Methodology to Evaluate Efficacy and Ecotoxicology of Modified Wood

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ABSTRACT

Modified wood can be seen as a new product group for which new evaluation criteria are needed. This paper wants to elaborate on methodology combining ecotoxicology of modified wood using leachates and decay resistance of the treated wood. Leaching procedures based on European standards EN 84 and OECD part 1 were performed prior to fungal testing according to the natural durability approach. This combination proved to be suitable for evaluation of both furfurylated or heat treated wood. It allowed concluding that next to wood species also the overall and exact process parameters influence the efficacy and ecotoxicology of the final modified product.

INTRODUCTION

To prolong the service life of wood and lower the maintenance costs wood can be treated in several ways. Whatever treatment or product is used to modify wood, it induces changes in the structure of wood, either when chemicals are added or new ones are formed. These changes lead to different degrees of improved wood properties like durability, dimensional stability, etc. Drawbacks are some reduced wood properties or the potential loss to the environment of (newly formed) chemicals. Finding a good balance between benefits and costs is a challenge. Therefore it is important to have a reliable and balanced evaluation system. In this research it was the purpose to assess both the efficacy of the treated wood against basidiomycetes attack and the ecotoxicology of the wood leachates against the crustacean *Daphnia magna* into one overall procedure.

MATERIALS AND METHODS

Both thermally modified and furfurylated wood were considered. Spruce (*Picea abies*) was sampled during the development of the hydrothermal Plato-process, while southern yellow pine (SYP) and maple were sampled during two different furfurylation scaling up processes. In the first process a monomeric furfuryl alcohol solution lead to 30% weight percent gain (WPG) for SYP and 20-25% WPG for maple. For the second furfurylation process an oligomeric furfuryl alcohol was used gaining 20-30% WPG for SYP.

Leaching procedures

It was the purpose of this study to set up a methodology to evaluate both the fungal resistance and ecotoxicity of modified wood. Since no specific approach exists yet for fungal resistance evaluation of modified wood the natural durability approach (CEN/TS 15083-1, 2006) was chosen over the preservative efficacy approach (EN 113, 1996; EN 599-1, 1996). The specimens were first leached according to the European Standard EN 84 (1996) and then subjected to fungal decay testing. The 24 hours and 14 day EN84-leachates were considered for ecotoxicity estimation. The first one refers to a worst case scenario while the 14 day EN84-leachate simulates wood in service (Wegen *et al.* 1998). Since it is not self-evident to generate a leachate containing realistic concentrations of depleted components (Melcher and Wegen 1999) a second series of wood blocks was subjected to the milder OECD part 1-leaching procedure (CEN/TR 15119, 2005), developed for applications in line with use class 3.

Full description of the leaching conditions can be found in De Vetter *et al.* (2008). In brief for the EN84-leaching procedure the specimens were initially impregnated with distilled water (562.5 ml per 6 specimens) which was then replaced 9 times in the next 14 days. Both first (24h) and last leachates were retained for further use in ecotoxicity tests. The OECD part 1 leaching procedure uses immersions instead of an impregnation. The end-sealed specimens were submerged in water (600 ml per 6 specimens) three times a day during 1 minute. Between the submersions the specimens were allowed to dry under ambient conditions. During 14 days submersions were performed every third day. Only leachates of the first and fifth ‘rain’ day were put aside for ecotoxicity determination. Regardless the leaching procedure the pH was always adjusted with NaOH (0.5 mol/l) until neutral.

Ecotoxicity testing

The basis for the ecotoxicity evaluation in this research was the Daphtoxkit F^{TM} magna (2001) procedure being based on OECD guideline 202 (1984) and using the crustacean *Daphnia magna* as test species. A total of 20 neonates were transferred to five dilutions (1:2 series from 6.25% till 100%) of each leachate. After 48 hours exposure in the dark at 20°C the mobility of the neonates was determined, leading to the concentration at which 50% of the neonates became immobile (EC_{50}s). Therefore the Trimmed Spearman-Karber method (Hamilton et al., 1977; US-EPA, 2006) was used, after which these concentrations were recalculated to toxic units (TUs) according to the formula of Sprague and Ramsay (1965) as cited in Manusadžianas et al. (2003) (Eqn. 1).

$$TU = \frac{1}{EC_{50}(\%)} \times 100 \qquad (1)$$

Since each leaching procedure yielded two leachates (both after 1 and 14 days) a multi-stage evaluation of the four leachates was considered. First of all the leachates originating from the harshest leaching procedure were evaluated, being the EN 84-leachates obtained after 1 day. It was considered that these leachates had potentially the highest environmental impact. If no significant toxicity for *D. magna* was observed, the evaluation stopped here, concluding that real life leaching, which is milder, would not cause any toxic effect. If, in contrast, a considerable ecotoxicity was detected a second step was performed. In this step both the EN 84-leachates after 14 days and the OECD part 1-leachates of the first ‘rain’ day were examined. When these latter leachates still exhibited a toxic response, then the leachates of the fifth rain day (OECD part 1) were also evaluated.

Decay resistance

Wood modification changes the structure of wood, leading to various improved parameters, depending on the process used. In this way a new product is created and the efficacy of the treated wood against fungal decay cannot just be regarded as some kind of wood preservation. Therefore the evaluation of this efficacy for use in use class 3 was based on the natural durability approach (CEN/TS 15083-1 2006, Van Acker 2003). This means that from all treated material as well as from control wood species Scots pine (*Pinus sylvestris* L.), spruce (*Picea abies* L. Karst) and maple (*Acer pseudoplatanus*) specimens with the sizes 50 × 25 × 15 mm were sawn. After γ-sterilization the blocks were put two by two according to wood species and treatment procedure on a malt-agar culture medium overgrown with fungal mycelium. Each Kolle-flask was thus inoculated with *Coniophora puteana* or *Postia placenta* for softwood testing or with *C. puteana* or *Trametes versicolor* for hardwood testing. After 16 weeks the blocks were taken out of the flasks and superficially cleaned, weighed and dried to 103 °C. These masses allowed calculating the mass loss of each block (Eqn. 2), indicating the durability of the modified material.

$$MassLoss(\%) = \left[\frac{m_{before\_testing} - m_{after\_testing}}{m_{abefore\_testing}} \times 100 \right] \qquad (2)$$

RESULTS AND DISCUSSION

Ecotoxicological evaluation

Furfurylated wood

De Vetter *et al*. (2008) already indicated the importance of the leaching procedure and this is confirmed again in this paper. Taking into account that the EN 84-procedure is harsh, due to the water impregnation stage (Hingston *et al*. 2001), it is not astonishing that this procedure generates higher toxicities than the OECD part 1-procedure, although both tests are designed to yield leachates of wood used under use class 3 conditions (Willeitner and Peek 1998) (Table 1). The higher the toxicity, the more obvious the difference between the methods become. Table 1 also shows that besides the leaching procedure the furfurylation process as well as the wood species itself influences the ecotoxicity value of the resulting leachates. Despite what was observed for untreated and preservative treated wood (De Vetter *et al*. 2009 De Vetter *et al*. 2008), the toxicity of the leachates of furfurylated wood does not diminish going from 1 to 14 days exposure. These results stress the importance of the multi-stage approach as evaluating leachates at a single moment would mask this tendency. The table clearly indicates that SYP furfurylated according to processes 1 and 2 generate significant different toxicities towards *D. magna*, regardless comparable WPGs (30% for process 1 and 20-30% for process 2). Although wood treated with oligomeric FA yielded much lower toxicities than wood treated with monomeric FA, also other process parameters, like curing and drying, may play an important role in the leachate-toxicity of the final product. Table 1 shows that furfurylated maple leads to more toxic EN 84-leachetes than SYP, although the same treatment process was used and maple had a lower WPG (20-25%) than SYP (30%).

Lande et al. (2004a) used the EN 84-procedure to obtain leachates of VisorWood treated Scots pine sapwood. They found only low toxicity (1.5 TUs after 48 hours) towards *D. magna*. Since wood species, treatment solution and furfurylation process differ from the ones used in this research it is hard to just compare the obtained toxicity values. However, it is clear this value is low and comparable to the value obtained for the SYP furfurylated according to process 2, indicating again that the achieved leachate-ecotoxicity can be steered by optimising the treatment procedure as a whole.

Thermally modified wood

Spruce obtained during the optimisation phase of thermal modification generates leachates that show low ecotoxicity values for *D. magna.* After 1 day EN 84-leaching a toxicity higher than the one of Scots pine sapwood could be observed (De Vetter *et al.* 2008), but this diminished with increasing time of exposure and from the harshest to the mild leaching method. These low values confirm the tendency to low ecotoxicity values found before by Van Eetvelde et al. (1998) for Plato modified Scots pine and beech, respectively 2.3 and <2 TUs for ENV1250.2 leachates.

Taking these different considerations into account it is clear that a range of factors influence the ecotoxicity for *D. magna* of leachates of furfurylated and thermally modified wood. Since no full understanding is attained for each factor yet, it is not self-evident to make a general statement about the ecotoxicology of leachates originating from furfurylated or thermally modified wood. However, the results presented here do show that the ecotoxicity can be altered by means of process parameter optimisation. Nevertheless it needs highlighting that the leaching procedure itself has a major influence on the obtained values and the corresponding interpretation. Since the 1-day OECD part 1-leachates and consecutive evaluation with *D. magna* seems the most suited procedure for ecotoxicity assessment of wood under use class 3 conditions it should be concluded that the furfurylated wood in this research does not pose any threat to the environment. Major drawback however is that only one organism of only one trophic level was used in this study. For a more extensive profile organisms of different trophic levels should be used in (sub)chronic/long-term testing.

Table 1: Toxic units (TUs) of leachates tested against D. magna

Wood species	**Process**	**Leaching method**		
		EN 84		**OECD part 1**
		1 day	14 days	1 day
SYP	Furfurylation 1	5.8	7.5	<2
Maple	Furfurylation 1	>16	>16	<2
SYP	Furfurylation 2	<2	<2	<2
Spruce	Thermal modification	3.6	<2	<2

Efficacy against fungi

Furfurylated wood

Figure 1 illustrates that only furfurylated maple achieved mass loss below 5% against attack by *P. placenta* and *T. versicolor* after 16 weeks exposure and can therefore be classified as very durable. For SYP the improvement in durability class seems to depend on the furfurylation process. The first process, using a monomeric FA solution was able to improve the durability to class 3, whereas the second process (with an oligomeric FA treating solution) gained only one durability class. While the former process already meets the requirements for treatment of wood to be used under use class 3 conditions both for maple and SYP, the second process can further be optimised as to reach the same level of efficacy. It is therefore shown that not only the level of modification has its influence on the level of protection against biodegradation (Lande *et al.* 2004b), but that also the treatment process as a whole plays an important role. This again shows that not only the ecotoxicology, but also the fungal resistance is influenced both by the wood species as well as by the modification process parameters.

Thermally modified wood

A major discrepancy was observed in the protective efficacy of heat treated spruce after 16 weeks exposure, depending on the fungal species. Mass loss induced by *C. puteana* was below 5% and consequently classified as 1, whereas *P. placenta* resulted in mass loss similar to untreated spruce, leading to durability class 5. Besides reported improvements in durability of thermally modified wood (Boonstra *et al.* 1998 Kamdem et al. 2002) Tjeerdsma *et al.* (1998) already stated that heat treatment according to the Plato-process revealed the highest improvement for its resistance against brown rot fungi and more specific against *C. puteana*. The authors also claimed that wood species and exact treatment conditions alter the properties of the obtained product. It therefore seems plausible to improve resistance against multiple biodegrading organisms by altering the treatment conditions.

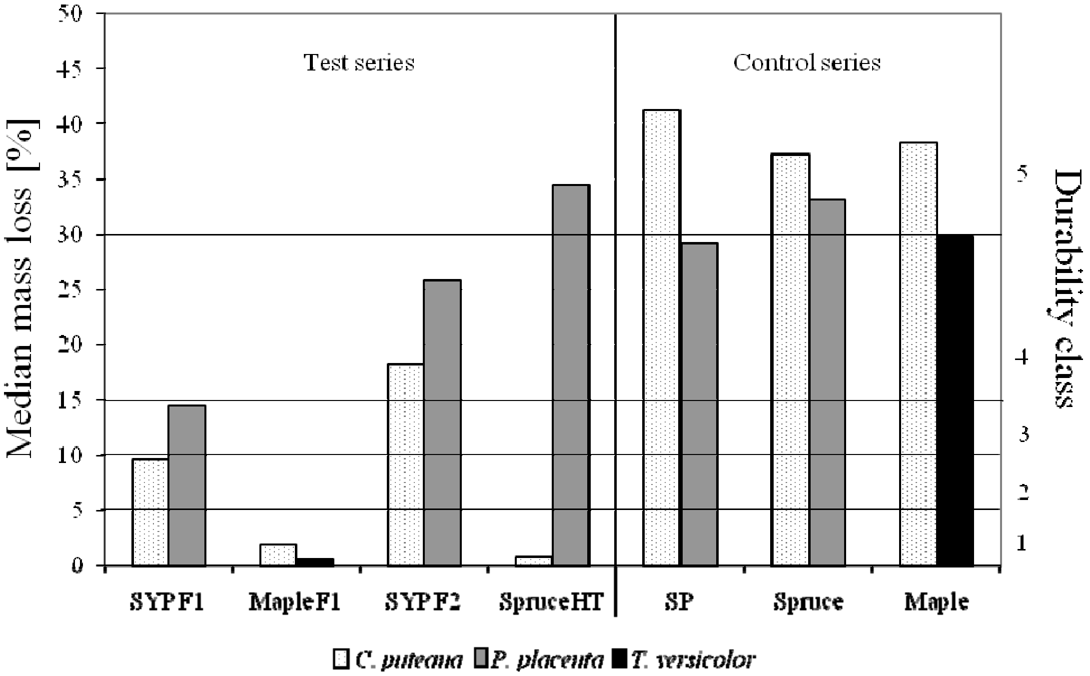

Figure 1: Median mass loss and corresponding durability class of modified wood and reference material. F1: furfurylated according to process 1, F2: furfurylated according to process 2, HT: heat treated

Combining ecotoxicology and efficacy

On the one hand the EN 84-leachates of furfurylated maple have a high toxicity towards *D. magna*, but on the other hand they are very effective in protecting wood against brown- and white rot. Leachates of SYP furfurylated according to the same process are less toxic to *D. magna*, but do not reach the same level of protection. Moreover SYP furfurylated by the second process leads to even less toxic leachates, but consigns some protective effectiveness. It therefore seems that for furfurylated wood improving fungal resistance is at the expense of leachate toxicity. However this is not fully true for thermal treated wood. The ecotoxicity of leachates of thermally modified spruce is only slightly toxic and the protective effectiveness against *T. versicolor* is low, while good protection is observed against *C. puteana*.

CONCLUSIONS

The methodology presented allows to obtain reliable results on the ecotoxicology of leachates of modified wood against *D. magna* and to get an idea about the protective effectiveness against basidiomycetes attack of the modified wood. Combining both results makes it possible to get a more generalized picture of the performance. The methodology can further be used as a first screening of both parameters during development of new modification processes. For a full product evaluation the method should be extended with more test organisms to get a broader basis for conclusions. This is especially the case for the ecotoxicological part.

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