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CHEMICAL COMPOSITION OF FIRED ALEPPO PINE (*Pinus halepensis* Mill.) BIOMASS

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ABSTRACT

The Republic of Croatia, as well as the rest of the Mediterranean European countries, is increasingly faced with the problem of forest fires and their immediate aftermath. After the forest fires, significant quantities of fired trees as lignocellulosic biomass are left behind, and the question arises as to what degree they are chemically degraded or whether they still possess all the properties for further application in mechanical or chemical processing. Therefore, the aim of this study was to research the impact of forest low ground fire and high fire of the treetops on the Aleppo pine (*Pinus halepensis* Mill.) chemical composition as a biomass quality property. The study was carried out by determining the group chemical composition of fired and non-fired wood anatomical parts for comparison with the fired ones, by sampling the rings at the height of the trees 0 m, 2 m 4 m. The results obtained show that the non-fired bark contains a appreciably higher content of ash, accessory materials (extractives) and lignin, and a considerably lower content of polysaccharides cellulose and polyoses (hemicellulose) than sapwood and heartwood, which is similar in comparison to the results of previous studies. The bark results show a notable difference in reduced ash, cellulose and lignin content, and in increased accessory materials and wood polyoses (hemicellulose) content between the non-fired and fired wood. Furthermore, the content of individual chemical components of fired bark at different forest fires heights of 0, 2 and 4m for each sample did not differ substantially. Contrary to fired bark, sapwood and heartwood does not have considerable differences in the chemical composition of non-fired and fired wood, as well as on different forest fires heights. The results obtained show that forest fires do not have any effect on overall Aleppo pine sapwood and heartwood; it is fired wood bark that takes on all the damage caused by the high temperature during a forest fire. In addition, the fired sapwood and heartwood still possess all the chemical properties for further application.

Key words: forest fires, Aleppo pine (*Pinus halepensis* Mill.), fired wood, group chemical composition

1. INTRODUCTION

A bioeconomy (biobased economy), as well as circular economy, uses as many renewable raw materials as possible for products such as chemicals, materials and energy in biorefineries. A key factor in its realisation is the production of a range of biobased products and bioenergy to substitute their fossil-derived equivalents by processing a wide variety of biological feedstock. The EU has declared the biobased products sector to be a priority area with high potential for future growth, reindustrialisation, and addressing societal challenges (IEA Bioenergy, 2017; AEBIOM, 2017).

A biorefinery is a multidisciplinary and complex concept addressing, at the same time, the production of value-added bioproducts (chemical building blocks, materials), and bioenergy (biofuels, power, and heat) from biomass, within a sustainability assessment carried out along the entire value chain and life cycle. It can use various combinations of feedstock and conversion technologies to produce a variety of products, and includes key technologies to effectively use (components from) biomass, involves converting biomass into valuable components and marketable products. Contrary to petro-resources, whose nature and composition variations are relatively limited, the terms *bioresource* or *biomass* cover compounds of very different natures. Biomass is defined as biodegradable products, wastes, and residues of biological origin from agriculture, forestry, and aquaculture, and comes from a wide range of raw materials that includes wood, agricultural crops, by-products of wood processing, manure, and the organic fraction of waste products (Directive 2008/28/EC). Biomass as a form of renewable raw material has the advantages of being easily stored, transported, and utilized with a flexible load and applications at the place and time of raw material needed. This makes biomass unique among other renewable raw materials options (AEBIOM, 2017). In addition, the European Commission has set a long-term goal to develop a competitive, resource effcient and low carbon economy by 2050, and biorefinery products are expected to play an important role (IEA Bioenergy, 2017).

Wood as a lignocellulosic biomass is a multicomponent, hygroscopic, anisotropic, fibrous, porous, biodegradable and renewable raw material. It is generally clear that wood has unique structural and chemical characteristics that show a wide spectrum of end-use possibilities. For these reasons, it can be assumed that basic knowledge of the structure and chemical composition of wood is of essential importance, considering the choice optimization of certain wood species for different applications. Every wood species is unique in its chemical composition and varies from species to species, as well as their chemical, physical, and mechanical properties. Wood is a complex heterogeneous mixture of key structural organic components such as cellulose, hemicellulose, and lignin, along with accessory organic and inorganic composites. From chemical point of view, wood consists of 40–45% cellulose, 25–35% hemicelluloses, 15–30% lignin and up to 10% other compounds. All the main wood components are high-weight-molecular polymers and form an interwoven network in the wood cell wall; consequently, we could say that wood is a natural polymer. The chemical composition of wood tissues (sapwood and heartwood), as well as bark, is equally complex, and varies between and within species. Comparing chemical composition of tissues and bark, it can be concluded that bark contains a higher content of ash, accessory materials (extractives) and lignin, and a lower content of polysaccharides cellulose and polyoses (hemicellulose). The qualitative and quantitative characterization of such components in the biomass is essential for its application perspectives. Hence, an overall characterization of biomass is indispensable to expand the bioeconomy sector worldwide (Antonović, 2010).

Open-air fires or forest fires become a key factor in reducing forest surface areas, and the former are one of the major factors for devastation and degradation of forests and forest land and their ecosystems in the Mediterranean, mainly at coastal karst. They are causing extremely large material and economic damage, and they negatively affect biological and landscape diversity. The impact of open space fire in ecological sense was explored by many authors. These are extremely important problems of natural renewal and vegetation succession; the emergence of erosion processes after the fire and the prevention of forest soil degradation (Saracino et al., 1997; Espelta et al., 2002; Rodrigo et al., 2004; Tapias et al., 2004; Prgin, 2005; Pausas et al., 2008; Španjol et al., 2011; Pentek et al., 2011; Pentek et al., 2014). Another aspect often neglected refers to the technical properties of the fired wood which was the aim of this study (Antonović et al., 2017).

When trees are exposed to forest fires elevated temperatures, changes can occur in their chemical composition that affect their technical properties. The extent of the changes depends on the temperature level and the duration of exposure. Combustion of cellulose, and lignin is preceded by thermal degradation, where gaseous and liquid products are formed, as well as a solid residue of charcoal. Some of the gases and liquids, when mixed with air, burn with a flame, whereas the charcoal burns in air by glowing without flame. Wood burns “indirectly”, in the sense that wood does not actually burn; rather, combustion takes place as a reaction between oxygen and the gases released from wood (high molecular weight components). Under influence of heat, wood easily produces substances that react eagerly with oxygen, leading to high propensity of wood to ignite and burn. Ignition and combustion of wood is mainly based on thermal decomposition of cellulose and the reactions of thermal degradation products with each other and with gases in the air, mainly oxygen. When temperature increases, cellulose starts to degrade. Decomposition products either remain inside the material or are released as gases. Gaseous substances react with each other and oxygen, thus releasing a large amount of heat that further induces degradation and combustion reactions (Thomas and McAlpine, 2010).

The end-use processing pathways of the fired wood, as a lignocellulosic biomass for biorefinery products, depend on its physicochemical properties. These properties are the following: (1) biochemical composition (a) wood chemistry – cellulose, hemicellulose and lignin; (b) non-wood chemistry – saccharides, lipids and proteins; (2) moisture content (a) intrinsic moisture; (b) extrinsic moisture; (3) mineral matter content (a) major elements; (b) trace elements; (c) nutrients; (d) salts; (4) elemental composition of organic matter (C, H, N, S, O); (5) physical properties (a) density; and (b) grindability. Two fundamental aspects related to such fired biomass are: (1) to extend and improve the basic knowledge of composition and properties; and (2) to apply this knowledge for the most advanced and sustainable utilisation of biomass. Pursuant to that, systematic identification, quantification and characterisation of chemical composition of such biomass are the initial and most important steps during the research and application of biorefinery products. The primary aspect in utilizing fired biomass for such products is to understand its basic composition and properties (Strezov and Evans, 2015).

In accordance with the above mentioned, after forest fires, significant quantities of fired Aleppo pine trees (*Pinus halepensis* Mill.) as a wood species which most often represents coastal karst and as lignocellulosic biomass, are left behind, and the question araises as to what degree they are chemically degraded or whether they still possess all the properties for further application in mechanical or chemical processing. The main aim of this study was to chemically characterize fired Aleppo pine as a technical quality property of biomass, and to contribute to better understanding of the possibility of using fired wood species, as a very large raw material base in the Republic of Croatia, in further production of biorefinery products. Therefore, the impact of forest fires on Aleppo pine wood group chemical composition was studied as a quality property. The study was carried out by determining the group chemical composition (accesory materials, mineral substances, cellulose, hemicellulose and lignin) on Aleppo pine fired wood anatomical parts (bark, sapwood and heartwood) and non-fired for comparison with the fired, by sampling the rings at the height of the trees 0 m, 2 m 4 m (also referred as forest fire heights). Based on the chemical analysis results of the fired Allepo pine wood, the impact of forest fires on chemical composition changes was determined by comparison with the non-fired, and its possibility for further application in production of biorefinery products.

Based on the obtained research results in this paper, very valuable information on the group chemical composition of Aleppo pine before and after forest fires will be presented, and we will have an answer to the question whether fired wood retains the possibility of further and wider application. Furthermore, the results will contribute to better understanding of application possibilities of fired wood (ecological-productive potential) and will serve as it is for further research and development of bioproducts production based on fired wood as a huge raw material base in the Republic of Croatia.

2. MATERIALS AND METHODS

For studying the chemical quality of fired wood, as one of the technical qualities, Aleppo pine (*Pinus halepensis* Mill.) was chosen as wood species which most often represents coastal karst, especially in Dalmatia, the islands and the Dalmatian Zagora of the Republic of Croatia. Aleppo pine increasingly occupies larger areas thanks not only to new afforestation, but also to its biological properties of natural expansion and regeneration on fired surfaces. Monoculture of Aleppo pine favours faster spread of fires than mixed forests of the Mediterranean hardwoods (Meštrović, 1977; Matić, 1986).

2.1 Wood sampling location and forest fires characteristics

Sampling of non-fired and fired Aleppo pine was carried out under the jurisdiction of the company Croatian Forests Ltd., in the Forest Administration Split – Forest department Shibenik unit Jelinjak. Wood sampling location information and forest fire characteristics were as follows: (a) fire type – ground fire (low) and treetops fire (high); (b) fired surface size – 19.25 ha; (c) forest breeding: high (Aleppo pine forest culture) – 3.15 ha (16.36%), low (garrigue) – 14.9 ha (77.40%), agriculture land (perennial crops) – 1.20 ha (6.23%); (d) forest description – old Aleppo pine forest culture (*Pinus* *halepensis* Mill.) 53 years old, the bushy layer and plants ground floor layer is very rare, rocky ground very expressed, 10º incline, 50m altitude; (e) sample mark: a – non-fired tree and b – fired tree.

2.2 Sampling and preparation of wood for chemical analysis

For the purpose of studying the influence of different types of forest fires (ground fire – low and treetops fire – high) on the chemical composition of fired (b), as well as non-fired (a) wood of Aleppo pine for comparison with fired wood, ring samples of 10–30 cm thickness were taken at three different tree heights (fires heights) in the following manner: (a) first ring sample at height of 0 m (the first ring from the cut felling point, next to the stump); (b) second ring sample at height of 2 m; (c) the third ring sample at height of 4 m. Rings were taken immediately after cutting trees according to the standard TAPPI T257 cm 02 – Sampling and preparation of wood for analysis and take-away to laboratory.

After laboratory drying during 14 days, wood anatomical (macroscopic) parts were mechanically separated on each ring. That means separately bark (B), sapwood (S) and heartwood (H). The sapwood (S) was additionally divided into two parts and marked as S1 (the part of sapwood till bark) and S2 (the second part of sapwood up to the heartwood) (Figure 1). The aim of that separation was to determine the influence of fire heat and temperature penetration into the wood depth on wood chemical composition as a quality property.

Furthermore, after macroscopic parts separation of each ring, all samples were prepared in compliance with previous studies (Antonović et al., 2007; Hames et al., 2008; Antonović et al., 2008; Antonović et al., 2010). Air-dried sapwood samples were milled using a knife-mill Fritsch – Pulverisette 19 on different particles size. After milling, samples were sieved through standardized sieves. The milled particles which passed the screen of sieve 0.71 mm and stay on sieve 0.325 mm were used in further chemical analysis, due to their ideal particle size for all isolation methods of group chemical composition, and which is recommended in previous studies. For screening, laboratory electromagnetic sieves shaker Cisa RP.08 (shaking time t=15±1 min) was used (TAPPI T 264 cm-97).

For better understanding and a complete overview of the chemical composition of all anatomic wood parts, bark (B) and both parts of sapwood (S1+S2), group chemical composition results of the same Aleppo pine from the previous study (Antonović et al., 2017a; Antonović et al., 2018a; Antonović et al., 2018b) were taken for comparison with the heartwood (H) results.

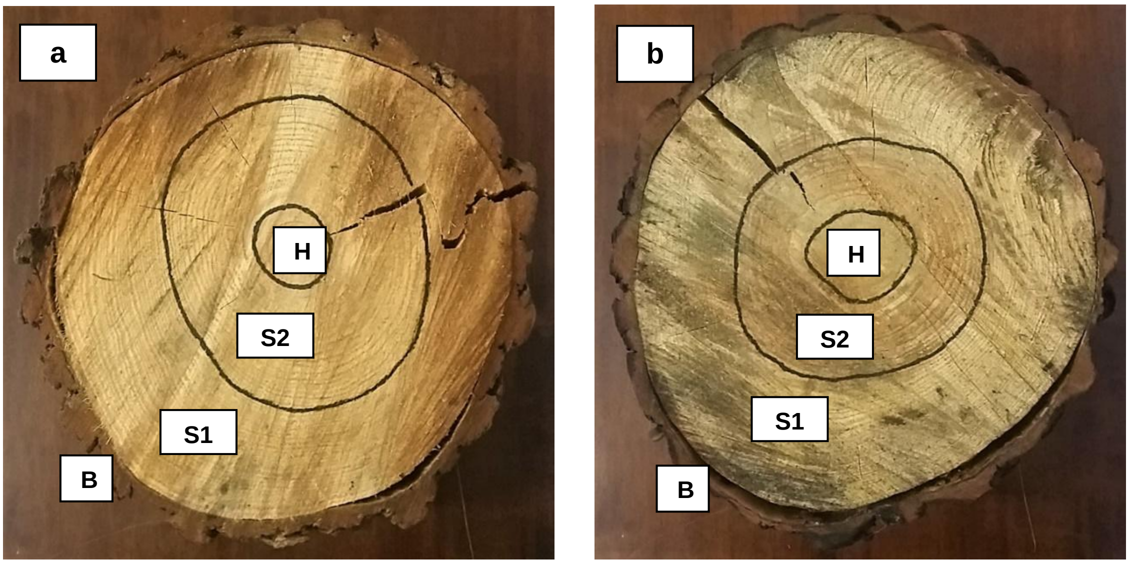


Figure 1. *Non-fired wood (a) and fired wood (b) of Aleppo pine with wood anatomic (macroscopic) parts*

2.3 Wood group chemical components isolation

After samples grinding and sieving, ten smaller samples were taken of each criterion, on which all the chemical analysis were performed, and the results were statistically analysed in Statistica program and are presented in Table 1 and Table 2.

Isolation methods for determining the content of heartwood sample group chemical composition, namely ash, accessory materials (extractives), cellulose, hemicellulose (polyoses) and lignin were conducted in compliance with previous study (Antonović et al., 2007; Antonović et al., 2008; Sluiter et al., 2005a; Sluiter et al., 2005b; Sluiter et al., 2008). Sample compositional analysis comprised a series of isolation methods of the main components, which can be schematically presented as shown in Figure 2.

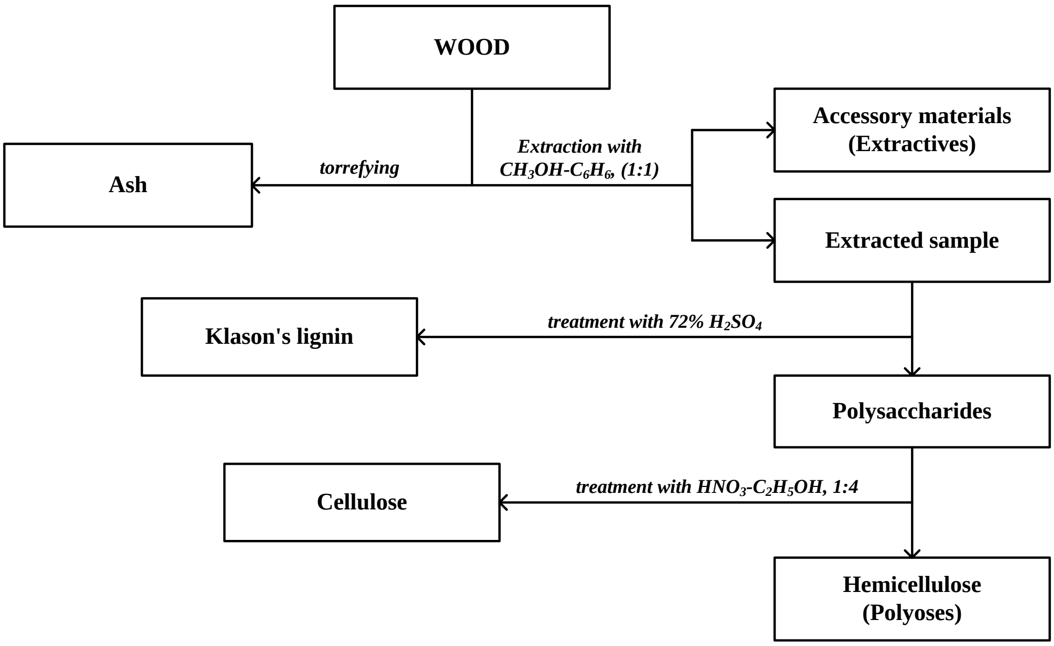


Figure 2. Schematic view of sample chemical analysis

A small portion of the prepared sample was first used to determine the ash content, and the other major part for prior sample extraction (treatment with a solvent mixture of methanol, CH_3OH and benzene, C_6H_6 in volume ratio 1:1) to remove the accessory materials from sample which could interfere with the further chemical analysis. Thus, additional residual solid content was determined as content of accessory materials or extractives. Furthermore, sulfonic acid lignin or Klason's lignin (treatment with 72% sulfuric acid, H_2SO_4) and the polysaccharides cellulose (by treatment with a solvent mixture of nitric acid, HNO_3 and ethanol, C_2H_5OH in a volume ratio of 1:4) was isolated from the extracted sample. The content of hemicellulose (polyose) was determined by calculation according to the share of other mentioned components in the samples. Hemicellulose content was calculated by means of the following expression: $WP = 100 - (\% A + \% AM + \% C + \% L)$ in %. All used chemicals were high purity (p.a.) and were obtained from commercial sources.

3. RESULTS WITH DISCUSSION

Forest fires occur when all of the necessary elements of a fire triangle come together in a susceptible area: an ignition source is brought into contact with a combustible material such as vegetation, that is subjected to sufficient heat and has an adequate supply of oxygen from the ambient air. Forest fires front is the portion sustaining continuous flaming combustion, where unfired material meets active flames, or the smoldering transition between non-fired and fired material. As the front approaches, the fire heats both the surrounding air and woody material through convection and thermal radiation. First, wood is dried as water is vaporized at temperature of 100°C. Next, the pyrolysis of wood at 230°C releases flammable gases. Finally, wood can smoulder at 380°C or, when heated sufficiently, ignite at 590°C. Even before the flames of a forest fires arrive at a particular location, heat transfer from the forest fires front warms the air from 800 to 900°C, which pre-heats and dries flammable materials, causing materials to ignite faster and allowing the fire to spread faster. A high moisture content usually prevents ignition and slows propagation, because higher temperatures are required to evaporate any water within the material and heat the material to its fire point. Dense forests usually provide more shade, resulting in lower ambient temperatures and greater humidity, and are therefore less susceptible to forest fires. Less dense material such as grasses and leaves are easier to ignite because they contain less water than denser material such as branches and trunks. Plants continuously lose water by evapotranspiration, but water loss is usually balanced by water absorbed from the soil, humidity, or rain. When this balance is not maintained, plants dry out and are therefore more flammable, often a consequence of droughts (Prgin, 2005; Bakšić et al., 2015).

Forest fires in wood emit a complex mixture of particles and gases into the atmosphere. Diversity in composition of combustion products results from wide range of wood species, wood chemistry, and fire behaviour. The chemical characteristics of wood affect the rate of combustion and influence the overall forest fire behaviour. At temperatures above 100°C, chemical bonds begin to break. The rate at which the bonds are broken increases as the temperature increases. Between 100°C and 200°C, non-combustible products, such as carbon dioxide, traces of organic compounds and water vapour, are produced. Above 200°C cellulose breaks down producing tars and flammable volatiles that can diffuse into the surrounding environment. If the volatile compounds are mixed with air and heated to the ignition temperature, combustion reactions occur. The energy from these exothermic reactions radiates to the solid material, thereby propagating the combustion reactions. If the burning mixture accumulates enough energy to emit radiation in the visible spectrum, the phenomenon is known as flaming combustion. Above 450°C all volatile material is gone. The residue that remains is an activated char that can be oxidized to carbon dioxide, carbon monoxide and water vapour. Oxidation of the char is referred to as afterglow (Alexander, 1982; Basin, 2011).

Thermal degradation of wood caused by forest fires can be represented as a sum of the thermal degradation reactions of the individual wood chemical components (group chemical composition), namely ash, accessory materials, cellulose, lignin and polyoses (hemicellulose) (Antonović et al., 2016; Krička et al., 2016). The influence of the individual chemical components on thermal degradation reactions of all macroscopic wood parts depends on the species and its moisture content, and forest fires exposure period as a function of temperature for the components and for wood itself. The chemical components of wood are thermally degraded at different speeds, and the degradation takes place in the following order: hemicellulose → cellulose → lignin. The degradation of holocellulose, which consists of cellulose plus hemicelluloses, most closely follows that of wood. Lignin generally degrades at a slower rate than holocellulose, although the degradation period begins somewhat earlier than for the holocellulose. Cellulose and wood appear to degrade at similar rates, although wood begins to degrade at slightly lower temperatures than cellulose but higher temperatures than holocellulose. This lower degradation temperature of wood is primarily due to the hemicelluloses in the wood and holocellulose. Wood degradation resembles more closely the degradation pattern of cellulose and holocellulose than the degradation pattern of lignin. This is reasonable because cellulose and holocellulose account for approximately 50% and 75% of the wood, respectively (Antonović et al., 2017a; Jurišić et al., 2017; Krička et al., 2017).

Table 1. *Bark (B) and sapwood (S1+S2) from previous study and heartwood (H) group chemical composition results of non-fired Aleppo pine wood (a)*

		N	Unit	Minimum	Median	Maximum	Mean	Std. dev.	Variance
Ash content									
0	B	10	%	3,48	3,67	3,74	3,63	0,1086	0,0118
	S1	10	%	0,36	0,39	0,51	0,40	0,0464	0,0022
	S2	10	%	0,36	0,57	0,82	0,59	0,1462	0,0214
	H	10	%	0,44	0,48	0,78	0,54	0,1225	0,0150
2	B	10	%	3,28	3,44	3,51	3,42	0,0780	0,0061
	S1	10	%	0,36	0,42	0,49	0,42	0,0389	0,0015
	S2	10	%	0,26	0,39	0,66	0,42	0,1235	0,0152
	H	10	%	0,48	0,65	0,91	0,66	0,1377	0,0190

4	B	10	%	5,71	5,90	6,06	5,89	0,1249	0,0156
	S1	10	%	0,36	0,42	0,52	0,42	0,0517	0,0027
	S2	10	%	0,33	0,63	0,85	0,58	0,1608	0,0258
	H	10	%	0,48	0,50	0,86	0,56	0,1246	0,0155
Accessory materials content									
0	B	10	%	8,44	8,57	8,86	8,61	0,1288	0,0166
	S1	10	%	1,06	1,20	1,26	1,19	0,0631	0,0040
	S2	10	%	1,36	1,79	2,11	1,78	0,2552	0,0651
	H	10	%	3,12	3,51	3,61	3,45	0,1546	0,0239
2	B	10	%	9,44	9,58	9,74	9,58	0,0959	0,0092
	S1	10	%	1,45	1,61	1,72	1,60	0,0810	0,0066
	S2	10	%	2,06	2,72	2,89	2,58	0,3258	0,1061
	H	10	%	3,33	3,61	3,78	3,57	0,1528	0,0234
4	B	10	%	8,11	8,37	8,55	8,37	0,1393	0,0194
	S1	10	%	0,91	1,04	1,16	1,04	0,0785	0,0062
	S2	10	%	0,90	1,10	1,55	1,14	0,2055	0,0422
	H	10	%	3,06	3,30	3,51	3,29	0,1596	0,0255
Cellulose content									
0	B	10	%	22,85	23,94	25,61	24,12	0,9368	0,8776
	S1	10	%	48,02	49,44	50,74	49,41	0,9136	0,8346
	S2	10	%	47,99	49,46	50,65	49,51	0,9714	0,9436
	H	10	%	43,25	44,32	45,90	44,49	1,0248	1,0502
2	B	10	%	23,06	23,93	25,79	24,15	0,8196	0,6718
	S1	10	%	48,28	49,55	50,86	49,53	0,8139	0,6624
	S2	10	%	41,06	42,13	43,95	42,30	0,8992	0,8085
	H	10	%	42,85	45,21	45,69	44,81	1,0845	1,1762
4	B	10	%	23,34	25,03	25,84	24,79	0,8012	0,6419
	S1	10	%	48,44	49,83	50,96	49,74	0,7449	0,5549
	S2	10	%	41,85	43,03	44,77	43,20	1,0144	1,0291
	H	10	%	44,01	44,99	46,69	45,25	0,8798	0,7741
Lignin content									
0	B	10	%	48,12	49,69	50,66	49,45	0,8495	0,7216
	S1	10	%	30,47	31,44	32,86	31,59	0,7659	0,5866
	S2	10	%	25,33	26,73	28,11	26,71	0,9482	0,8991
	H	10	%	30,33	31,15	33,03	31,38	0,8616	0,7424
2	B	10	%	48,22	49,90	50,74	49,55	0,9073	0,8232
	S1	10	%	30,08	31,30	32,78	31,30	0,8570	0,7344
	S2	10	%	28,74	30,14	31,02	29,93	0,7312	0,5347
	H	10	%	30,09	31,25	32,86	31,44	0,8771	0,7694
4	B	10	%	48,64	49,89	51,33	49,94	0,8392	0,7042
	S1	10	%	30,87	31,88	33,51	32,02	0,8341	0,6957
	S2	10	%	30,06	31,33	32,58	31,25	0,7591	0,5763
	H	10	%	29,77	31,50	32,70	31,18	1,0650	1,1342
Wood polyoses content									
0	B	10	%	-	-	-	14,18	-	-
	S1	10	%	-	-	-	17,40	-	-
	S2	10	%	-	-	-	21,41	-	-
	H	10	%	-	-	-	20,14	-	-
2	B	10	%	-	-	-	13,30	-	-
	S1	10	%	-	-	-	17,16	-	-
	S2	10	%	-	-	-	24,76	-	-
	H	10	%	-	-	-	19,51	-	-
4	B	10	%	-	-	-	11,01	-	-
	S1	10	%	-	-	-	16,77	-	-
	S2	10	%	-	-	-	23,83	-	-
	H	10	%	-	-	-	19,72	-	-

0 – height 0 m; 2 – height 2 m; 4 – height 4 m; B – bark; S1 – sapwood till bark; S2 – sapwood up to heartwood; H – heartwood; Std. dev. – standard deviation

Table 2. *Bark (B) and sapwood (S1+S2) from previous study and heartwood (H) group chemical composition results of fired Aleppo pine wood (b)*

		N	Unit	Minimum	Median	Maximum	Mean	Std. dev.	Variance
Ash content									
0	B	10	%	2,63	2,71	2,84	2,72	0,0769	0,0059
	S1	10	%	0,41	0,47	0,55	0,47	0,0412	0,0017
	S2	10	%	0,25	0,40	0,59	0,41	0,1124	0,0126
	H	10	%	0,39	0,56	0,75	0,55	0,1391	0,0194
2	B	10	%	2,36	2,51	2,79	2,53	0,1255	0,0150
	S1	10	%	0,39	0,44	0,51	0,45	0,0453	0,0021
	S2	10	%	0,32	0,54	0,76	0,54	0,1614	0,0261
	H	10	%	0,43	0,67	0,78	0,65	0,1226	0,0150
4	B	10	%	2,76	3,19	3,32	3,10	0,1940	0,0376
	S1	10	%	0,45	0,52	0,55	0,51	0,0327	0,0011
	S2	10	%	0,40	0,63	0,82	0,63	0,1328	0,0176
	H	10	%	0,37	0,53	0,72	0,52	0,1023	0,0105
Accessory materials content									
0	B	10	%	12,25	12,48	12,69	12,47	0,1489	0,0222
	S1	10	%	1,12	1,26	1,43	1,27	0,1017	0,0103
	S2	10	%	1,88	2,27	2,51	2,22	0,2272	0,0516
	H	10	%	2,90	3,25	3,47	3,22	0,1868	0,0349
2	B	10	%	12,99	13,14	13,41	13,17	0,1554	0,0241
	S1	10	%	1,05	1,18	1,30	1,17	0,0664	0,0044
	S2	10	%	1,95	2,37	2,66	2,32	0,2395	0,0574
	H	10	%	3,34	3,81	4,01	3,74	0,2300	0,0529
4	B	10	%	13,00	13,16	13,36	13,17	0,1305	0,0170
	S1	10	%	0,99	1,08	1,29	1,11	0,1039	0,0108
	S2	10	%	1,48	1,95	2,44	1,96	0,3348	0,1121
	H	10	%	2,92	3,14	3,44	3,18	0,1970	0,0388
Cellulose content									
0	B	10	%	17,01	18,35	19,76	18,44	0,8110	0,6577
	S1	10	%	47,75	49,10	50,26	49,03	0,7608	0,5788
	S2	10	%	45,89	47,07	48,36	47,05	0,8905	0,7930
	H	10	%	44,03	45,73	47,11	45,60	1,0312	1,0634
2	B	10	%	19,02	20,57	21,74	20,50	0,8307	0,6901
	S1	10	%	48,12	49,57	50,36	49,40	0,7117	0,5066
	S2	10	%	42,39	43,74	44,87	43,65	0,9344	0,8731
	H	10	%	45,09	46,22	47,88	46,31	0,8034	0,6454
4	B	10	%	17,94	19,12	20,44	19,20	0,7561	0,5717
	S1	10	%	47,89	49,07	50,44	49,06	0,8751	0,7658
	S2	10	%	42,01	43,44	44,74	43,37	1,0168	1,0338
	H	10	%	42,88	43,82	45,69	44,04	1,0454	1,0929
Lignin content									
0	B	10	%	45,48	46,80	48,00	46,71	0,8558	0,7323
	S1	10	%	31,00	32,38	33,65	32,28	0,9716	0,9441
	S2	10	%	27,64	28,74	30,14	28,83	0,7936	0,6299
	H	10	%	30,98	32,54	33,66	32,44	0,7544	0,5691
2	B	10	%	45,95	47,28	48,44	47,18	0,8550	0,7310
	S1	10	%	30,60	31,71	33,10	31,84	0,7766	0,6031
	S2	10	%	30,01	31,16	32,54	31,19	0,7295	0,5322
	H	10	%	29,68	30,87	32,36	30,95	0,9108	0,8296
4	B	10	%	45,99	47,11	48,44	47,13	0,8158	0,6656
	S1	10	%	31,07	32,02	33,62	32,37	0,8737	0,7634
	S2	10	%	31,66	32,96	34,25	32,93	0,8471	0,7175
	H	10	%	30,89	32,55	33,44	32,37	0,7733	0,5980

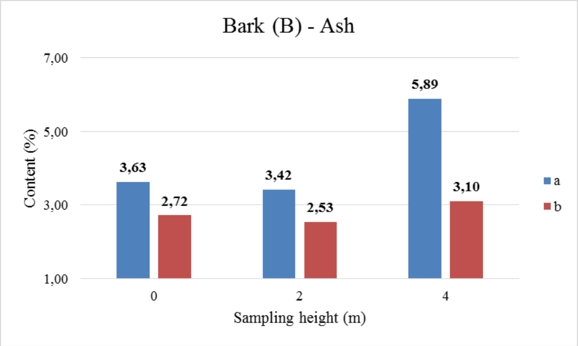
Wood polyoses content									
0	B	10	%	-	-	-	19,67	-	-
	S1	10	%	-	-	-	16,94	-	-
	S2	10	%	-	-	-	21,49	-	-
	H	10	%	-	-	-	18,19	-	-
2	B	10	%	-	-	-	16,61	-	-
	S1	10	%	-	-	-	17,14	-	-
	S2	10	%	-	-	-	22,30	-	-
	H	10	%	-	-	-	18,35	-	-
4	B	10	%	-	-	-	17,40	-	-
	S1	10	%	-	-	-	16,96	-	-
	S2	10	%	-	-	-	21,11	-	-
	H	10	%	-	-	-	19,89	-	-

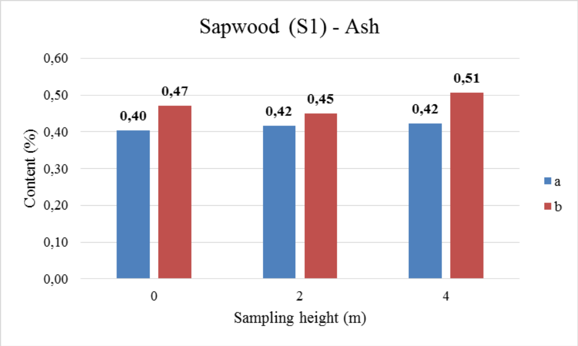
0 – height 0 m; 2 – height 2 m; 4 – height 4 m; B – bark; S1 – sapwood till bark; S2 – sapwood till heartwood; H – heartwood; Std. dev. – standard deviation

Table 1 and Table 2 show chemical composition of non-fired and fired wood bark (B) and sapwood (S1+S2) from previous studies (Antonović et al., 2017; Antonović et al., 2018a; Antonović et al., 2018b) for comparison with the heartwood (H) chemical components contents of the Aleppo pine depending on the sampling heights or forest fires heights. Notice that the bark (B) and sapwood (S1+S2) are from the same Aleppo pine wood as heartwood (H), for better understanding and a complete overview of the chemical composition of all anatomic wood parts.

Comparing the results of the Aleppo pine non-fired bark (B), sapwood (S1+S2) and heartwood (H) with the results of previous studies of the same wood species (Antonović et al., 2007), a conclusion can be made that the distribution of chemical components is similar. When comparing non-fired wood bark (B) with sapwood (S1+S2) and heartwood (H) chemical composition results the distribution is also similar, which means that the bark contains a significantly higher content of ash, accessory materials (extractives) and lignin, and an appreciably lower content of polysaccharides cellulose and polyoses (hemicellulose) than heartwood. The same was noticed for fired wood bark (B) in comparison with fired sapwood (S1+S2) and heartwood (H).

The statistical analysis of non-fired and fired wood bark (B) chemical composition results (Antonović et al., 2017) showed a substantial difference in the increased ash content between different forest fire heights, i.e. increased content at 4m respectively. Furthermore, fired wood bark (B) chemical composition results showed remarkably reduced ash content in comparison with non-fired wood. Based on the sapwood (S1+S2) (Antonović et al., 2018a; Antonović et al., 2018b) and heartwood (H) results there is no significant differences of ash content in non-fired and fired wood, between non-fired and fired wood, as well as on different forest fires heights (Figure 3). The inorganic content of wood species usually refers to its ash content, which is an approximate measure of its mineral salts and other inorganic matters content. The ash content of fired wood bark decreased in comparison to non-fired, which is probably a result of rapid water evaporation, where mineral salts were dissolved at high temperatures caused by fires. Furthermore, during burning in presence of oxygen and the appearance of the flame, a part of inorganic substances were evaporated and thus the loss of mass of inorganic substances is assumed.





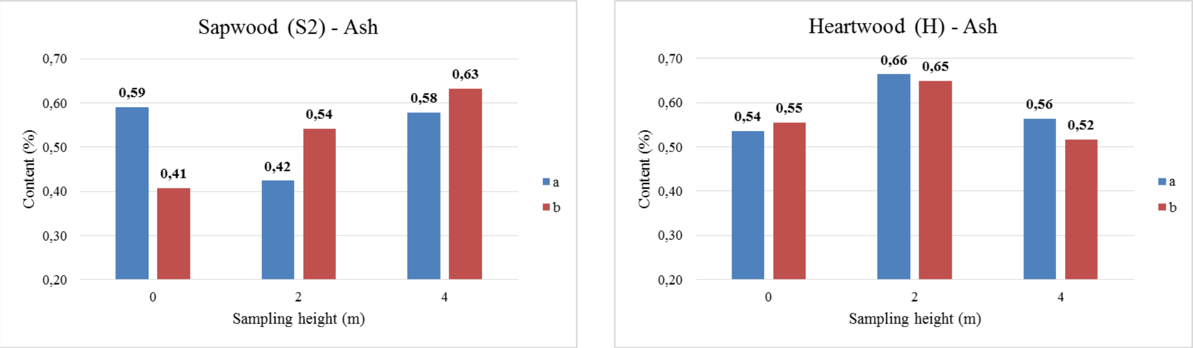


Figure 3. *Ash (mineral matter) content of non-fired and fired Aleppo pine in dependence on sampling height (forest fire height)*

Statistical analysis of fired wood bark (B) chemical composition results (Antonović et al., 2017) showed a significant difference in the increased accessory materials content in comparison with non-fired wood. Furthermore, the same results showed neither in non-fired wood nor in fired wood a substantial difference in the accessory materials content among different forest fire heights. Based on the sapwood (S1+S2) (Antonović et al., 2018a; Antonović et al., 2018b) and heartwood (H) results, it is apparent that there are no significant differences of the accessory materials content in non-fired and fired wood, between non-fired and fired wood, as well as on different forest fires heights (Figure 4). Previous study (Antonović et al., 2017) showed that the chemical components of the bark (B) wood cell wall (cellulose, hemicellulose, and lignin) were thermally degraded under the influence of high temperatures caused by forest fires, i.e. the high polymeric compounds are degraded into compounds with low molecular weight. It is assumed that many new low molecular weight compounds which had occurred during the fire and elevated temperatures, due to their chemical character similar to the different accessory materials groups mentioned above, during Soxhlet extraction were extracted together with the original accessory materials and thus joined their total content. The same applies to for recondensation (repolymerisation) explained in previously mentioned research.

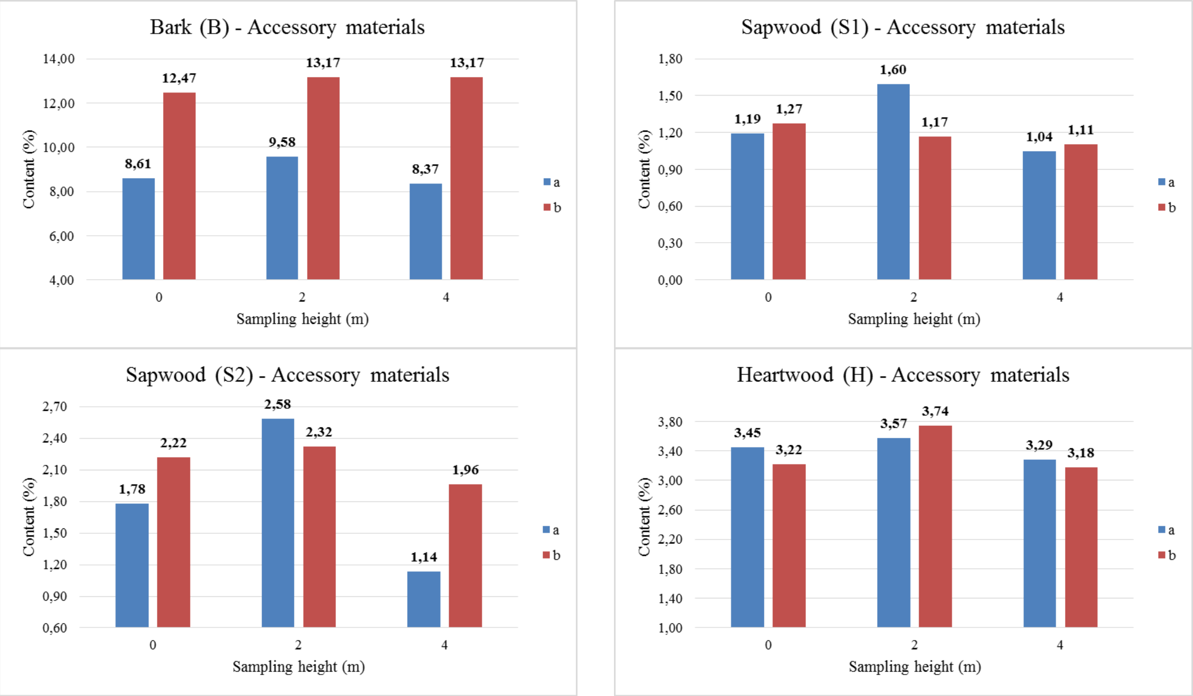


Figure 4. *Accessory materials (extractives) content of non-fired and fired Aleppo pine in dependence on sampling height (forest fire height)*

Statistical analysis of fired wood bark (B) chemical composition results (Antonović et al., 2017) showed a appreciable difference in the decreased cellulose content in comparison with non-fired wood. Furthermore, the same results showed neither in non-fired wood nor in fired wood a drastic difference in the cellulose content between different forest fire heights. Based on the sapwood (S1+S2) (Antonović et al., 2018a; Antonović et al., 2018b) and heartwood (H) results there are no significant differences of cellulose content in non-fired and fired wood, between non-fired and fired wood, as well as on different forest fires heights (Figure 5). Cellulose is principally responsible for production of flammable volatiles. The decrease in cellulose content occurs through dehydration, hydrolysis, oxidation, decarboxylation and transglycosylation. The primary reaction of the high-temperature pathway is depolymerization. This takes place when cellulose structure has absorbed enough energy to activate the cleavage of the glycosidic linkage to produce glucose, which is then dehydrated to levoglucosan (1,6-anhydro-ß-D-glucopyranose) and oligosaccharides. During thermal degradation, water and acids are produced from both hemicellulose and cellulose. The degradation reaction of cellulose is an exothermic reaction and it begins at 240–350 °C, and thus decomposes in anhydrocellulose and levoglucosan.

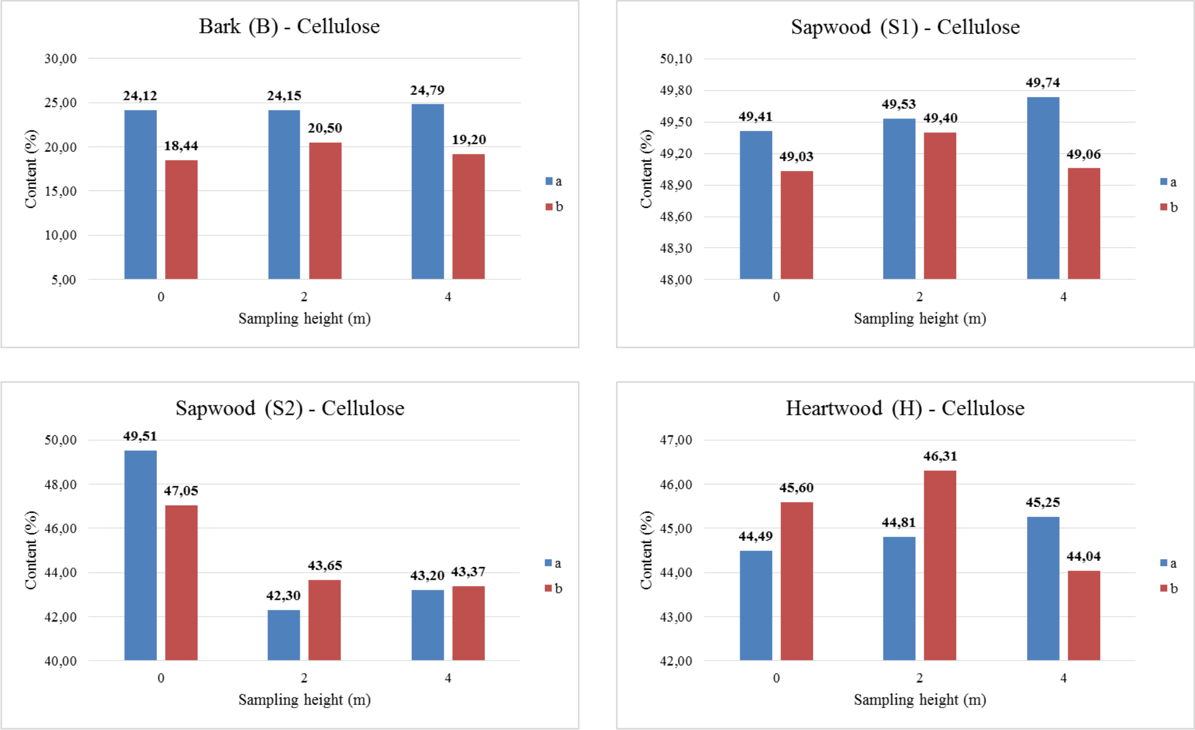


Figure 5. *Cellulose content of non-fired and fired Aleppo pine*
in dependence on sampling height (forest fire height)

As well as in cellulose content, statistical analysis of fired wood bark (B) chemical composition results (Antonović et al., 2017) showed a significant difference in the decreased lignin content in comparison with non-fired wood. Furthermore, the same results showed neither in non-fired wood nor in fired wood a significant difference in the lignin content between different forest fire heights. Based on the sapwood (S1+S2) (Antonović et al., 2018a; Antonović et al., 2018b) and heartwood (H) results, there are no considerable differences of the lignin content in non-fired and fired wood, between non-fired and fired wood, as well as on different forest fires heights (Figure 6). Thermal degradation of lignin yields phenols from cleavage of ether and carbon–carbon linkages and produces more residual char than does thermal degradation of cellulose. Dehydration reactions around 200°C are primarily responsible for thermal degradation of lignin and one part of decreased content. Second part of lignin decreased content part occurs between 150°C and 300°C and cleavage of a- and ß–aryl-alkyl-ether linkages, around 300°C, aliphatic side chains start splitting off from the aromatic ring, and finally, the carbon-carbon linkage between lignin structural units is cleaved at 370–400°C. The degradation reaction of lignin is also an exothermic reaction, with peaks occurring between 225°C and 450°C.

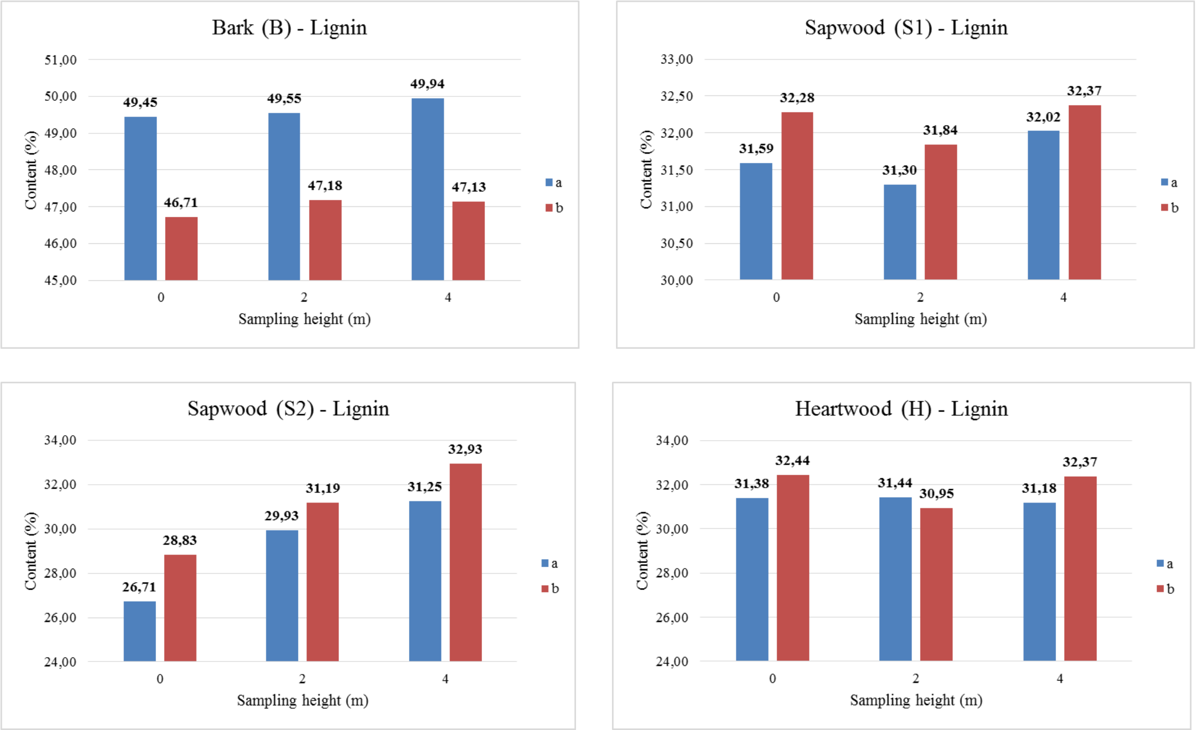
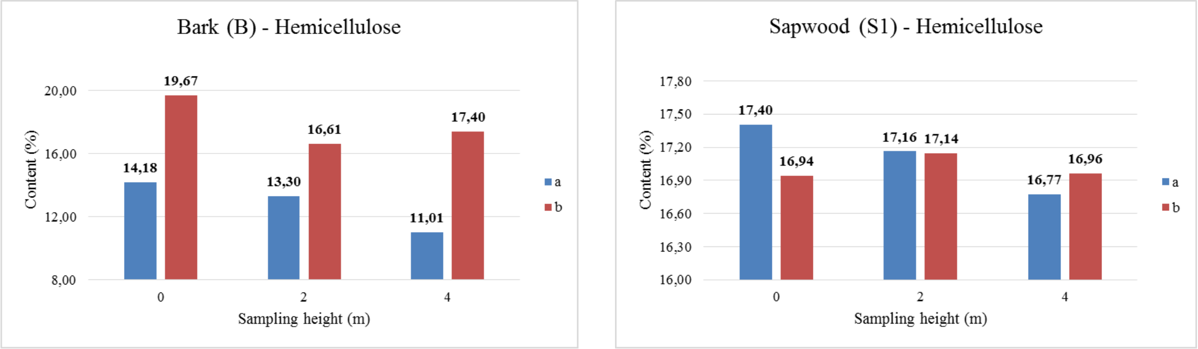


Figure 6. *Lignin content of non-fired and fired Aleppo pine in dependence on sampling height (forest fire height)*

Statistical analysis of fired wood bark (B) chemical composition results (Antonović et al., 2017) showed a significant difference in the increased hemicellulose content in comparison with non-fired wood. Based on the sapwood (S1+S2) (Antonović et al., 2018a; Antonović et al., 2018b) and heartwood (H) results there are no significant differences of hemicellulose content in non-fired and fired wood, between non-fired and fired wood, as well as on different forest fires heights (Figure 7). Although belonging to the same group of polysaccharides, wood polyoses (hemicellulose) differs from cellulose by the composition of different sugar units, by a much shorter molecular chain and by molecule chain branching. Accordingly, hemicelluloses are less stable thermally than cellulose and they evolve more non-combustible gases and less tar. As the obtained results show increased hemicellulose content in the fired wood bark compared with non-fired, and with the comprehension that hemicellulose was mathematically calculated, it should be assumed that increased hemicellulose content is caused by thermal decomposition of other chemical components of the wood bark group chemical composition (cellulose and lignin) into low molecular weight compounds that are joined to the sum of the hemicellulose total content.



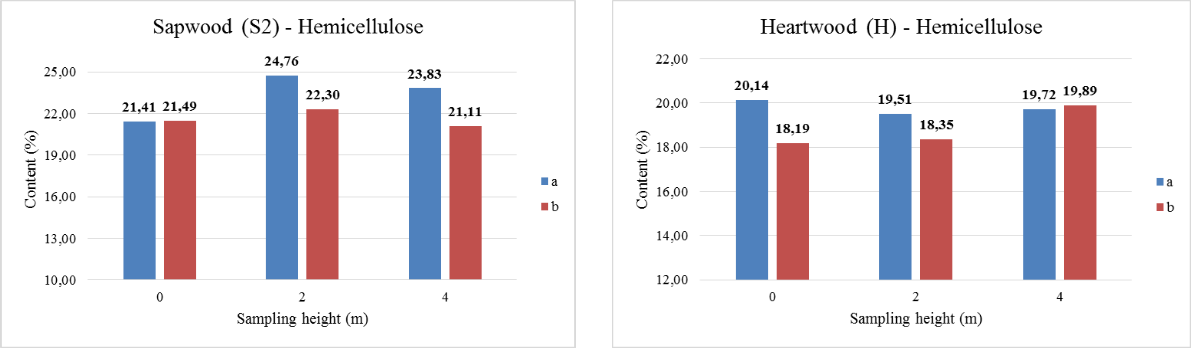


Figure 7. *Polyoses (hemicellulose) content of non-fired and fired Aleppo pine in dependence on sampling height (forest fire height)*

4. CONCLUSIONS

The main aim of this study was to study the group chemical composition of the Aleppo pine (*Pinus halepensis* Mill.) anatomical (macroscopic) wood parts before and after the impact of low ground fire and high fire of the treetops at the height of the trees of 0, 2 and 4 m. Therefore, the impact of forest fires on the Aleppo pine bark B), sapwood (S1+S2) and heartwood (H) group chemical composition was studied as a chemical quality property, as one of the technical properties, for further application. In addition, chemical composition results of non-fired and fired Aleppo pine bark (B) and sapwood (S1+S2) from previous studies were used for comparison with heartwood (H) from this study.

Obtained results show that the distribution of main chemical components of Aleppo pine non-fired wood bark (B), sapwood (S1+S2) and heartwood (H) is similar to results of previous studies for the same wood species. Chemical composition distribution is also similar, when bark (B) is compared with sapwood (S1+S2) and heartwood (H) of different wood species. That means that the bark contains notably higher content of ash, accessory materials (extractives) and lignin, and significantly lower content of polysaccharides cellulose and polyoses (hemicellulose) than sapwood and heartwood.

The bark results from previous study show drastic difference in reduced ash, cellulose and lignin content, and in the increased accessory materials and wood polyoses (hemicellulose) content between the non-fired and fired wood. Furthermore, the content of individual chemical components of fired bark at different forest fires heights of 0, 2 and 4m for each sample does not differ appreciably, except for ash, which can be explained by phytocoenological criteria of different sampling locations. Based on the results, there are no substantial differences for sapwood and heartwood, in the chemical composition between non-fired and fired wood, as well as on different forest fires heights.

It can be concluded that the forest fire did not have any effect on Aleppo pine overall sapwood and heartwood. Therefore, the fired wood bark takes on all the damage caused by the high temperature during the forest fire. It can be assumed that fired sapwood and heartwood still possess all the chemical properties for further application in mechanical or chemical processing. Furthermore, in practical terms it is necessary to ascertain the possible utilization and use of wood biomass that has been exposed to forest fires. This can reduce the extremely high costs of recovery after forest fires.
The study and results presented in this paper contributes to a better understanding of the possibility of using fired wood species as an enormous raw material base in the Republic of Croatia.

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