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EFFECT OF THERMAL MODIFICATION ON FLAMELESS COMBUSTION OF SPRUCE WOOD

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ABSTRACT

The paper deals with the effect of heat treatment of spruce wood (*Picea abies* (L) Karst.) at the temperatures of 160°C, 180°C and 210°C - on the change of properties that characterize its relation to fire and burning,in particular in the phase called flameless combustion. A test method, which is sufficiently sensitive to monitor these changes, has been used for the evaluation of these changes. The results show that thermally modified spruce wood has positive assessment even in this regard.

KEYWORDS: Flameless combustion, burning rate, spruce, thermal modification of wood.

INTRODUCTION

The term « burning » can be defined as a chemical oxidation-reduction reaction where a flammable substance reacts with an oxidant and the reaction is accompanied by heat release and emission of light. Flammable substance and oxidising agent form a flammable aggregate i.e. components entering the chemical reaction of combustion (Balog 1986).

During combustion, a reaction is taking place in the mixture of flammable substance and oxygen (flammable aggregate). To catch fire, the mixture must be heated to a certain temperature, set off by an initiating source. Exposure of solid materials to a heat source leads to their degradation accompanied by mass loss and formation of volatile products. If the mixture of volatile products is flammable, the mixture - in contact with oxygen and an initiating source - catches fire (ignites), creating flame burning and releasing heat necessary to boost the follow-up burning process (Osvald 1997).

For most solid substances, combustion takes place in two stages. First stage is represented by flame-burning of gaseous products of degradation. Second stage is represented by flameless combustion of the rest of the substance enriched by carbon. Since the fire development process may take up to a few hours without being spotted, it is important to know which materials have the propensity for flameless burning (Babrauskas 2001, Balog 1986, Ohlemiller 1991). Despite numerous efforts, no unequivocal and more precise data on initialization and propagation of burning - for traditional materials such as wood, wood-based products, paper, and cotton - have been collected.

Temperature above 100°C has an influence on the changes in chemical, physical and structural characteristics of wood. Besides temperature coefficient, other factors have an effect on these changes i.e. time, atmosphere, pressure and volume of water, so under certain conditions, changes in wood structure can be observed also at temperatures below 100°C (Kačíková and Netopilová 2006, Osvald 2006, Karlsson and Quintiere 2000).

Wood is now used in many areas, e.g. as a construction and facing material. From all construction materials, wood has the best weight and load capacity ratio and therefore it is possible to carry out wooden constructions in hard to reach areas. This material is used in the exterior as well as the interior of wooden constructions. The main disadvantage of wood is its ability to catch fire and burn so lots of attention has been fastened on this issue for many years and tendencies to modify fire and technical proprieties of woodhave emerged. (Osvald 1997).

Methods which change the basic properties of the material are called modification methods. Depending on the purpose, it is possible to divide the types of modifications into mechanical (densification of wood); physical - by various types of radiation (infrared and high frequency plastification), by layering, by the effect of increased moisture interacting with heat - plastification; chemical (anhydrides, carboxylic acids, isocyanates, epoxides, etc.). Thermal modification starts to be commonly used and is considered to be an environmental type of modification (Hill et al. 2006, Kubovsky and Babiak 2009, Gašparík and Barcík 2013, 2014, Svoboda et al. 2015, Miftieva et al. 2016, Hrčka and Babiak 2012). From the point of view of fire protection, it is necessary to test any type of modification in terms of its fire-technical properties. Modifications may change wood proprieties in a negative as well as positive way.

The interest in thermally modified wood has significantly increased lately. This interest aroused due to reduced production of wood as durable material, increased interest in durable construction material and legislative changes which restrict toxic substances usage. The largest commercial importance is currently represented by five different modifications in particular, one in Finland (Termowood), the Netherlands (Plato Wood) and Germany

(OHT - Oil Heat Treatment Wood) and two methods in France (Bois Perdure and Rectification). Temperatures range between 160 - 260°C and the differences between various modifications arise when using gas environment (nitrogen, steam, etc.), oils, having different humidity levels, and so on. Wood treated in such way has more appropriate properties when used in the exterior as well as the interior, e.g. dimensional stability, durability, change incolour, and so on. (Reinprecht and Vidholdová 2008, Esteves 2008).

One of the disadvantages of thermally treated wood is the deterioration of its mechanical properties which restrict the use of the modified wood in certain applications - as a structural material in particular. Degradation of hemicellulose is probably the most important factor influencing the changes of mechanical properties of thermally modified wood, bend strength and tensile strength in particular; the changes in crystalline and amorphous share of cellulose can also have a big impact on mechanical properties of such wood. In the process of thermal modification, deterioration in mechanical properties of spruce wood and reduction of cellulose proportion have been detected, hemicellulose in particular (Yildiz et al. 2006, Kacik et al. 2015). The correlation between hemicellulose content and bend strength has been published by multiple authors (Winandy and Lebow 2001, Esteves et al. 2008). Correlations between strength properties, hemicellulose content, degree of polymerisation and cellulose crystallinity have been detected during thermal modification of spruce wood (Kacikova et al. 2013). This can also influence the ignition, burning or flameless burning of the modified wood.

The impact of thermal modification on anatomical, mechanical, physical, biological and chemical properties of wood have been the subject of many studies. In scientific literature, however, no knowledge about fire characteristics of this material is available. Fire characteristics are important especially in terms of its usage in wooden constructions (ThermoWood Handbook 2002, Tewarson et al. 1994, Baysalet al. 2014, Yinodotlgör et al. 2010). Even though there are studies dealing with thermally modified wood and its combustion (Martinka et al. 2013), the information on modification of thermally modified wood against fire and the impact of these modifications on its properties is missing.

The aim of this work has been to assess, by a standard method which simulates fire (open flame; flame of burner in an open space, not in an enclosed area of laboratory equipment), properties of thermally treated wood which is characterised by its ability of flameless burning.

MATERIAL AND METHODS

Material

Norway spruce (*Picea abies* (L) Karst.) - is the second most widespread type of wood in Slovakia and the most important one from the economical point of view. Spruce wood is yellowish to yellow-brown, glossy, with colourless heartwood, very bright, light, soft, elastic, splits easily and is easy to stain but more difficult to impregnate. It is characterized by a symmetrical and narrow annual rings (1 to 4 mm) with a share of summer wood in an annual circle ranging from 5 to 20 % (Wagenführ 2007).

Thermal treatment of spruce wood

Parameters and time intervals of thermal modification are stated and shown in Fig. 1.

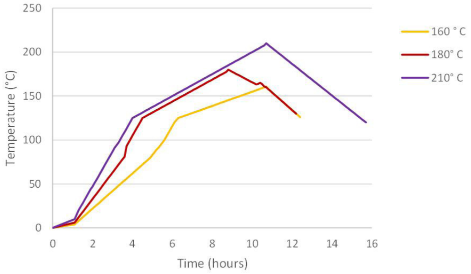


Fig. 1: Time course of thermal modification for each end temperature.

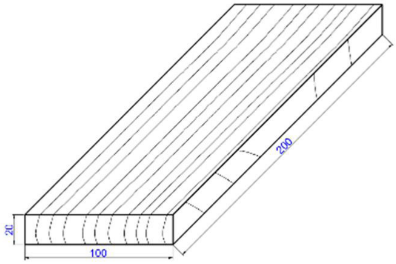


Fig. 2: Size of test samples (mm) to verify the thermal modification on the ignition and burning of the modified wood.

Spruce wood has been subjected to experiments - without heat treatment (20°C), with heat treatment (160°C, 180°C and 210°C). For all types of modifications, samples of 200 x 100 x 10 mm have been used Fig. 2). Thermal modification was even visible to the naked eye (Fig. 3).

This change in colour has initiated the experiment to be done for each temperature of thermal modification. Modifications have caused changes in colour that have occurred due to a change in the chemical composition as well as the structure of the modified wood. No burning occurred at the given temperature and no charred layer has been observed on the surface of the samples, just the overall thermal degradation within the sample. Samples had been thermally modified to the extent as they were later subjected to experiment.

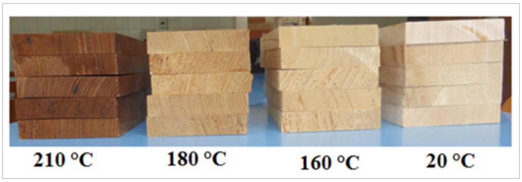
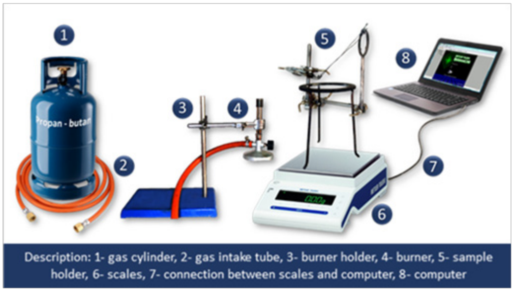


Fig. 3: Change in colour caused by thermal modification.

Test apparatus

From the large quantity of test methods available, a test method simulating the conditions of real fire has been selected. Open flame - of a constant value in an open space, not in an enclosed laboratory facility - serves as a heat source. It concerns a non-normalized EU method but with a tradition of materials evaluation and their fire-retarding treatments.

In this way, each test sample is directly exposed to propane gas burner flame for 10 minutes. Test sample is placed at an angle of 45° to the horizontal plane. Flame had a size of 100 mm and the centre of sample is 90 mm from the mouth of the burner. Basic measurements were carried out for 10 minutes, the auxiliary measurements took additional 5 minutes (without using any heat source). The apparatus, which was relatively uncomplicated, consisted of USBEC 1011/1 propane gas burner, which served as a regulated source of flame (DIN-DVGW reg. Pan NG-2211AN0133) 1.7 kW. To pinpoint the weight, Mettler Toledo scales with 0.01 g readability were used, (MS 1602S / MO1, Mettler Toledo, Geneva, Switzerland). Weight changes of the sample (evaluation criteria) have been recorded and the test has been carried out using BalanceLink 4.2.0.1 (Mettler Toledo, Switzerland). Weight change interval was set to 10 seconds during the experiment. Diagnostic laboratory equipment is depicted in Fig. 4.



Description: 1- gas cylinder, 2- gas intake tube, 3- burner holder, 4- burner, 5- sample holder, 6- scales, 7- connection between scales and computer, 8- computer

Fig. 4: Test apparatus scheme (Mitrenga 2016).

Evaluation criteria

Mass loss

The main evaluation criterion was the mass loss of the test samples which was calculated according to Eq. 1,

$$\Delta m = \frac{m_1 - m_2}{m_1} .100 \qquad (\%) \tag{1}$$

where: Δm- mass loss (%),
m_1 - sample's weight before the test (g),
m_2 - sample's weight after the test (g).

Burning rate

The burn rate was calculated according to Eq. 2,

$$v = \left| \frac{m_t - m_{t+10}}{m_t .10} \right| .100 \tag{2}$$

where: v - burning rate (%·s^{-1}),
m_t- weight (g) at the time t,
m_{t+10}- weight (g) of the sample 10 s later.

RESULTS AND DISCUSSION

The results are presented in Figs. 5 to 11. Fig. 5 (averages from five measurements) shows mass loss courses during the experiment from 0 to 900 seconds. In 600th second, heat source - flame burner- was shut down. We also monitored the mass loss of the samples of thermally treated and untreated wood, which occurred due to heat accumulation within the material and due to flame as well as so-called flameless burning. Chart symbols mark the values of heat treatment (colour coding) and the "No" note means that no further treatment has been applied, e.g. fire retardant. All charts depict average values of the measurements. Courses in Fig. 5 indicate that heat treatment does not substantially change the property observed; the curves, in the initial stage of the measurement, inosculate, which was given by the natural non-homogenous nature of the samples; mass losses are not significantly different with different types of modifications. Notice that Fig. 5 shows the curve course of spruce 20 No - blue colour, without heat treatment which has continuously increased from approximately 500th second compared to other monitored measurements. A similar case applies to Fig. 6, depicting burning rate courses for the different modifications. Two strong peaks - Spruce 180 No in 180th second and spruce 210 No in 250th second - are not very relevant for our measurements. Spruce wood crackles when burning and „shoots„ pieces of burning or charred particles. Two peaks represent this phenomenon. These "pieces" had greater weight which is represented by the peaks in Fig. 6 of the chart.

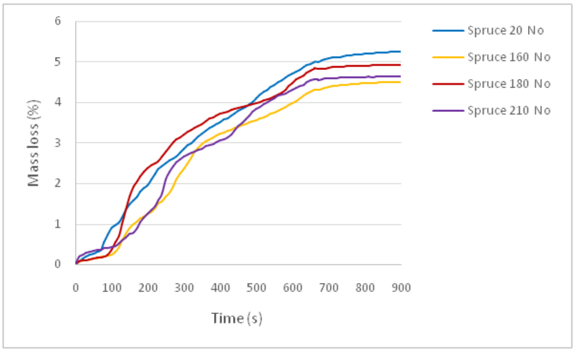


Fig. 5: Mass loss course during the test depending on thermal modification.

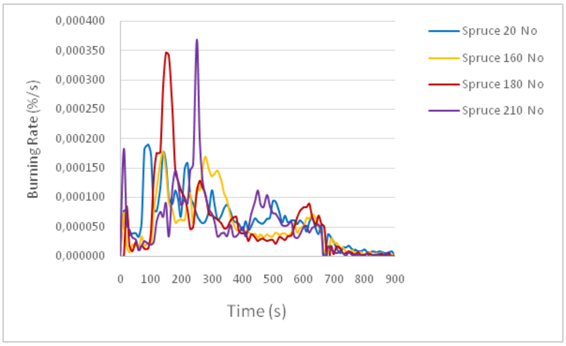


Fig. 6: Burning rate course during the test depending on thermal modification.

Figs. 7 and 8 have more informative value. They show the same values as Figs. 5 and 6, but in more details, at time interval from 600 to 900 of the experiment, not exposed to a heat source - gas burner. The figures show that thermally untreated spruce wood 20 No shows the greatest mass loss during the monitored period of time (Fig. 7 - blue curve). Also, the samples cool down and thereby reduce burning rate from approx. 750th second of the experiment, spruce 20 No having the highest burning rate (see blue curve in Fig. 8). Both selected evaluation criteria show negative evaluation for Spruce 20 No compared with the spruce which is thermally modified.

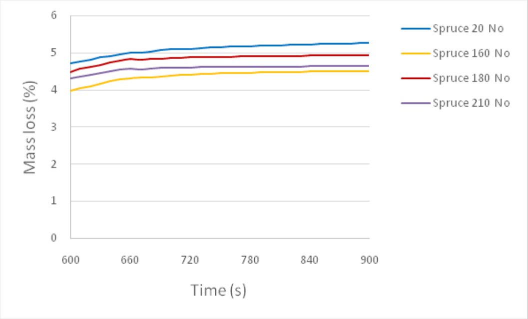


Fig. 7: Mass loss course during the test depending on thermal modification during flameless burning phase (no heat source).

Fig. 9 shows, in a bar chart, mass losses in 600th and 900th second of the experiment. It is logical that mass losses are higher in 900th second. If, however, we draw the differences between these mass losses in the given time intervals, depending on thermal modification (see Fig. 10), we can see that the differences in mass losses are decreasing. This fact was confirmed even by statistical dependence (Fig. 11) where the linear dependence y = 0.004x + 1.1723 is confirmed and R2 has a value of 0.9997. On the basis of these observations, we can sum up that the higher the temperature of thermal modification is, the more degraded the wood structure and, in particular, its chemical composition is. Changes (change in colour is the evidence of it) can be expected in the share and structure of hemicellulose and cellulose. Due to temperature, lignified part changes chemically and it is supposable that physically as well. We suppose that lignin in the central lamella is going to melt and thus "reimpregnates" the primary wall, increasing its resistance in the later stage of burning and stopping the process of flameless combustion.

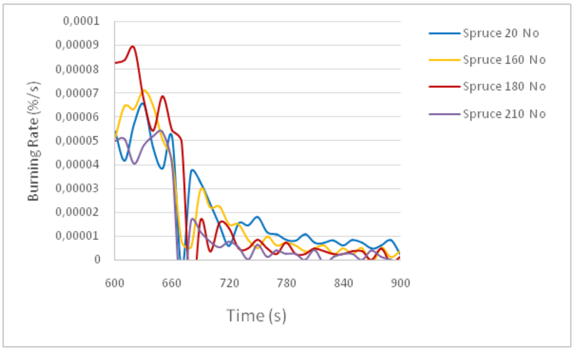


Fig. 8: Burning rate course during the test depending on thermal modification in the phase of flame burning (no heat source).

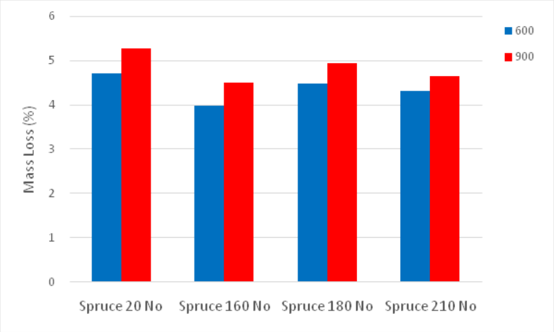


Fig. 9: Mass loss values in 600th and 900th second of the experiment.

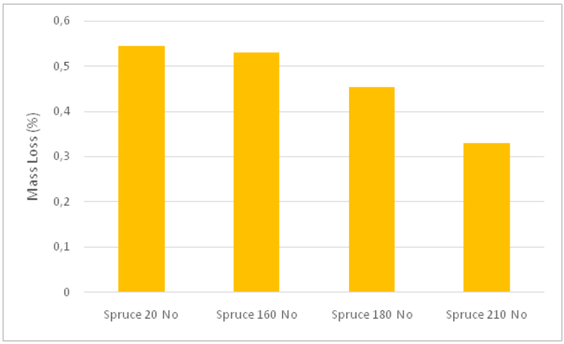


Fig. 10: Differences in mass loss in 600th and 900th second of the experiment.

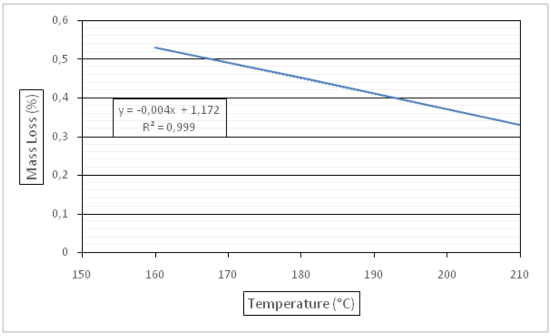


Fig. 11: Linear dependence of mass loss differences for thermally modified spruce wood at the temperatures of 160°C; 180°C and 210°C.

On the basis of the values of the significance level P shown in Tab. 1, we can state that the effect of the applied thermal modification is a statistically insignificant factor at the Mass Loos values at 600th and 900th seconds.

Tab. 1: Basic statistical characteristics evaluation the effect of thermal treatment on the values of the monitored characteristics.

Effect	Sum of squares	Degrees of freedom	Variance	Fisher's F - Test	Significance level P
Mass Loss –600 s (%)					
Intercept	382.042	1	382.042	93.892	0.000
Thermal modification	1.460	3	0.487	0.120	0.947
Error	65.103	16	4.,069		
Mass Loss –900 s (%)					
Intercept	467.500	1	467.500	105.447	0.000
Thermal modification	1.688	3	0,.563	0.127	0.943
Error	70.936	16	4.433		

Comparing the results with similar works is possible tangentially only. Although we might come across the evaluation of certain changes in physical parameters of spruce wood assessing its burning and ignition (Babrauskas, 2001; Kačíková, Netopilová, Osvald, 2006; Mitrenga, 2016), the works don´t treat the issue of thermally modified wood.

In other works, these parameters are observed by other laboratory methods (Kacikova, Kacik, Cabalova, Durkovic, 2013; Hrcka, Babiak, 2012; Yildiz, Gezer, Yildiz, 2005) necessary for a comprehensive assessment of materials, yet not in terms of their burning. When evaluating fire performance characteristics, these were evaluated by other instrumental methods (Tewarson, 1994; Ohlemiller, 1991) which do not simulate real fire conditions unlike our method. The monitoring of flameless burning of thermally treated spruce wood using our method is original in its own way. The results need to be further analyzed.

CONCLUSIONS

In conclusion, thermal modification has a positive effect on the length and intensity of flameless burning of the wood modified in such way. This applies for this very type of thermal modification only. Each method of thermal modification needs to be individually evaluated for fire protection purpose. To improve thermal modification technologies and gain more knowledge in the field (e.g. for fire protection purpose), we recommend chemical and microscopic analysis of modified wood for each tree type to be done separately.

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