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Hydrothermally modified wood: some reasons for durability

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The aim of the work:

To come closer to the understanding of the reasons for durability of hydrothermally modified wood by analysis of our experimental data.

Materials and treatment:

Soft deciduous wood: aspen (*Populus tremula*), birch (*Betula* spp.), grey alder (*Alnus incana*)

(moisture content 8-12%; boards (28-32) x (100-105) x 1000 mm)

The modification method: one-stage hydrothermal modification (HTM) in WTT experimental equipment in water vapour medium at elevated pressure.

The treatment regimes: holding for 3 h at 160^{o}C and for 1 h at 170^{o}C (pressure 0.8-0.9 MPa).

Investigations

- The durability of wood against brown (*Coniophora puteana, Postia placenta*) and white (*Trametes versicolor*) rot fungi (EN 113 (CEN/TS 15083-1), and after leaching according to EN 84).
- The enzymatic activity of the fungi according to standard methods*
- Chemical components' analysis:
    - holocellulose (according to the Wise method);
    - cellulose (Kirschner-Hoffer method);
    - hemicelluloses were determined from the amounts of holocellulose and cellulose analyses data.

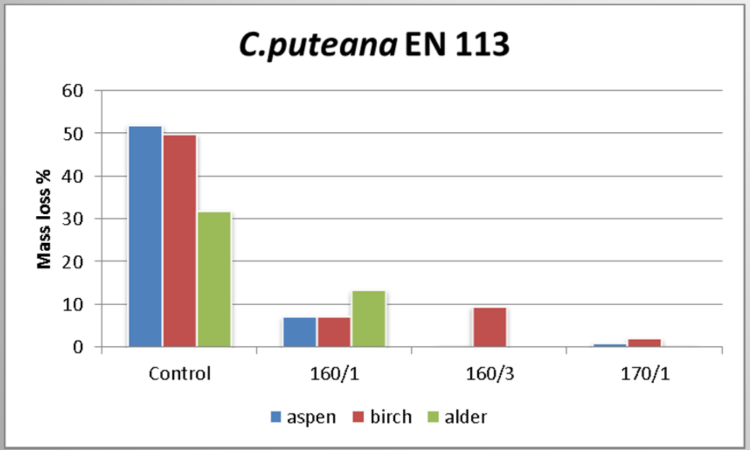
*Irbe I. et al. , 2014, *Int.Biodeterioration and Biodegradation*

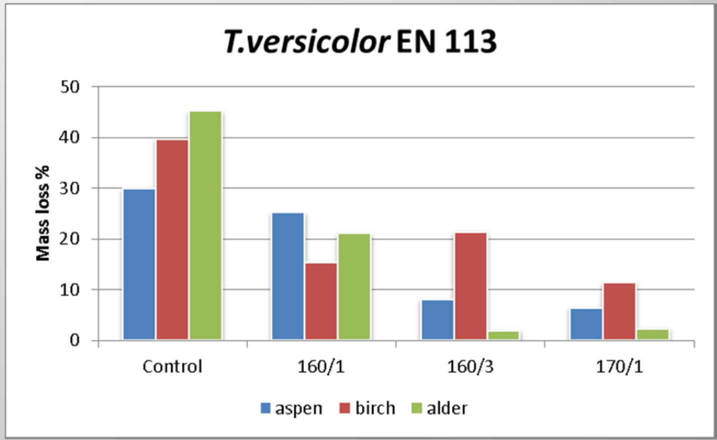
Possible reasons for thermowood durability from literature data:

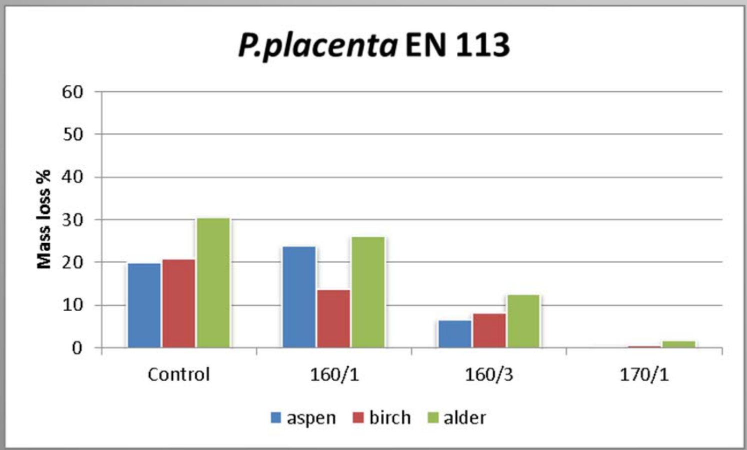
- thermowood hydrophobicity as the limiting factor of water sorption in wood, hence, the development of fungi;
- extractives with biocide properties formed in thermo treatment;
- wood polymers are modified and become unrecognisable for fungal enzymes;
- hemicelluloses - the necessary nutrient source at the first stages of the fungal attack - are degraded;
- after the treatment, the material acquires a higher size stability; respectively, cell wall porosity decreases, which hinders the penetration of enzymes in the cell wall, etc.

Weiland, and Guyonnet (2003). *Holz als Roh- und Werkstoff*

Differences in HTM aspen, alder and birch biodegradation with rot fungi (EN 113)







All the test fungi degrade the HTM **birch** wood most intensively (the highest hemicellulose (xylose) content?), while **alder** is the most durable (the highest lignin content?).

The moisture of HTM wood:

after the fungal attack was sufficiently high (40-60% on the average):

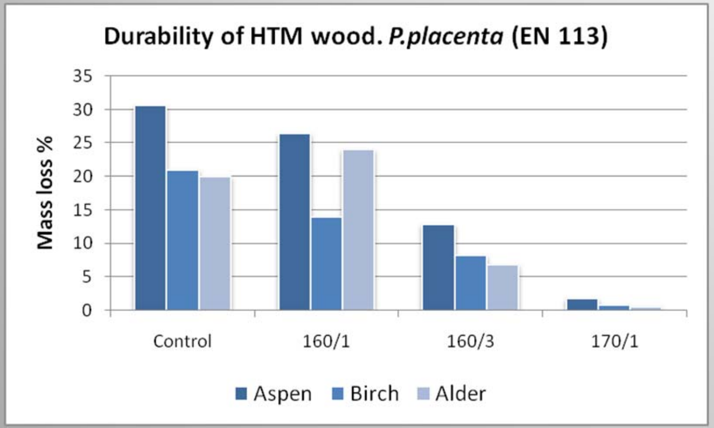
- *C.puteana* - 47%,
- *P.placenta* - 42%,
- *T.versicolor* - 56%,

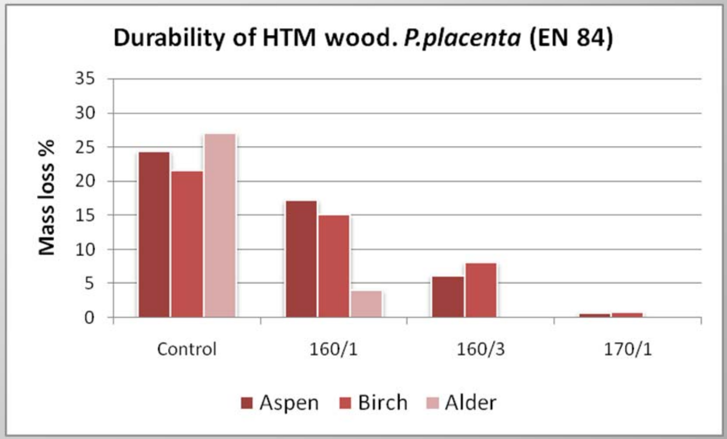
so that to ensure the development of fungi.

This makes it possible to conclude:

the **hydrophobicity** of thermowood, which is testified by the higher contact angle, lower capillary water uptake and smaller specific surface accessible for water vapours, comparing with the case of unmodified wood, **is not only the reason** for its durability.

Effect of leaching (EN 84) on the fungal resistance of HTM wood





The leaching according to EN 84 prior to the fungi test changes wood durability.

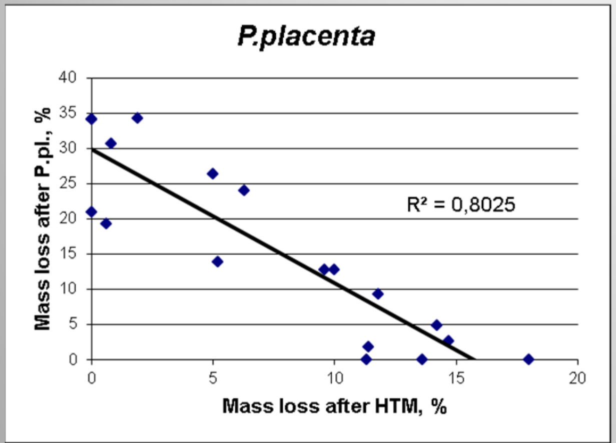
The HTM wood contains water-soluble compounds which hampers or favours the degradation with different rot fungi.

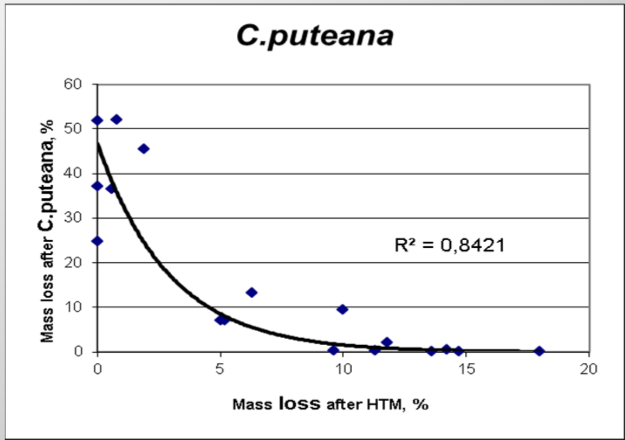
Water extracts contain **sugars, esters, acids, tannins**.

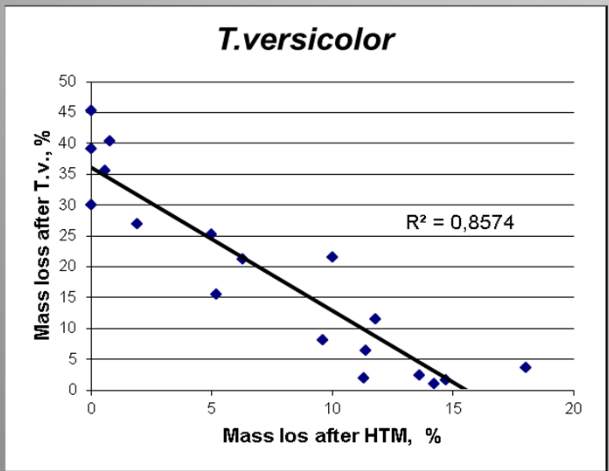
- For the wood modified in the regime 170^{o}C/1 h, leaching does not affect the mass losses (the wood does not contain the corresponding water-soluble compounds any more, or those are transformed, and the wood has become inaccessible for fungi).

- The water-soluble compounds formed during the HTM process in wood determine the thermowood fungal resistance; hence, it can change, depending on the service life conditions (in constantly high moisture conditons).

Correlation *between the mass losses (ML) of aspen, birch, alder after the HTM treatment and those after the attack of rot fungi*







Wood durability can be forecasted from the ML after HTM.

To reach the durability class 2 according to CEN/TS 15083-1 (mass losses after the fungi < 10%) against all test fungi, the birch mass losses after HTM should be ~12%, and those for aspen and alder ~10%. Such mass losses in the HTM process used are reached, modifying alder at 160º/3 h, and aspen and birch at 170ºC/1 h.

Lignocellulolytic activity in decay of HTM soft deciduous woods

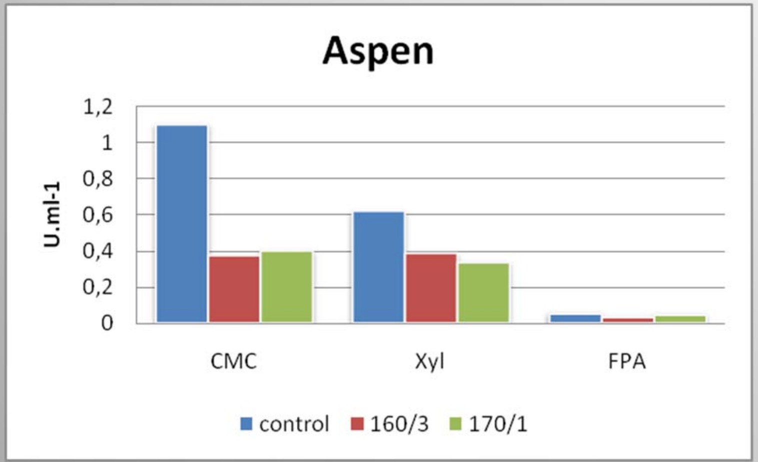
We determined:

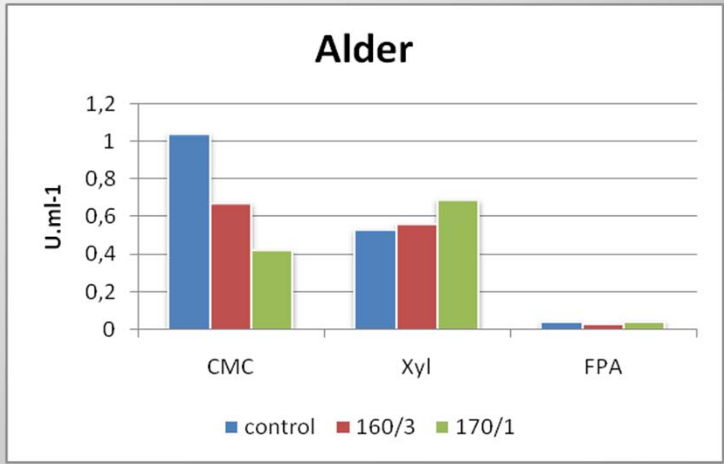
- wood mass losses *(ML),*
- xylanase (Xyl),
- laccase,
- endoglucanase (carboxymethylcellulase, CMCase) activity,
- Filter paper activity (FPA) for total cellulase activity,
- manganese-dependent peroxidase (MnP) activity

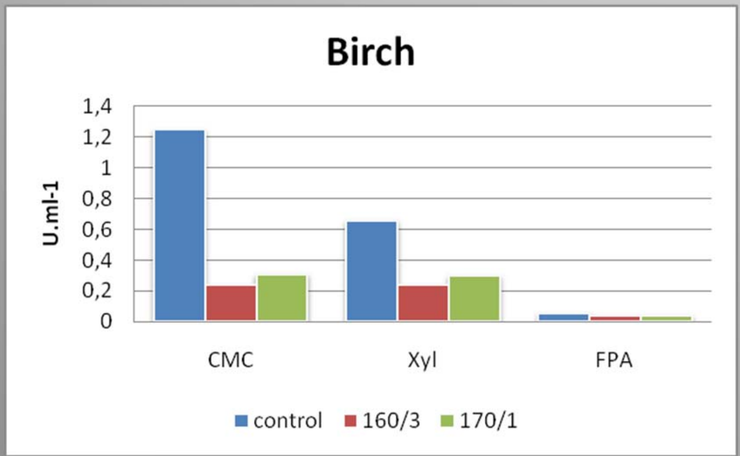
after 10, 20 and 42 days of incubation. Data are given for total released enzyme amounts.

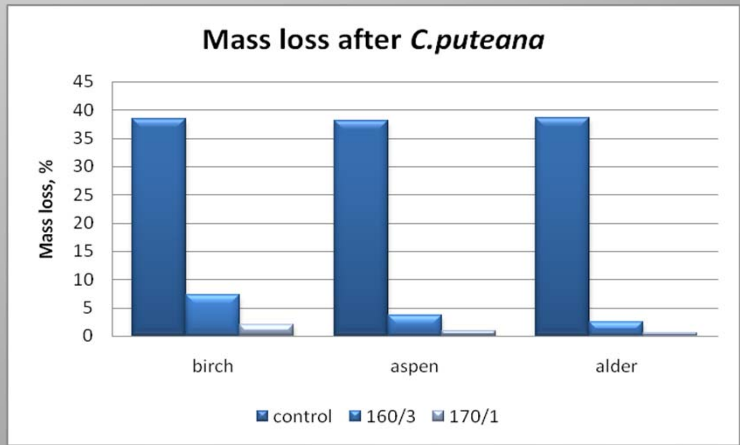
Enzyme formation dynamics are different for different wood and fungi.

C.puteana. Unmodified wood: values of CMCase and Xyl production are similar, but Xyl activity is about twice lower. HTM wood: CMCase and Xyl production is lower (except alder).

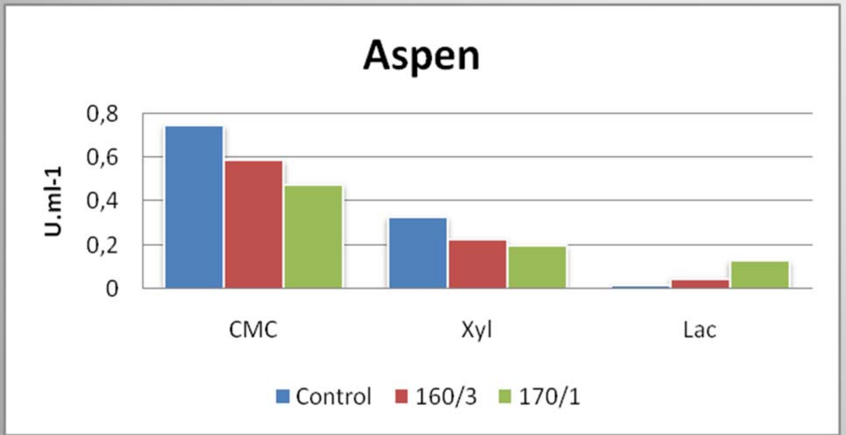


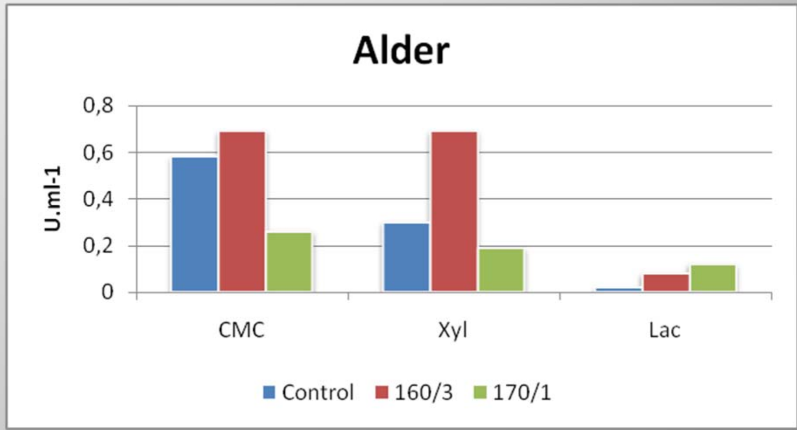


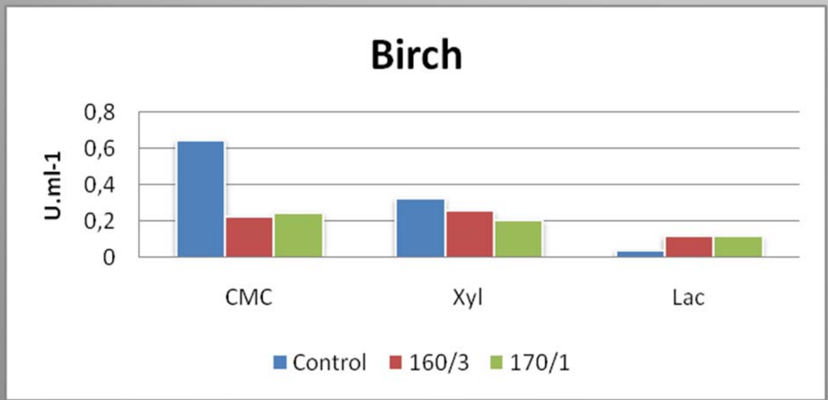


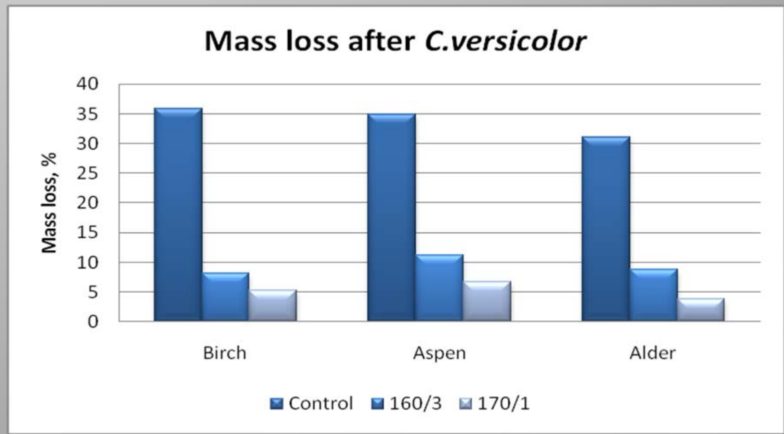


T.versicolor, in comparison with *C.puteana*, produced somewhat less CMCase and about twice less Xyl. HTM wood: CMCase and Xyl production is lower (except alder at 160/3).

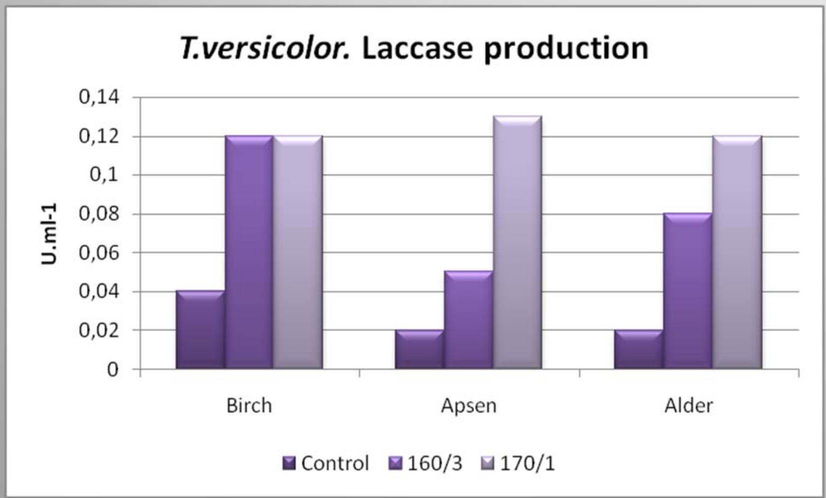








T.versicolor in contact with HTM wood, compared with unmodified wood, produced several times more **laccase**.



Enzyme production is closely connected with the presence of the inducing agent and the deficit of the readily available carbon sources*.

Probably, laccase production is induced by the low-molecular aromatic or heterocyclic compounds formed in HTM, the presence of which in modified wood is confirmed by our Py/GC-MS analyses data **.

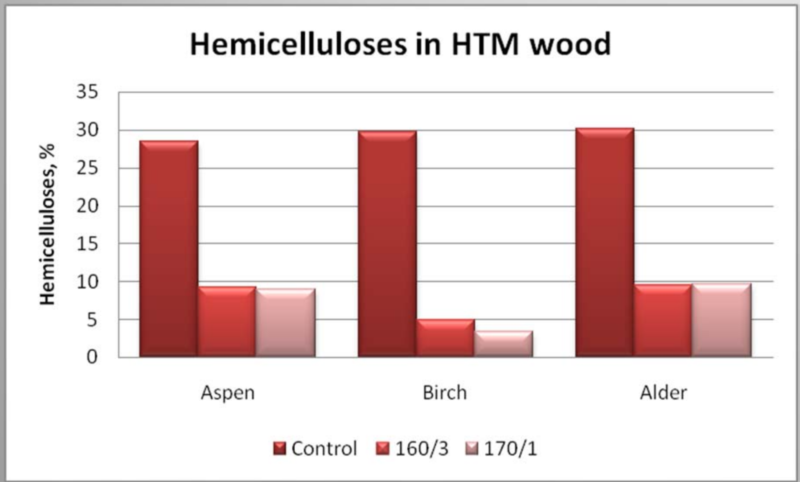
*Aro (2005). *FEMS Microbiology Reviews*
**Grinins (2013). *J.Anal.Appl.Pyrolysis*

The activity of individual enzymes or the sum of the produced enzymes does not directly correlate with the wood mass losses – this is obviously determined by the action of the enzyme complex on wood.

The results make it possible to conclude that the contact of fungi with HTM wood, although decreases, however, does not fully inhibit the cellulolytic enzymes' production, but initiates the laccase production for the white rot fungus. This partly agrees with the conclusion of other authors *.

** Lekounougou et al.(2009). Wood Sci. Technol.*

Hemicelluloses in HTM wood

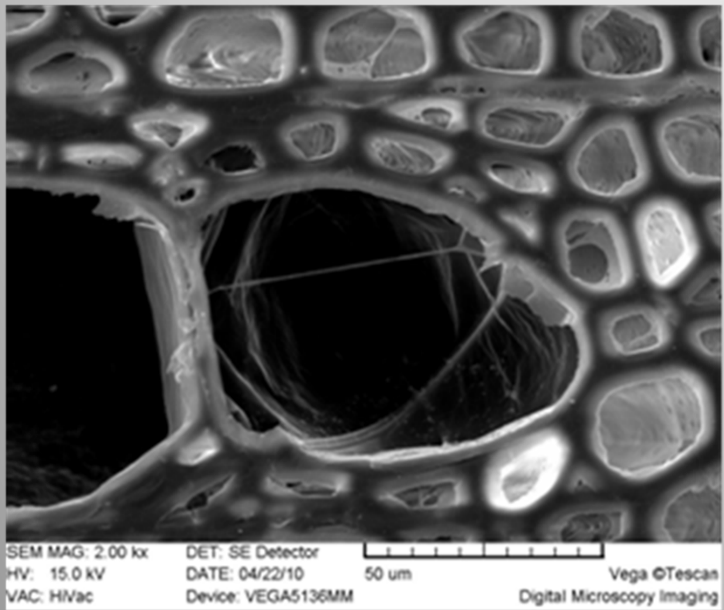


An important reason for the durability of HTM wood is the components' composition: more than 3 times lower content of hemicelluloses - most accessible wood polymer for rot fungi, and by ~10% higher relative lignin content.

Cross-linking of hemicelluloses with the lignin* or of cellulose with the lignin** probably occurs.

*Hakkou *et al.* (2006). *Polymer Degradation and Stability*
** Košikova *et al*. (2010) . *Wood Sci.Technol.*

Despite the hemicelluloses' degradation, the fungal attack occurs.



HTM wood is overgrowing with fungi mycelia more intensively in comparison with unmodified wood.

HTM treatment reduces the cellulose DP. The fungi reduce the HTM wood cellulose DP further.

For example, in our tests, as a result of the action of *C.puteana*, the cellulose DP of HTM aspen (170ºC/1 h) after 42 test days decreases from 608 to 526.

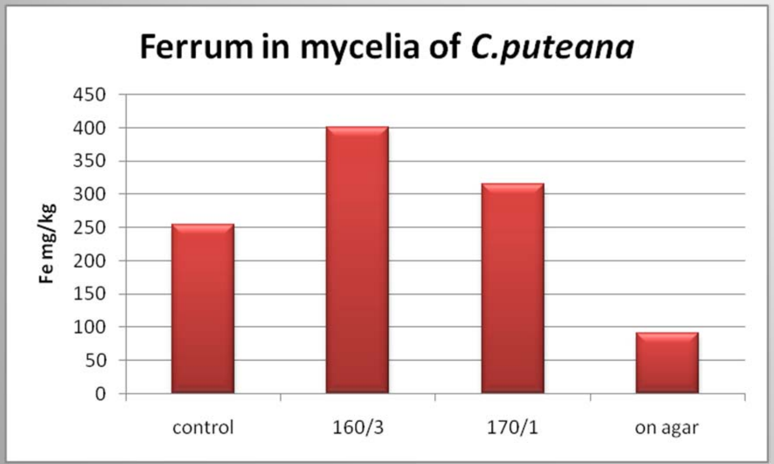
Picture from *Irbe I. *et al*. (2014) *Int.Biodeterioration and Biodegradation*

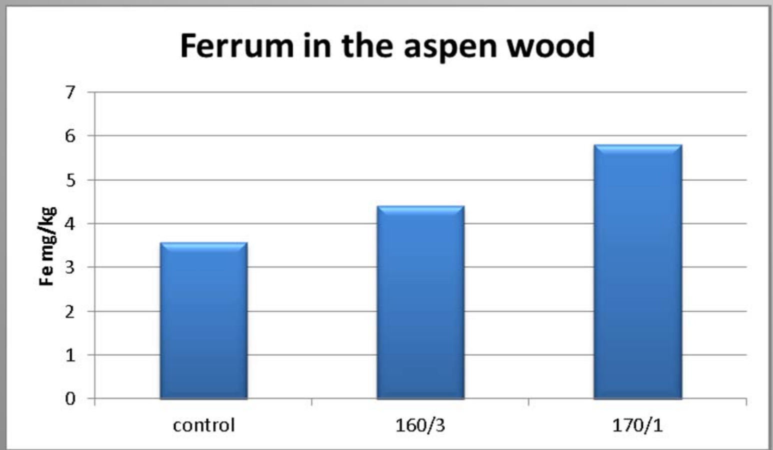
- It is demonstrated (Arantes *et al.* 2010)* that of great importance for degradation with brown fungi and selective white fungi are **low-molecular phenolate compounds**, which bind and reduce iron, forming oxygen radicals. Free radicals, which are generated by low-molecular systems, are important so that to open the wood structure prior to or simultaneously with the fungal attack.

- Analyses of our autoclave condensates testify the formation of volatile aromatic compounds. Py/GC-MS analyses testify the presence of heterocyclic compounds and lignin (mainly syringyl-) derivates in HTM wood. Those compounds can hinder the formation of oxygen radicals.

*Arantes et al. (2010). IRG/WP

Role of Fe in HTM wood degradation?

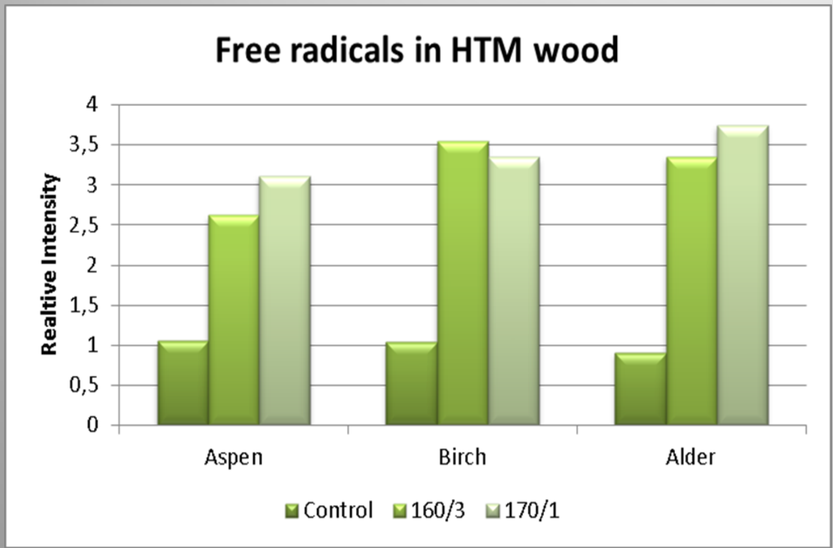




The amount of Fe in *C.puteana* mycelia growing on HTM wood is 50-90 times greater in comparison with the Fe content in wood.

By the ESR method ferric compounds (Fe III) are not found.

Long-lived stable free radicals in thermowood



Those can influence the fungi low-molecular compounds' reactions at the starting stage of biodegradation.

Experimental data were obtained in 1 month after the modification*.

Our studies in this direction are under way. We have not yet managed to elucidate the free radicals' stability in time.

*Example of the experimental data obtained by Michael Altgen

Conclusions

- **Durability against brown and white rot fungi** for aspen, alder and birch is **noticeably improved at a hydrothermal modification** temperature of 160^{o}C.
- The correlation between the mass losses of all modified woods under study after HTM treatment and the mass losses after the action of rot fungi is linear for the fungi *P.placenta* and *T.versicolor*, but exponential for *C.puteana;* respectively, the **HTM wood is degraded by *P.placenta* and *T.versicolor* more intensively, and less by *C.puteana.***
- The durability of HTM wood, leached prior to the fungi test according to EN 84, changes; hence, the **modified wood contains water-soluble compounds, the presence of which influences variously the wood degradation with different fungi.**

Conclusions

- Hydrothermal modification enhances the durability of soft deciduous wood against brown and white rot fungi, although hyphae are found in the wood cell wall lumens, **the fungi, in contact with wood, produce enzymes, and the DP of cellulose as a result of the fungal action is decreased.**
- To obtain soft deciduous wood with the durability against rot fungi corresponding to the durability classes 1 or 2, hydrothermal modification in the regime 170^{o}C/1 h is required.
- In our opinion, **an important aspect of thermally modified wood durability against fungi is the chemical composition of the wood and the interaction of the formed compounds with the low-molecular and enzymatic systems of rot fungi.**

THANK YOU FOR YOUR ATTENTION!