The Quality of Fired Aleppo Pine Wood (*Pinus Halepensis* Mill.) Biomass for Biorefinery Products

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Abstract

Open-air fires or forest fires are becoming a key factor in reducing the forest surface areas and they are one of the major factors of devastation and degradation of forests and forest land and their ecosystems in the Mediterranean, mainly in coastal karst. They cause extreme material and economic damage, and they negatively affect biological and landscape diversity. After the forest fire, significant quantities of fired trees are left behind, representing a significant amount of lignocellulosic biomass available for conversion into a variety of biobased products. The question arises as to what degree they are chemically degraded, or whether they still have the properties required for further application in mechanical or chemical processing.

*The main aim of this paper was to study the group chemical composition as a biomass chemical property of the Aleppo pine (*Pinus halepensis Mill.*) sapwood before and after the impact of low ground fire and high fire of the treetops at tree height of 0, 2 and 4 m. Therefore, the impact of forest fires on the Allepo pine sapwood group chemical composition was studied in terms of quality for further application in production of biorefinery products. In addition, research results on group chemical composition of the same unfired and fired Aleppo pine wood bark from previous study were used for comparison with sapwood from this study.*

The obtained results show that the distribution of the main chemical components of Aleppo pine unfired wood bark and sapwood is similar to the results of previous studies for different wood species. That means that the bark contains a significantly higher content of ash, accessory materials (extractives) and lignins, and a significantly lower content of polysaccharides cellulose and polyoses (hemicellulose) than sapwood. The bark results from previous studies show a significant difference in reduced ash, cellulose and lignin content, and in the increased accessory materials and wood polyoses (hemicellulose) content between the unfired and fired wood. Furthermore, the content of individual chemical components of fired bark at different forest fires heights of 0, 2 and 4 m for each sample did not differ significantly. Contrary to fired bark, no significant differences have been observed in the chemical composition of sapwood between unfired and fired wood, not even resulting from different forest fires heights. It can be concluded that the forest fire did not have any effect on Aleppo pine sapwood, where the fired wood bark took over all the damage caused by high temperature during the forest fire. In addition, the fired sapwood still retains the chemical properties required for further application in biorefinery biobased products.

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

1. Introduction

The current model of production and consumption, which largely relies on fossil-based resources and has a decisive impact on the environment and the availability of natural resources, is approaching its peak. Significant steps are being taken around the world to move from today's fossil based economy to a more sustainable economy based on biomass. A key factor in the realization of a successful biobased economy or bio-economy 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, reindustrialization, and addressing societal challenges. Furthermore, the circular economy is defined as an economy that is restorative and regenerative by design, and which aims to keep products, components and materials at their highest utility and value at all times, distinguishing between technical and biological-cycles. It focuses on the efficient use of finite resources and ensures that these resources are reused as long as possible (IEA Bioenergy 2017, AEBIOM 2017).

A bioeconomy, as well as circular economy, uses as many renewable raw materials as possible for products such as chemicals, materials and energy. As a part of bioeconomy and circular economy, biorefining, as the sustainable processing of biomass into a range of marketable biobased products and bionenergy/biofuels, is an innovative and efficient approach to use the available biomass resources for the synergistic co-production of chemicals, materials and energy. A biorefinery is a multidisciplinary and complex concept addressing, at the same time, the production of value-added bio-products (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. The development and implementation of biorefinery processes is of the upmost importance and constitutes the keystone for establishing a bioeconomy based on bioresources, and it is an absolute necessity and the key to meet this vision of a biobased economy. 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. In addition, the European Commission has set a long-term goal to develop a competitive, resource efficient and low carbon economy by 2050, and biorefinery products are expected to play an important role (IEA Bioenergy 2017).

Contrary to petro-resources, whose nature and composition variations are relatively limited, under the terms bioresource or biomass, compounds are gathered of very different nature. 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 include 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 used as a flexible load where and when the raw material is needed. This makes biomass unique among other options of renewable raw materials (AEBIOM 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 the 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 its 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 the 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 it can be said that the 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 the chemical composition of tissues and bark, it can be concluded that the 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, Antonović, 2017).

The end-use processing pathways of wood, as a lignocellulosic biomass for biorefinery products, depend on its physicochemical properties. These properties are composed of the following:

⇒ biochemical composition (a) wood chemistry – cellulose, hemicellulose and lignin; (b) non-wood chemistry – saccharides, lipids and proteins

⇒ moisture content (a) intrinsic moisture; (b) extrinsic moisture

⇒ mineral matter content (a) major elements; (b) trace elements; (c) nutrients; (d) salts

⇒ elemental composition of organic matter (C, H, N, S, O)

⇒ physical properties (a) density; and (b) grindability.

Two fundamental aspects related to such biomass are:

⇒ to extend and improve the basic knowledge on composition and properties

⇒ apply this knowledge for the most advanced and sustainable utilization of biomass.

According to that, the systematic identification, quantification and characterization 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 biomass for such products is to understand its basic composition and properties (Strezov and Evans 2015).

Recently in Croatia, and worldwide, concern has arisen with respect to the increasing number of forest fires. The causes of fires, as a result of certain human activities, are manifold and numerous. Open-air fires or forest fires are becoming a key factor in reducing the forest surface areas and they are one of the major factors of devastation and degradation of forests and forest land and their ecosystems in the Mediterranean, mainly in coastal karst. In addition to causing extreme material and economic damage, in a large number of cases they negatively affect biological and landscape diversity (Prgin 2005). The impact of open space fire, in terms of ecology, was explored by many authors. These are extremely important problems of natural renewal and vegetation succession, occurrence of erosion processes after the fire and prevention of forest soil degradation. Another aspect, often neglected, refers to the technical properties of the fired wood. Therefore, an important species for the Croatian Mediterranean karst was studied in this paper, the Aleppo pine (*Pinus halepensis* Mill.), the most important species for the afforestation of the Dinaric karst (Saracino et al. 1997, Pentek 1998, Espelta et al. 2002, Rodrigo et al. 2004, Tapias et al. 2004, Pausas et al. 2008, Španjol et al. 2011, Pentek et al. 2011, Pentek et al. 2014).

Forest fires occur when all the 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. 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 higher 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 become more flammable; this being often a consequence of droughts (Prgin 2005).

According to the occurrence method, fires are grouped into:

⇒ natural (uncontrollable, wild, sifted)

⇒ artificial (controlled, planned) (Dimitrov 1987, Španjol 1996).

According to the fuel material type, fires are classified as follows:

⇒ underground fire or soil fire (roots and peat);

⇒ ground or low fire

⇒ fire in the tops or high fire

⇒ fire of lonely trees and shrubs (Španjol 1996).

Underground fire or soil fire (roots and peat) is affected by humus and peat layers beneath forestry mats. It advances very slowly but constantly. Peat fires may last (smolder) for several months and constantly threaten to emerge from the surface and become a dangerous groundwater fire. Damage is great because of the damage to the roots of trees that are then dried. Such fire is very difficult to detect and it is difficult to extinguish. Ground fire or low fire occurs when the upper layer of forest mats, booming shrubs and young stands, are ignited. This is the most common type of fire that occurs in all types of forests. Strong ground fire in forests, where the trees have a thin bark, damages the tree roots, and causes cambium dying and trees drying, as well as dying of the whole stands. The temperature of 54 °C is sufficient for destroying the cambium. Fire in the tops or high fire is the kind of fire that surely destroys the entire forest ecosystem, and it is most frequent in coniferous forests. With the so-called flying fires, fire spreads from one top to another. With the help of the wind, this fire can destroy large forest complexes. The fire of lonely trees and shrubs is mainly caused by the lightning strike and in that case the tree burns down. It is most often connected to large forest areas. However, the cause may also be the burning of the fire close to the trees (Španjol 1996).

When trees are exposed to elevated temperatures caused by forest fires, changes can occur in their chemical composition, affecting their properties. The extent of changes depends on the temperature level and length of time under exposure conditions. 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 gases and liquids, when mixed with air, burn with a flame, whereas the charcoal burns in the air without flame. Wood burns »indirectly«, in the sense that wood does not actually burn, but combustion takes place as a reaction between oxygen and the gases released from the wood (high molecular weight components). Under the influence of heat, wood produces easily substances that react eagerly with oxygen, making wood susceptible to

fire. Ignition and combustion of wood is mainly based on thermal decomposition of cellulose and reactions of thermal degradation products with each other and with gases in the air, mainly oxygen. When temperature increases, cellulose starts to degrade. The decomposition products either remain inside the material or are released as gases. Gaseous substances react with each other and oxygen, releasing a large amount of heat that further induces degradation and combustion reactions (Thomas and McAlpine 2010).

According to the above mentioned, after the forest fires, significant quantities of fired Aleppo pine trees (*Pinus halepensis* Mill.) are left behind as a lignocellulosic biomass. The question arises as to what degree they are chemically degraded or whether they still have all the properties required for further application in mechanical or chemical processing. The main aim of this study was to chemically characterize fired Aleppo pine in terms of biomass quality and contribute to a better understanding of the possibility of using fired wood species, as a very large raw material base in the Republic of Croatia, in the further production of biorefinery products. Therefore, the impact of forest fires on chemical composition of the Aleppo pine sapwood group was studied as a quality property. The study was carried out by determining the group chemical composition (accessory materials, mineral substances, cellulose, hemicellulose and lignin) of Aleppo pine fired wood sapwood and unfired wood sapwood for comparison, by sampling the rings at the tree height of 0 m, 2 m 4 m (also referred as forest fire heights). Based on the results of the chemical analysis of the fired Allepo pine wood sapwood, the impact of forest fires on changes of chemical composition was determined by comparison with the unfired wood sapwood, as well as its possibility for further application in production of biorefinery products. In addition, research results on group chemical composition of unfired and fired Aleppo pine wood bark from previous study (Antonović et al. 2017) were used for comparison with sapwood from this study.

2. Materials and methods

For studying the quality of fired wood as biomass for the production of biorefinery products, Aleppo pine wood (*Pinus halepensis* Mill.) was chosen, as the most common wood species in the coastal karst, especially in Dalmatia, the islands and the Dalmatian Zagora of the Republic of Croatia.

Aleppo pine wood covers more and more 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 favors faster spread of fires than mixed forests of Mediterranean hardwoods. The use of Aleppo pine wood in Mediterranean countries has a wide application. It is especially appreciated as quality wood in pulp production, and in some countries, wood industry is based on the Aleppo pine raw materials. Furthermore, it is used for heating, small technical wood in agriculture, mining wood, in construction for internal joinery, sawmill boards and others. Aleppo pine forests favor the development of economic activities, employment of the population, raising the quality of life of people and creating their local culture identity. With the opportunities offered by Aleppo pine forests, as well as other forest areas, new possibilities will emerge for the development of forestry and wood processing, providing employment of the local population, with a clear concept of forestry development on karst areas that have been passive until now (Meštrović 1977, Matić 1986).

2.1 Wood sampling location and forest fires characteristics

Sampling of unfired and fired Aleppo pine wood was carried out by the company »Croatian Forests Ltd.«, in Split Forest Administration – Forest Department Šibenik, management unit Jelinjak. Wood sampling location and forest fire characteristics were as follows:

⇒ fire type – ground fire (law) and treetops fire (high)
⇒ fired surface size – 19.25 ha
⇒ forest breeding
⇒ high (Allepo pine forest culture) – 3.15 ha (16.36%)
⇒ low (garrigue) – 14.9 ha (77.40%)
⇒ agriculture land (perennial crops) – 1.20 ha (6.23%
⇒ forest description – old Allepo pine forest culture (*Pinus halepensis* Mill.) 53 years old, the bushy layer and plants ground layer are very rare, ground is very rocky, 10º inclination, 50m altitude
⇒ sample mark
⇒ »a« unfired tree
⇒ »b« fired tree (Fig. 1, 2 and 3).

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), and unfired (a) wood of Aleppo pine for comparison, ring samples of 10–30 cm thickness were taken at three different tree heights (fires heights) as follows:

Fig. 1 Forwarder pulling out the fired Aleppo pine biomass from the fired forest

Fig. 2 Removal of fired Aleppo pine biomass from fire site

⇒ first ring sample at a height of 0 m (the first ring from the cutting point, next to the stump)

⇒ second ring sample at a height of 2 m

⇒ third ring sample at a height of 4 m.

Fig. 3 Fired Aleppo pine biomass on fire site

Rings were taken immediately after cutting trees according to the standard TAPPI T257 cm 02 – Sampling and preparation of wood for analysis, and taken to the laboratory.

After 14 days of drying in the laboratory, wood macroscopic parts were mechanically separated on each ring. This means that bark (B), sapwood (S) and heartwood (H) were separated. The sapwood (S) was additionally divided into two parts and labeled as S1 (the part of sapwood close to the bark) and S2 (the second part of sapwood close to the heartwood) (see Fig. 4). 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. The first part of sapwood close to the bark (S1) was taken for this research. The results of chemical composition of bark (B) group of the same Allepo pine wood was also taken from the previous
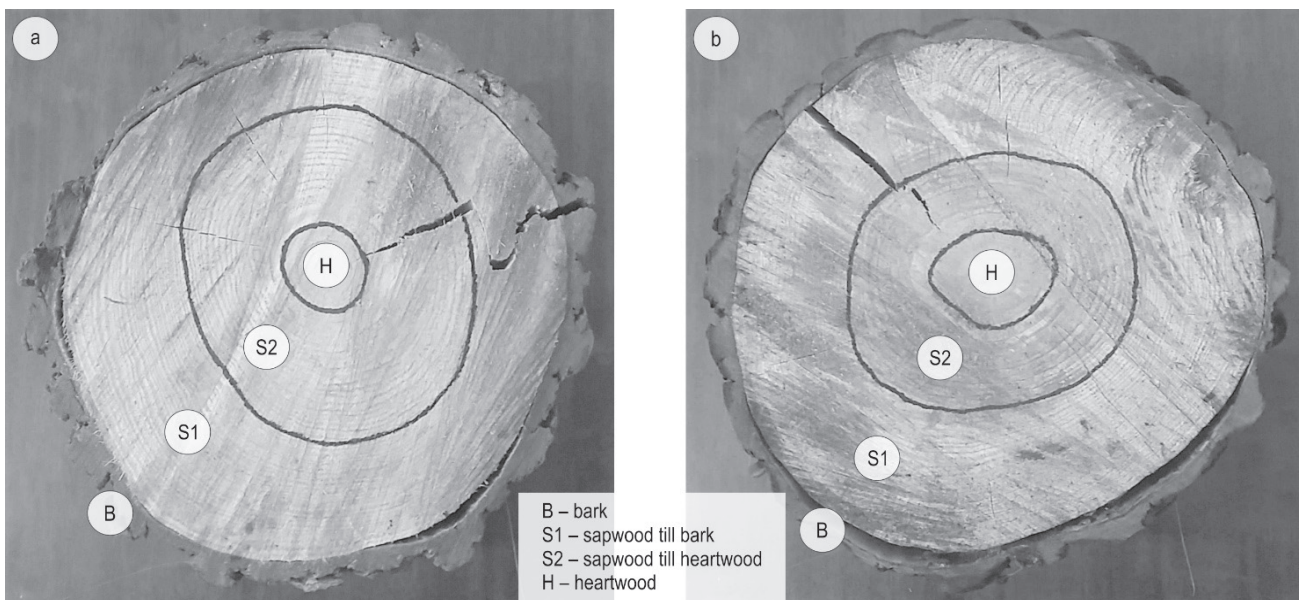

Fig. 4 Unfired wood (a) and fired wood (b) of Allepo pine with wood macroscopic parts
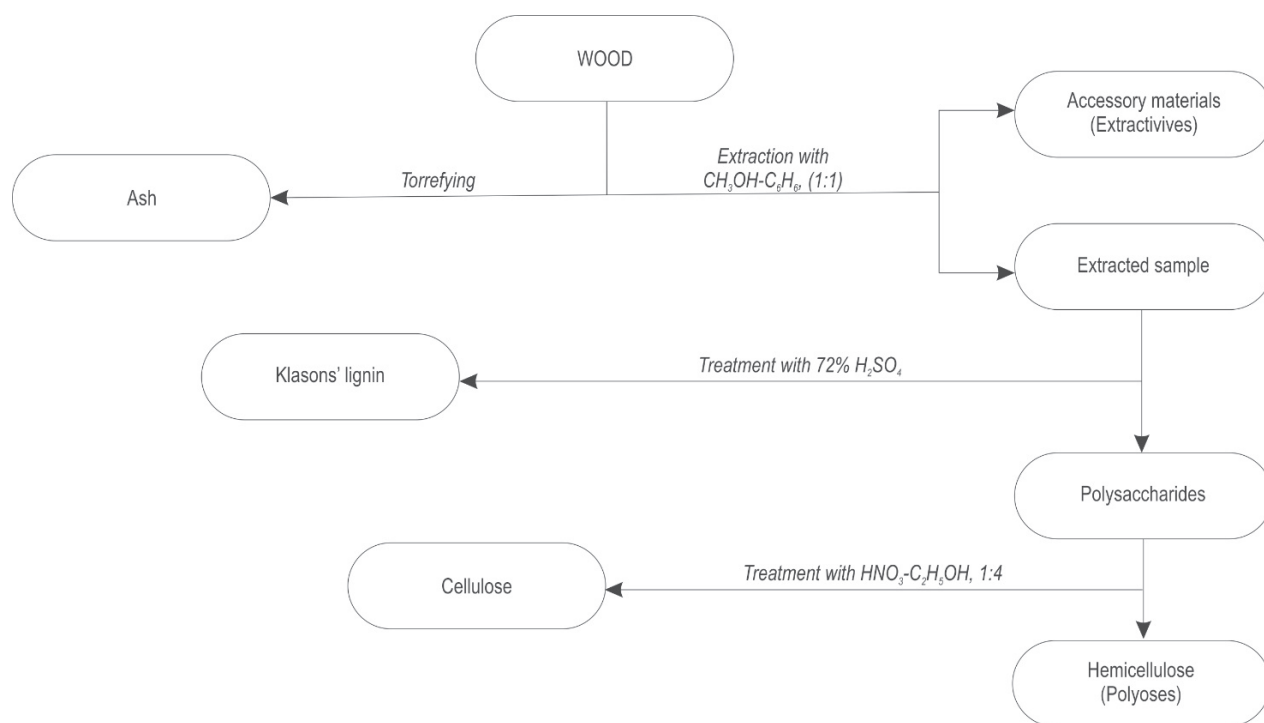
Fig. 5 Schematic view of sample chemical analysis

study (Antonović et al. 2017) for comparison with sapwood (S1) results obtained in this research.

Furthermore, after the separation of macroscopic parts of each ring, sapwood (S1) samples were prepared according to previous studies (Antonović et al. 2007, Antonović et al. 2008, Antonović et al. 2010) and in accordance with the laboratory analytical procedure Preparation of Samples for Compositional Analysis (Hames et al. 2008). Air-dried sapwood samples were milled to different particle sizes using a knife-mill Fritsch – Pulverisette 19. After milling, samples were sieved through standardized sieves. The milled particles, which passed the sieve screen of 0.71 mm and remained on the sieve of 0.325 mm, were used for further chemical analysis, due to their ideal particle size for all isolation methods of group chemical composition, as recommended in previous studies. For screening, laboratory electromagnetic sieves shaker Cisa RP.08 (shaking time t=15±1 min) was used.

After sapwood (S1) grinding and sieving, three smaller samples were taken of each criterion, on which all the chemical analysis were performed, and the results are presented as the mean values of these three samples.

2.3 Wood group chemical components isolation

Isolation methods for determining the content of the chemical composition of sapwood (S1) sample

group, namely ash, accessory materials (extractives), cellulose, hemicellulose (polyoses) and lignin, were conducted in compliance with previous studies (Antonović et al. 2007, Antonović et al. 2008, Sluiter et al. 2005a, Sluiter et al. 2005b, Sluiter et al. 2008). Sample compositional analysis consisted of a series of isolation methods of the main components, which can be schematically presented as shown in Fig. 5. 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 the volume ratio 1:1) to remove the accessory materials from the sample which could interfere during further chemical analysis. Thus, additional residual solid content was determined as a content of accessory materials or extractives. Furthermore, sulfonic acid lignin or Klason's lignin (by treatment with 72% sulfuric acid, H_2SO_4) and 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) were 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. The hemicellulose content was calculated according to following expression: WP = 100 – (% A + % AM + % C + % L) in %. All used chemicals were of high purity (p.a.) and were obtained from commercial sources.

3. Results with discussion

Forest fires front is the portion sustaining continuous flaming combustion, where unfired material meets active flames, or the smoldering transition between unfired 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 a temperature of 100 °C. Next, the pyrolysis of wood at 230 °C releases flammable gases. Finally, wood can smolder at 380 °C or, when heated sufficiently, ignite at 590 °C. Even before the flames of a forest fire 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 (Bakšić et al. 2015).

Forest fires emit a complex mixture of particles and gases into the atmosphere. The diversity in composition of combustion products results from a wide range of wood species, wood chemistry, and fire behavior. The chemical characteristics of wood affect the rate of combustion and influence the overall forest fire behavior. 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, noncombustible products, such as carbon dioxide, traces of organic compounds and water vapor, are produced. Above 200 °C, the cellulose breaks down, producing tars and flammable volatiles that can diffuse into the surrounding environment. If 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 enhancing 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 vapor. Oxidation of the char is referred to as afterglow (Alexander 1982, Basin 2011).

The thermal degradation of wood caused by forest fires can be represented as the 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 individual chemical components on thermal degradation reactions of sapwood 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 the cellulose plus hemicelluloses, follows most closely the degradation 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 at higher temperatures than holocellulose. This lower degradation temperature of wood is primarily due to hemicelluloses in wood and holocellulose. The 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 wood, respectively (Antonović et al. 2017, Jurišić et al. 2017, Krička et al. 2017).

Table 1 Bark (B) from previous study and average values of sapwood (S1) group chemical composition of unfired and fired Aleppo pine wood

Sample			Wood chemical component				
			A	AM	C	L	WP
			%	%	%	%	%
a	0	B	3.63	8.61	24.12	49.45	14.18
		S1	0.40	1.19	49.41	27.24	21.76
	2	B	3.42	9.58	24.15	49.55	13.30
		S1	0.42	1.60	44.51	25.99	27.48
	4	B	5.89	8.37	24.79	49.94	11.01
		S1	0.42	1.04	53.85	29.85	14.83
b	0	B	2.72	12.47	18.44	46.71	19.67
		S1	0.47	2.68	47.11	33.35	16.38
	2	B	2.53	13.17	20.50	47.18	16.61
		S1	0.45	1.58	49.40	31.84	16.73
	4	B	3.10	13.17	19.20	47.13	17.40
		S1	0.51	1.11	44.81	32.37	21.20

A – ash; AM – accessory materials; C – cellulose; L – lignin; WP – polyoses (hemicellulose); a – unfired wood; b – fired wood; 0 – height 0 m; 2 – height 2 m; 4 – height 4 m; B – bark; S1 – sapwood

Table 1 and Fig. 6 show the unfired and fired wood bark (B) from previous study (Antonović et al. 2017) for comparison and chemical components contents of the first part of sapwood close to the bark (S1) of the Aleppo pine depending on the sampling heights or forest fires heights. The bark and sapwood were from the same Aleppo pine wood. Comparing the results of the Aleppo pine unfired bark and sapwood with the results of previous researches of different wood species (Antonović et al. 2007), it can be concluded that the distribution of chemical components is similar. When comparing the unfired wood bark with sapwood chemical composition, the distribution is also similar, which means that the bark contains a significantly higher content of ash, accessory materials (extractives) and lignins, and a significantly lower content of polysaccharides cellulose and polyoses (hemicellulose) than sapwood. The same was noticed for fired wood bark in comparison with fired sapwood.

The inorganic content of wood species, usually referred to as its ash content, is an approximate measure of its mineral salts and other inorganic matter content. The ash content of fired wood bark decreased in comparison to unfired wood bark, which is probably due to rapid water evaporation, where mineral salts were dissolved at high temperatures caused by fires. Furthermore, during the burning in the presence of oxygen and the appearance of flame, a part of inorganic substances were evaporated and thus the loss of mass of inorganic substances was assumed.

Previous research (Antonović et al. 2017) showed that the chemical components of the bark wood cell wall (cellulose, hemicellulose, and lignin) was thermally degraded under the influence of high temperatures caused by forest fires, i.e. the high polymeric compounds were degraded into compounds of low molecular weight. It is assumed that many new low molecular weight compounds, which occurred during the fire and elevated temperatures, due to their chemical character similar to the different accessory materials groups mentioned above, were extracted during Soxhlet extraction together with the original accessory materials and thus joined their total content. The same is explained for re-condensation (re-polymerization) in the above mentioned previous studies. Based on the sapwood results, there is no significant difference in the accessory materials content between unfired and fired wood, not even resulting from different forest fires heights.

Cellulose is principally responsible for the 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 the 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, beginning at 240–350 °C, where it is decomposed to anhydrocellulose and levoglucosan. The bark results from the previous study (Antonović et al. 2017) show a significant difference in reduced cellulose content between the unfired and fired wood. Based on the sapwood results, there are no significant differences in the cellulose content between unfired and fired wood, not even resulting from different forest fires heights.

Although belonging to the same group of polysaccharides, wood polyoses (hemicellulose) differ from cellulose by the composition of different sugar units, by a much shorter molecular chain and by molecule chain branching. Hemicelluloses are less stable thermally than cellulose and evolve more noncombustible gases and less tar. As the obtained results show, increased hemicellulose content in the fired wood bark compared with unfired wood bark, and considering that hemicellulose was mathematically calculated, it should be assumed that the 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 hemicelulose total content. Based on the sapwood results, there are no significant differences in the hemicellulose content between unfired and fired wood, not even resulting from different forest fires heights.

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. The other part of lignin decreased content 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. Similarly as in cellulose content, the bark results show a significant difference in reduced lignin content between the unfired and fired wood. Based on the sapwood results, there are no significant differences in the lignin content between unfired and
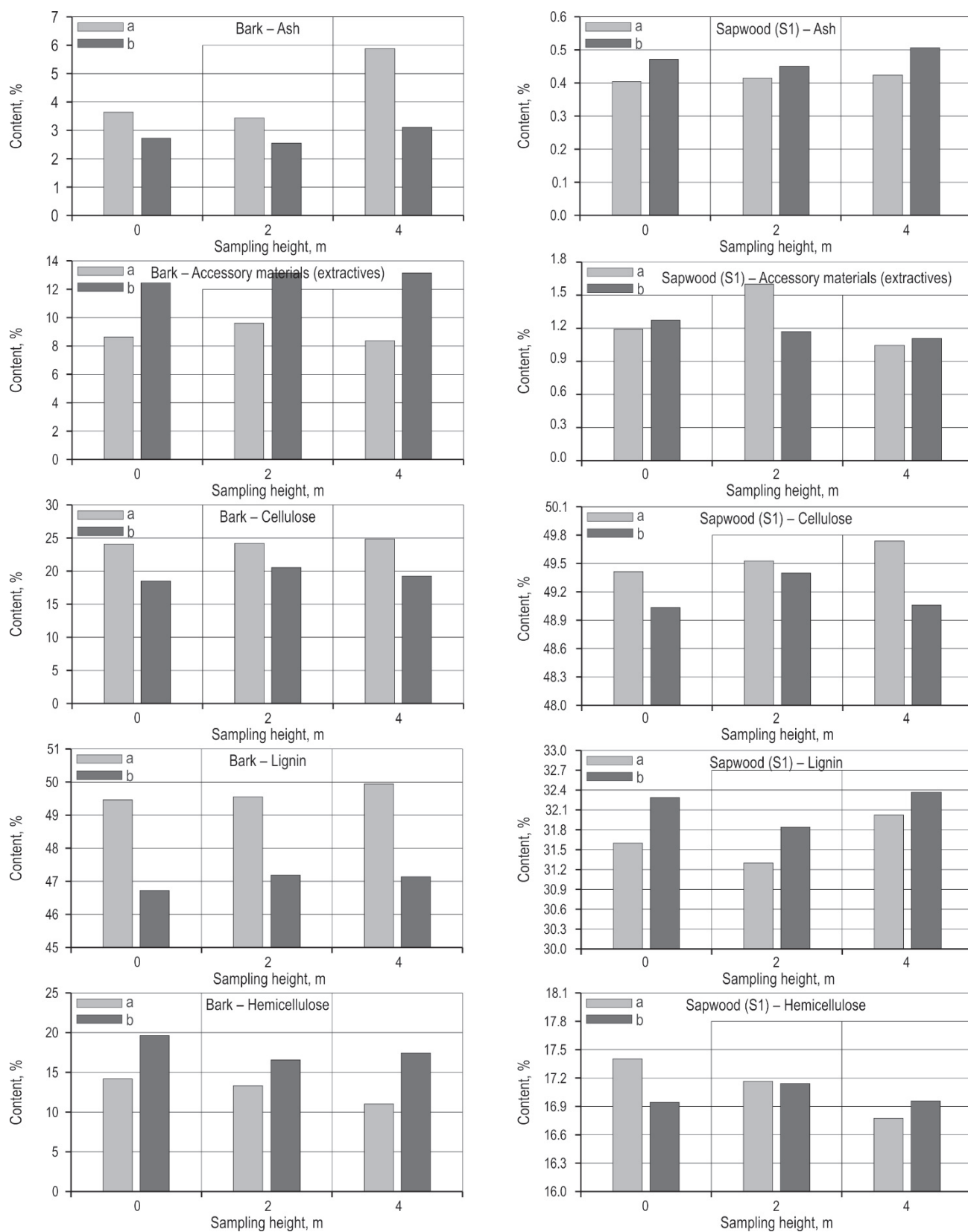
Fig. 6 Bark (B) and sapwood (S1) group chemical components content of unfired and fired Aleppo pine wood in dependence on sampling height (forest fire height)

fired wood, not even resulting from different forest fires heights.

Further research on the same wood samples should analyze the impact of forest fires on the second part of sapwood and heartwood at different tree heights (fire heights) to see if the fire has affected their chemical composition, and to make comparison with the results of the present study.

4. Conclusions

The main aim of this paper was to study the group chemical composition of the Aleppo pine (*Pinus halepensis* Mill.) first part of sapwood close to the bark before and after the impact of low ground fire and high fire of the treetops at tree height of 0, 2 and 4 m. Therefore, the impact of forest fires on the Allepo pine sapwood group chemical composition was studied in terms of quality for further application in production of biorefinery products. In addition, research results on group chemical composition of unfired and fired Aleppo pine wood bark from previous studies were used for comparison with sapwood from this study.

The obtained results show that the distribution of the main chemical components of Allepo pine unfired wood bark and sapwood is similar to the results of previous studies for different wood species. The distribution is also similar when bark is compared to chemical composition of sapwood of different wood species. This means that the bark contains a significantly higher content of ash, accessory materials (extractives) and lignins, and a significantly lower content of polysaccharides cellulose and polyoses (hemicellulose) than sapwood.

The bark results from previous studies show a significant difference in reduced ash, cellulose and lignin content, and in the increased accessory materials and wood polyoses (hemicellulose) content between the unfired 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 significantly, except for ash, which can be explained by phytocenological criteria of different sampling locations. Based on the results, there are no significant differences for sapwood in the chemical composition between unfired and fired wood, not even resulting from different forest fires heights.

It can be concluded that the forest fire did not have any effect on Aleppo pine sapwood. The fired wood bark takes over all the damage caused by the high temperature during the forest fire. It can be assumed that fired sapwood still has all the chemical properties for further application in mechanical or chemical processing. Therefore, 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 the forest fires.

The study presented in this paper contributes to a better understanding of the possibility of using fired wood species, as a very large raw material base in the Republic of Croatia, in the further production of biorefinery products.

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