and stability result from the application of heat. Various degradation and condensation reactions are joined (BREBU, VASILE 2010). At the temperatures ranging between 100–180°C, plasticisation happens (NUOPPONEN *et al.* 2003, KAČÍKOVÁ *et al.* 2008).

The phase of stabilized combustion occurs after forming the charred layer on the exposed surface of samples. Heat release stays almost constant. It is followed by the phase of burning the overheated sample described with substantial pyrolysis through the whole sample (RANTUCH *et al.* 2015).

The depth of charred area and the speed of carbonization is one of the most important fire properties of wood and wood products. The standard (Eurocode 5) is used to analyse the depth of charred area, which is considered the most reliable figure in terms of assessing the flame spread. In accordance with the standard STN EN 1995-1-2 (2004), the depth of charred area is defined as a distance between the outer surface of the original element and the position of the line between the charred layer and the rest of the cross-section. The line of the charred

layer of timber construction is specified in the standard as the place with a temperature of 300°C. As it is mentioned by FONSECA and BARREIRA (2009), the charred layer is the dividing line between thermally degraded and non-degraded wood bounded by a black and a brown wood layer and it is characterised by a temperature of 300°C. According to the statement of WHITE and NORDHEIM (1992), the charred layer corresponds to the temperature of 288°C. FINDORÁK *et al.* (2016) agree with the mentioned statement, i.e. rapid thermal decomposition of wood (in the case of short-term exposure) starts just below the temperature of 300°C.

The aim of the paper was to observe the effectiveness of two flame retardants, first standard flame retardant based on the chemical principles and the second atypical following the physical principals, used for the protection of thermal loaded spruce wood.

MATERIAL AND METHODS

Samples

Four samples of spruce wood (*Picea abies* L. Karst.) (harvested in the east part of Slovakia in Dobšiná, trunk diameter approximately of 35 cm, age of 85 years) were cut into the shapes of blocks with the dimensions of 150 × 150 × 1,000 mm (thickness × width × length). The wood surface was treated by 80 grit sandpaper.

The retardant was applied by painting to the air-dry wood (moisture of 8 %) in two coats in a time interval at least of 40–60 minutes. The overall coating thickness was 300 g/m² in line with the instructions of producer, which is our case 81 g of retardant per sample. The weight of applied retardant was less than 1% of the weight of the test sample.

Flame retardants used

HR prof

It is a fire protection paint restricting ignition and spread of flame of timber constructions, staircases, cassette ceilings, wood flooring and other products made of wood and cellulose. It can be used in interior as well as exterior spaces. Once dry it is not broken down by water or humidity. At the high temperatures, there is no smoke emission and charred dust dispersion. Therefore, it is not harmful to the environment. When material treated with HR prof is exposed to the temperatures higher than 1700 °C, it turns black with smoke and the flame stops spreading.

Striebrenka (Silver paint)

Aluminium paint is determined to protect derusted metal items against oxidation during heat exposure up to the temperature of 600 °C. Properties: dispersion of sodium silicate solution, heat-resistant inorganic fillers, organic ingredients and aluminium powder.

It is used to protect metal items against corrosion at high temperatures up to 600 °C. According to the instructions of the producers, the clean surface must be covered with 1-3 layers of undiluted retardant. During the first exposing the treated unit to the heat, thermal shock (due to fast emission of volatile components) is to be avoided to give the volatile components time to penetrate slowly with no impact on the surface integrity. The reflection of thermal radiation is the principle of Striebrenka; therefore, it does not act as a chemical retardant and it is not used as a flame retardant. Due to its properties it belongs to the fourth class – retardants with physical characteristics. Most of retardants in this group are of solid state, therefore there is a chance to create a microclimate after their application to wood. On the contrary, Striebrenka is a liquid, it must be dried before thermal loading.

Radiant heating

Three samples were thermally loaded, namely the sample treated with HR prof, with the Striebrenka retardant and control (untreated) sample of original wood.

A ceramic radiated panel used for model testing to evaluate the building elements in terms of fire protection was used as the source of radiant heating. The heat source can be characterized by the following data: the dimensions of the radiation zone – 480×280 mm, maximum performance of the radiation zone – $50.5 \text{ kW}\cdot\text{m}^{-2}$, the total reached temperature of the radiation zone – 935°C . The radiating flow ($30.9 \text{ kW}\cdot\text{m}^{-2}$) must supply the body of the radiant with propane at the constant flow of $13 \text{ l}\cdot\text{hour}^{-1}$ in order to achieve the requested performance. The support stand was placed 30 cm from the radiation panel. The thermos-element of K type K (Ni-Cr-Ni) to measure the temperature on the surface of the block were placed there as well. Second thermos-element of K type measuring the temperature of the environment during the experiments ($T = 25.0 \pm 0.7^\circ\text{C}$) was located in the same room.

The first thermocouple (M0.0) was placed on the side directly exposed to the radiant heat from the radiant panel. Another five thermocouples were inserted into drilled holes (75 mm deep below the surface, i.e. in the centre of the sample) on the top side of the wooden block (M1.0 – M5.0) at a distance of 10 mm from each other. During measurement, the thermocouples on the top side of the sample were covered with mineral wool. The last thermocouple was freely placed in the testing laboratory to measure the ambient temperature. The samples were gradually placed on the stand in front of the radiation panel (at a distance of 20 cm) affected by the radiation heat for 30 minutes per each sample. The procedure was monitored and recorded by digital measurement device (Almemo 2290-8). The recorded data were evaluated.

Size and depth of charred area

The thickness of the charred layer or the depth of charring is defined as the thickness of the layer of material at the surface of the timber cross-section that burned out and charred (thickness added to the original cross-section) and lost the ability to transfer stresses due to degradation of mechanical properties. The material in this layer is charred, with no strength or even fallen off.

The measurement was conducted using a laboratory measuring instrument and a digital calliper. Firstly, the length of the charred layer was measured. The charred layer must be removed to measure its depth. After removing the charred layer, the depth was measured in nine predetermined points (starting in the centre of the sample and continuing at a distance of 100 mm from the centre).

Sampling for the purpose of chemical analysis

Sawdust must be used to determine the chemical composition of wood. Two layers were removed by a circular saw. The thickness of the first layer was up to 20 mm, dark brown coloured wood (layer 1) and the thickness of the second one, light brown coloured wood, was from 20 to 40 mm (layer 2) below the charred layer.

Chemical composition of wood

Samples were disintegrated into sawdust and fractions 0.5 mm to 1.0 mm in size were used for the chemical analyses. The extractive content was determined in a Soxhlet apparatus with a mixture of ethanol and toluene (2:1) according to ASTM D1107-96 (2007). The lignin content was determined according to SLUITER *et al.* (2012), the cellulose content was determined according to the method by SEIFERT (1956) and the holocellulose content according to the method by WIESE *et al.* (1946). Hemicelluloses were calculated as a difference between the holocellulose and cellulose content. Measurements were performed on four replicates per sample. The results were presented as oven-dry wood percentages.

RESULTS AND DISCUSSION

When samples were exposed to radiant heat from the radiant panel, the changes to various extent could be monitored in each of them. In the case of the sample treated with no retardant, so-called control sample, the most significant changes occurred.

Changes in a temperature when loading by radiant heat

The sample with HR prof

The changes in temperatures in individual thermocouples are presented in the graph (Fig. 1). The temperature on the thermally loaded side of the sample rose substantially and there was a gradual fall to the depth (10–50 mm). In the case of this sample, an increase in a temperature of the first two thermocouples M0.0 and M1.0 placed on wood close to the radiant panel could be seen. The final value of the temperature was 175 °C during the first 60 s. Furthermore, the temperature rose slowly to 190.6 °C (maximum). In the case of the thermocouple M1.0, rapid increase in a temperature during the measurement was observed. The temperature values measured in this place were 479 °C. There was no fluctuation in temperatures, they increased steadily after the third minute. In the case of the thermocouple M2.0, the value was lower than in the case of M1.0. The thermocouple M2.0 was placed 20 mm far from the loaded side. The temperature recorded increased very slowly to the value of 170.4 ° at the end of measurement. The temperatures recorded in the case of other thermocouples were not higher than 150 °C during the measurement. Following the data, it can be stated that there was the biggest load of the sample with the high temperature in the depth of 10 mm from the loaded side of wood.

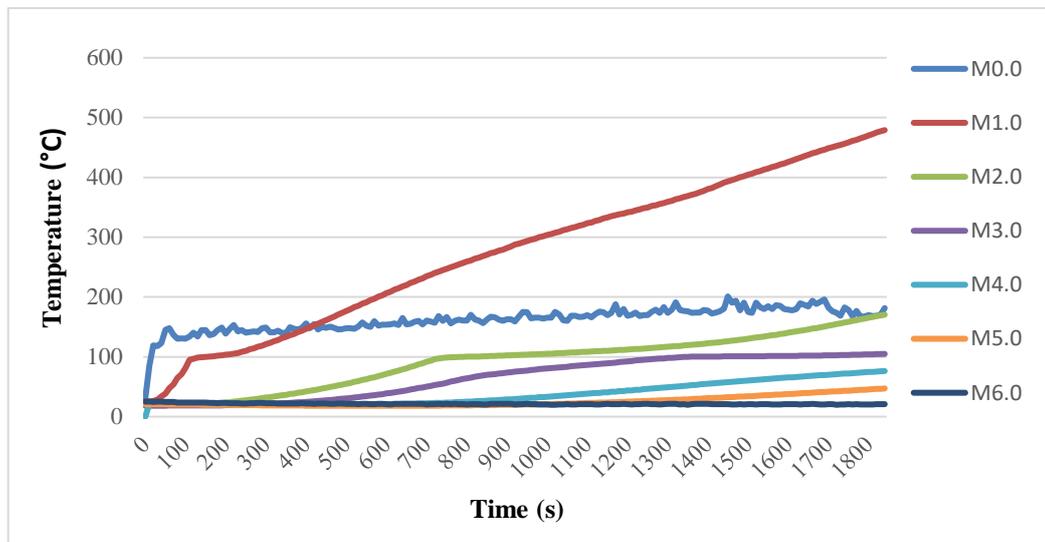


Fig. 1 Changes in temperatures during the thermal loading, the sample treated with HR prof (M0.0, M1.0, M2.0, M3.0, M4.0, M5.0, M6.0 - thermocouples).

In the case of the sample treated by retardant HR prof, on thermocouple M 1.0, the temperature of 300°C was reached in time of 990 sec which correspond to the thickness of charred layer 10 mm below the thermal loaded surface. On other thermocouples (M2.0 – M5.0) (Fig. 1), the limit temperature 300°C was not reached in time up to 1800 sec.

The sample with Striebrenka

The temperatures when the sample was thermally loaded under the same conditions are mentioned in the graph (Fig. 2). However, the development of temperatures was different.

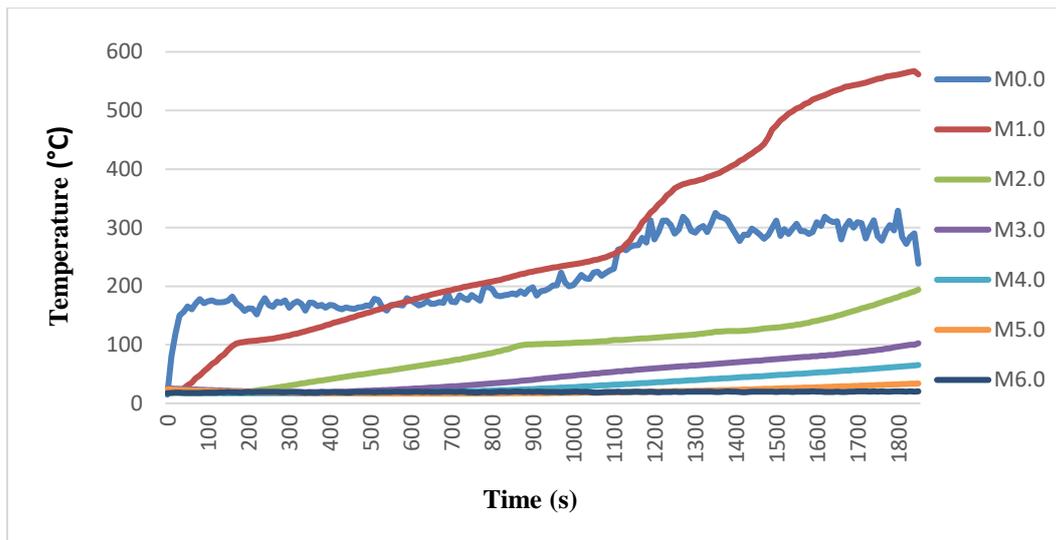


Fig. 2 Changes in temperatures during the thermal loading, the sample treated with Striebrenka (M0.0, M1.0, M2.0, M3.0, M4.0, M5.0, M6.0 - thermocouples).

A significant increase in the temperatures in the case of the thermocouples M0.0 and M1.0 in comparison to other thermocouples could be monitored. The temperature recorded by the thermocouple M0.0 placed on the surface of loaded side rose from the beginning of the measurement. From the beginning to the 10th minute, the temperature recorded in this place was lower than 200 °C. Later, the temperature started to increase to the value of 328 °C after 28 minutes. From this point, the temperature started to fall down to the value of 238°C. There were differences in the development of temperatures recorded by the thermocouple M1.0. The temperature of the material after 5 minutes from the beginning of the thermal loading was 100 °C. Since then, the temperature increased steadily without significant differences. After 18 minutes, there was a radical change in a temperature, from 263 °C to 377 °C during 3 minutes. From this point, the temperature increased steadily for next 24 minutes when another, albeit not so radical, change occurred. The temperature value was 436 °C and continued rising until the end of the measurement, to the value of 567 °C. The temperatures recorded by the thermocouple M2.0 were significantly lower. At the end of the measurement the temperature recorded by the thermocouple was approaching the value of 200 °C. The temperatures recorded by other thermocouples were lower with growing tendency during the measurement.

In case of sample treated by Striebrenka, on thermocouple M 1.0, the temperature of 300°C was reached in time of 1 170 sec which correspond to the thickness of charred layer 10 mm below the thermal loaded surface. On other thermocouples (M2.0 – M5.0) (Fig. 2), the limit temperature 300°C was not reached in the time interval up to 1800 sec.

Control sample

The sample was used as a control sample in order to determine the impact of a retardant during the thermal loading of wood. In the case of this sample, the faster increase in temperature as well as higher temperatures comparing to treated wooden blocks occurred. The most significant change was observed in the case of the first two thermocouples M0.0 and M1.0. The temperature recorded by the thermocouple M0.0 in one minute was 100 °C. Sharp rise in temperature lasted for two minutes and the achieved temperature was 235 °C. Since then the temperature was rising steadily for 21 minutes when the sample started burning. In this point, a significant change (Fig. 3) and subsequent increase in temperature can be seen. The flames were visible for 3 minutes. At the end of flame burning, a substantial fall in values of measured temperatures was monitored. The temperature plummeted from

the value 506°C to 362 °C. The same fluctuation in temperatures was similarly recorded by the thermocouple M1.0. In the case of this thermocouple, there was a steady increase during the first 20 minutes. At this point, there is a significant change from 336 °C to the value of 441.7 °C, and the flames could be seen as well. In the case of this thermocouple, there was a steady rise in a temperature during the time of burning. The temperature achieved was 553.5 °C. After burning, the temperature decreased significantly to the value of 384 °C. Since then the temperature rose steadily to the value of 424°C. Furthermore, there was a falling tendency to the temperature of 351 °C (the end of measurement). In the case of other thermocouples, slower increase in the temperature was recorded.

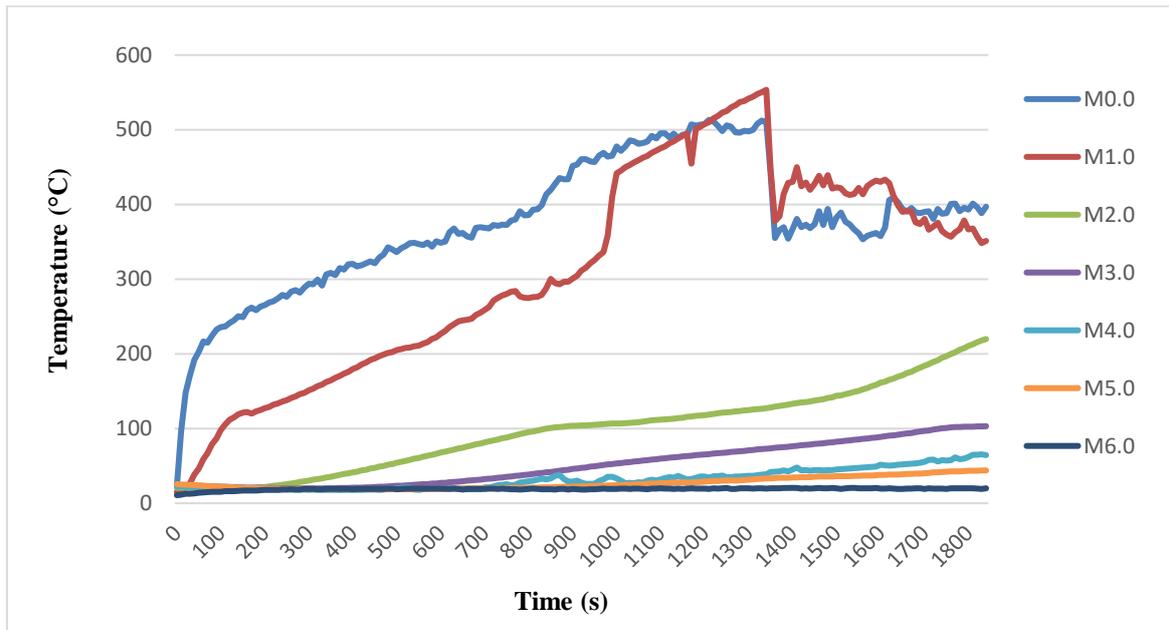


Fig. 3 Changes in temperatures during the thermal loading, control sample (M0.0, M1.0, M2.0, M3.0, M4.0, M5.0, M6.0 - thermocouples).

In the case of untreated sample, on thermocouple M 1.0, the temperature of 300°C was reached in time of 860 sec which correspond to the thickness of charred layer 10 mm below the thermal loaded surface. On other thermocouples (M2.0 – M5.0) (Fig. 3), the limit temperature 300°C was not reached in time up to 1800 sec.

Size and depth of charred area

The sample with HR prof

Following the nine measured data, it was found out that the average depth of charred area was 14.9 mm, up to maximum 19.4 mm and minimum 9.3 mm (Table 1). Total carbonisation of the sample occurred on the area of 416 × 150 mm (in the middle of the sample). Significant change in colour of wood (black) could be to a distance of 413 mm from the centre of the sample on both sides, of the wooden block on the loaded side. During the thermal loading, a visible protective layer similar to bitumen emerged on the wood surface as a result of the effect of a retardant. This protective layer reduced the effect of radiant heating in the sample and at the same time the spread of charred area



Fig. 4 Sample treated with flame retardant HR prof after thermal loading.

The sample with the retardant Striebrenka

After painting, a light grey matt coat was formed. The average depth of the charred area was 15.18 mm, up to maximum 20.2 mm and minimum 8.2 mm that can be compared to the effect of the retardant HR prof (Table 1). Only approximate measurement of the area of charred layer was carried out because it was symmetrical with the dimensions of 458.3 mm \times 150 mm (in the middle of the sample). In the place with the most intensive loading, the protective layer of Striebrenka broke off and subsequently, wood degradation and carbonisation occurred exactly in this place. Striebrenka degradation emerged on the edges of wooden block and spread towards the centre. When Striebrenka broke off completely, burning the wood without flames occurred and the material began to smoulder.



Fig. 5 Sample treated with Striebrenka after thermal loading.

Control sample with no treatment

The sample was treated with no retardant, thus the effect of fire and the spread of flame was natural and slowing down with nothing. The average depth of charred layer was 15.4 mm. It is more in comparison to the samples treated with a retardant, however, the differences in the nine measured points were not significant so much. Maximum depth was 17.9 mm and minimum one was 10.1 mm (Table 1). It can be stated that burning the control sample was steadier comparing to treated samples. The area of charred layer was 569.6 \times 150 mm (in the middle of the sample). In the case of this sample, the surface of material was getting black, therefore it can be assumed that during further heat loading this area would spread. The change in colour (black) occurred on the area with the length of 750 mm, i.e. it is less than in the case of the retardant HR prof used. Surface carbonisation started earlier than in the case of treated samples. An increase in the temperature in shorter time was seen. In the two thirds of loading time, the beginning of burning the already charred surface was observed. The flame could not be seen; it was not spread to other parts of the surface or deeper to the sample. It was only in the place exposed to heat. The flame could be seen for 204 seconds and then it went out.



Fig. 6 Control sample, with no treatment, after thermal loading.

Tab. 1 Thickness of the charred layer of samples loaded for 30 minutes.

Treatment	Type of treatment	Thickness of charred layer (mm)		
		min	max	average
Control sample	-	10.10	18.40	15.41 ± 0.25
Treated sample	HR prof	9.30	19.40	14.90 ± 0.36
	Striebrenka	8.20	20.20	15.18 ± 0.79

According to the findings of HADVIG (1981) and BABRAUSKAS (2005), the speed of carbonisation is the topic in the centre of attention of structural engineers who want to determine the load-bearing capacity of timber beams or columns during post-flashover. During their research on the samples of Nordic spruce, the oven was run at the temperature ranging between 920–1 070 °C. The depth of the charred layer resulting from the experiment was 7–9 mm (when the time of loading was 300 s), 20–21 mm (when the time of loading was 1200 s) and 30–32 mm (when the time of loading was 2400 s). It can be compared to the samples in our experiment.

According to DÚBRAVSKÁ *et al.* 2019, charred layer in the test samples exposed to thermal loading corresponded to the parametric fire curve. In the case of 120 mm thick test sample, 20 mm charred layer appeared in the 22nd minute. In the case of 240 mm thick test sample, 20 mm charred layer appeared in 29th minute.

According to SU *et al.* 2019, charred layer of the wood stud specimens estimated based on their experiment was 15 mm when the time of loading was 30 min. It can be compared to the samples in our experiment (on control sample average thickness of charred layer was 15.41 ± 0.25 mm).

Chemical analysis of wood during the thermal treatment

Chemical composition of original wood, wood treated with the retardant HR prof, Striebrenka and the control sample after thermal loading are mentioned in Table 1. The analysis of original wood was carried out due to the opportunity for comparing the changes in chemical composition before and after the thermal treatment. The values of basic chemical composition in the case of original sample show the extent of wood degradation treated and untreated with retardants and at the same time, the effect of the retardants used for the protection.

Following the table, it can be seen that in the case of the control sample there was a decrease in all wood components. In the layer 1, an increase in average number of extractives from the value 2.12 to 3.55 occurred. An increase of these components after thermal degradation of wood was mentioned by other authors as well (KUČEROVÁ *et al.* 2011, ČABALOVÁ *et al.* 2013). Their amount is higher because of degradation products of thermal decomposition of lignin and carbohydrates in wood (KUČEROVÁ *et al.* 2011). During thermal degradation of wood, degradation of thermally least stable wood components, especially hemicelluloses was

monitored. It was confirmed in our experiment as well. As a result of radiant heating, these components decreased by 20.25 % (layer 1) and by 13.57 % (layer 2). A decrease in hemicelluloses after thermal degradation of spruce wood with radiant heating was mentioned in our further work (ČABALOVÁ *et al.* 2014). Together with a decrease in these wood components, there was a decrease in thermally more stable wood components, especially cellulose and lignin. The average values of cellulose decreased by 13.88 % (layer 1) and by 9.63 % (layer 2) and in the case of lignin, there was a decrease by 12.26 % (layer 1) and by 8.34 % (layer 2). At the temperatures over 250 °C, intensive decomposition of cellulose can be seen and at a temperature over 300 °C, the decomposition of lignin occurs (ČABALOVÁ *et al.* 2013). Following the graph in Fig. 3, it can be seen that in the case of material loaded, the achieved temperatures were higher than 500 °C in the thermocouples M0.0 a M1.0.

Following the chemical analysis of the sample treated with the retardant HR prof after thermal loading, it can be stated that in comparison to original wood sample there was less decrease in the main chemical components of wood than in the control sample. Especially in the case of cellulose, the mentioned decrease in both investigated layers was slight. During thermal loading, cellulose stability comparing to hemicelluloses is evident. It is in compliance with other published works (WINDEISEN, WEGENER 2009, POLETO *et al.* 2012). Due to thermal treatment, there was a decrease in average amount of saccharides (holocellulose) by 3.06 % (layer 1) and only by 2.39 % (layer 2). In the case of main wood components, the most stable component – lignin suffered from the most significant degradation. There was a decrease in lignin by 8.10 % (layer 1) and by 7.66 % (layer 2) comparing to original wood. The thermocouple M0.0, placed on the loaded side, recorded the maximum temperature of 181.9 °C and the temperature recorded by the thermocouple M1.0 was up to 479 °C. The effect of the retardant is evident as the highest temperature achieved in the case of the control sample was in the thermocouple M0.0 – 506.6 °C and in the thermocouple M1.0 – 538.6°C. The degradation of sample treated with the retardant HR prof occurred to a lesser extent in comparison to the control untreated sample. Lignin degradation could be compared but the saccharide stability was evident.

Tab. 2 Chemical analysis of untreated wood and wood after thermal degradation.

Sample and treatment	Layer	Extractives (%)	Lignin (%)	Holocellulose (%)	Cellulose (%)	Hemicelluloses (%)
Original wood sample*	-	2.12 ± 0.02	29.12 ± 0.27	78.32 ± 0.73	41.63 ± 0.06	36.69 ± 0.79
Control sample	1	3.55 ± 0.01	25.55 ± 0.06	65.11 ± 1.50	35.85 ± 0.45	29.26 ± 1.06
	2	3.24 ± 0.07	26.69 ± 0.04	69.33 ± 0.02	37.62 ± 0.01	31.71 ± 0.02
HR prof	1	2.04 ± 0.02	26.76 ± 0.01	75.92 ± 0.39	40.67 ± 0.57	35.25 ± 0.96
	2	1.88 ± 0.05	26.89 ± 0.06	76.45 ± 1.64	41.45 ± 0.44	35.00 ± 2.08
Striebrenka	1	2.23 ± 0.09	28.89 ± 0.16	71.82 ± 2.02	37.21 ± 0.10	34.61 ± 1.92
	2	2.57 ± 0.03	29.24 ± 0.01	73.75 ± 1.12	37.78 ± 0.92	35.97 ± 0.20

*original sample from the wood trunk, without any surface and heat treatment

Chemical composition of thermally loaded wood sample treated with physical retardant called Striebrenka is given in Table 1 as well. Following the results of chemical analysis, it can be seen that in comparison to original wood, the amount of lignin stayed the same, however, the degradation of saccharides (decrease of 8.5% in layer 1 and 8.9% in layer 2) comparing to the sample treated with the retardant HR prof. occurred. Nevertheless, the effect of the retardant is evident when the results were compared to the control sample.

The amount of the chemical components of wood (Extractives, Lignin and Holocellulose) ranged between 94–108% what is in compliance with the statement of

FENGEL and WEGENER (2003), They mentioned that the amount of the components of the analysed wood can exceed 100%. At the same time, during thermal degradation of wood, an increase in the amount of cellulose determined by SEIFERT (1956) and lignin determined by SLUITER *et al.* (2012) as a result of condensation reactions of lignin and saccharides was observed (KAČÍK *et al.* 2006).

CONCLUSION

In this study, the effect of thermal loading by radiant heat source on spruce wood samples treated with a HR prof retardant and Striebrenka was investigated. While the retardant HR prof is a common retardant based on chemical principles, the Striebrenka retardant is not used to protect wood and its nature is physical. During and after the thermal loading, the degree of its charring (extent and depth) was evaluated. It was found out that once a continuous carbon layer was formed, the degradation of the wood slowed down. This is due to the well-known fact that the carbonized layer itself acts as a flame retardant for specific time. As the temperature on the surface of the sample rose, the coating foamed and increased its volume, creating a kind of protective barrier that slowed down the degradation of the wood. The results related to the thickness of charring layer by reaching a critical temperature of 300 °C, specified also in Eurocode 5, which was determined by thermocouples placed in the cross section of the sample and further manually measured (at nine places on the sample surface) were compared. A significant deviation between those values was found. HR prof and Striebrenka has a demonstrable wood protective function due to its prohibitive capability to reach a critical temperature of 300 °C, in the depth of 10 mm below the surface of the sample. However, when the thickness of the average charred layer is manually measured, it reached a value of 15.41 mm (control sample), 15.18 mm (Striebrenka) and 14.90 mm (HR prof).

During the thermal loading of wood, the changes in its properties and the degradation of main wood components were monitored.

Following the changes of chemical components as a result of thermal loading:

- the amount of extractives in the control sample increased from the value 2.12 to 3.55 by the products resulting from the lignin and saccharide degradation;
- a decrease in lignin (from 8.34 to 12.26%), cellulose (from 9.63 to 13.88%) and hemicelluloses (from 13.57 to 20.25%) in the control sample was observed;
- a decrease in lignin (from 7.66 to 8.10%) in the case of the sample treated with HR prof occurred but the percentage of saccharides in wood stayed the same comparing to the original wood sample;
- the proportion of lignin treated with the retardant Striebrenka did not change in comparison to untreated wood;
- a decrease in the amount of cellulose (from 9.25 to 10.62%) of sample treated with Striebrenka and the control sample (in the layer 2) is similar.

HR prof retardant was more effective in terms of saccharides and the Striebrenka retardant in terms of lignin protection.

REFERENCES

- ASTM D1107-96. 2007. Standard test method for ethanol-toluene solubility of wood, ASTM International, West Conshohocken, PA.
- BABRAUSKAS, V. 2005. Charring rate of wood as a tool for fire investigations. In *Fire Safety Journal*, 40(6): 528–554. DOI: 10.1016/j.firesaf.2005.05.006

- BREBU, M., VASILE, C. 2010. Thermal degradation of lignin – A review. In *Cellulose Chemistry and Technology*, 44(9): 353–363.
- ČABALOVÁ I., KAČÍK, F., KAČÍKOVÁ, D., ORAVEC, M. 2014. The influence of cross-section of spruce wood specimens on saccharides changes at thermal loading (in Slovak). In *Acta Facultatis Xylogologiae Zvolen*, 56(2): 81–86.
- ČABALOVÁ, I., KAČÍK, F., KAČÍKOVÁ, D., ORAVEC, M. 2013. The influence of radiant heating on chemical changes of spruce wood (in Slovak). In *Acta Facultatis Xylogologiae Zvolen*, 55(2): 59–66.
- DÚBRAVSKÁ, K., ŠPILÁK, D., TEREŇOVÁ, L., ŠTEFKOVÁ, J. 2019. Charring layer on a cross-laminated timber panel construction. In *Acta Facultatis Xylogologiae Zvolen*, 61(2): 109–119, DOI: 10.17423/afx.2019.61.2.11
- FENGEL, D., WEGENER, G. 2003. *Wood: Chemistry, Ultrastructure, Reactions*, Verlag Kessel, Remagen, Germany.
- FINDORÁK, R., FRÖHLICHOVÁ, M., LEGEMZA, J., FINDORÁKOVA, L. 2016. Thermal degradation and kinetic study of sawdusts and walnut shells via thermal analysis. In *Journal of Thermal Analysis and Calorimetry*, 125:689–694. DOI:10.1007/s10973-016-5264-6
- FONSECA, E.M.M.A., BARREIRA, L.M.S. 2009. Charring rate determination of wood pine profiles submitted to high temperatures. In *Safety and Security Engineering III. Polytechnic Institute of Bragança, Portugal. WIT Transactions on the Built Environment*, 108, 2009: 449–457.
- GAFF, M., KAČÍK, F., GAŠPARÍK, M., TODARO, L., JONES, D., CORLETO, R., MAKOVICKÁ OSVALDOVÁ, L., ČEKOVSÁ, H. 2019a. The effect of synthetic and natural fire-retardants on burning and chemical characteristics of thermally modified teak (*Tectona grandis* L. f.) wood. In *Construction and building materials*, 200: 551–558. DOI: 10.1016/j.conbuildmat.2018.12.106
- GAFF, M., KAČÍK, F., SANDBERG, D., BABIAK, M., TURČÁNI, M., NIEMZ, P., HANZLÍK, P. 2019b. The effect of chemical changes during thermal modification of European oak and Norway spruce on elasticity properties. In *Composite structures*, 220: 529–538. DOI: 10.1016/j.compstruct.2019.04.034
- GAŠPARÍK, M., MAKOVICKÁ OSVALDOVÁ, L., ČEKOVSÁ, H., POTŮČEK, D. 2017. Flammability characteristics of thermally modified oak wood treated with a fire retardant, In *Bioresources*. 12(4): 8451–8467.
- HADVIG, S. 1981. *Charring of Wood in Building Fires*. Lyngby : Technical University of Denmark.
- KAČÍK, F., LUPTÁKOVÁ, J., ŠMÍRA, P., EŠTOKOVÁ, A., KAČÍKOVÁ, D., NASSWETTROVÁ, A., BUBENÍKOVÁ, T. 2017. Thermal analysis of heat-treated silver fir wood and larval frass. In *Journal of Thermal Analysis and Calorimetry*, 130(2): 755–762. DOI: 10.1007/s10973-017-6463-5
- KAČÍK, F., KAČÍKOVÁ, D., BUBENÍKOVÁ, T. 2006. Spruce wood lignin alterations after infrared heating at different wood moistures. In *Cellulose Chemistry and Technology*, 40(8): 643–648.
- KAČÍKOVÁ D., KAČÍK F., BUBENÍKOVÁ T., KOŠÍKOVÁ B. 2008. Influence of fire on spruce wood lignin changes. In *Wood Research*, 53(4): 95–103.
- KAČÍKOVÁ, D., KAČÍK, F., ČABALOVÁ, I., ĎURKOVIČ, J. 2013. Effects of thermal treatment on chemical, mechanical and colour traits in Norway spruce wood. In *Bioresource Technology*, 144: 669–674. DOI: 10.1016/j.biortech.2013.06.110
- KUČEROVÁ, V., KAČÍKOVÁ, D., KAČÍK, F. 2011. Alterations of extractives and cellulose macromolecular characteristics after thermal degradation of spruce wood. In *Acta Facultatis Xylogologiae Zvolen*, 53(2): 77–83.
- KUČEROVÁ, V., LAGAŇA, R., VÝBOHOVÁ, E., HÝROŠOVÁ, T. 2016. The effect of chemical changes during heat treatment on the color and mechanical properties of fir wood, In *BioResources* 11(4): 9079–9094. DOI: 10.15376/biores.11.4.9079-9094
- LUPTÁKOVÁ, J., KAČÍK, F., EŠTOKOVÁ, A., KAČÍKOVÁ, D., ŠMÍRA, P., NASSWETTROVÁ, A., BUBENÍKOVÁ, T. 2018. Comparison of activation energy of thermal degradation of heat sterilised silver fir wood to larval frass regarding fire safety. In *Acta Facultatis Xylogologiae Zvolen*, 60(1): 19–29. DOI: 10.17423/afx.2018.60.1.03
- NUOPONNEN, M., VUORINEN, T., JÄMSÄ, S., VIITANIEMI, P. 2003. The effect of a heat treatment on the behaviour of extractives in softwood studied by FTIR spectroscopic methods. In *Wood Science and Technology*, 37: 109–115.

- NUOPPONEN, M., VUORINEN, T., JAMSÄ, S., VIITANIEMI, P. 2005. Thermal modifications in softwood studied by FT-IR and UV resonance Raman spectroscopies. In *Journal of Wood Chemistry and Technology*, 24: 13–26. DOI: 10.1081/WCT-120035941.
- OČKAJOVÁ, A., KUČERKA, M., KMINIAK, R., KRIŠŤÁK, E., IGAZ, R., RÉH, R. 2020. Occupational Exposure To Dust Produced When Milling Thermally Modified Wood. In *International Journal of Environmental Research and Public Health*, 17: 1478. DOI: 10.3390/ijerph17051478
- POLETTI, M., ZATTERA, A. J., SANTANA, R.M.C. 2012. Thermal decomposition of wood: Kinetics and degradation mechanisms. In *Bioresource Technology*, 126: 7–12. DOI: 10.1016/j.biortech.2012.08.133
- RANTUCH, P., KAČÍKOVÁ, D., MARTINKA, J., BALOG, K. 2015. The influence of heat flux density on the thermal decomposition of OSB (in Slovak). In *Acta Facultatis Xylogiae Zvolen*, 57(2): 125–134. DOI: 10.17423/afx.2015.57.2.13 125.
- SEIFERT, V.K. 1956. Über ein neues Verfahren zur Schnellbestimmung der Rein-Cellulose (About a new method for rapid determination of pure cellulose). In *Das Papier* 10(13/14): 301–306.
- SLUITER, A., HAMES, B., RUIZ, R., SCARLATA, C., SLUITER, J., TEMPLETON, D., CROCKER, D. 2012. Determination of Structural Carbohydrates and Lignin in Biomass (NREL/TP-510-42618). In National Renewable Energy Laboratory, Golden, CO.
- STN EN 1995-1-2 (Eurokód 5). 2004. Navrhovanie drevených konštrukcií (všeobecné pravidlá a navrhovanie konštrukcií na účinky požiaru).
- SU, H. C., TUNG, S. F., TZENG, C. T., LAI, C. M. 2019. Variation in the charring depth of wood studs inside wood-frame walls with time in a fire. In *Wood Research*, 64(3): 449–460.
- WHITE, R.H., NORDHEIM, E.V. 1992. Charring rate of wood for ASTM E 119 exposure. In *Fire Technology*, 28: 5–30.
- WINDEISEN, E., WEGENER, G. 2009. Chemical characterization and comparison of thermally treated beech and ash wood. In *Material Science Forum*, 599: 143–158. DOI: 10.4028/www.scientific.net/MSF.599.143
- WISE, L.E., MURPHY, M., D'ADDIECO, A.A. 1946. Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses. In *Paper Trade Journal*, 122(2): 35–44.
- ZAIKOV, G.E., LOMAKIN, S.M. 2002. Ecological issue of polymer flame retardancy. In *Journal of Applied Polymer Science*, 86: 2449–2462. DOI: 10.1002/app.10946.
- ZELENÁ SPRÁVA 2019. Available on: <https://www.mpsr.sk/zelena-sprava-2019/123---14927/>

ACKNOWLEDGEMENT

This work was supported by the Slovak Scientific Grand Agency (Contract No. VEGA 1/0397/20 (50%) and No. VEGA 1/0387/18 (20%) and the Slovak Research and Development Agency under the contract No. APVV-16-0326 (30%).

ADDRESSES OF AUTHORS

Doc. Ing. Iveta Čabalová, PhD.
 Ing. Michal Bélik
 Technical University in Zvolen
 Department of Chemistry and Chemical Technologies
 T. G. Masaryka 24
 960 01 Zvolen
 Slovakia
 cabalova@tuzvo.sk
 xbelik@is.tuzvo.sk

Doc. Ing. Martin Zachar, PhD.
Technical University in Zvolen
Department of Fire Protection and Safety
T. G. Masaryka 24
960 01 Zvolen
Slovakia
zachar@tuzvo.sk

Mgr. Žaneta Balážová, PhD.
Technical University in Zvolen
The Institute of Foreign Languages
T. G. Masaryka 24
960 01 Zvolen
Slovakia
balazova@tuzvo.sk