

# Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy

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**Abstract** A mild thermal treatment of wood leads to improved macroscopic properties (dimensional stabilization and resistance against fungal degradation). The chemical modifications induced by the thermal treatment were investigated by means of DRIFT spectroscopy on wood blocks in order to explain the new macroscopic properties on a molecular level. The formation of new ether linkage was observed in addition to the well-known acidic hydrolysis reactions of wood. Fungal attack was found to take place even after thermal degradation of pentosanes by a standard oxidative way. A competition between depolymerization and condensation reactions was observed.

## **DRIFT Untersuchung chemischer Veränderungen sowie des Pilzabbaumechanismus von wärmebehandelten Hölzern**

**Zusammenfassung** Eine milde thermische Behandlung führt zu verbesserten makroskopischen Holzeigenschaften (Dimensionsstabilität und Pilzwiderstandsfähigkeit). Chemische Veränderungen von Holzstücken während der thermischen Behandlung wurden mit Hilfe von DRIFT Spektroskopie untersucht, um die neuen Eigenschaften auf molekularer Basis zu erklären. Die Entstehung neuer Etherbrücken sowie bekannte saure Hydrolysereaktionen von Holz wurden beobachtet. Obwohl die Pentosan-Moleküle nach der thermischen Behandlung abgebaut waren, konnte ein Pilzangriff auf normalem oxidativen Weg stattfinden. Eine Konkurrenz zwischen Depolymerisierungs- und Kondensationsreaktionen konnte beobachtet werden.

## 1

### Introduction

Heating wood at higher temperatures than normal drying conditions has been shown to appreciably reduce the hygroscopicity and the subsequent swelling and shrinking of the ligno-cellulosic material (Stamm et al. 1937, Stamm et al. 1946, Kubinsky 1971, Giebeler 1983, Bourmester 1974). The Ecole Nationale Supérieure des Mines of Saint-Etienne has developed a thermal process (Guyonnet

et al. 1986) named 'retification' in order to produce heat modified wood called 'retified wood' (Bourgois et al. 1988). This thermally modified wood has undergone a mild pyrolysis in inert atmosphere at a temperature between 200°C and 260°C under atmospheric pressure. The thermal modifications of wood result in changes of lignin and hemicelluloses (De Groot et al. 1988) that become less hygroscopic (Nebesarova 1996). The new properties of such wood consist principally of a lower swelling and shrinking, and also of a good resistance against fungi (Dirol et al. 1993, Weiland et al. 1997) without strong losses in strength.

The retification process can therefore be considered as a wood preservative treatment without external addition of chemicals which allows the modifications of the properties of fast-growing non-durable wood (such as poplar) in order to produce a durable material which can compete with tropical woods (teak, red cedar...). This study was performed in order to understand the origin of the high durability of retified wood and chemical changes during thermal treatment using infrared spectroscopy in a diffuse reflection mode on solid samples.

## 2

### Experimental

Maritime pine (*Pinus pinaster*) and beech (*Fagus sylvatica*) were treated in a 0.3 m<sup>3</sup> laboratory reactor under various conditions of temperature in nitrogen as shown in Table 1.

Thermally treated and non-treated wood specimens' resistance against fungal degradation was estimated by normalized European tests NF-EN-113. Maritime pine specimens were degraded by a brown-rot fungus (*Poria placenta*) during 16 weeks.

Infrared spectra of the treated and non-treated wood specimens before and after fungal attack were obtained with a Digilab BIORAD FTS 185 spectrometer equipped with a DRIFT accessory composed of a modified HARRICK model in order to obtain spectra on wood blocks (dimension 5 mm×5 mm×1 mm). Each DRIFT spectrum was transformed into an absorption spectrum with the help of the Kubelka–Munk theory (Kubelka et al. 1931). The validity of the Kubelka–Munk theory was confirmed in the case of wood blocks for the whole infrared and near infrared spectral region by Tsuchikawa and coworkers (Tsuchikawa et al. 1996). This technique permits to obtain an excellent reproducibility of the recorded spectrum.

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**Table 1.** Schedules used for the treatment of thermally modified wood

**Tabelle 1.** Bedingungen für die Wärmebehandlung von Meerkiefer und Buche

	Temperature(°C)	Atmosphäre
Maritime pine	230	nitrogen
	240	nitrogen
	250	nitrogen
	260	nitrogen
Beech	230	nitrogen
	235	nitrogen
	240	nitrogen

### 3 Results and discussion

As shown in Table 2, the macroscopic properties of wood changed during the thermal treatment.

The thermally modified wood is less hygroscopic than the untreated one. Contact angle measurements of water and organic solvents on the treated wood (Nebesarova 1996) proved the hydrophobic nature of the new material. The first consequence of the retification treatment is an improvement of the dimensional stability. Some authors attributed this stabilization to cross-linking of wood polymers during the treatment (Tjeerdsma et al. 1998) but as noticed by Seborg and coworkers (Seborg et al. 1953), thermally modified wood does shrink in organic solvents (DMF, DMSO, pyridine, methanol.) even more than the untreated control samples do. Dimensional stabilization can be explained by an important degradation of the hemicelluloses of wood. This heat-sensitive polymer mainly undergoes dehydration reactions with the destruction of numerous hydroxyl groups. The thermal treatment principally affects the most hydrophilic polymer of wood (hemicelluloses) and as a result, the treated wood has a low affinity to water and therefore a good dimensional stability.

The improved durability of retified (thermally treated) maritime pine against fungi may be mainly explained by 3 theories:

- the thermal treatment causes the creation of new free molecules in the retified wood. These compounds, acting like fungicides, can be considered as new *in situ* preservation agents of wood
- some molecules arising from thermal degradation (like furfural for example) may reticulate on the lignin network (Weiland et al. 1998). The enzymatic system of

the fungi (the lignase in particular) can no longer recognize the wood substrate and is therefore incapable of degrading it. The cellulose might also be modified (possible esterification by the acetic acid released by the hemicelluloses during the thermal treatment)

- the thermal treatment causes the elimination of the pentanes (hemicelluloses), which compose the elementary nutritive elements of wood, and therefore inhibits the initial colonization of fungi.

In this paper, we will try to bring forth some evidence concerning the last two theories.

#### 3.1 Chemical modifications of wood during thermal treatment

In Fig. 1, infrared spectra of several maritime pine samples treated under nitrogen atmosphere are represented. The bands attributions were made according to Kuo and coworkers (Kuo et al. 1988). The treatment affected the C=O band of acetyl groups present in the hemicelluloses ( $1750\text{ cm}^{-1}$ ) and a general decrease in C=O functions during the treatment ( $1650\text{ cm}^{-1}$ ) is observed at temperatures below  $250^\circ\text{C}$ . The  $1600\text{ cm}^{-1}$  band decreases while the  $1510\text{ cm}^{-1}$  slightly increases. These two bands correspond to C=C vibration of the aromatic skeleton of lignin. The  $1460\text{ cm}^{-1}$  band corresponding to hemicelluloses and to methyl groups of lignin decreases. We also noticed an increase of the  $1160\text{ cm}^{-1}$  band probably due to new C-O-C linkages in the treated wood.

According to Kosikova and coworkers (Kosikova et al. 1993), the modification of the hydrogen bonding system in cellulose and hemicelluloses induces a broadening of the  $1110\text{ cm}^{-1}$  band. The hydrogen bonding system of wood seems to be disrupted at elevated temperatures.

An increase in C=O and C=C bands is observed for  $250^\circ\text{C}$  and  $260^\circ\text{C}$  treatments.

Figure 2 shows the infrared spectra obtained for thermally treated beech. The C=O bands decrease ( $1730\text{ cm}^{-1}$  and  $1660\text{ cm}^{-1}$ ) at temperatures as high as  $240^\circ\text{C}$ . The aromatic skeleton of lignin is also slightly affected (decrease of the  $1600\text{ cm}^{-1}$  band and increase of the  $1500\text{ cm}^{-1}$  band).

The observations made in the case of maritime pine are still true: a destruction of the hemicelluloses and a modification of the linkages of lignin's aromatic ring is noticed. The cellulose environment is modified (spectral region  $1200\text{ cm}^{-1}$ – $1010\text{ cm}^{-1}$ ). The  $980\text{ cm}^{-1}$  band decreases as the treatment temperature increases. This band is

**Table 2.** Properties of thermally treated wood  
**Tabelle 2.** Eigenschaften von wärmebehandelten Hölzern

	Volumic swelling (%)	Modulus of rupture(MPa)	Weight loss* (%)
Maritime pine			
Non-treated	13,22	99.7	17.13
Thermal-treated**	9.90	92.1	9.76
Treatment efficiency (%)	25	–8	43
Beech			
Non-treated	22.89	113.7	22.92
Thermal-treated**	14.56	106.8	5.94
Treatment efficiency (%)	36	–6.1	74

\* after a 16 weeks fungal attack  
\*\* standard industrial treatment

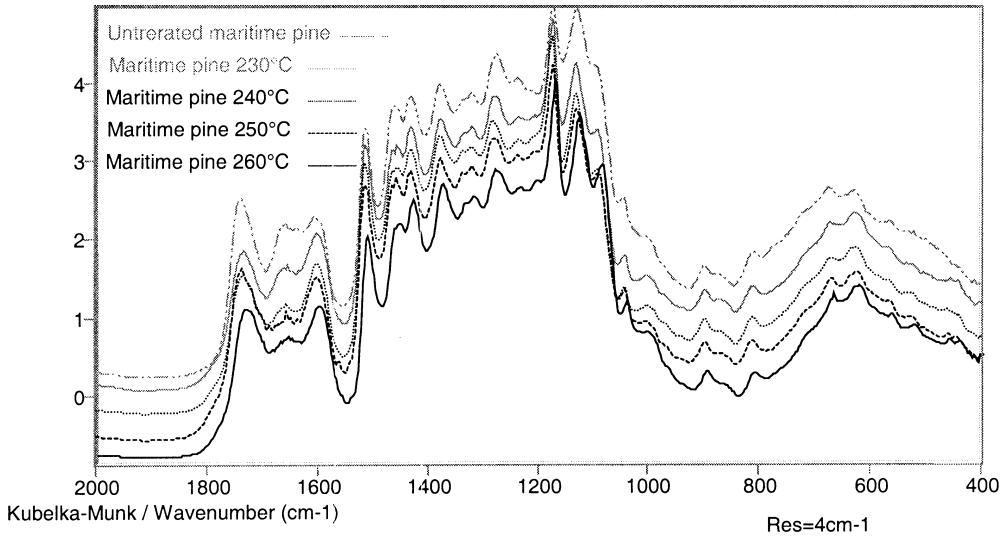


Fig. 1. Infrared spectra of several maritime pine samples treated in nitrogen

Bild 1. Infrarotspektren von verschiedenen Meerkiefer Proben nach thermischer Behandlung unter Stickstoffatmosphäre

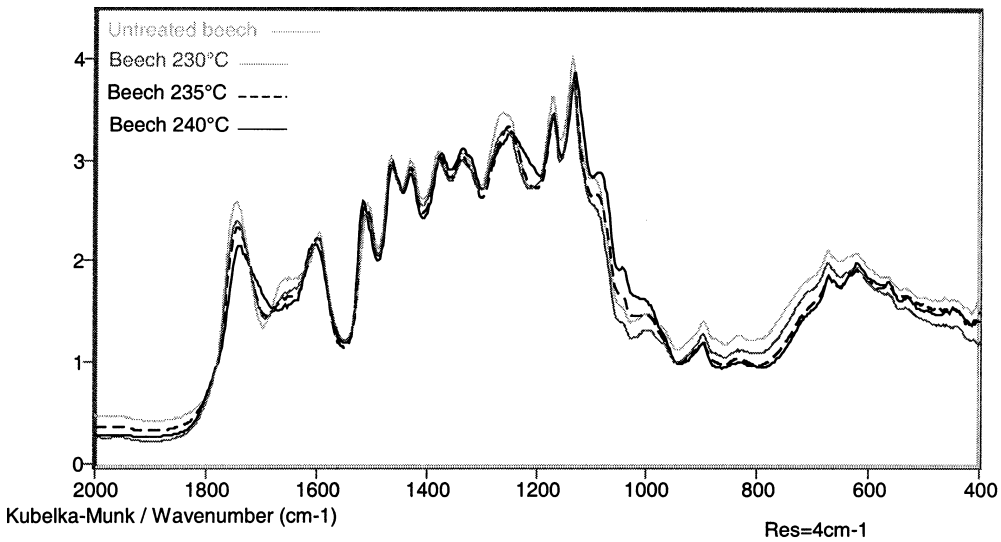


Fig. 2. Infrared spectra of several beech samples treated in nitrogen

Bild 2. Infrarotspektren von verschiedenen Buche-Proben nach thermischer Behandlung unter Stickstoffatmosphäre

characteristic for the  $\beta$ -(1,4)-linkage between sugar units in wood. The numerous acetyl groups present in beech wood are released during the thermal treatment and induce a depolymerization of the wood polysaccharides.

The heat treatment of wood in the temperature range between 200°C and 260°C causes strong hemicellulose degradation (Weiland et al. 1998) with an important release of acetic acid. A low pH and high temperatures are conditions which give rise to acidic hydrolysis of polysaccharides and lignin.

Two main reactions occur during acidic hydrolysis of polysaccharides:  $\beta$ -(1,4)-bond breaking between saccharide units and intramolecular dehydration reactions (Fengel et al. 1984). The depolymerization reactions mostly affect amorphous polysaccharides and the loss of intramolecular water generate furaldehyde-like compounds (Fig. 3).

Acidic hydrolysis of lignin alters ether linkages (Hon 1990) to form carbonium ions (Fig 4).

The presence of carbonium ions induces further condensation reactions that are catalyzed by high temperature and presence of acetic acid (Fig. 5).

### 3.2

#### Degradation patterns of heat treated wood

One of the most important effects is a spectacular increase of wood resistance against fungal attack. But unfavorable

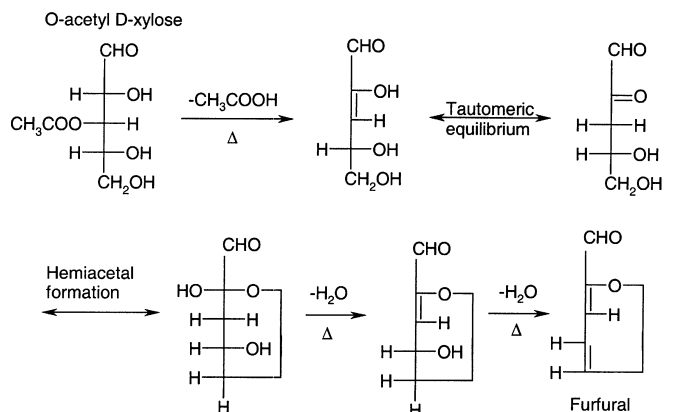


Fig. 3 Intramolecular dehydration of O-acetyl D-xylose

Bild 3. Intramolekulare Dehydrierung von O-Acetyl D-Xylose

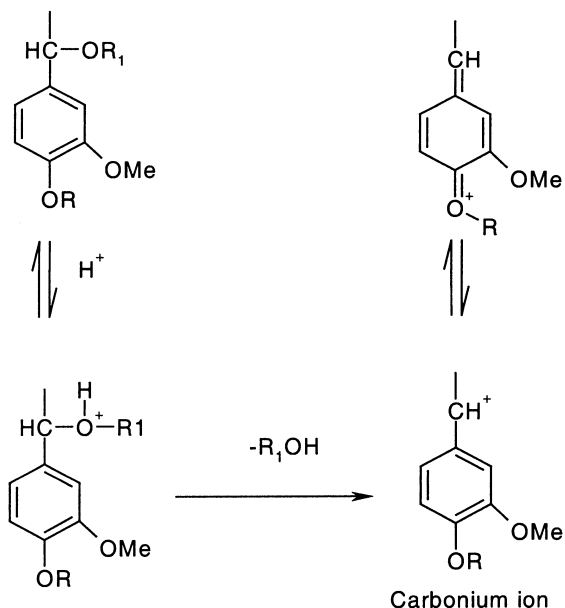
C $\alpha$  ether linkage

Fig. 4. Carbonium ion formation during acidic hydrolysis of lignin  
 Bild 4. Bildung von Carbonium-Ionen während saurer Hydrolyse von Lignin

process parameters reduce fungal resistance of heat treated wood even at high temperature. The study of degradation patterns of heat treated wood still sensible to fungal attack by means of infrared spectroscopy will be discussed below.

Untreated maritime pine has undergone a brown-rot fungal attack (*poria placenta*). In Fig. 6, deep chemical changes of the sample are observed. The hemicelluloses degradation leads to a decrease of peaks in the spectral

region 1800  $\text{cm}^{-1}$ –1500  $\text{cm}^{-1}$ , as the typical guaiacyl (1275  $\text{cm}^{-1}$ ) and syringyl (1230  $\text{cm}^{-1}$ ) peaks increase. These results are in agreement of those of Kuo and coworkers (Kuo et al. 1988), who observed an important increase of the typical lignin bands. The fungus consumes the polysaccharides leaving a lignin-rich material after biodegradation. Gilardi (Gilardi 1995) also attributed the peaks increase 1200  $\text{cm}^{-1}$ –1300  $\text{cm}^{-1}$  to phenolic -OH groups emergence in accordance to known brown-rot fungal patterns. Unlike Gilardi, we did not observe an increase of C=C and C=O bands. However, these band increases could be concealed by the hemicelluloses degradation.

The 1160  $\text{cm}^{-1}$  (C–O–C linkage of polysaccharides) and 895  $\text{cm}^{-1}$  bands decrease while the 1110  $\text{cm}^{-1}$  band (-OH linkage of polysaccharides) shows an important broadening after fungal attack. An important polysaccharide depolymerization (decrease of the  $\beta(1,4)$  linkage band at 1000  $\text{cm}^{-1}$ ) is observed.

The thermally treated wood degradation pattern is shown in Fig. 7. In the spectral region 1800  $\text{cm}^{-1}$ –1600  $\text{cm}^{-1}$ , we can notice that the residual hemicelluloses are no longer assimilated by the fungi. Furthermore an increase of the C=O linkage (1660  $\text{cm}^{-1}$  and 1730  $\text{cm}^{-1}$ ) due to an oxidizing degradation pathway is observed. The lignin amount of the degraded material increases (1230  $\text{cm}^{-1}$ –1280  $\text{cm}^{-1}$ ). The cellulose environment is deeply affected and changed after fungal attack (1100  $\text{cm}^{-1}$ –1200  $\text{cm}^{-1}$ ). As observed for untreated wood, polysaccharides undergo depolymerization reactions (decrease of 1050  $\text{cm}^{-1}$  and 895  $\text{cm}^{-1}$  bands).

In spite of a strong hemicellulose degradation by the heat treatment, the fungal attack still takes place. The hypothesis of an initial colonization inhibition due to the

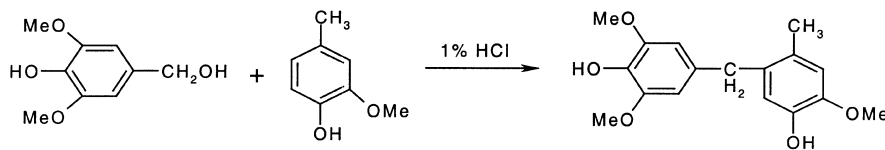


Fig. 5. Condensation reactions of model compounds of lignin (Hon et al. 1990)  
 Bild 5. Kondensationsreaktionen von Lignin (Hon et al. 1990)

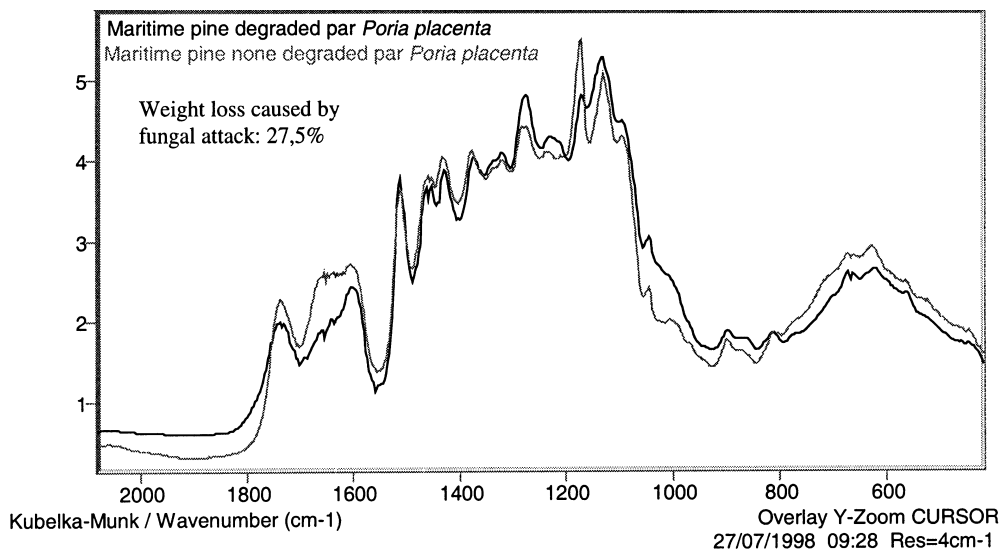


Fig. 6. Infrared spectra of untreated maritime pine degraded by *Poria placenta*  
 Bild 6. Infrarotspektren von unbehandelter Meerkiefer nach Angriff von *Poria placenta*

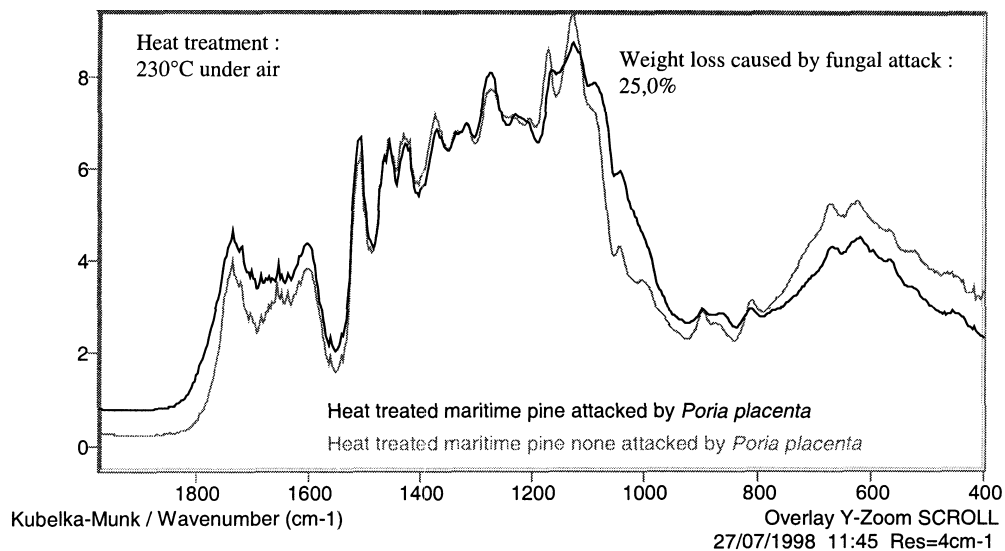


Fig. 7. Infrared spectra of thermal treated maritime pine degraded by *Poria placenta*  
Bild 7. Infrarotspekren von thermisch behandelter Meerkiefer nach Angriff von *Poria placenta*

destruction of pentosanes seems to be wrong in the case of heat treated maritime pine. The modifications of lignin and the creation of new ether linkages in the material could possibly create a denaturation phenomenon and lead to an obsolescence of the fungi's enzymatic system against retified woods.

Wood polymers undergo both depolymerization and condensation reactions. The optimization of process parameters will probably consist in minimizing the polymer depolymerization reactions in order to avoid mechanical degradation without affecting the condensation reactions necessary for optimal fungal resistance.

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