

## Emissions from Thermally Modified Beech, their Reduction by Solvent Extraction and Fungicidal Effect of the Organic Solvent Extracts

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### ABSTRACT

The characterization and removal of odorous substances caused by thermal treatment of wood were investigated using chromatographic and spectroscopic methods. Two different thermally modified samples of Beech (*Fagus sylvatica* L.) were analysed in comparison with the respective untreated wood. The resulting volatile substances were analysed, described and quantified with Headspace SPME and Gas chromatography/mass spectrometry. Emissions of pentanal and hexanal, probably formed by oxidation of unsaturated fatty acids, were the prevailing aldehydes in untreated wood samples. Their amount decreased during thermal treatment, while furfural and 5-methylfurfural – degradation products of hemicelluloses – accounted for almost 100% of the aldehyde fraction. Furthermore, it can be assumed that odorous emissions of thermally modified wood can be strongly reduced by solvent extraction. Good results were obtained by an ethanol/cyclohexane mixture that produces wood samples without significant odour emissions. Certain organic solvent extractives from thermally modified beech have fungicidal properties. Methanol extracts, resolubilized in propanone, caused a significant retardation of fungal growth on native beech specimen. Beech specimen impregnated with these extractives could be assigned to the durability class 4 (not permanent). The analysis of methanol extracts using gas chromatography coupled with mass spectrometry (GC-MS) showed an increased share of phenolic compounds known to cause resistance effects. Their presence in organic extracts of thermally modified wood may explain the improvement of the resistance of the impregnated specimen.

### INTRODUCTION

Thermal treatment is a suitable method for improving the properties of wood like spruce, beech or poplar, and thus to open up new fields of application that used to be limited to tropical woods or woods treated with timber preservatives. Thermally modified woods are characterized by considerable changes in structural, mechanical, physical, and chemical properties, resulting in increased dimensional stability and durable resistance to fungi and microorganisms as well as discoloration and a significant odour (e.g. (Kamdem *et al.* 2002). Degradation products of miscellaneous wood components cause this typical odour (e.g. Boonstra and Tjeerdsma 2006, Windeisen *et al.* 2007, Peters *et al.* 2008). The formation of toxic polyaromatic compounds during heat treatment has been discussed in the literature (Kamdem *et al.* 2000). It was

supposed that the formation of these products caused resistance of thermally modified wood against fungal decomposition and microorganisms. Increasing indoor application of thermally modified wood enhances interest in elucidating the chemical composition of those emissions and to elaborate ways to reduce them. The aim of this investigation was to provide opportunities to reduce odour emissions and to review fungicidal effect of organic solvent extracts of thermally modified wood on the example of the European beech (*Fagus sylvatica* L.).

## MATERIALS AND METHODS

### **Materials**

Two different thermally modified samples of beech (*Fagus sylvatica* L.) were analysed in comparison with the respective untreated wood. The thermal modification was performed in a single stage dry process at 180°C and at 200°C for 4 h in a commercial plant at Mitteramskogler GmbH in Gaflenz (Austria).

### **Methods**

First, during the modification process resulting volatile substances were analysed, described and quantified with Headspace SPME and Gas chromatography/mass spectrometry. GC/MS analyses were performed on an Agilent Technologies HP 6890 gas chromatograph equipped with a split/splitless injection port and an Agilent Technologies MSD 5973. The substances were separated on an Optima5 capillary column (Macherey-Nagel, 5 % diphenyl – 95 % dimethylpolysiloxane, 30 m x 0.25 mm ID, 0.25 µm film thickness). Helium with a constant flow of 1 ml/min was used as the carrier gas. Electron impact mass spectra were recorded at 70eV in the m/z range of 10-550. The substances were identified by analysis of the individual mass spectra and comparison with the NIST 2.0 mass spectral library. Major substances not included in the NIST 2.0 mass spectral library were identified on the basis of mass spectra of reference standards analyzed at the same conditions as the sample material. For Headspace SPME analysis the injector initial temperature was 280 °C, and chromatograms were obtained in splitless mode. Column temperature was held at 50 °C for 5min, increased to 240 °C at 5 °C/min, and then held for 7 min. The volatile substances were assessed on their health and environmentally relevance.

As a second step the effect of solvent extraction to these volatiles was examined. Above-mentioned samples of modified and unmodified beech wood were milled and soxhlet extracted with several organic solvents or water. Organic solvent extracts were directly transferred to GC analysis, while water extracts were analysed after evaporation or freeze-drying and dissolution in methanol. In general, 1µl of the concentrated organic solvent extracts or of the freeze-dried aqueous extracts diluted in methanol, respectively, was directly injected at a temperature of 280 °C. Column temperature was held at 100 °C for 5 min, increased to 300 °C at 5 °C/min, and held for 15 min. Furthermore, chips of beech were thermally modified at 170°C and at 200°C for 4 h in a laboratory scale (Wienhaus 1999).

Following Sjöström and Alén (1999) 10 grams of milled chips were soxhlet extracted with 250 millilitre of several organic solvents or water (Table 1). By evaporation in a rotary evaporator the extractive content was determined. Following Grohs and Kunz (1998) the extracts were re-dissolved in 200 ml of solvent (Table 1).

**Table 1: Used extractives and solvents**

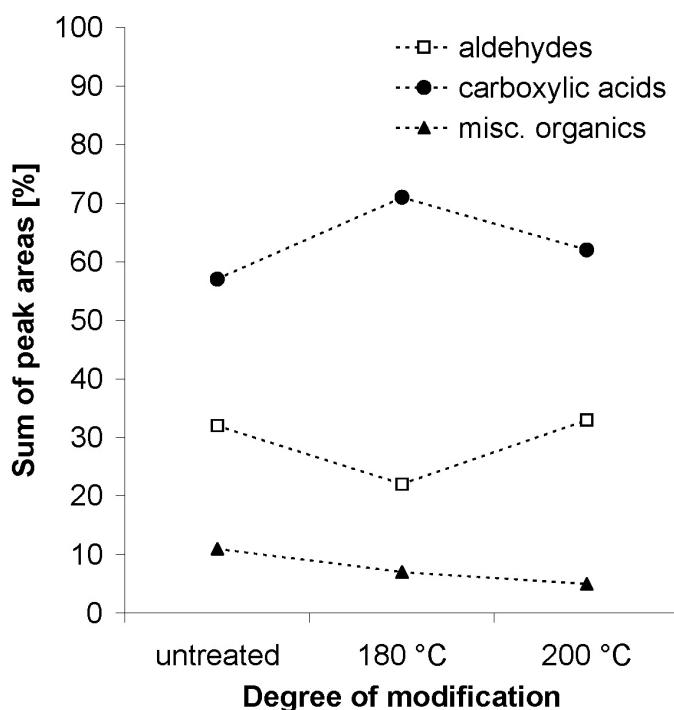
<b>Solvent</b>	<b>Mixing ratio</b>	<b>Solvent for re- dissolution</b>	<b>Mixing ratio</b>
Propanone / Purified H <sub>2</sub> O	10:1	Propanone / Purified H <sub>2</sub> O	10:1
Methanol	-	Propanone	-
Methanol / Purified H <sub>2</sub> O	2:1	Propanone / Purified H <sub>2</sub> O	2:1
Purified H <sub>2</sub> O	-	Purified H <sub>2</sub> O	-

Samples from beech ( $50 \pm 0,5$  mm x  $25 \pm 0,5$  mm x  $13 \pm 0,5$  mm) were impregnated with extracts for 30 min. With extract impregnated and not impregnated samples were used for fungal durability evaluation. Three impregnated and one not impregnated sample were placed in petri dishes and exposed to *Coriolus versicolor* (L.) during 8 weeks. After this period, mycelia were removed and the blocks were dried and weighed to determine the mass loss caused by the fungal attack.

## RESULTS AND DISCUSSION

### Analyse of volatile substances

SPME headspace extracts of the beech sample mainly consisted of aldehydes (pentanal, hexanal, furfural), carboxylic acids (acetic acid) and esters, ketones as well as aliphatic and aromatic hydrocarbons. The most noticeable changes in the chemical composition of volatiles after thermal treatment could be observed in the emission of carboxylic acids and aldehydes (Figure 1).

**Figure 1: Comparison of emission profiles of untreated and thermally modified beech**

Emissions of pentanal and hexanal, probably formed by oxidation of unsaturated fatty acids, were the prevailing aldehydes in untreated wood samples. Their amount decreased during thermal treatment, while furfural and 5-methylfurfural – degradation

products of hemicelluloses – accounted for almost 100 % of the aldehyde fraction (Table 2).

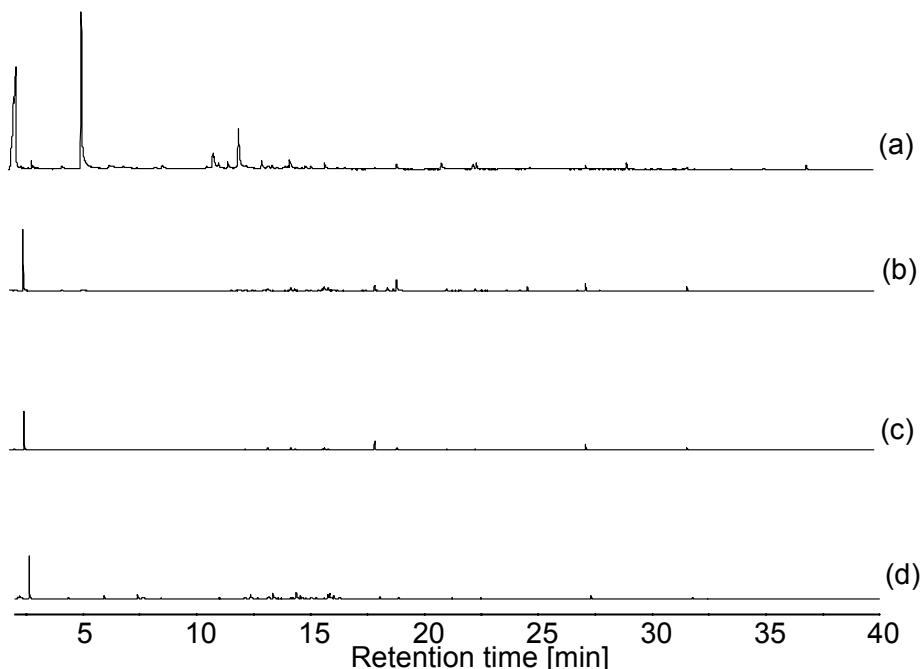
**Table 2: Changes in Aldehyde Distribution according to thermal modification**

Samples	Fraction of aldehydes [%]				
	Pentanal	Hexanal	Furfural	5-Methylfurfural	Other
Beech native	1.4	91.1	1.4	-	6.2
Beech 180 °C	-	1.1	83.9	14.8	0.3
Beech 200 °C	-	-	83.1	2.3	2.1

Toxic compounds, such as products of thermal process suspected polycyclic aromatic hydrocarbons (Kamdem *et al.* 2000), could not be proven as ingredient of the emissions. Nevertheless, the emissions of furfural have to estimate as critical. This compound is a carcinogen category 3.

#### **Reduction of odorous emissions by solvent extraction**

Additionally, the effect of solvent extraction on the composition and amount of emissions from the wood samples was verified. Based on all of the experiments considered, it can be assumed that odorous emissions of thermally treated wood can be strongly reduced by solvent extraction. A solvent extraction with an ethanol/cyclohexane mixture produces wood samples without significant odour emissions. SPME-GC analysis of the solvent-treated wood samples validates this subjective odour test (Figure 2). Extraction not only affected the emissions from the investigated natural wood samples; process products of thermal treatment were also removed by this method, and volatiles such as acetic acid, furfural or 5-methylfurfural were no longer detectable in significant amounts.

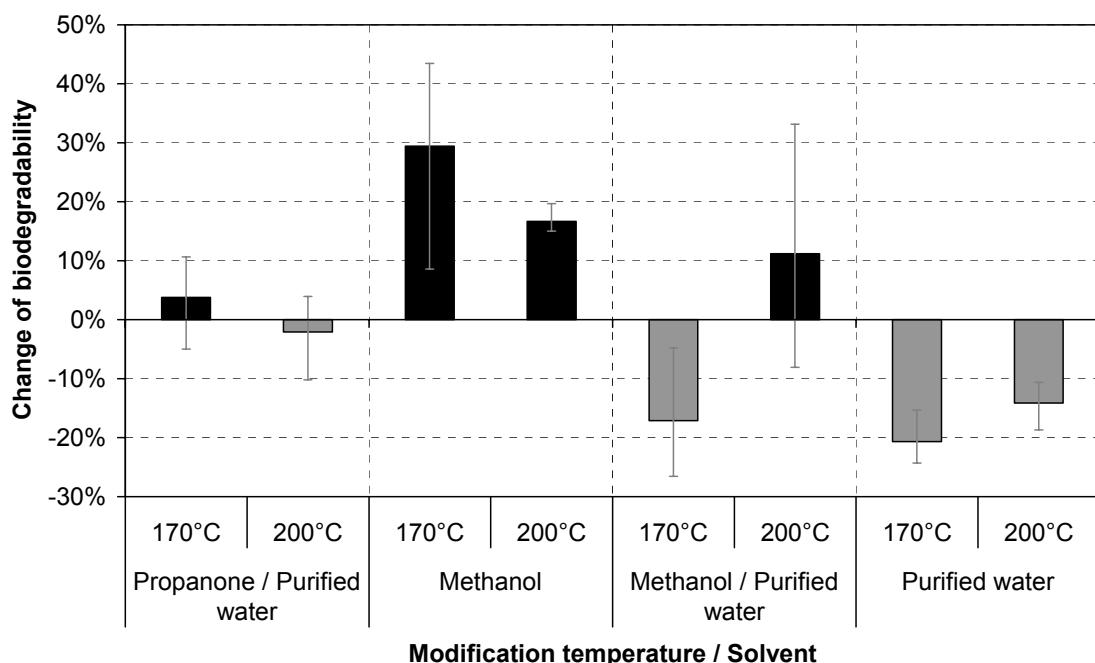


**Figure 2: SPME-GC analysis of (a) native beech wood and (b) extracted native beech wood samples; (c) 180 °C; (d) 200 °C**

Furthermore, the reduction of odorous emissions caused by thermal treatment due to solvent extraction with different solvents is a result to be followed up, and first attempts were made to extract wood before thermal modification. It has been shown that thermally treated hardwood that had been solvent extracted on a laboratory scale led to specimens with barely noticeable odour (Peters *et al.* 2008).

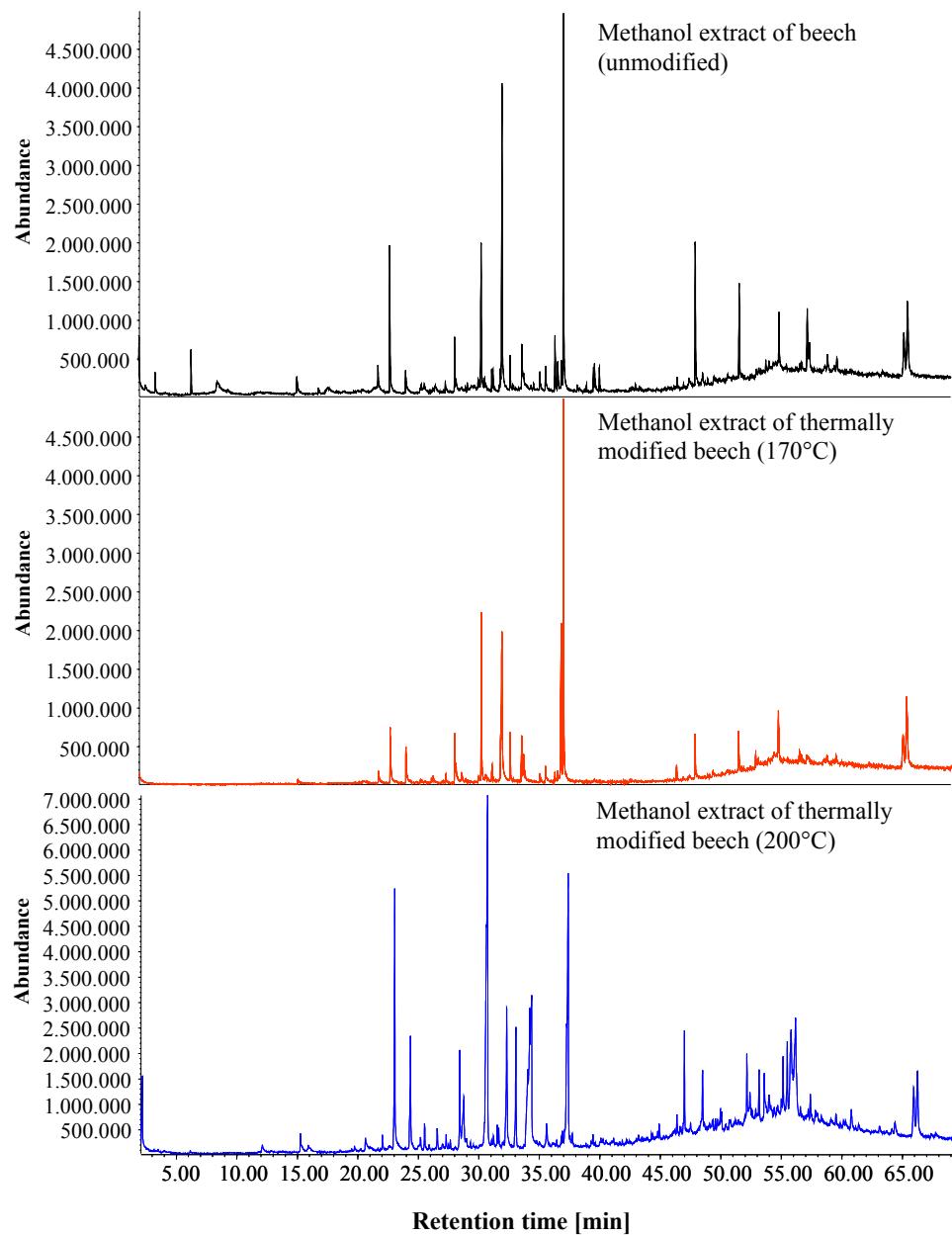
### **Proof of the fungicidal effect of extracts**

Certain organic solvent extractives from thermally modified beech have fungicidal properties. Methanol extracts, resolubilized in propanone, caused a significant retardation of fungal growth on native beech specimen (Figure 3). Beech specimen impregnated with these extractives could be assigned to the durability class 4 (not permanent).

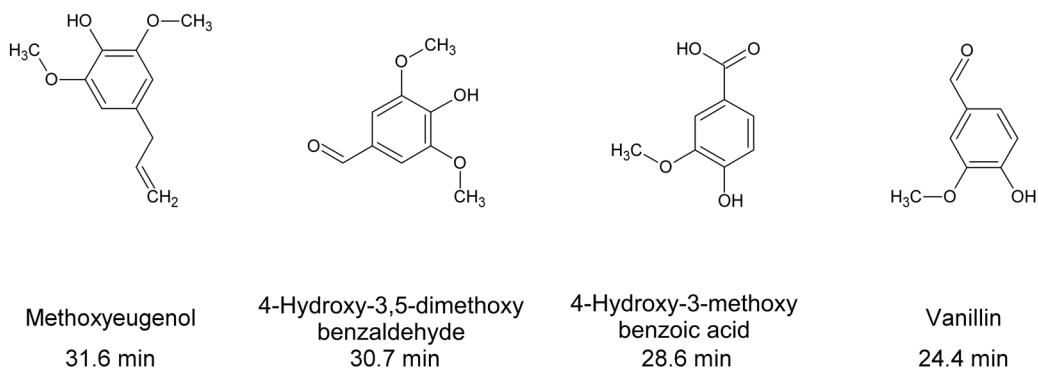


**Figure 3: Change of biodegradability by *Coriolus versicolor* (L.) of native beech specimen after impregnation with extracts of thermally modified beech (black: reduction of biodegradability, grey increase of biodegradability)**

The analysis of methanol extracts using GC/MS showed an increased share of phenolic compounds known to cause resistance effects (Figure 4). In the area of retention from 20 to 45 minutes the same phenolic substances were detected in independence of the level of modification. They are varying in their proportions. During the peak at 32.4 min (4-(3-hydroxy-1-propenyl)-2-methoxyphenol) with increasing modification temperature decreased, the other chemical substances remain in their relationship relatively stable. The peak of the dimethoxy-dihydroxyzimtaldehyde at 37.6 min, which split off from reductive reaction, is dominated in the extracts of native and 170°C modified beech. In the extract of the highest level of modification the peak of the dimethoxycinnamaldehyde at 37.4 min outweighed. The proven substances which have fungicidal effects were methoxyeugenol (31.6 min), 4-hydroxy-3,5-Dimethoxybenzaldehyde (30.7 min), 4-hydroxy-3-methoxybenzo acid (28.6 min) and vanillin (24.4 min) (Figure 5). Their presence in organic extracts of thermally modified wood may explain the improvement of the resistance of the impregnated specimen.



**Figure 4:** Overview of the chromatograms of methanol extracts of native beech (top) and thermally modified beech (centre: 170°C, below: 200°C)



**Figure 5:** Phenolic compounds with fungicidal effects found in the methanol extracts

## CONCLUSIONS

The characterization and removal of odorous substances caused by thermal treatment of wood were investigated using chromatographic and spectroscopic methods. Two different thermally modified samples of Beech (*Fagus sylvatica* L.) were analysed in comparison with the respective untreated wood. Emissions of pentanal and hexanal, probably formed by oxidation of unsaturated fatty acids, were the prevailing aldehydes in untreated wood samples. Their amount decreased during thermal treatment, while furfural and 5-methylfurfural – degradation products of hemicelluloses – accounted for almost 100% of the aldehyde fraction. Solvent extracts of thermally modified wood primarily consisted of degradation and condensation products of extracted lignin components. Advances were made in the reduction of malodorous emissions of thermally modified wood by solvent extraction. Certain extractives from thermally modified beech have fungicidal properties. Methanol extracts, resolubilized in propanone, caused a significant retardation of fungal growth on native beech specimen. Beech specimen impregnated with these extractives could be assigned to the durability class 4 (not permanent). Other extracts of thermally modified beech, in particular water extracts, did not show significant improvement in resistance. The analysis of methanol extracts using gas chromatography coupled with mass spectrometry (GC-MS) showed an increased share of phenolic compounds known to cause resistance effects. Their presence in organic extracts of thermally modified wood may explain the improvement of the resistance of the impregnated specimen.

## ACKNOWLEDGEMENTS

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