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COMPOSITION OF HYDROLYSATES OF SOME HARDWOODS OCCURRING IN THE PROCESS OF THEIR HYDROTHERMAL TREATMENT BY COOKING

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Abstract

Oak wood samples were hydrothermally treated at 80 and 120° C. The times of treatment varied from 2 to 32 hours according to the temperature. Obtained hydrolysates were analysed for the contents of acetic acid, 2-furaldehyde and monosaccharides prior to and after the inversion. Also the specific gravity, pH, contents of reducing substances and the weights of dry residua were determined.

Key words: hydrothermal treatment, oak wood, hydrolysates, acetic acid, 2-furaldehyde, saccharides

ZGRADBA HIDROLIZATOV NEKATERIH LISTAVCEV DOBLJENIH S HIDROTERMIČNO OBDELAVO PRI KUHANJU

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Izvleček

Vzorci hrastovega lesa smo hidrotermično obdelali pri 80° C in 120° C, časi obdelave so se glede na temperaturo spreminjali od 2-32 ur. Dobljeni hidrolizati so vsebovali očetno kislino, 2-furaldehid in monosaharide pred in po inverziji. Hidrolizatoma smo določili njihovo gostoto, pH, količino reducirajočih substanc in vsebnosti suhe snovi.

Ključne besede: hidrotermična obdelava, hrastov les, hidrolizati, očetna kislina, 2-furaldehid, saharidi

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CONTENTS

1	INTRODUCTION.....	175
2	EXPERIMENTAL.....	176
3	DISCUSSION.....	177
4	CONCLUSIONS.....	181
	POVZETEK.....	182
	REFERENCES.....	182

Part I
(oak wood hydrolysates)
(hidrolizati hrastovega lesa)

1 INTRODUCTION

Steaming and modifying the wood properties by immersion into hot water (boiling) are the basic methods of wood plastification. Steaming is preferentially used prior to bending, and boiling is often applied when cutting and slicing the wood. There are also other methods of wood plastification (so called "chemical") based on the wood penetration with ammonia or with its derivatives. The practical utilisation of these is negligible because of the odour, toxicity as well as the costs of used chemicals.

The plasticizing effect of steaming and boiling is based predominantly on the softening the middle lamella lignin and on the relaxation of the lignin-polysaccharidic matrix of the wood (1). Depolymerisation of wood polyoses and the moisture content of the plasticized wood above FSP also contribute to wood plasticity (2)

The principle of the plasticizing effect of amines is due mainly to the rupture of hydrogen bonds in the wood substance, in the cleavage of less stable covalent bonds between lignin and polysaccharides, as well as among polysaccharides themselves (3, 4).

The hydrolysis of ester bonds between acetyls and xylans (in the case of hardwood species) plays an important role in both types of plastification thus enhancing hydrophilic nature of the wood (5).

It can be concluded that the final properties of plasticized wood are the reflection of great number of various physico-chemical, chemical and structural alterations of this substance.

Despite of the fact that the hydrothermal plastification of wood is a technological process which is not proceeding with the application of chemicals it produces some emitants (gaseous compounds, condensates and hydrolysates, respectively) which are potentially harmful to the environment. The composition and the quantity of wood degradation products in the above mentioned emitants are dependent on the conditions (temperature, time, method applied and possibly the wood species processed) of

treatment. The aim of the presented paper was to assess the influence of time and temperature of hydrothermal treatment on the composition of oak wood hydrolysates.

2 EXPERIMENTAL

A series of comparable oak wood specimens with dimensions 2 x 2 x 30 cm (the longer dimension parallel with the fibres) were hydrothermally treated at 80° and 120° C. The time of treatment was 8, 16, 24 and 32 hours at the lower temperature and 2, 4, 8 and 16 hours, respectively, at 120° C.

The experiments were carried out in a stainless steel autoclave with an automatic temperature control. The wood to distilled water ratio was in each case 1 to 4. The initial pH values of the medium were 4, 75 ± 0, 1. The treatments were performed in the absence of the air, which was removed from the autoclave by the vacuum, prior to cooking.

The obtained treated wood specimens were desintegrated and submitted to various analyses. The analytical data are presented in (6, 7). The hydrolysates were subjected to the following analyses:

- pH values of hydrolysates were measured with a digital MV 781 pH-meter.
- the specific gravity was determined by a pycnometer
- the dry residua of hydrolysates were determined by drying in a dryer with the forced air circulation at the temperature of 98° C
- amounts of 2, 4-dinitrophenyl hydrazones (2, 4 DNPH-ones) were determined following the method in (8)
- the content of acetic acid in examined hydrolysates was determined by GLC (9)
- the amounts of 2-furaldehyde were estimated by GLC (9)
- the inversion of oligosaccharides present in hydrolysates was performed by the addition of H₂SO₄ so that the final concentration of acid was 3 %. Time of hydrolysis was 3 h, and the temperature 98° C.
- contents of monosaccharides in the investigated samples were determined by the GLC of their aldonitrileacetates (10) - the reducing substances were determined according to the method of Bertrand (11)

3 DISCUSSION

Data in Tab. 1 and 2 provide the basic information about the low and high temperature oak wood hydrolysates. As it follows from displayed data the pH value of resulting hydrolysates are more temperature than time dependent. The drop in pH values of examined hydrolysates is a result of the hydrolysis of acetyl as well as of the formyl esters (these are present in negligible amounts as reported in the literature (12) of hemicelluloses (xylans) in treated material.

Tab. 1

*Analysis of hydrolysates at 80° C**Preglednica. 1**Analiza hidrolizatov pri 80° C*

	8h	16h	24h	32h
pH	3, 59	3, 45	3, 40	3, 26
Density (g. cm ⁻³)	1, 0020	1, 0016	1, 0017	1, 0033
Reducing substances (g. dm ⁻³)				
Dry residua (g. dm ⁻³)	1, 40	2, 45	2, 62	4, 13
DNPH-ones (g. dm ⁻³)	2, 15	3, 66	3, 88	6, 70
CH ₃ COOH (g. dm ⁻³)	0, 80	1, 09	1, 36	2, 13
2-furaldehyde (g. dm ⁻³)	0, 69	0, 80	1, 02	1, 33
	0, 02	0, 03	0, 05	0, 09

Tab. 2

*Analysis of hydrolysates at 120° C**Preglednica. 2**Analiza hidrolizatov pri 120° C*

	2h	4h	8h	16h
pH	3, 10	2, 94	2, 82	2, 82
Density (g. cm ⁻³)	1, 0020	1, 0044	1, 0078	1, 0119
Reducing substances (g. dm ⁻³)				
Dry residua (g. dm ⁻³)	2, 95	5, 61	5, 48	20, 48
DNPH-ones (g. dm ⁻³)	5, 17	9, 96	20, 30	26, 41
CH ₃ COOH (g. dm ⁻³)	1, 38	2, 68	4, 51	6, 13
2-furaldehyde (g. dm ⁻³)	0, 90	1, 62	3, 45	5, 00
	0, 25	0, 44	1, 02	1, 86

The extremely low pH of hydrolysates after 8 and 16 hours of hydrothermal treatment maintained at 120° C might be explained by the liberation or formation of some extra formic acid or some other acid with the K dis ranging within values from 10-2 to 10-3. The formation of such acidic compounds might be a result of saccharidic moieties decomposition. We are

also of the opinion that it might be a consequence of certain cation-exchange activity of uronides as well as of acidic groups of lignin (though these are known to be present in lignin in the minor quantities only) which may promote the liberation of some additional acids (oxalic, hydrochloric, phosphoric etc. - by origin from the salts present in the wood), too. We do not consider any strong influence of tannins on the pH as their acidity (K dis) is lower than that of acetic acid.

The values of specific gravity of examined hydrolysates change with the time very little in the case of oak wood treatment at 80° C. The increase in the treatment temperature to 120° C results in an ascending specific gravity of hydrolysates, especially after 8 hours of treatment.

The amounts of dry residua of hydrolysates are both time and temperature dependent. Treatment at 120° C causes a deeper wood decomposition and more intensive diffusion of wood degradation products into the cooking medium. This processes are reflected in increased amounts of soluble hydrolysis products in hydrolysates arising in the case of cooking the wood at 120° C. At this temperature, however some condensation of newly formed products in both wood matrix and cooking medium cannot be avoided. This leads to the formation of resin like materials precipitated on the surfaces of autoclave and treated wood specimens (probably in the inner spaces of the wood substance also) in later stages of cooking.

As for the amounts of precipitated carbonyl containing compounds (incl. saccharides, unfortunately) in the form of their 2, 4 DNPH-ones, these are also the time and temperature dependent, and all gravimetric data may be influenced by the secondary reactions of saccharides yielding insoluble osazones. The higher time and temperature of treatment the higher amounts of 2, 4 DNPH-ones were determined. It is difficult to explain the discrepancy between higher total amounts of reducing compounds in the hydrolysates (their amounts being expressed as D- glucose in accordance with the Bertrand method applied) and lower amounts of dinitrophenyl hydrazones precipitated (probably most of the reducing compounds are of lower relative molecular weight than D-glucose and there is also a possibility of incomplete condensation reaction or of formation of soluble intermediates).

The concentration of liberated acetic acid in the low temperature (80° C) oak wood hydrolysates is gradually rising with the time of treatment, but the final concentration after 32 hour lasting experiment was very low - 1,33 g.l⁻¹. The increase in the treatment temperature to 120° C is reflected in

the gradually ascending concentration of this acid up to many times higher values as were detected in the case of hydrolysates of the low temperature wood treatment.

Relatively high acetic acid concentrations in the hydrolysates arising in the treatment at a temperature of 120° C are sufficient to cause pronounced hydrolytic reactions of polyoses and condensation reactions (known to proceed even under the mild acidic conditions at elevated temperatures (13, 14) of the lignin macromolecules. The 2-furaldehyde formation in the hydrothermal treatment is strongly dependent on the temperature and time of oak wood cooking.

At lower temperature (80° C) the formation of this moiety is nearly negligible, thus indicating a very low rate of pentosan hydrolysis and further conversion of liberated pentoses. The formation of 2-furaldehyde is much more intensive when experiments are carried out at 120° C. This refers to a deep decomposition of hemicelluloses, particularly of pentosans.

Data presented in the in Tab. 3 and 4 are concerned with the contents of saccarides in hydrolysates investigated. From comparison of these data it follows that concentrations of both mono- and oligosaccharides in hydrolysates are also strongly dependent on the temperature and the time of hydrolytic treatment to which the wood was exposed. The most sensitive polysaccharides of oak seem to be those containing arabinose, since concentration of this monosaccharide is unexpectedly high even in the case of the hydrolysates produced in low temperature treatments. The low stability of arabans is probably given by the furanose form of this compound incorporated in the chains of arabans as well as in the side chains of some other hemicelluloses. The arabinofuranose being generally the prevailing building unit in arabanes is reported to be liberated very easily in the hydrolytic treatments (15). The contents of L- arabinose in the low temperature hydrolysates do not increase fluently with the time of treatment. In the interval of 16 and 24 hours of treatment at 80° C the liberation of L-arabinose slows down and remains nearly constant (cca 250 mg. l⁻¹, see tab. 3), and afterwards increases rapidly. A very similar trend (with exception of D-glucose) can be observed in amounts of other monosaccharides, though in general their concentrations ere several times lower. The inversion of low temperature oak wood hydrolysates increased the total amounts of monosaccharides determined a little and with respect to the contents of individual monosaccharides also very irregularly. The effect of inversion on amounts of monosaccharides in hydrolysates produced by treatment at a temperature of 80° C is less pronounced with the time

Tab. 3

Contents of monosaccharides in hydrolysates obtained at the temperature of 80° C, before and after inversion with 3% sulphuric acid (data in brackets) (mg.dm⁻³)

Preglednica. 3

Količine monosaharidov v hidrolizatih pred in po inverziji s 3 % žveplovo (VI) kislino (podatki v oklepajih) pri temperaturi 80° C (mg.dm⁻³)

	8h	16h	24h	32h
L-rhamnose	12. 24 (23. 12)	45. 56 (46. 13)	42. 37 (72. 10)	63. 75 (65. 28)
L-arabinose	143. 10 (221. 54)	240. 62 (328. 60)	255. 32 (502. 44)	638. 12 (722. 92)
D-xylose	25. 87 (56. 67)	74. 55 (174. 48)	71. 39 (165. 25)	187. 26 (158. 69)
D-mannose	0 (0)	0 (12. 33)	8. 22 (16. 45)	24. 66 (22. 20)
D-galaktose	6. 93 (48. 51)	27. 41 (61. 23)	29. 91 (71. 20)	82. 58 (72. 07)
D-glukose	0 (24. 50)	58. 80 (139. 65)	129. 85 (166. 61)	196. 00 (178. 85)
Σ	188. 14 (374. 34)	446. 94 (762. 42)	537. 06 (994. 42)	1192. 77 (1219. 19)

Tab. 4

Contents of monosaccharides in hydrolysates obtained at the temperature of 120° C, before and after inversion with 3% sulphuric acid (data in brackets) (mg.dm⁻³)

Preglednica. 4

Količina monosaharidov v hidrolizatih pred in po inverziji s 3 % žveplovo (VI) kislino (podatki v oklepajih) pri temperaturi pri 120° C (mg.dm⁻³)

	8h	16h	24h	32h
L-rhamnose	63. 11 (70. 72)	122. 40 (165. 92)	462. 05 (481. 44)	92. 41 (429. 75)
L-arabinose	364. 64 (394. 32)	542. 72 (646. 60)	845. 58 (884. 04)	223. 35 (1026. 08)
D-xylose	199. 58 (857. 47)	1089. 09 (3811. 81)	7365. 07 (10762. 75)	2123. 00 (13588. 96)
D-mannose	8. 40 (14. 00)	30. 80 (49. 28)	123. 34 (81. 20)	46. 99 (156. 80)
D-galaktose	72. 07 (243. 94)	158. 000 (449. 89)	1005. 21 (1302. 84)	231. 72 (1240. 77)
D-glukose	14. 56 (129. 85)	210. 71 (308. 70)	272. 25 (262. 15)	110. 96 (436. 10)
Σ	722. 36 (1710. 30)	2153. 71 (5432. 20)	10073. 50 (13774. 42)	2828. 43 (19706. 89)

of treatment. This indicates the very low resistance and amounts of short chain hemicelluloses, or their oligomeric fragments, that passed from the treated wood into the cooking medium (distilled water)

The data in Tab. 4 point out the rapid decomposition of wood polyoses at increased treatment temperatures (120° C). The concentration of monosaccharides in hydrolysates is time dependent. After first 8 hours of treatment the even increase in single monosaccharides concentration becomes reverse thus indicating the enhanced thermo-hydrolytic degradation of saccharidic moieties as compared to the speed of new saccharides liberation from wood. The most abundant monosaccharide (except of arabinose in the early stages of hydrothermal treatment at 120° C) in examined hydrolysates is D-xylose. This fact is undoubtedly due to the high amount of xylans in the oak wood polyoses (6). Relatively low concentrations of other monosaccharides in the cooking media are a natural reflection of their low representation in the treated wood. As for the presence of D-glucose in hydrolysates it is rather low and probably given by the very limited contents of wood starch and by the increased resistance of cellulose (except of some of its amorphous and short chain portions) towards hydrolysis under experimental conditions. The inversion of hydrolysates produced at 120° C results in an irregular increase in the amounts of monosaccharides determined. The comparison of amounts of monosaccharides determined prior and after inversion gives rise to the conclusion of the parallel diffusion of mono- and oligomeric saccharides from the oak wood into the cooking media. The ratio of monomeric units prior to inversion to monomeric units after inversion is variable within the range of 1 : 4 to 1 : 7, approximately.

4 CONCLUSIONS

Obtained analytical data allow to formulate the following conclusions:

- the mild conditions of oak wood hydrothermal treatment are reflected in the minute concentrations of wood degradation products
- L-arabinose is the most abundant saccharide in hydrolysates obtained in the mild conditions of treatment
- severe conditions of hydrothermal treatment maintained at 120° C yielded increased concentrations of wood degradation products
- relatively high concentrations of acetic acid, 2-furaldehyde and of saccharidic moieties in the high temperature hydrolysates (could be much higher if the lower wood to water ratio and higher temperatures were

- used) might be interesting from the view-point of their chemical or biochemical utilisation
- the low pH values of oak wood hydrolysates together with the high amount of tannins in this wood species may cause the increased rate of metallic surface corrosion (16), which is much undesired possibility
 - experiments point out possible negative impact of produced hydrolysates on the environment in the proximity of wood processing plants applying the methods of hydrothermal treatment

POVZETEK

Iz dobljenih analiznih podatkov lahko izvedemo naslednje ugotovitve:

- mili pogoji hidrotermične obdelave se odražajo v nizkih koncentracijah razgradnih produktov lesa
- v hidrolizatih dobljenih pod milimi pogoji obdelave je izmed saharidov najpogosteje nastopala L-arabinoza
- nekateri pogoji hidrotermične obdelave pri 120° C so vodili k povečanju koncentracij razgradnih produktov
- relativno visoke koncentracije očetne kisline, 2-furaldehida in saharidov v hidrolizatih, dobljenih pri višjih temperaturah, bi lahko bile zanimive s stališča kemijske in biokemijske uporabe. Te koncentracije bi lahko povezali z zmanjšanjem razmerja med količino vode in lesa.
- nizke pH vrednosti hidrolizatov hrastovega lesa skupaj z veliko količino taninov v teh vzorcih lesa pospešijo korozijo kovinskih površin, kar je seveda nezaželeno.
- poskusi tudi nakazujejo možne negativne vplive proizvedenih hidrolizatov na okolje kar se še posebej nanaša na lesne proizvodnje, kjer uporabljajo metode hidrotermične obdelave lesa.

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