

## CHEMICAL CHANGES OF HARDWOODS AT THERMAL LOADING BY RADIANT HEATING

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### ABSTRACT

This paper describes the chemical changes of three hardwood species, white willow (*Salix alba* L.), alder (*Alnus glutinosa* (L.) Gaertn.), and poplar (*Populus tremula* L.) with dimensions 50 × 50 × 1000 mm after thermal loading by radiant heating for 30 minutes.

We determined the amounts of extractives, cellulose and lignin in degraded and sound wood by wet chemistry methods. The influence of thermal loading on carbohydrates changes was investigated by high-performance liquid chromatography (HPLC).

After thermal loading the increase of cellulose content (approx. 2–19%), lignin (approx. 26–61%) and also extractives (approx. 83–125%) except for alder sample, where the decrease of extractives content for approx. 20% was observed. Increase of cellulose content is probably due to changes in its structure (carbonization and crosslinking). The lignin content increase due to its greater thermal stability compared to carbohydrates, as well as a result of its condensation. Increased extractives content is due to the creation of new extractive components by thermal decomposition of hemicelluloses.

Hemicelluloses were degraded to the greatest extent in the case of poplar (42.91%), less in the willow wood (29.20%) and the most resistant was in the alder wood (loss of hemicelluloses were only 17.60%). The least thermally stable monosaccharide was galactose, which was completely removed in all three investigated samples. Resistance other carbohydrates depends on the species - in alder were more labile pentosans, contrary to poplar and willow wood.

**Key words:** lignin, cellulose, hemicelluloses, carbohydrates, radiant heating.

### INTRODUCTION

Thermal loading has a negative influence on wood properties. It degrades its mechanical properties, especially dynamic and static bending strength and toughness (SANTOS 2000, ESTEVES *et al.* 2008 a,b, 2009). On the contrary, it positively influences its durability and dimensional stability (REINPRECHT, VIDHOLDOVÁ 2008, CADEMARTOR *et al.* 2014, 2015). By the influence of high temperatures on wood, its main components as well as extractive matters of wood change (NAKANO, MIYAZAKI 2003).

Temperature above 100 °C has a significant influence on physical, structural and chemical changes of wood. The changes are also influenced by pressure, time, moisture, and the environment (FENGEL, WEGENER 2003, FUNAOKA *et al.* 1990, BUČKO *et al.* 1994). Thermal degradation of wood takes place also at temperatures below 100 °C. These changes can be characterised by lowering of weight, and also include changes in components of

lignin-saccharine matrix, and changes in chemical and physical properties. The low borderline of thermal degradation cannot be more precisely determined; therefore, the rate of degradation is very low (MELCER *et al.* 1990).

Except the weight drop of main wood components, thermal degradation also causes is active degradation of saccharides ratio, change in toughness properties, flame and flameless burning (HORSKÝ *et al.* 1984).

At increasing temperatures, both hemicelluloses and cellulose undergo pyrolysis and oxidation reactions, which are created by inflammable gases. Lignin contributes more to the creation of coal rather than cellulose and hemicelluloses. The increased creation of coal lowers the creation of inflammable gases and this way it protects wood against further thermic degradation (ROWEL *et al.* 1984). Hemicelluloses are the most stable thermic element of wood. Their thermic decomposition has two phases, since they have a heterogeneous structure. At first long patterns get shorter, which are then in the second stage degraded into monosaccharides and sometimes even to evaporative substances. In the second stage the process of degradation is so fast that semi-products cannot be detected (FENGEL 1966). The final products of thermal degradation are evaporative heterocyclic compounds (furane,  $\gamma$ -valerolactone), acetic acid and methanol.

The percentage of the amount of basic compounds and the presence of inherent matter varies depending on the wood species type. This also influences the different resistance properties of individual wood species towards thermal decomposition and a different burning process under the same loading conditions (ZACHAR 2009).

The thermal process of degradation also significantly influences the density of wood. But wood species with higher content of hemicelluloses are more flammable even though they have a higher density (ZACHAR 2009). Anatomic composition has a significant influence on the wood degradation process. When we compare individual elements we can state that the most sensitive to thermal load are parenchymatic cells in wrinkled beams and axial parenchyma. Also, individual anatomic elements react to thermal degradation according to mutual bonds in wood. It therefore depends on whether the wood species are deciduous, coniferous, broadleaved circular-porous or scattered-porous (BUČKO, OSVALD 1998).

The aim of this paper is to characterise the content of saccharides, cellulose, lignin and extractive agents before and after thermal degradation of the selected deciduous trees by radiated heating.

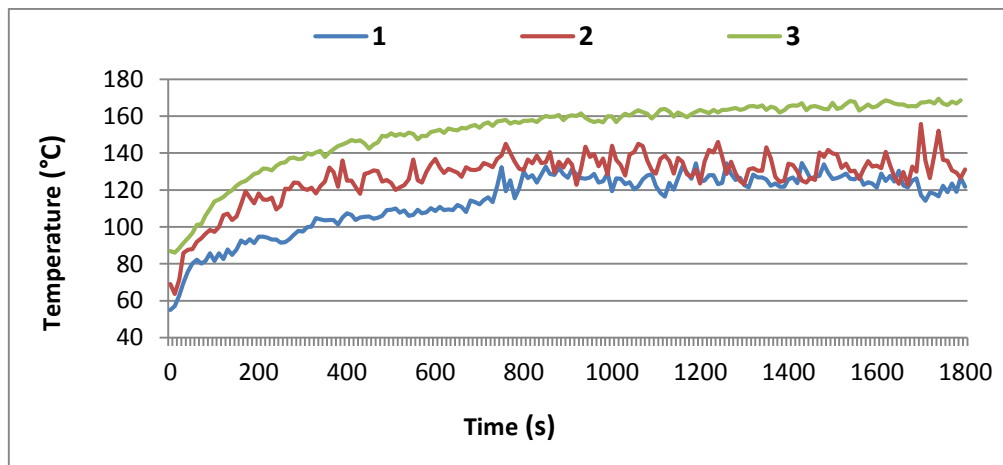
## MATERIAL AND METHODS

The experiment included the following tree wood species common or black alder (JL) (*Alnus glutinosa* (L.) Gaertn.), trembling poplar (TO) (*Populus tremula* L.) and white willow (VB) (*Salix alba* L.). Three pieces of samples were extracted from the trunk of the same tree in each of the mentioned wood species. The samples were cut into the shapes of blocks with the dimensions of 50 × 50 × 1,000 mm and were climatized for 90 days at the relative humidity of 60%. The surface of the samples was not further treated. Before the thermal load the density was set for all the samples (according to STN 49 0108) and the humidity was set by gravimetric method (Tab. 1). For each setting, three repetitions were carried out.

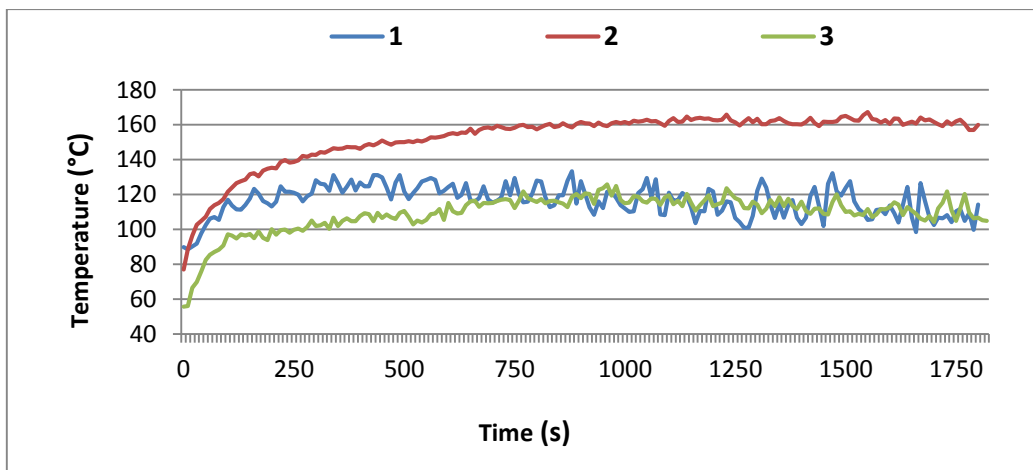
**Tab. 1 Density and moisture of samples before thermal degradation.**

Property	Poplar	Willow	Alder
Density (kg/m <sup>3</sup> )	463	443	529
Moisture (%)	8.50	8.84	8.63

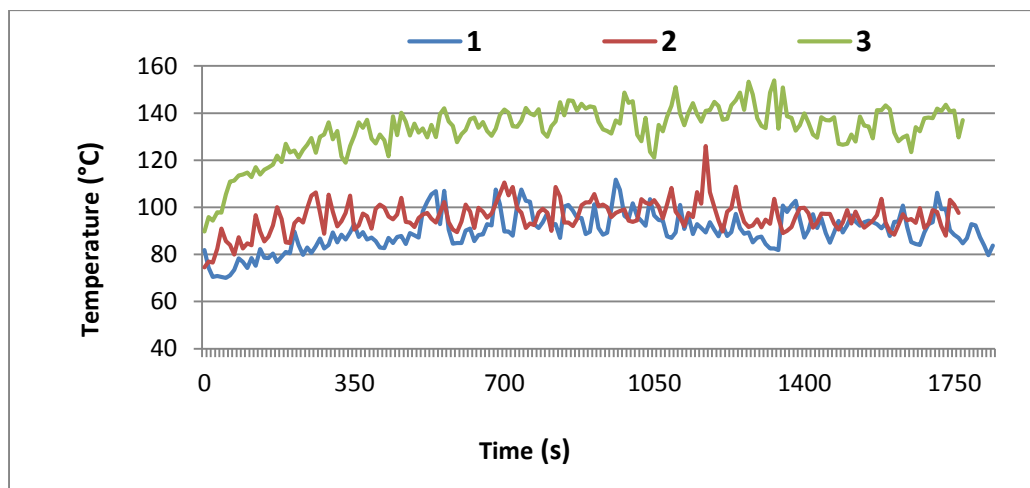
The source of the radiated heating was a ceramic radiated panel used for model testing of the evaluation of building elements from the fire protection point of view. The heat source can be characterized by the following data: the dimensions of the radiation zone –  $480 \times 280$  mm, max. performance of the radiation zone –  $50.5 \text{ kW/m}^2$ , the total reached temperature of the radiation zone –  $935^\circ\text{C}$ . To achieve the requested performance – the radiating flow ( $30.9 \text{ kW/m}^2$ ) needed to supply the body of the radiant with propane at the constant flow of 13 l/hour. We placed the support stand 30 cm from the radiation panel on which we placed the thermos-element of K type K (Ni-Cr-Ni), which measured the temperature on the surface of the block. We also placed in the same room a second thermos-element of K type which measured the temperature of the environment during the experiments ( $T = 25.0 \pm 0.7^\circ\text{C}$ ). The samples were gradually placed on the stand in front of the radiation panel with the impact of radiation heat for 30 minutes per each sample. The procedure was monitored and recorded by digital measurement device (Almemo 2290-8). Measurements were performed on three replicates per sample. The recorded data were then evaluated (Fig. 1–3).



**Fig. 1 Graphical representation of running of samples heating – poplar.**



**Fig. 2 Graphical representation of running of samples heating – willow.**



**Fig. 3 Graphical representation of running of samples heating – alder.**

After the samples were taken from the scope of the radiation panel they were allowed to cool down at the laboratory temperature and were stored for another phase of the experiment.

For chemical analysis, we chose samples from the thermally degraded part of the wood and these were disintegrated and by grain size analysis arranged to fractions. The width of the carbonized layer for the grain size analysis was for poplar of 2 mm, willow of 4 mm and alder of 4.5 mm. A fractional piece of wood of 0.5 to 1.0 mm was used for the chemical analysis. Extractive agents were set in a Soxhlet apparatus by the mixture of ethanol and toluene (2:1) according to the Standard ASTM D 1107-96. Lignin was set according to the Standard ASTM D 1106-96, cellulose according to SEIFERT (1956). Saccharides were set according to the modified method NREL (National Renewable Energy Laboratory) (SLUITER *et al.* 2011, KAČÍK *et al.* 2014).

## RESULTS AND DISCUSSION

Increased temperature has a significant influence on degradation of individual wood components, while parts of extractive agents (e.g. terpenes) evaporate. Degradation reactions of the main wood components though lead to the development of new, less evaporative low molecule compounds which can be extracted by polar or non-polar dissolvent. Their concentration in thermally modified wood grows, which leads to the increased ratio of extractive agents (KAČÍKOVÁ *et al.* 2008, NUOPPONEN *et al.* 2004, WINDEISEN *et al.* 2009). This was also proved in this experiment, monitoring wood species of TO and VB but in case of JL the drop of their ratio was monitored (Tab. 2). According to ESTEVES *et al.* (2008a) the thermal load on wood at first causes the increase of extractive agents and, later, their amount in the wood decreases. When heating up the eucalyptus wood (*Eucalyptus globulus*), new extractive compounds are created due to the decomposition of hemicelluloses and the majority of original extractive agents such as e.g. glycerol, oleic acid, linoleic acid and  $\beta$ -sitosterol degrade. NUOPPONEN *et al.* (2003) states that fat and wax are the first compounds which due to thermal treatment disappear These are followed by fat and resin acids that can be the result of the agents in thermally degraded alder wood, since alder consists of considerable amount of the mentioned extractive agents (KAČÍK, LAUROVÁ 2008, BIKOVENS *et al.* 2013).

The impact of the radiated heating in the distance of 30 cm from the source has a significant influence on the changes of the main chemical compounds of the monitored fast growing wood species (Tab. 1). After the thermal treatment there was an increase of the relative ratio of more stable wood compounds: cellulose and lignin and on contrary degradation of hemicelluloses which results from the data obtained from determination of saccharides (Tab. 2) by the HPLC method. Increased extracts of cellulose are probably due to the changes in cellulose structure while is subjected to carbonisation and crosslinking (TJEERDSMA *et al.* 1998, ESTEVES *et al.* 2008b, KUČEROVÁ *et al.* 2009, ČABALOVÁ *et al.* 2013). The amount of lignin after thermal loading was increased in the case of poplar by 61.4 %, alder by 29.9 % and willow by 26.3 %. The reason may be condensation reactions with the products of saccharides degradation as well as of lignin self-condensation (KAČÍK *et al.* 2007). In comparison with polysaccharides, lignin is thermally the most stable wood compound, even though its changes depend on the form of thermal loading. With slow heating at the atmospheric pressure conditions for growth, condensation reactions and the extraction of evaporative products is relatively low (ELDER 1984, KAČÍK *et al.* 2007). Hemicelluloses undergo degradation process at relatively low temperatures (ESTEVES, PEREIRA 2009). From the presented results (Tab. 2), it is clear that degradation of hemicelluloses was the most significantly visible at TO wood species, which proves also the highest ratio of cellulose to hemicelluloses (cel/hemi), that is according to KAČÍK *et al.* (2010) increasing due to faster decomposition of hemicelluloses in comparison with cellulose.

**Tab. 2 Amounts of extractives, cellulose and lignin in analyzed samples (% odw).**

Sample/ Wood	Extractives (%)			Cellulose (%)			Lignin (%)		
	JL	TO	VB	JL	TO	VB	JL	TO	VB
Untreated	7.25	4.55	3.01	36.62	40.20	45.18	23.52	18.61	19.91
Charred	5.77	8.33	6.77	43.51	45.20	45.49	31.04	28.51	24.16

**Tab. 3 Relatives amounts of saccharides in analyzed samples (% odw).**

Sample		XYL	GAL	ARA	MAN	GLC-hemi	GLC-cel	SUM hemi	RATIO cel/hemi
JL	Untreated	24.02	0.58	1.17	6.19	2.06	65.97	34.03	1.94
	Charred	18.77	0.00	1.09	6.14	2.05	71.96	28.04	2.57
TO	Untreated	22.89	0.43	1.39	5.43	1.81	68.05	31.95	2.13
	Charred	15.34	0.00	0.81	1.57	0.52	81.76	18.24	4.48
VB	Untreated	19.73	0.50	2.28	4.59	1.53	71.37	28.63	2.49
	Charred	15.98	0.00	0.82	2.61	0.87	79.73	20.27	3.93

XYL = D-Xylose, GAL = D-Galactose, ARA = L-Arabinose, MAN = D-Mannose, GLC = D-Glucose, hemi = hemicelluloses, cel = cellulose, SUM Hemi = XYL + GAL + ARA +MAN +GLC-hemi

The highest wood density and the amount of hemicelluloses were monitored in common or black alder. This wood species from all the monitored samples had the thickest burned layer of wood (4.5 mm), which is in accordance with statement of ZACHAR (2009), who declares that wood species with higher amount of hemicelluloses are more inflammable even though they have greater density.

From the results it is obvious that radiated heating of samples caused the decrease of the relative ratio of hemicelluloses type saccharides (XYL, GAL, ARA, MAN) and on contrary the increase of glucose due to bigger thermal cellulose stability.

The least thermally stable saccharide was galactose which was completely degraded due to thermal loading. Resistance of individual saccharide types differed depending on individual

wood species. Pentosanes are generally more unstable than hexosans, and during our experiments degraded only in case of alder wood (pentosanes – degradation of 21.16%, hexosans – degradation of 7.25%). A thermal load on willow and poplar wood hexosans degraded much faster (TO: degradation of hexosans of 72.75%, pentosanes of 33.48%, VB: degradation of hexosans 47.43%, pentosanes 13.67%).

## CONCLUSION

The experimental results gained from the chemical composition analysis of the selected deciduous wood species (alder, poplar, willow) show that when exposed to thermal loading, the relative number of saccharides of hemicelluloses type drops. On the contrary, more stable compounds of wood such as cellulose and lignin as well as the ratio of extractive agents grow. Hemicelluloses degraded on large scale in poplar wood (42.91%), less in willow wood (29.20%) and the most resistant were in case of alder wood (degradation of hemicelluloses was 17.60%). Of saccharides, the least stable is galactose, which is completely degraded in cases of all researched wood species. The resistance of other saccharides depends on wood type – in alder wood saccharides were less stable pentosanes. In poplar and willow wood hexosans degraded faster.

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