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THE ENVIRONMENTAL CHEMICAL FEATURES OF THE WASTE WATER ORIGINATED FROM THE THERMAL TREATMENT OF WOOD

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ABSTRACT

The thermal treatment of wood improves beneficially several parameters of wood products. Significant amount of waste water having strong acidic and corrosive effect originates during the production of thermally modified wood. Waste waters originating from the thermal treatment of spruce and ash wood have been examined. The determination of the main environmental-chemical parameters (pH value, acidity, conductivity and COD) and the analysis of the chemical compounds by GC-MS showed that pH values of the waters altered between 2.3 and 2.6 and the samples contained high amount of organic matter. The main compounds were acetic acid, furfural and its derivatives.

KEY WORDS: thermal treatment, chemical composition, waste water, spruce, ash

INTRODUCTION

The industrial production of the thermally (~200 °C) treated wood increases year by year (Bächle and Niemz 2007b). The main reason of this tendency is the improvement of some technological parameters (swelling, shrinkage) which extends the industrial application (Yildiz et al. 2006, Bächle and Niemz 2007a). Other beneficial effects are the improvement of the aesthetical value of the heterogeneously colored wood and the decreasing of the environmental burden of the surface wood protection due to the increased durability (Giebler 1981).

From among the main components of wood hemicelluloses degrade most intensively during the general thermal processes (Boonstra and Tjeerdsma 2006). Different compounds evolve in the complex reactions (Hill 2006). A part of them have volatile feature which evaporate with the volatile extractives into the environment during the manufacturing process (Hofmann et al. 2008). The significant part of the moisture content from wood turns to steam in the heating process which condensate on the cold surfaces of the manufacturing equipments constituing - with the mentioned volatile organic compounds - a strong aggressive and acidic fluid.

The environmental friendly management of the waste water is unsolved up today. The first step of the answer is the recognizing the chemical composition and the chemical parameters. The composition and the environmental-chemical parameters of the waste water originating from the thermal treatment of two wood species, spruce (*Picea abies* Karst.) and ash (*Fraxinus excelsior* L.) wood in nitrogen atmosphere have been examined in this article.

MATERIAL AND METHODS

Material and treatment

Wood samples (ash and spruce) were treated thermally in an autoclave in N_2 gas according to the method described by Giebler (1981) in three steps. Intensity of the modification increases with the number of steps. The two steps of the modification process differ in terms of pressure, residual oxygen content, temperature and duration. The reference samples were not modified (Step 0). After closing the autoclave, the vacuum is generated, which is followed by the establishment of an overpressured atmosphere using N_2 gas. The initial moisture content of the wood is between 8-10 %. The mixture of nitrogen, residual oxygen and steam, which is produced during the treatment, remains in the autoclave during the whole process. The waste water generated after the complete modification process has been investigated.

Determination of the main chemical parameters

The most relevant environmental chemical parameters were determined using the following techniques:

pH value. 50 ml of the liquid samples have been measured using OAKTON PC510 pH/Conductivity meter (Eutech Co.) and OP 0808P pH glass electrode. The pH meter was calibrated before each determination using standard buffers of pH 4.00 and 9.00.

Acidity. The determination of the acidity was carried out by the end-point titration using 0.10 M NaOH solution. The amount of the sodium hydroxide at the neutralization point has been derived from titration curve. The acid content of samples is equal to the amount of the NaOH at the neutralization point.

Conductivity. The specific conductivity was measured by OK-114 conductivity meter with OK 0907P electrode (Radelkis, Hungary). The conductrometric standard solution was 0.01 M KCl (Radelkis, Hungary).

COD. The Chemical Oxygen Demand is widely used for measuring the organic compounds in water solutions. The standard Hungarian method (MSZ ISO 6060:1991) was applied for determination of COD.

Liming. Liming is the general industrial treatment of the waste water. It is modeled with continuous adding of $Ca(OH)_2$ solution until reached pH 7.

Determination of the chemical compounds by GC-MS

Volatility is the common feature of the main organic compounds found in the waste water due to their origin. The identification of the chemical compounds in the waste waters has been carried out by the gas chromatograhy coupled with mass spectrometry. This method is very versatile for the determination of the huge numbers of different volatile or semi-volatile components from any type of complex mixtures (Fernandez et al. 2001, Manninen et al. 2002). The advantage of this method is the unnecessity of any sample preparation since the water sample has been injected directly into the injector after the filtration through a glass filter.

The GC-MS equipment was Shimadzu QP 2010 type with AOC 5000 Autosampler. The column type: Supelco SLB 5-MS (middle polarity). The injection temperature was 275 °C, the split ratio was 200. The temperature of the column starts at 35 °C for 3 min, then raised up to 300 °C at 15 $°C.min^{-1}$ rate.

The MS recording mode was TIC (33-600 m/z). The mass spectrometry detection was performed by electron impact ionisation (70 eV). The ion source temperature was 200 °C. Wiley and NIST MS libraries were used for identify the compounds.

Since the main components seemed to be the acetic acid and the furfural and its derivates, while many other components have been detected in much lower concentration, the chromatographic method was divided in two parts: the main component analysis (A) (up to retention time 8 min) and the micro component analysis (B) (retention time 8-20 min). The direct aqueous injected (DAI) volume was 1 µl with 200 split ratio and 2 µl with 10 split ratio, respectively.

RESULTS AND DISCUSSION

General chemical parameters

The values of the important environmental chemical parameters can be found in Tab. 1. The waste waters have strong acidic characters. The acid content of waste water originating from the heat treatment of the ash wood is five times higher compared to that of spruce. Despite of this fact no correlation can be observed between the acid content and the pH value which is generally used for describing the acidity. This contradiction may base on the buffer capacity of the waste water. This experience cautions not to make decision by the pH value alone.

Tab. 1: The main chemical parameters of the investigated waste waters

	pH	Acidity[a]	Conductivity[b]	COD[c]	
Spruce	2.30	0.273	1578	41665	29350*
Ash	2.60	1.343	2190	115122	112460*

[a]: acidity is expressed in base equivalent value, mol $NaOH/dm^3$
[b]: specific conductivity, µS/cm
[c]: Chemical Oxygen Demand, mg Oxygen $consumption/dm^3$
*: COD values after liming

The high conductivity values refer to the high ion- and organic matter concentrations. The result of the Chemical Oxigen Demand investigation for waste water samples originating from ash, exceeds the acceptable limit value of the waste waters (100 000 $mg.L^{-1}$). The examined values are higher in the case of ash wood compared to spruce except of the pH value.

The beneficial effect of liming is the decreasing of the corrosion damage while the influence of environment burden caused by organic content does not alter considerably.

Chemical composition of the waste waters

The knowledge on the chemical composition is fundamental to qualifying and handling of the waste waters. The toxicity of any component group determines the classification of the waster water.

The parameters of the identified components by GC-MS are shown in Tab. 2 and Tab. 3. The major component groups in the waste water are the following: carbonic acids, ketones, aldehydes, and several phenolic components, while many other compounds can be determined in small quantities. These components are originated from the heat degradation of hemicelluloses, lignin and extractives.

Since the components could be detected in different quantities, two methods with different sample intake amounts have been applied. Thus the areas of the chromatographic peaks can be compared *only in the same method* (Fig. 1.). The main components of the waste waters are acetic acid, furfural and 5-methyl furfural. The compounds originate from the thermal degradation of the hemicelluloses. Furfural and 5-methyl furfural are degradation products of pentoses and hexoses respectively. The degradation reactions are also catalysed by acetic acid (Fengel and Wegener 1989). The volatile organic content of the waste waters originating from the thermal treatment of hard- and softwood are similar but some differences can also be found. Terpenoids and coniferyl-alcohol type components (e.g.4-hydroxy-2-methoxycinnamaldehyde) refer to softwood, while sinapyl-alcohol derivatives (4-hydroxy-3,5-dimethoxybenzoic acid, 3,5-dimethoxy-4-hydroxycinnamalde) originate from hardwood from the phenyl-propane-type structural compounds.

CONCLUSION

The waste water originating from the thermal treatment of wood has a strong acidic character and has high organic content. The values of the acid content, the COD and specific conductivity characterize the composition the waste water better, compared to the generally used pH value. This observation is confirmed by GC-MS results. The composition of waste waters originating from the thermal treatment of the hard- and softwoods are similar, the small deviations can be explained with the differences between the composition of the two wood types. The main components are acetic acid, furfural and its derivates.

Waste water needs further treatment. Liming is generally used for neutralization but this process does not decrease the organic content significantly. Another alternative possibility may be the application of the waste water as wood preservative.

Tab. 2: Volatile organic compounds in the waste water originating from the thermal modification of ash. A: Main component analysis, B: Micro component analysis

	Retention Time	Compound name	Area*
A	3.241	2,3-butanedione	3473438
	4.054	Acetic acid	204269540
	4.135	3-methyl-butanal	83427
	4.453	1-hydroxy- 2-propanone	846463
	4.643	1-methoxy-2-propanone	183601
	4.787	2,3-pentanedione	375347
	5.014	Propionic acid	2376812
	5.202	3-hydroxy-2-butanone	284028
	6.235	1-hydroxy-2-butanone	583496
	7.318	Furfural	50261034
	8.633	1-(2-furanyl)-ethanone	370478
	8.700	Butyrolactone	293136
	8.922	2,5-hexanedione	63978
	9.117	5-methyl-2(5H)-furanone	91965
	9.425	5-methyl-furfural	5489972
B	10.801	4-oxo-pentanoic acid	34355578
	10.880	2-furancarboxylic acid	8887595
	11.128	2-methoxy-phenol	2852988
	11.524	Maltol	9426876
	12.432	1,2-benzenediol	7901331
	12.790	5-hydroxymethyl-furfural	56289943
	14.091	2,6-dimethoxy- phenol	11416106
	14.676	Vanillin	25759304
	14.900	4-hydroxy-benzeneethanol	22705462
	15.497	Acetovanillone	4376276
	15.856	1-(4-hydroxy-3-methoxyphenyl)-2-propanone	6594803
	16.124	Vanillic acid	10740874
	17.013	4-hydroxy-3,5-dimethoxy-benzaldehyde	28988740
	17.596	1-(4-hydroxy-3,5-dimethoxyphenyl)- ethanone	2846732
	17.705	4-hydroxy-2-methoxycinnamaldehyde	7848213
	18.173	4-hydroxy-3,5-dimethoxybenzoic acid	2187070
	19.539	3,5-dimethoxy-4-hydroxycinnamalde	3972230

Tab. 3: Volatile organic compounds in the waste water originating from the thermal modification of spruce. A: Main component analysis, B: Micro component analysis

	Retention Time	Compound name	Area*
A	3.253	2,3-butanedione	1644222
	3.708	Acetic acid	34761195
	4.459	1-hydroxy-2-propanone	370465
	4.889	Propanoic acid	202003
	6.191	1-pentanol	313828
	6.477	Butanoic acid	185348
	6.735	Hexanal	216777
	7.325	Furfural	5650696
	7.982	1-Hexanol	102541
	8.126	Pentanoic acid	112282
	8.658	1-(2-furanyl)-ethanone	100692
	8.711	Butyrolactone	213994
	9.444	5-methyl-furfural	520332
	9.572	Hexanoic acid	503615
B	10,637	Methyl-2-methoxypropenoate	10520825
	10.776	2-furancarboxylic acid	3125684
	11.014	5-methyl-resorcinol	795197
	11.509	Maltol	2201412
	11.604	Fenchol	745438
	11.963	Dihydro-4-hydroxy-2(3H)-furanone	3363260
	12.283	Borneol	508467
	12.406	1,2-benzenediol	1066645
	12.487	α-terpineol	991314
	12.754	5-hydroxymethyl-furfural	11290380
	13.791	4-hydroxy-4-trimethyl-cyclohexanemethanol	5928257
	14.091	2,6-dimethoxy-phenol	608021
	14.220	4-hydroxy-benzaldehyde	930118
	14.673	Vanillin	21993657
	15.495	Acetovanillone	1762399
	15.738	Vanillic acid, methyl ester	629824
	16.110	Vanillic acid	3186492
	17.002	4-hydroxy-3,5-dimethoxy-benzaldehyde	2881353
	17.702	4-hydroxy-2-methoxycinnamaldehyde	3465004

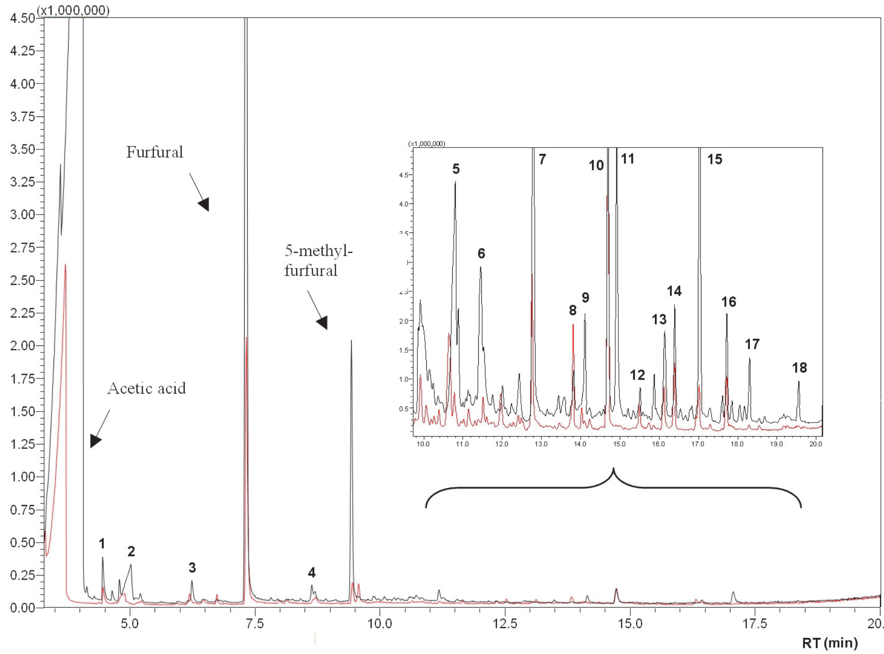

Fig. 1: Comparison of the GC-MS chromatograms of the waste waters originated from Ash and Spruce thermowood producing (black: Ash, red: Spruce)

1: 1-hydroxy-2-propanone, **2**: propionic acid, **3**: 1-hydroxyde-2-butanone, **4**: 1-(2-furanyl)-ethanone, **5**: 4-oxo-pentanoic acid, **6**: maltol, **7**: 5-hydroxymethyl-furfural, **8**: 4-hydroxy-4-trimethyl-cyclohexanemethanol, **9**: 2,6-dimethoxy-phenol, **10**: vanillin, **11**: 4-hydroxy-benzeneethanol, **12**: acetovanillone, **13**: vanillic acid, **14**: unknown component, **15**: 4-hydroxy-3,5-dimethoxy-benzaldehyde, **16**: 4-hydroxy-2-methoxycinnamaldehyde, **17**: 4-hydroxy-3,5-dimethoxybenzoic acid, **18**: 3,5-dimethoxy-4-hydroxycinnamaldehyde

REFERENCES

1. Bächle, F., Niemz, P., 2007: Deutlich geringere Quellwerte bei Thermoholz. Holz-Zentralbl. 134 (23): 622-623
2. Bächle, F., Niemz, P., 2007: Thermisch vergütetes Laubholz. Wald und Holz 4, 37-40
3. Boonstra, M.J., Tjeerdsma, B.F., 2006: Chemical analysis of heat treated sofals Roh- und Werkstoff 64: 204-211
4. Callum Hill, A.S., 2006: Wood modification – chemical, thermal and other processes. John Wiley & Sons. Chichester, 239 pp.
5. Fengel, D., Wegener, G., 1989: Wood: Chemistry, Ultrastructure, Reactions. Walter Gruter. New York
6. Fernandez, M.P., Watson, P.A., Breuil, C., 2001: Gas chromatography-mass spectrometry Journal of Chromatography A., 922: 225-233
7. Giebler, E., 1981: Dimensionsstabilisie rung von Holz durch Feuchte/Wärme/Druck-Behandlung. Holz als Roh- und Werkstoff, 41: 87-94
8. Hofmann, T., Rétfalvi, T., Albert, L., Niemz, P., 2008: Investigation of the chemical changes in the structure of wood thermally modified within a nitrogen atmosphere autoclave. Wood research, 53 (3): 85-98
9. Manninen, A-M., Pasanen, P., Holopainen, J.K., 2002: Comparing the VOC emissions between air-dried and heat-treated Scots pine wood. Atmospheric Environment 33: 1763-1768
10. Yildiz, S., Gezer, E.D., Yildiz, U.C., 2006: Mechanical and chemical behavior of spruce wood modified by heat. Building and Environment, 41: 1762-1766

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