

International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

Volume 4, Issue 2, August 2024

# Evaluation of a Combined Thermal/Chemical Wood Modification by the Use of FTeIR Spectroscopy and Chemometric Methods

Ms. Priya Panday

Lecturer (Department of Chemistry), Government Polytechnic College, Adityapur, Jamshedpur, Jharkhand, India

**Abstract:** In this study, the combined effects of chemical (with tricine and bicine) and thermal treatments were investigated. The modifications which appeared in the wood structure were evaluated by infrared spectroscopy and chemometric methods (principal component analysis and hierarchical cluster analysis). After the treatment, about 6e7% of WPG was identified in treated samples, but further thermal treatment decreased the WPG to about 5%. The modifications appearing in the spectra were mostly related to increase of the intensities of the bands assigned to C]O groups but also to NeH and CeN groups, with shifting of some bands to higher wave number values.

Keywords: chemometric methods

#### **I. INTRODUCTION**

Wood is an important natural resource used in many applications, from construction to furniture and different domestic or industrial objects, tools and artworks. Despite its properties, wood presents some limitations in exterior environment use, such as dimensional instability, susceptibility to fungal decay or weathering, etc . In order to prevent these, several thermal or chemical treatments have been applied.

Thermal treatment of wood has been well established over the past decades, with several commercialised processes . The treatment causes transformations in wood composition, through a series of hydrolysis, oxidation and decarboxylation reactions, which are coupled with heat and mass transfer and/or other physical changes (conformational changes and molecular rearrangements). The reactions involved during heating, as well as the final properties of the wood material, depend strongly on several factors, like: treatment time, normal atmosphere condition or vacuum, temperature applied, and the relative humidity, but also on the wood species used Even the resulted endeproduct possesses improved physical characteristics, like lower hygroscopicity, better dimensional stability, durability, if wood is to be exposed to different chemical or biological agents, or to frequent use under natural environmental conditions, the mechanical properties are often reduced. Another type of wood modification is the reaction with different chemicals e chemical modification, where chemical moieties are covalently bonded to the wood cell wall polymers. Different chemical modifications can be applied to change the properties of wood, especially to improve the dimensional stability, decay resistance, water sorption, and mechanical properties As a result of this treatment, the hydroxyl groups in the cell wall are substituted partially and the cell wall of the wood is bulked with the bonded chemicals. The substitution of the hydroxyl groups reduces the number of primary sorption sites (which are generally assumed to be the OH groups); while the bulking reduces the volume in the wood cell wall which is accessible to water molecules The most common chemical modification process involves the reaction with different anhydrides. Although the literature presents a wide range of anhydrides used for the treatment, acetylation using acetic anhydride is the most studied one and it is also produced commercially. Apart of anhydrides, many other chemicals have been used in order to improve the properties of wooden material. For example, treatments using dimethylol dihydroxy ethylene urea (DMDHEU) [i.e. melamine resin, silane, siloxane or silicon polymers were found to improve the mechanical strength of wood.

Recently, a new approach uses the Maillard reactions for the treatment of wood. This method proved to be promising modification method for the improvement of some properties of the wood. In this context, a recent work of Hauptmann

Copyright to IJARSCT www.ijarsct.co.in DOI: 10.48175/IJARSCT-19495





International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

#### Volume 4, Issue 2, August 2024

and co-workers has considered the use of tricine for the modification of wood, though the studies have been limited to a maximum temperature of 103 C. The authors observed increased hardness and tensile strength of their modified wood species. Another work from Peeters and co-workers describe preliminary results of their experiments based on a Maillard type of reaction at 120 C by using nontoxic chemicals in order to decrease the wood decay.

Maillard type reactions are a cascade of reactions, known also as nonenzymatic browning. The initial step consists in reaction between a reducing end of a saccharide and an amino acid to give a condensation product. This reaction takes place usually during the heat processing of food with a low relative humidity, and it is considered to cause the brown stains during wood kiln drying with temperatures higher than 80 C due to the presence of natural amino acids and reduced sugars.

Subsequently, a range of reactions takes place, including cyclization's, dehydrations, retro aldolizations, rearrangements, isomerization and further condensations, which ultimately lead to the formation of polymers and copolymers, known as melanoidins. Generally, the composition is relatively unknown due to the complexity of the products that are generated in the reaction. Overall, Maillard reaction is an aqueous process initiated by heat, which makes it relatively straightforward to apply to wood in a commercial process. In addition, the reaction does not require the use of strong acids or bases, which could degrade the wood structure.

The most efficient characterization method, to identify the modifications appearing in the wood structure during heating and to identify the possible interaction and bonds formed between the wood components and the used reagents in chemical modification is infrared spectroscopy. This technique proved to be an efficient tool to identify differences between wood species small modifications in the wood structure as a result of different treatments , decay or photodegradation , but also to identify the changes taking place during thermal treatment , chemical treatment , and/or impregnation or coating . Moreover, due to the use of small amount of sample and little or no processing, this method is also considered as being non-destructive.

In the present study, the combined effects of chemical treatment (using bicine and tricine) and the thermal modification (using a temperature of 160 C) was investigated. To identify and better understand the structural changes appearing during these processes in the wood cell wall, infrared spectroscopy was used, combined with chemometric methods, such as principal component analysis and hierarchical cluster analysis

### Materials

### **II. MATERIALS AND METHODS**

For this study we used spruce (Picea abies) and beech (Fagus sylvatica) wood blocks, and as chemicals bicine [2-(Bis(2hydroxyethyl)amino)acetic acid] and tricine [N-(2-Hydroxy-1,1bis(hydroxymethyl)ethyl)glycine] from Merch. Their chemical structure is presented in Fig. 1



Fig. 2. Infrared spectra and their derivatives in the 3700e2500 cm<sup>1</sup> region of the spruce (a, b) and beech (c, d) wood samples.

Copyright to IJARSCT www.ijarsct.co.in





International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

Volume 4, Issue 2, August 2024

### Treatment

Spruce and beech wood samples were separated in 6 categories (control, thermal treated, impregnated with bicine/tricine, impregnated and thermal treated).

Impregnation procedures e aqueous solution of 10 wt% bicine/ tricine were introduced using a vacuumpressure impregnation (VPI) process according to the fullcell process in a laboratory impregnation setup (Kambic, Semic, Slovenia). The impregnation process comprised 30 min of vacuum (10 kPa), 40 min of pressure (1000 kPa) and 10 min of vacuum (15 kPa). The WPG were determined gravimetrically, and the impregnated specimens were conditioned for 2 weeks prior to thermal modification.

Thermal modification was performed according to a modified Silvapro® commercial procedure developed by Rep and Pohleven , at a temperature of 165 C for a period of 3 h, to limit the degree of thermal degradation of the chemicals impregnated into the wood prior to thermal modification. The mass loss (ML) of the samples after thermal modification was determined gravimetrically and the samples stored in the laboratory for 4 weeks (at 23 C; 65% relative humidity) before subsequent testing. Table 1 shows the sample categorisation relative to their respective bicine and tricine treatments.

### Method

The infrared spectra of the wood samples were recorded in KBr pellets on a Bruker ALPHA FTeIR spectrometer with 4 cm<sup>1</sup> resolution. The concentration of the sample was constant (2 mg powdered sample/200 mg KBr). Processing of the spectra was performed using the Grams 9.1 program (Thermo Fisher Scientific). Five recordings were performed for each sample, and their average spectra were further used in interpretation of the data. Principal component analysis (PCA) and hierarchical cluster analysis (HCA) were performed using the Chemo Spec package in R software

	ОН							
Fig. I. Ch	nemical structu	are of bicine (a) and tricine (b).						
Species	Code	Treatment description						
Spruce	S_C	control						
	S_HT	heat treatment only						
	S_B	bicine pre-treatment and drying						
	S_B_HT	bicine pre-treatment and heat						
		treatment						
	S_T	tricine pre-treatment and drying						
	S_T_HT	tricine pre-treatment and heat						
		treatment						
Beech	B_C	control						
	B_HT	heat treatment only						
	B_B	bicine pre-treatment and drying						
	в в нт	bicine pre-treatment and heat						
		treatment						
	B_T	tricine pre-treatment and drying						
	B_T_HT	tricine pre-treatment and heat						
		treatment						

Table 1: Samples, codes and the applied treatment

Copyright to IJARSCT www.ijarsct.co.in DOI: 10.48175/IJARSCT-19495





International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

#### Volume 4, Issue 2, August 2024

### **III. RESULTS AND DISCUSSION**

The mass loss (ML) and the weight percent gained (WPG) after thermal and thermochemical treatment were calculated. The ML during the thermal treatment is about 1.2% for S\_HT and of about 1.6% for the B\_HT. The bicine chemically treated samples presented a WPG of about 13.9% for S\_B, and 8.0% for B\_B. When both treatments are applied (thermal and chemical) the final WPG is of about 8.3% for the S\_B\_HT samples and of about 5.2% for the B\_B\_HT. For the tricine treated samples the WPG was of about 12.6% for S\_T and 6.8% for B\_T, while the final WPG for the thermal and chemical treated ones was of 10.7% for S\_T\_HT and 4.8% for B\_T\_HT sample, respectively.

Bands assignments	Bands posi	tion						
	S_C/B_C S_HT/ B_HT		_B	S_B/B_B S_ B_	B_HT/ B_HT	_T	S_T/B_T S_T_H B_T_H	IT/ IT
				3521/ 35 3523	22/3522	3517 3	3521 / 3522	
OeH stretching (B, T)				3439 3458 3456	3455	/3456	3455 3455	5/3455/3454
O2eH2/O6 intramolecular stretching modes (in cellulose)	3418/ 3418	3414 3423	4/ 3	3419/ 3419	3419	/3420	3417/ 3419	3418/3421
OH in carboxylic acid and NeH in secondary amine	5110	5125		3384 3375 3374	/3370/	/3372	3359 3370	)/3373/3376
O5eH5/O3 intramolecular in cellulose	3344/ 3340	3349 3343	9/ 3	3342/ 3345	3343/	/3344	3344/ 3345	3345/3341
O6eH6/O3 intermolecular in cellulose Ib (3270)	3279/ 3275	3279 3279	9/ 9	3280/ 3280	3280/	/3276	3281 3281 3279	/3280/3280
O6eH6/O3 intermolecular in cellulose $I_a(3240)$	3233/ 3213	3227 3227	7/ 2.	3224/ 3209	3229	/3222	3229/ 3216	3232/3211
OH and NeH stretching	5215	5221	_	3193	/ 3181		3197 / 3177	/ 3184
CeH stretching absorption in methyl and methylene groups in cellulose I	3133/ 3142	3141 3142	1/ 1 2	3139 3137 3140	/3135/	/3140	3110 3139 3139	0/3132/3136
multiple formation of an intermolecular hydrogen bond between biphenol and other phenolic groups (in lignin)	3067/ 3067	3067 3071	- 7/ 1		/ 3067		3067/ 3068	3068/3070
	3018/ 3013	3018 3014	8/ : 4	3025 3022 3018	/3022/	/3014	3029 3026 3021	5/3021/3018
CH stretching				2976			2997	
asymmetric methoxyl CeH stretching	2935/ 2936	2934 2936	4/ 6	2937/ 2936	2935	/2935	2946 2936 2936	5/2936/2936
symmetric CH <sub>2</sub> stretching	2885/ 2881	2883 2881	3/ 1 1	2905 2902 2889	/2888/	/2881	2888 2885 2882	5/2885/2882
CH stretching				2841 2847 2846	/2849/	/2848	2824 2839 2847	0/2839/2848

Table 2 Bands position and their assignment in the 3700e2500 cm<sup>1</sup> region [6,29,34,39,40].

### **Infrared spectra**

Generally, the infrared spectra of the wood present two absorbed water weakly bound and intramolecular hydrogen bond in a phenolic group (in 3521/important regions, namely the 3700e2500 cm<sup>1</sup> assigned to different stretching vibration of OH groups and methyl and methylene groups and 1800e800 cm<sup>1</sup> (fingerprint region) where the specific stretching vibration and deformation bands from the all wood components can be found. Therefore, for the evaluation of our samples we separated the spectra according to these two regions.

Copyright to IJARSCT www.ijarsct.co.in DOI: 10.48175/IJARSCT-19495





International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

#### Volume 4, Issue 2, August 2024

The spectra of the first region  $(3700e2500 \text{ cm}^1)$  for all the studied samples are presented in Fig. 2. The spectrum of control wood shows the characteristic bands of both softwoods and hardwoods, with a large band at about 3420 cm<sup>1</sup> which is an envelope of the specific bands assigned to inter and intramolecular hydrogen bonds in the wood components, and the band from about 2870 cm<sup>1</sup> which, in this case, is an envelope of the symmetric and antisymmetric stretching vibration of the methyl and methylene groups (Fig. 2a and c).

During thermal treatment (see S\_HT and B\_HT comparing to S\_C and B\_C), almost no change was possible to identify through the normal spectra or their second derivatives.

When the samples were exposed to chemical modification with bicine and tricine and further to thermochemical modification, the spectra of S and B clearly showed the presence of the chemicals in wood structure, with higher modifications encountered for the bicine treated samples for both series of wood, but because the bands from bicine and tricine almost totally overlapped with the bands from the wood components, it was difficult to specify the presence of the interactions. The band positions and their assignments are presented in Table 2.

The second region (Fig. 3) presented more detailed information concerning the structure of wood, and the modifications that took place during the thermal, chemical and thermochemical treatments.

As previously mentioned for the other region, both the infrared spectra and their derivatives for control (S\_C and B\_C) and thermal treated (S\_HT and B\_HT) samples did not indicate any significant differences occurring as a result of the thermal process.



Fig. 3. Infrared spectra and their derivatives in the 1800e800 cm<sup>1</sup> region of the spruce (a, b) and beech (c, d) wood samples.

Copyright to IJARSCT www.ijarsct.co.in DOI: 10.48175/IJARSCT-19495





International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

#### Volume 4, Issue 2, August 2024

The samples treated with bicine (S\_B and S\_B\_HT and B\_B and B\_B\_HT) presented increased intensities of the bands assigned to carbonyl and carboxyl groups stretching vibration (at about 1740 and 1647 cm<sup>1</sup>), but also of those assigned to methyl and methylene deformation vibration (1493, 1465, and 1422 cm<sup>1</sup>), to OH stretching and deformation vibration (1402, and 1317 cm<sup>1</sup>), to CeN stretching vibration in amine groups (1267 and 1208 cm<sup>1</sup>), and of those assigned to CeO groups stretching vibration (at about 1166, 1118, 1074, 1045 and 1024 cm<sup>1</sup>) (Fig. 3). Because the samples treated with tricine presented a lower WPG% than those modified with bicine, the modifications mentioned before and observed for the treatment with bicine are not that obvious. In Table 3, all the bands in this region and their assignment are presented.

Table 3: Bands position and their assignment in the 1800e800 cm<sup>1</sup> region [3,6,29,34,39,40].

Bands assignments Bands position								
		S_C	S_HT	_B S_B	S_B_HT	_T S_T	S_T_HT	
		/B_C	/B_HT	/B_B	/B_B_HT	/B_T	$/B_T_HT$	
C <sup>1</sup> / <sub>4</sub> O stretching vibration of carboxyl and acetyl groups		1740/	1741/	1734 1741/	1740/	1734 1741/	1741/	
		1739	1740	1740	1741	1740	1740	
C <sup>1</sup> /4O stretching of various groups		1729	1724	1726	1724	1725	1726	
C <sup>1</sup> /4O stretching in conjugated persubstituted aryl ketones		1690	1662/	1694	1702	1701 1702	1704	
and conjugated acid (B, T) conjugated CeO in quinones		1662/	1661	1658/	1658/	1658/	1659/	
		1661		1662	1657	1658	1659	
absorbed OeH; C]O stretching in carbox	xylic acid (B, T)	1637	1640	1647 1645/	1644/	1630 1635/	1637/	
				1645	1646	1635	1641	
NeH bending (T)						1602 1601	1602	
C <sup>1</sup> / <sub>4</sub> C of aromatic skeletal (lignin)		1592	1592	1589/	1590/	1590/	1590/	
				1593	1593	1593	1593	
conjugated CeO		1553/	1554/	1552/	1554/	1558/	1551/	
		1552	1551	1550	1551	1552	1550	
C <sup>1</sup> / <sub>4</sub> C of aromatic skeletal (lignin)		1512/	1512/	1512/	1512/	1512/	1512/	
		1506	1507	1507	1507	1507	1507	
CH <sub>2</sub> bending				1493		1488		
CeH deformation in lignin and carbohyd	drates; CH <sub>2</sub> bending	1465/	1465/	1455 1462/	1463/	1469 1465/	1464/	
(B, T)		1465	1465	1465	1465	1466	1465	
CeH deformation in lignin and carbohyd	drates; CH <sub>2</sub> bending	1425/	1425/	1422 1426/	1426/	1412 1426/	1426/	
(B, T)		1425	1425	1426	1425	1425	1426	
CeOH from carboxylic acid bending (B	,T)			1402 1402/	1400/	1394 1399/	1402/	
				1399	1399	1398	1397	
CeH deformation in cellulose and hemic	cellulose; CH <sub>2</sub>	1375/	1375	1388 1384/	1374/	1365 1374/	1374/	
bending (B, T)		1376	1376	1380	1376	1376	1377	
CeH vibration in cellulose and C <sub>1</sub> eO vib	ration in syringyl	1332/	1333/	1334/	1335/	1336/	1335/	
derivatives		1329	1330	1327	1327	1328	1330	
$CH_2$ rocking vibration in cellulose; CeO acid (B T)	H from carboxylic	1318	1318	1311 1317	1317	1320 1317	1318	
CeH bending mode in cellulose and Ce	O stretch in lignin Co	eN	1270	1260 1268/	1268/	1259 1269/	1269/	
stretching from amine (B 1270/	s succen in righti, et		1262	1260 1200,	1266	1261	1265	
T)		1262	2	1202	1201	1201	1201	
CeO linkage in guiacyl aromatic methor	kyl groups and acetyl	l /	/	/	/	/	/	
groups in xyloglucan		1244	1244	1243	1244	1243	1245	
CeOeC stretching mode of the pyranose	ring	1228/	1228/	1230/	1228/	1223 1228/	1229/	
		1229	1228	1229	1226	1229	1230	
C <sup>1</sup> / <sub>4</sub> O stretch in lignin and xylem; CeN s	stretching in amine	1209/	1209/	1204 1207	1207	1209/	1208/	
Copyright to IJARSCT	DOI: 10.48175/IJARSCT-19495			10 11 11 11 11	81-9429 ARSCT	829		

1011010101 + 10010HP

www.ijarsct.co.in



International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

ctor: 7.53 Volume 4, Issu	ie 2, Aug	ust 2024					
(B, T)	1203	1203		1207	1207	1208	1206
CeOeC vibration in cellulose and hemicellulose; CeO	1164/	1164/	1166	1163/	1163/	1161 1164/	1164/
stretching (B, T)	1163	1163		1162	1163	1163	1163
CeO stretching	1113/	1113/	1118	1113/	1112/	1115 1112/	1112/
	1127	1126		1126	1126	1125	1126
CeO stretching mainly from C(3)O(3)H in cellulose I; CeO	1062/	1062/	1074	1063/	1060/	1071 1061/	1062/
stretching (B, T)	1071	1071		1070	1068	1070	1071
CalkyleO ether vibrations methoxyl and beOe4 in guaiacol;	/	/	1045	/	/	1047 /	/
CeO stretching (B, T)	1046	1046		1046	1047	1051	1055
CeO and CeC stretching ring in cellulose and hemicelluloses	s 1025/	1025/	1024	1025/	1027/	1029 1026/	1027/
	1020	1020		1020	1020	1020	1020
CeO stretching	988/987	988/987	978	987/988	987/987	980988/987	988/986
Aromatic CeH out of plane deformations	957/961	957/961	953	958/963	959/961	952958/960	958/961
Pyran ring stretching	939/926	936/926	933	931/929	931/926	920933/925	936/926
CeH deformation in cellulose	896/896	896/896	907	894/896	895/896	896/896	896/897
			887				
CH out of plane vibrations in position 2, 5 and 6 of guaiacyl units	862/871	862/871	854	856/870	858/870	878 863/871	864/872

The increase of intensity of the bands mentioned above and their shifting to lower or higher wavenumber values indicated the presence of the chemicals in the wood structure. Furthermore, an increase of the C]O groups content indicate the presence of Amadori products (mentioned before in literature by Hauptmann and co-workers as a result of the interaction between the bicine and tricine with the wood carbohydrates.

In order to show the possible interactions taking place between the bicine/tricine and the wood structure, the theoretic spectra were calculated through the additivity law and using as initial values the spectra of control and thermal treated samples and the pure components (S\_C/B\_C, S\_HT/B\_HT, \_B and \_T). As for the experimental spectra, the calculated spectra versus experimental ones were separated into the two main regions (3700e2700 cm<sup>1</sup> and 1800e830 cm<sup>1</sup>).





In Fig. 4, the spectra and their derivatives in the first region are presented. From the spectra, only slight differences can be noticed here, but the second derivative spectra reveal differences among the both series of spectra, mostly in the CH stretching vibration region. If no interaction would occur between the wood and the chemicals, then the theoretic spectra should look similar to experimental ones. In reality, we can observe that in theoretic spectra we have bands which present higher intensities than in the experimental spectra, and these are located at about 2935 and 2888 cm<sup>1</sup> for the samples treated with bicine, and at about 3280, 3205, 3030, 2938 and 2884 cm<sup>1</sup> for the samples treated with tricine. Lower intensities in the experimental spectra indicate that those groups may be involved in the interactions which takes place between the wood and the used chemical compounds

Copyright to IJARSCT www.ijarsct.co.in





International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

#### Volume 4, Issue 2, August 2024

In the second region (Fig. 5), the spectra show higher variations. For example, for the S samples, the bands located at about 1739, 1591, 1462, 1426, 1384, 1360, 1268, 1097 and 1025 cm<sup>1</sup> present higher intensities in the theoretic spectra comparing to the experimental ones. These bands belong mostly to bicine and tricine structure. The most important differences are indicated by reduced intensity in the experimental spectra of the bands from 1738, 1600, 1384, 1268, 1093 and 1024 cm<sup>1</sup>, assigned to C]O stretching vibration of carboxyl and acetyl groups, conjugated CeO and CeO and CeN stretching vibration. For the samples S\_T and S\_T\_HT, the bands from 1070 to 1051 cm<sup>1</sup> present a decreased intensity in the experimental spectrum and were merged in one band with the maximum at 1061 cm<sup>1</sup>. These bands also presented larger width when comparing similar bands from the theoretic spectra. Further increased intensities were noticed of the bands around 1645, 1550, 1400, 1061 cm<sup>1</sup> assigned to CeO and conjugated CeO stretching vibration. Moreover, the band from 1400 cm<sup>1</sup> was not observable in the theoretic spectra.



Fig. 5. Experimental (full line) and theoretic (dotted line) infrared spectra and their derivatives in the 1800e830 cm<sup>1</sup> region of spruce (S) (a, b) and beech (B) (c, d) wood samples.



Fig. 6. PC1 versus PC2 scores plot of the spruce (a) and beech (b) wood samples. Larger variations were identified in the spectra of the B samples, comparing to the other set of samples (S). Here, the most important differences were observed for the bands from 1735, 1650, 1550, 1380, 1727, 1162, 1126, 1093, 1070

Copyright to IJARSCT www.ijarsct.co.in DOI: 10.48175/IJARSCT-19495

ISSN 2581-9429 IJARSCT



International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

#### Volume 4, Issue 2, August 2024

and 1045 cm<sup>e1</sup> which presented lower intensities and were wider in the experimental spectra compared to their equivalent bands from the theoretic spectra. As in the previous case, was observed the presence of the band from 1400 cm<sup>1</sup> only in experimental spectra. At the same time were observed higher intensities for the band from 1205 cm<sup>1</sup>. Moreover, these bands were shifted to lower or higher wavenumbers in the experimental spectra comparing to theoretic ones, indicating the formation of new bonds between the chemicals structure and wood.

It has been mentioned before by Hauptmann and co-workers (2015) that the spectra of tricine treated cellulose and lignin did not indicate any chemical reaction. Therefore, the variation of the infrared bands indicates that the C]O and CeO groups mainly probably from the hemicelluloses are involved in the reaction with the bicine or tricine compounds, as would be expected if a Maillard reaction had taken place.

### Principal component analysis

Principal component analysis (PCA) gives, generally, detailed information regarding the differences which appear between the series of similar samples . To perform the PCA, the fingerprint regions ( $1800e800 \text{ cm}^1$ ) for the spectra of the studied samples were used.

For spruce wood (Fig. 6a), the PC1 (principal component factor 1) describes 86% and PC2 (principal component factor 2) 8.4% of data variance, therefore more than 94% of the existed variances in all spectra can be captured using these two dimensions instead of the initial data.

The bicine treated samples presented positive values on PC1, the tricine treated ones had values close to 0 while the control and thermal treated samples presented negative scores. On PC2, control, tricine and bicine treated samples presented negative values, while the thermal treated and thermochemical treated ones presented positive values.

Therefore, PC1 is the most informative latent variable for the description of chemical treatments, differentiating the chemical and thermochemical treated samples from the control and thermal treated control samples, while PC2 separated the samples according to thermal and nonthermal treatment, indicating the negative relationship between these two series of samples.

Almost the same behaviours can be observed for the beech wood samples (Fig. 6b). The only difference is that the samples treated with bicine present more distinct groups than the other samples.

Hierarchical cluster analysis

In addition to principal component analysis, a hierarchical cluster analysis (HCA) was performed, which allow us to emphasize the natural grouping in the data set, making possible at the same time to visualize the relationships among different groups [6,48].



Fig. 7. HCA plots of the spruce (a) and beech (b) wood samples.

The dendrograms of the two series of samples (spruce and beech wood) are presented in Fig. 7, showing two main clusters with different heterogeneities.

The spruce wood samples dendrogram (Fig. 7a) was separated in two main clusters, the bicine treated samples in the first one, and the other samples in the second one. Further, the second cluster was divided into two other superclusters, which separated the control and thermal treated samples from the tricine treated samples.

Copyright to IJARSCT www.ijarsct.co.in





International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

#### Volume 4, Issue 2, August 2024

On the other hand, the beech wood samples (Fig. 7b) dendrogram was separated in two main clusters, differentiating between the control and thermal treated sample and the chemically and thermochemically treated samples. The second cluster was further divided in several subclusters, which discriminated between the bicine and tricine treated samples. As observed in the PCA analysis, there was a higher difference in the samples treated with bicine and those thermoses treated with bicine, comparing to spruce wood.

In a previous paper the colour measurements indicated that the treatment with tricine and thermal modification had the greatest impact on the samples, showing a considerable darkening even when compared to the thermal modification only. The treatment with bicine induced less darkening. Thermal treatment usually induce some darkening of the material and it has been mentioned that during thermal treatment the darkening of the wood samples is due to the lignin. The additional darkening of the samples treated with bicine/tricine, indicated additional process, which may be due to Maillard process occurred as a result of the combined treatments possibly as a result of the formation of polymerisation products such as melanoidins.

At the same time, the contact angle measurements indicated that the combination of the both treatments increases the contact angles compared to control and simple thermal treatment.

The preliminary experiments of the thermally and thermochemically modified wood indicated the occurrence of the reactions between the functional groups from bicine and tricine and those present in wood structure, which could suggest that there was chain displacement from the bicine to create the Amadori products and activation of the N via a quaternary ammonium intermediate typical of a Maillard reaction.

### **IV. CONCLUSION**

Two types of wood were thermally and chemically treated, as well as combined treatment between them was applied. The modifications which appeared in the wood structure were evaluated by infrared spectroscopy and chemometric methods (principal component analysis and hierarchical cluster analysis). These indicated the occurrence of the reactions between the functional groups from bicine and tricine and those present in wood structure.

Moreover, it was observed that the softwood samples were more susceptible to chemical/thermal modification than the hardwood samples, indicated both by the increased WPG values, but also by the infrared spectra.

### ACKNOWLEDGEMENTS

The wood specimen's treatment was performed in the framework of COST Action FP1407, while the infrared analysis was performed in the framework of COST Action FP1303. Dennis Jones acknowledge the financial support for both COST Actions.

### APPENDIX A. SUPPLEMENTARY DATA

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2019.127133.

### REFERENCES

[1] R.E. Ibach, Biological properties, in: R.M. Rowell (Ed.), Handbook of Wood Chemistry and Wood Composites, CRC Press, 2005, pp. 99e120.

[2] R.S. Williams, Weathering of wood, in: R.M. Rowell (Ed.), Handbook of Wood Chemistry and Wood Composites, CRC Press, 2005, pp. 139e186.

[3] C.-M. Popescu, P. Gradinariu, M.-C. Popescu, Structural analysis of lime wood biodegraded by white rot fungi through infrared and two dimensional correlation spectroscopy techniques, J. Mol. Struct. 1124 (2016) 78e84, https://doi.org/10.1016/j.molstruc. 2016.04.029.

[4] R. HerreraeDíaz, V. SepúlvedaeVillarroel, N. Perez ePena, L. Salvo~ eSepúlveda, C. SalinaseLira, R. LlanoePonte, R.A. Ananías, Effect of wood drying and heat modification on some physical and mechanical properties of radiata pine, Dry. Technol. 36 (2017) 537e544, https://doi.org/10.1080/

07373937.2017.1342094.

Copyright to IJARSCT www.ijarsct.co.in





International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

Volume 4, Issue 2, August 2024

[5] I. Cabalova, F. Kacík, R. Lagana, E. Výbohova, T. Bubeníkova, I.Canova, J. Durkovic, Effect of thermal treatment on the chemical, physical, and mechanical properties of pedunculate oak (Quercus robur L.) wood, Bio 13 (2018) 157e170, https://doi.org/10.15376/biores.13.1.157e170.

[6] M.-C. Popescu, J. Froidevaux, P. Navi, C.-M. Popescu, Structural modifications of Tilia cordata wood during heat treatment investigated by FTeIR and 2D IR correlation spectroscopy, J. Mol. Struct. 1033 (2013) 176e186, https://doi.org/ 10.1016/j.molstruc.2012. 08.035.

[7] E.D. Marfo, E.Y. Wereko, K.O. Larbi, Chemical modification of the tropical hardwood species, Celtis mildbraedii (ESA FUFUO), to improve its durability, J. Wood Chem. Technol. 38 (2017) 51e56, https://doi.org/10.1080/02773813.2017.1372476.

[8] K.E. Okon, F. Lin, X. Lin, C. Chen, Y. Chen, B. Huang, Modification of Chinese fir (Cunninghamia lanceolata L.) wood by silicone oil heat treatment with microewave pretreatment, Eur. J. Wood Wood Prod. 76 (2018) 221e228, https://doi.org/10.1007/s00107-017-1165-z.

[9] A. Kumar, J. Richter, J. Tywoniak, P. Hajek, S. Adamopoulos, U. Segedin, M. Petric, Surface modification of Norway spruce wood by octadecyltrichlorosilane (OTS) nanosol by dipping and water vapour diffusion properties of the OTSemodified wood, Holzforschung 72 (2018) 45e56, https://doi.org/ 10.1515/hf-2017-0087.

[10] C.A.S. Hill, Wood ModificationeChemical, Thermal and Other Processes, John Wiley&Sons, Chichester, 2006.

[11] D. Jones, G.O. Ormondroyd, S.F. Curling, C.-M. Popescu, M.-C. Popescu, Chemical compositions of naturalfibres, in: M. Fan, F. Fu (Eds.), Advanced High Strength Natural Fibre Composites in Construction, Elsevier, 2017, pp. 23e58.

[12] K. Srinivas, K.K. Pandey, Effect of heat treatment on color changes, dimensional stability, and mechanical properties of wood, J. Wood Chem. Technol. 32 (4) (2012) 304e316, https://doi.org/10.1080/02773813.2012.674170.

[13] M. Jebrane, D. Harper, N. Labbe, G. Sebe, Comparative determination of thegrafting distribution and viscoelastic properties of wood blocks acetylated by vinyl acetate or acetic anhydride, Carbohydr. Polym. 84 (2011) 1314e1320, https://doi.org/10.1016/j.carbpol. 2011.01.026.

[14] C.A.S. Hill, A.N. Papadopoulos, D. Payne, Chemical modification employed as a means of probing the cellewall micropore of pine sapwood, Wood Sci. Technol. 37 (6) (2004) 475e488, https://doi.org/10.1007/s00226-003-0193-5.

[15] N. Ozmen, N.S. Çetin, P. Tingaut, G. Sebe, A new route for the functionalisation f wood through transesterification reactions, Eur. Polym. J. 42 (2006) 1617e1624, https://doi.org/10.1016/j.eurpolymj.2006.01.020.

[16] C. Mai, H. Militz, Modification of wood with silicon compounds. inorganic silicon compounds and solegel systems: a review, Wood Sci. Technol. 37 (2004) 339e348, https://doi.org/10.1007/s00226-003-0205-5.

[17] C.A.S. Hill, The reduction in the fibre saturation point of wood due to chemical modification using anhydride reagents: a reappraisal, Holzforschung 62 (2008) 423e428, https://doi.org/10.1515/HF.2008.078.

[18] C.A.S. Hill, J.G. Hillier, Studies of the reaction of carboxylic acid anhydrides with wood. Experimental determination and modelling of kinetic profiles, Phys. Chem. Chem. Phys. 1 (1999) 1569e1576, https://doi.org/10.1039/ A809830A.

[19] J.eZ. Li, T. Furuno, S. Katoh, T. Uehara, Chemical modification of wood by anhydrides without solvents or catalysts, J. Wood Sci. 46 (2000) 215e221, https://doi.org/10.1007/BF00776452.

[20] C.A.S. Hill, S. Mallon, The chemical modification of Scots pine with succinic anhydride or octenyl succinic anhydride. I. Dimensional stabilisation, Holzforschung 52 (1998) 427e433, https://doi.org/10.1515/hfsg.1998.52.4.427.

[21] Y. Xie, C.A.S. Hill, Z. Xiao, C. Mai, H. Militz, Dynamic water vapour sorption properties of wood treated with glutaraldehyde, Wood Sci. Technol. 45 (2011) 49e61, https://doi.org/10.1007/s00226-010-0311-0.

[22] C.-M. Popescu, C. Hill, S. Curling, G. Ormondroyd, Y. Xie, The water vapour sorption behaviour of acetylated birch wood: how acetylation affects the sorption isotherm and accessible hydroxyl content, J. Mater. Sci. 49 (5) (2014) 2362e2371, https://doi.org/10.1007/s10853-013-7937-x.

[23] R. Wascher, N. Leike, G. Avramidis, A. Wolkenhauer, H. Militz, W. Viol,€ Improved DMDHEU uptake of beech veneers after plasma treatment at atmospheric pressure, Eur. J. Wood Prod. 73 (2015) 433e437, https://doi.org/10.1007/s00107-015-0916-y.





International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

Volume 4, Issue 2, August 2024

[24] L. Emmerich, S. Bollmus, H. Militz, Wood modification with DMDHEU (1.3dimethylol-4.5-dihydroxyethyleneurea)eState of the art, recent research activities and future perspectives, Wood Mater. Sci. Eng. 14 (2019) 3e18, https://doi.org/10.1080/17480272.2017.1417907.

[25] B.C. Kielmann, S. Adamopoulos, H. Militz, C. Mai, Decay resistance of ash, beech and maple wood modified with Nemethylol melamine and a metal complex dye, Int. Biodeterior. Biodegrad. 89 (2014) 110e114, https://doi.org/ 10.1016/j.ibiod.2014.01.011.

[26] W. Lin, Y. Huang, J. Li, Z. Liu, W. Yang, R. Li, H. Chen, X. Zhang, Preparation of highly hydrophobic and antiefouling wood using poly(methylhydrogen) siloxane, Cellulose 25 (2018) 7341e7353, https://doi.org/10.1007/s10570018-2074-y.

[27] T. Meints, C. Hansmann, M. Müller, F. Liebner, W. GindleAltmutter, Highly effective impregnation and modification of spruce wood with epoxyefunctional siloxane using supercritical carbon dioxide solvent, Wood Sci. Technol. 52 (2018) 1607e1620, https://doi.org/10.1007/s00226-0181050-x.

[28] I. Ratajczak, M. Wozniak, P. KwasniewskaeSip, K. Szentner, G. Cofta, B. Mazela, Chemical characterization of wood treated with a formulation based on propolis, caffeine and organosilanes, Eur. J. Wood Wood Prod. 76 (2018) 775e781, https://doi.org/10.1007/s00107-017-1257-9.

[29] M. Hauptmann, W. GindleAltmutter, C. Hansmann, M. Bacher, T. Rosenau, F. Liebner, S. D'Amico, M. Schwanninger, Wood modification with tricine, Holzforschung 69 (8) (2015) 985e991, https://doi.org/10.1515/hf-2014-0122.

[30] K. Peeters, E. Larnøy, A. Kutnar, C.A.S. Hill, An examination of the potential for the use of the Maillard reaction to modify wood, Int. Wood Prod. J. 9 (3) (2018) 108e114, https://doi.org/10.1080/20426445.2018.1471840.

[31] C. Hauser, U. Müller, T. Sauer, K. Augner, M. Pischetsrieder, Maillard reaction products as antimicrobial components for packaging films, Food Chem. 145 (2014) 608e613, https://doi.org/10.1016/j.foodchem.2013.08.083.

[32] A.P. Echavarría, J. Pagan, A. Ibarz, Melanoidins formed by Maillard reaction in food and their biological activity, Food Eng. Rev. 4 (2012) 203e223, https:// doi.org/10.1007/s12393 -012-9057-9.

[33] J.S. Kim, Y.S. Lee, Enolization and racemization reactions of glucose and fructose on heating with aminoeacid enantiomers and the formation of melanoidins as a result of the Maillard reaction, Amino Acids 36 (2009) 465e474, https://doi.org/10.1007/s00726-008-0104-z.

[34] M.-C. Popescu, C.-M. Popescu, G. Lisa, Y. Sakata, Evaluation of morphological and chemical aspects of different wood species by spectroscopy and thermal methods, J. Mol. Struct. 988 (2011) 65e72, https://doi.org/10.1016/j.molstruc.2010.12.004.

[35] F. Ma, A. Huang, Rapid identification and quantification three chickenewing woods of Millettia leucantha, Millettia laurentii and Cassia siamea by FTeIR and 2DCOSeIR, J. Mol. Struct. 1166 (2018) 164e168, https://doi.org/10.1016/j.molstruc.2018.04.037.

[36] B. Mohebby, Application of ATR infrared spectroscopy in wood acetylation, J. Agric. Sci. Technol. 10 (2008) 253e259.

[37] O.€ Ozgenç, S. Durmaz, I.H. Boyaci, H. Eksi€ eKocak, Determination of chemical changes in heatetreated wood using ATReFTIR and FT Raman spectrometry, Spectrochim. Acta: Molec. Biomolec. Spectrosc. 171 (2017) 395e400, https:// doi.org/10.1016/j.saa.2016.08.026.

[38] A.U. Ferraz, J. Baeza, J. Rodrigues, J. Freer, Estimating chemical composition of biodegraded pine and eucalyptus by DRIFT spectroscopy and multivariate analysis, Bioresour. Technol. 74 (2000) 201e212, https://doi.org/10.1016/S0960-8524(00)00024-9.

[39] C.-M. Popescu, M.-C. Popescu, C. Vasile, Characterization of fungal degraded lime wood by FTeIR and 2D IR correlation spectroscopy, Microchem. J. 95 (2) (2010) 377e387, https://doi.org/10.1016/j.microc.2010.02.021.

[40] C.-M. Popescu, M.-C. Popescu, C. Vasile, Structural analysis of photodegraded lime wood by means of FTeIR and 2D IR correlation spectroscopy, Int. J. Biol. Macromol. 48 (4) (2011), https://doi.org/10.1016/j.ijbiomac.2011.02.009, 667e67.

[41] G. Capobianco, L. Calienno, C. Pelosi, M. Scacchi, G. Bonifazi, G. Agresti, R. Picchio, U. Santamaria, S. Serranti, A. Lo Monaco, Protective behaviour monitoring on wood photoedegradation by spectroscopic techniques coupled with

Copyright to IJARSCT www.ijarsct.co.in





International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

#### Volume 4, Issue 2, August 2024

chemometrics, Spectrochim. Acta: Molec. Biomolec. Spectrosc. 172 (2017) 34e42, https://doi.org/10.1016/j.saa.2016.05.050.

[42] A. Sikora, F. Kacík, M. Gaff, V. Vondrova, T. Bubeníkova, I. Kubovský, Impact ofthermal modification on color and chemical changes of spruce and oak wood, J. Wood Sci. 64 (2018) 406e416, https://doi.org/10.1007/s10086-018-1721-0.

[43] H. Shen, S. Zhang, J. Cao, J. Jiang, W. Wang, Improving antieweathering performance of thermally modified wood by TiO2 sol or/and paraffin emulsion,

Constr. Build. Mater. 169 (2018) 372e378, https://doi.org/10.1016/ j.conbuildmat.2018.03.036.

[44] S. Isaji, Y. Kojima, Application of copper monoethanolamine solutions as primers for semitransparent exterior wood stains, Eur. J. Wood Prod. 75 (2017) 305e314, https://doi.org/10.1007/s00107-016-1078-2.

[45] G. Rep, F. Pohleven, S. Kosmerl, Development of industrial kiln for thermal wood modification by a procedure with an initial vacuum and commercialisation of modified Silvapro wood, in: Proceedings of the Sixth European Conference on Wood Modification, 2012, pp. 11e17.

[46] B.A. Hanson, ChemoSpec: an R package for chemometric analysis of spectroscopic data. https://github.com/bryanhanson/ChemoSpec.

[47] S.eY. Park, J.eC. Kim, J.eH. Kim, S.eY. Yang, O. Kwon, H. Yeo, K.eC. Cho, I.eG. Choi, Possibility of wood classification in Korean softwood species using neareinfrared spectroscopy based on their chemical compositions, J. Korean Wood Sci. Technol. 45 (2) (2017) 202e212, https://doi.org/10.5658/ WOOD.2017.45.2.202.

[48] H. Chen, C. Ferrari, M. Angiuli, J. Yao, C. Raspi, E. Bramanti, Qualitative and quantitative analysis of wood samples by Fourier transform infrared spectroscopy and multivariate analysis, Carbohydr. Polym. 82 (2010) 772e778, https://doi.org/10.1016/j.carbpol.2010.05.052.

[49] D. Jones, C.-M. Popescu, D. Krzisnik, M. Hocevar, M. Humar, M.-C. Popescu, The use of bicine and tricine as possible Maillard reagents in a combined thermal/ chemical modification of beech, in: Proceedings IRG Annual Meeting, IRG/WP 19e40852, IRG, 2019, pp.1e13.

