

NATURAL DURABILITY AND PHENOLIC CONTENT IN DRIED SCOTS PINE HEARTWOOD

Margot Sehlstedt-Persson,^{a*} and Olov Karlsson^b

The durability of Scots pine heartwood has previously been shown to be affected by the industrial drying process of sawn lumber. The durability of heartwood from boards dried at temperatures between 20°C-110°C was studied by measuring the mass loss in a decay test with a brown rot fungus (*Coniophora puteana*), and the concentration of total phenolics was measured according to the Folin-Ciocalteu (FC) assay. The relation between mass loss and phenolics in dried heartwood showed a weaker negative correlation at lower levels of phenolics as compared to the strong relationship found in a study on heartwood from standing Scots pine trees. Mass loss in dried heartwood showed a weak negative correlation to density. Heating of extractives-rich green sawdust under moist conditions resulted in a reduction of phenolics with temperature up to 180 °C and with increasing time. The concentration of phenolics in heated, green sawdust was higher in extractives-rich pine heartwood than in heartwood with a normal extractives content.

Keywords: Drying; Durability; Phenolics; Scots pine; Heartwood; Folin-Ciocalteu assay

*Contact information: a, b: Division of Wood Physics, Luleå University of Technology, LTU Skellefteå, SE-931 87 Skellefteå, Sweden. *Corresponding author: Margot.Sehlstedt-Persson@ltu.se*

INTRODUCTION

During recent years there has been some indication that the durability of pine heartwood products has declined, and one hypothesis is that the drying process might negatively affect the natural durability of wood. In a recent study, Sehlstedt-Persson and Wamming (2010) found that air-dried heartwood showed better durability in decay tests compared to kiln-dried heartwood dried at various temperature levels up to 110°C.

According to European Standard EN350-2 (1994), Scots pine heartwood is classified into class 3–4 (moderately to slightly durable) in terms of natural resistance to wood-destroying brown rot fungus. Mass loss, expressed as a percentage of the original dry weight, is commonly used in laboratory tests to assess the natural durability of wood.

The chemical composition of wood varies considerably within any single tree as well as between different trees. This large variability leads to large variations in natural durability. It is generally agreed that extractives are “the principal source of decay resistance” in wood (Scheffer and Cowling 1966). The amount of extractives in green Scots pine heartwood varies greatly and might be substantial due to the ability of pine species to produce rich amounts of resin as a result of injuries, forming so called resinous wood (Hillis 1987), with extractives in resinous Scots pine reaching concentrations higher than 30% (Lindgren and Norin 1969) of the wood mass. However, normal

concentrations of extractives in pine heartwood are substantially lower: 8.6% ether-soluble (Lange *et al.* 1989), and 9.3% acetone-soluble (Sehlstedt-Persson 2001).

Extractives have been shown to have an inhibitory effect on fungal degradation in pine heartwood, but considerable differences in tolerance to toxic extractives are also found in various kinds of fungi (Martínez-Inigo *et al.* 1999). Resin acids, which are the major extractives constituent in Scots pine heartwood (Lindgren and Norin 1969; Martínez-Inigo *et al.* 1999) have been reported to cause severe inhibition to wood-inhabiting fungi (Micales *et al.* 1994; Eberhardt *et al.* 1994). Extractives contents in heartwood in many species show an overall pattern with decreasing amounts of extractives towards the pith and higher up the tree (Hillis 1987). This pattern of lower extractives content near the pith may reflect a degradation of extractives over time or an increase in extractives deposits with age (Taylor *et al.* 2002). A study on *Pinus sylvestris*, however, showed an increase in the total amount of extractives towards the pith (Lindgren and Norin 1969).

The chemical characteristics that separate decay-resistant from decay-susceptible pine heartwood in decay tests with the brown rot fungus *Coniophora puteana* were shown to be resin acids, pinosylvin, acetone-soluble extractives, and total phenolics measured according to the Folin-Ciocalteu (FC) assay (Harju and Venäläinen 2006 a).

The concentration of pinosylvin and resin acid content in heartwood is shown to vary considerably between individual Scots pine trees, with indications of a strong genetic control of the wide individual variation (Fries *et al.* 2000). The concentration of total resin acids in heartwood in decay-resistant Scots pine trees was found to be 1.6 to 2.1 times higher than the concentration in susceptible trees (Harju *et al.* 2002). The spatial distribution of pinosylvin in pine heartwood was found to decline in inner heartwood, while the concentrations were highest in outer heartwood at the transition between sapwood and heartwood (Bergström 2003).

The variation in durability within a single tree in the radial direction is also shown to be large, with the most decay-resistant specimens corresponding to the outer part of green Scots pine heartwood in decay tests with the brown rot fungus *Coniophora puteana* (Harju and Venäläinen 2006a). In contrast to these results, no significant difference was found in mass loss in similar decay tests between inner and outer Scots pine heartwood dried at various temperatures (Sehlstedt-Persson and Wamming 2010).

Chubinsky (2003) found that larch heartwood of high density was more resistant than larch heartwood with low density in decay tests with *Coniophora puteana*. In contradiction to this, Venäläinen *et al.* (2006) found no relationship between density and mass loss in decay tests with *Coniophora puteana* in larch heartwood. Boutelje and Nilsson (1985) found varying effects of density on mass loss for various fungi in decay tests with pine sapwood. A weak but significant negative correlation between mass loss and density was found in tests with the white rot fungus *Phlebiopsis gigantea* and significant positive correlation in tests with the brown rot fungus *Fomitopsis pinicola* (Boutelje and Nilsson 1985).

In decay tests with *Coniophora puteana*, Harju and Venäläinen (2006b) found a fairly strong negative correlation between mass loss and the concentration of total phenolics measured by the FC assay in Scots pine juvenile heartwood in standing trees. The authors suggest that measurements of total phenolics according to the FC assay could

be used for screening the variation in natural durability of Scots pine heartwood and as an alternative to time-consuming laboratory decay tests.

During drying of wood, a process that in fact can be seen as a hygrothermal treatment of wood, physical and chemical reactions occur that change the properties of wood and its constituents, including evaporation of volatile compounds, changes in colour, hygroscopicity, consistency of resin, and re-distribution of nutrients in sapwood, among other things. In addition, durability in Scots pine heartwood has been shown to be affected by the drying process (Sehlstedt-Persson and Wamming 2010).

The aim of this study is to investigate how industrial drying and heating of Scots pine heartwood affects the concentration of total phenolics measured according to the FC assay. Furthermore, the aim is to determine whether the large variation in mass loss in dried heartwood (Sehlstedt-Persson and Wamming 2010) can be explained by the concentration of total phenolics, by comparing the relation between mass loss in decay testing and total phenolics in dried heartwood in a similar way as the study done on Scots pine heartwood in standing trees performed by Harju and Venäläinen (2006b). In order to minimize the influence of variation in various wood properties, a study with heating of green mixed and sieved sawdust was also done.

EXPERIMENTAL

Lumber

Centre-sawn boards, 50x125 mm from Scots pine (*Pinus sylvestris* L.) felled in January 2007 were used in the tests. The location of the stand was within in a circle of 150 km around a sawmill in Piteå (N 65° 19', E 21° 28) in Norrbotten in the northern part of Sweden. The boards were sawn from high quality butt logs with top diameter 166-195 mm. All boards used in the test had heartwood class K60 and K40 (percent heartwood in cross-section of the sawn board).

36 green boards were cut into four one-meter-long samples (numbered 1-4 from butt to top end), which were end-sealed with Sikaflex polyurethane sealant and kept in a climate chamber at 0°C and 95% relative humidity (RH) until the start of drying. Out of 144 samples 66 samples were selected with regard to heartwood content, visually estimated resin content, and position along the board. These were sorted into six similar batches, one for each drying series.

Drying

Drying was performed in six different series, as summarized in Table 1. Series A, considered similar to industrial outdoor air-drying, was, due to the time of year, dried indoors at the laboratory on stickers at 20 to 25°C and 38% to 45% relative humidity (RH) for just under 9 weeks. Series B through F were dried in a small-scale laboratory air-circulation kiln at maximum temperature levels of 70°C, 90°C, and 110°C. For the 70°C and 90°C series (B through E), two different regulation principles were used after the initial preheating:

- I. Dry-bulb temperature (T_{db}) gradually rising to a maximum temperature level and wet-bulb temperature (T_{wb}) at one or two constant levels.

II. Constant T_{db} at the maximum level with the initial T_{wb} dropping to a constant level.

Table 1. Drying Series A through F

Series	Maximum temperature	Regulation principle
A	25°C	-
B	70°C	I
C	70°C	II
D	90°C	I
E	90°C	II
F	110°C	-

The difference between these two regulation principles concerns how fast the wood temperature reaches the maximum temperature level. In regulation principle II, the wood temperature reaches its maximum temperature level early in the capillary regime of drying when the moisture content (MC) is high, while the wood temperature in regulation principle I reaches maximum temperature considerably later in the drying process when the MC is substantially lower.

Series F was dried with a high-temperature schedule at a maximum temperature of 110°C. A detailed description of the material and industrial drying schedules is found in the paper by Sehlstedt-Persson and Wamming (2010).

Sampling of the Evaluation Material

For decay testing, 2 x 66 specimens (5 x 15 x 30 mm) were sawn from dried samples conditioned at equilibrium moisture content (EMC) 10% in all six series from inner and outer heartwood (Fig. 1).

The initial dry weight (m_{dry}) of each specimen before the decay test was measured after drying for 48 hours in a vacuum desiccator with silica gel at 60°C for specimens in series B through F and for specimens in series A, in order not to exceed the maximum drying temperature in series A, after drying for 144 hours in a vacuum desiccator with silica gel at 20°C. The density ($\rho_{dry,10}$) for each specimen was calculated without any volume correction for the difference in EMC because of miscellaneous drying in the six series.

Analysis of total phenolics according to the FC assay and of extractives content was done for chosen samples in series A through F on adjacent specimens (Fig. 1).

Decay Test

The decay test with the brown rot fungus *Coniophora puteana* (BAM Ebw.15) was performed according to the standardized EN113 decay test, but modified with respect to sample size and incubation time in the same way as described by Harju and Venäläinen (2006b) (with the exception of predrying temperature of 20°C instead of 60°C for controlling the initial dry weight (m_{dry}) in series A). The mass loss of the samples after an incubation time of 7 weeks, expressed as a percentage of the original dry mass before the decay test, was used as a measure of durability.

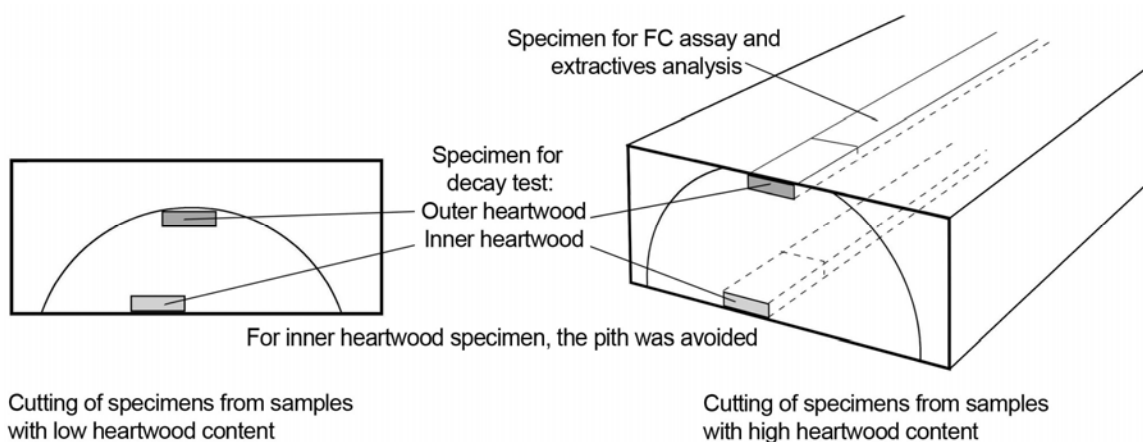


Fig. 1. Sampling of the evaluation material for decay test and analysis of concentration of total phenolics and extractives from dried, planed boards.

Based on the results from the decay test, four samples from each drying temperature level, 20°C, 70°C, 90°C, and 110°C, in series A through F with the two highest and two lowest mass losses were identified without regard to position in inner or outer heartwood. From these 16 samples, the concentration of total phenolics according to the FC assay was determined, as well as the concentration of extractives in specimens cut adjacent to the mass-loss specimen as in Fig.1. Furthermore, ten additional samples from series E, dried at maximum temperature 90°C with regulation principle II, which on average showed the highest mass loss of all series as described in Sehlstedt-Persson and Wamming (2010), were randomly chosen for phenolic and extractives analysis to cover the whole range of mass loss.

Concentration of Total Phenolics and Extractives Content

The specimens cut adjacent to the decay specimens were sawn into small parts using a small band saw carefully cleaned for each sample, and the sawdust was collected and sieved using a mesh grid of 1 mm. For each sample, approximately 1 gram of collected particles, dried in a vacuum dessicator at room temperature, was extracted twice with 15 ml of aqueous acetone solution (acetone-water 8:2) using magnetic stirring for 0.5 to 1 hour. After filtering of the extract and washing with 5 ml of solvent, the concentration of total phenolics was determined by the FC assay as described by Harju and Venäläinen (2006b) in their study on pine heartwood using tannic acid as a standard and absorptivity measured at 735 nm. Therefore, the results of the total phenolic concentration are expressed as milligrams tannic acid equivalents (TAE) per gram of dry mass of wood.

For determination of extractives content, half of the extract was put into Petri dishes and dried in the lab and in a dessicator. After evaporation of the aqueous acetone solution, the weight of the dry mass of the extract was calculated and expressed in percentage of dry wood weight.

Concentration of Total Phenolics in Heated Green Sawdust

Since the extractives content varies so much between trees as well as between positions in single trees, and since extractives content has an impact on the concentration of phenolics, a supplementary study was done using mixed sawdust from pine heartwood. Green heartwood sawdust from two trees, one with normal and one with high extractives content, was collected and sieved according to the earlier description. The average extractives content in the mixed sawdust from each tree was measured using a Soxhlet extractor for 24 hours (with four extraction cycles per hour) with Acetone 99.5% *pro analysi* as solvent.

10 grams of sieved, mixed, green sawdust was put into a cylindrical 90 ml Teflon tube vessel and heated. During heating, the vessel was closed and sealed using a steel support module.

In series I, with sawdust from heartwood with normal extractives content, heating was done in an oven at temperatures 20°C, 40°C, 90°C, and 110°C during 65 hours, respectively.

In series II, with sawdust from heartwood with high extractives content, heating was done at 20°C, 40°C, 70°C, 90°C, and 110°C during 72 hours, respectively.

In series III, with sawdust from heartwood with high extractives content, heating was done at 110°C, 130°C, 140°C, 150°C, 160°C, 170°C, and 180°C during 3 hours, respectively.

Approximately 2 grams of sawdust from each heated set was put into glass cups and dried at room temperature in a vacuum dessicator with silica gel for 6 days before performing the FC assay analysis. One gram of dry, heated sawdust from each set was used in FC assay analysis as earlier described.

RESULTS AND DISCUSSION

Mass loss in Decay Test—Impact of Concentration of Total Phenolics

Results from the measurements of total phenolics according to the FC assay, with mass loss after 7 weeks incubation time as a function of total phenolics, are shown in Fig. 2. Measurements were done on 16 samples with the two highest and two lowest mass losses in inner or outer heartwood from drying series A through F at 20°C, 70°C, 90°C, and 110°C.

No clear relation between mass loss and total phenolics was found in the limited samples shown in Fig. 2. The highest concentration of phenolics was found among the samples with low mass loss. At lower concentrations (in the region 3–6 mg TAE/g dry wood) samples with high as well as low mass loss were found. This indicates that not only concentration of phenolics affected the durability of the heartwood. Varying composition of extractives in the samples, such as varying concentrations of resin acids, which is known to contribute to decay resistance in Scots pine heartwood (Harju *et al.* 2002), might be one explanation.

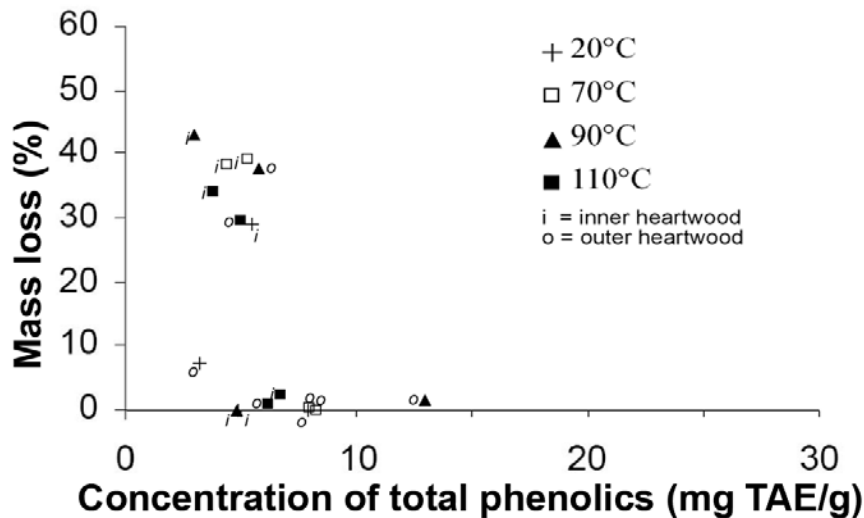


Fig. 2. Mass loss in decay test as a function of concentration of total phenolics according to FC assay in pine heartwood industrially dried at various maximum temperature levels. For each temperature level, samples with the two highest and two lowest mass losses were selected from inner or outer heartwood. Linear correlation coefficient $r = -0.52$ ($p < 0.05$)

The relation between mass loss and total phenolics in heartwood industrially dried at various maximum temperatures was not as clear as the relation found by Harju and Venäläinen (2006a, 2006b) in heartwood cut from standing trees (Fig. 3). The linear correlation coefficient presented by Harju and Venäläinen was $r = -0.82$ ($p < 0.001$), by comparison with $r = -0.52$ ($p < 0.05$) in dried heartwood presented in Fig. 2. The level of concentration of total phenolics was also found to be lower in industrially dried heartwood than in heartwood in standing trees.

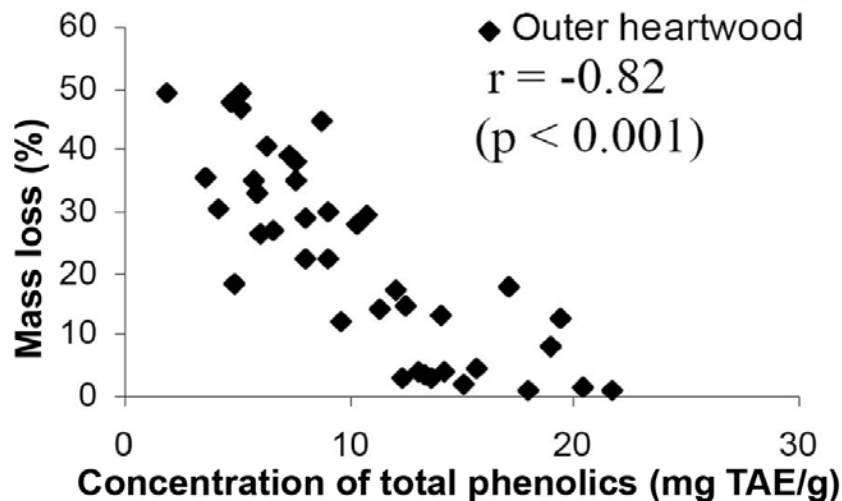


Fig. 3. Relation between mass loss in decay test and concentration of total phenolics according to FC assay in juvenile pine heartwood (cut from standing trees annual ring 3-6 from pith) according to the study by Harju and Venäläinen. Linear correlation coefficient $r = -0.82$. (Diagram from Harju and Venäläinen 2006a).

During drying, the extractives content in wood is lowered compared to wood in standing trees, due to evaporation of extractives compounds, but as the boiling point of most phenols in pine heartwood is considerably higher than the monoterpenes, they are less likely to evaporate during drying. A conceivable explanation for the lower levels of total phenolics might be a hygrothermal degradation of phenolics during industrial drying, and degradation of phenolics was studied in a separate experiment with heating of sawdust (see below).

In Fig. 2 samples with the two highest and two lowest mass losses were chosen for FC assay analysis at each temperature level in series A through F. In Fig. 4, a more continuous range of mass losses is presented as a function of total phenolics in samples from drying series E dried at maximum temperature 90° C. These samples showed on average the lowest durability after drying, compared to all other drying series (Sehlstedt-Persson and Wamming 2010).

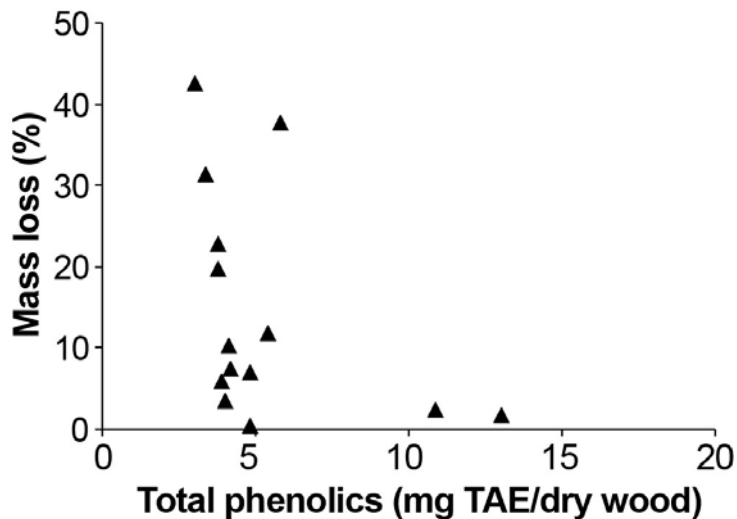


Fig. 4. Mass loss in decay test as a function of concentration of total phenolics according to FC assay in pine heartwood in series E dried at 90°C maximum temperature. Linear correlation coefficient $r = -0.42$ ($p < 0.2$)

The same pattern was found in series E in Fig. 4 as in Fig. 2 with the highest concentrations of phenolics showing low mass loss, and phenolics gathered in the region around 5 mg TAE/g showing high as well as low values of mass loss. The linear correlation coefficient was $r = -0.42$. Thus, the fairly strong linear relation between mass loss and total phenolics found in juvenile Scots pine heartwood in standing trees (Harju and Venäläinen 2006b) was not found in industrially dried heartwood in this study.

Mass Loss in Decay Test—Impact of Density

The relation between mass loss and density ($\rho_{dry,10}$) of each decayed sample in series E in Fig. 5 showed a weak negative correlation with a linear correlation coefficient of $r = -0.62$. The linear correlation coefficient between mass loss and density of chosen samples dried at various temperatures in series A through F is $r = -0.51$. This supports the results found in decay testing with *Coniophora puteana* in larch heartwood by Chubinsky (2003) and by Boutelje and Nilsson (1985), who found a weak, but significant, negative

correlation between mass loss and density in tests with a white rot fungus *Phlebiopsis gigantea* in pine sapwood.

Nilsson and Daniel (1992) have proposed the use of degradation susceptibility (DS) instead of percentage mass loss, where DS is the mass loss divided the volume. They hypothesised that the total amount of cellulose and hemicellulose should not have any significant influence on the decay rate of a decay organism and that the actual weight of similar sized wood blocks would have little or no effect on the decay rate during testing. Calculation of data with DS according to Nilsson and Daniel (1992) has been made with volume V at 10% and 0% MC with correction for difference in EMC because of miscellaneous drying. The result did not show any stronger relationship compared to mass loss, and this was true both for DS as a function of phenolics and of density.

A conceivable explanation as to why higher density showed better decay resistance in our study is that denser wood could be expected to have higher resistance to decay simply because of its more solid state and lower porosity during the limited time during which short-term *in vitro* tests are performed, in this study during 7 weeks. Higher density may also be related to higher extractives content, which is known to have an inhibitory effect on fungal degradation (Martínez-Inigo *et al.* 1999). However, no inhibiting effect of density on mass loss was found in long-term exposure outdoors above ground during 9 years for Norway spruce (Bergström *et al.* 2004) or Scots pine lumber (Rydell *et al.* 2005). This illustrates the difficulties in transferring conclusions from short-term decay tests using one specific fungus to the practical service life of wood in outdoor applications.

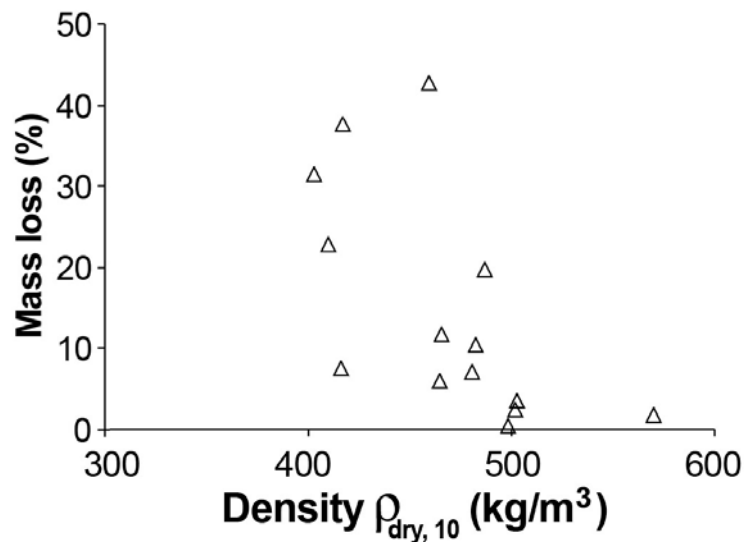


Fig. 5. Mass loss in decay test as a function of density ($\rho_{dry,10}$) in pine heartwood in series E dried at 90°C maximum temperature. Linear correlation coefficient $r = -0.62$ ($p < 0.02$).

Concentration of total phenolics—impact of density and extractives content

The concentration of total phenolics showed a weak positive correlation to wood density, with a linear correlation coefficient $r = 0.65$ for the 14 samples in series E, Fig. 6 and $r = 0.58$ for the 16 samples dried at various temperatures in series A through F, Fig.

7. The concentration of phenolics shows a weak positive correlation to extractives content determined in a short-term extraction, with a linear correlation coefficient $r = 0.60$ in series E, Fig. 8 and $r = 0.46$ for samples dried at various temperatures in series A through F, Fig. 9. The simplified way of determining extractives content by short-term extraction is not claimed to give the total concentration of extractives, but rather only a relative measure.

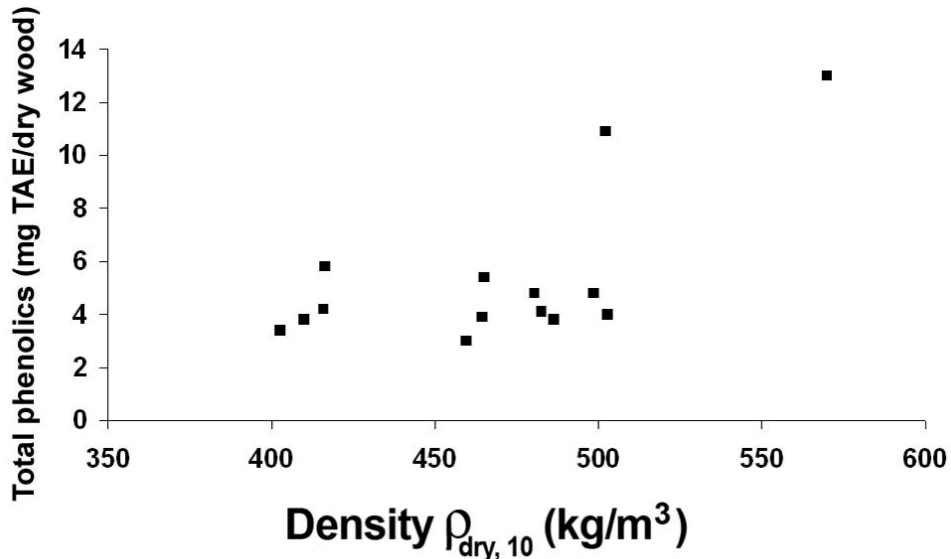


Fig. 6. Concentration of total phenolics (mg TAE/g dry wood) measured by the FC assay as a function of density ($\rho_{dry, 10}$) in pine heartwood in series E dried at 90°C maximum temperature. Linear correlation coefficient $r = 0.65$.

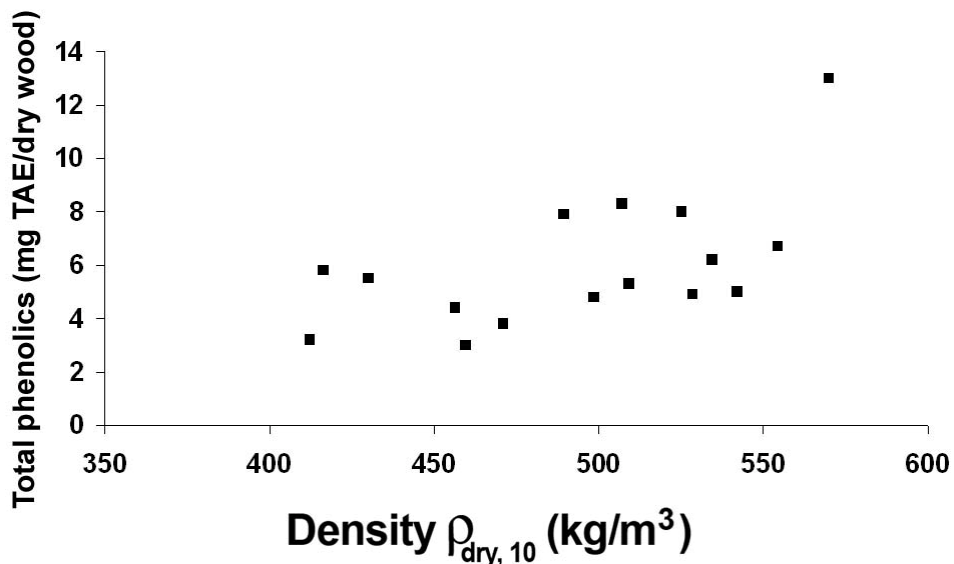


Fig. 7. Concentration of total phenolics (mg TAE/g dry wood) measured by the FC assay as a function of density ($\rho_{dry, 10}$) in pine heartwood in samples dried at various temperatures in series A–F. Linear correlation coefficient $r = 0.58$.

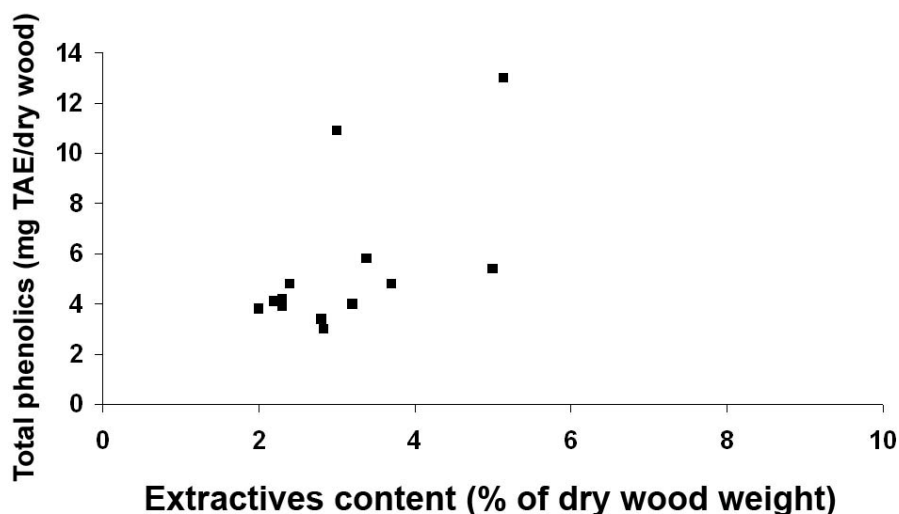


Fig. 8. Concentration of total phenolics (mg TAE/g dry wood) measured by the FC assay as a function of extractives content (% of dry wood weight) in pine heartwood in series E dried at 90°C maximum temperature. Linear correlation coefficient $r = 0.60$.

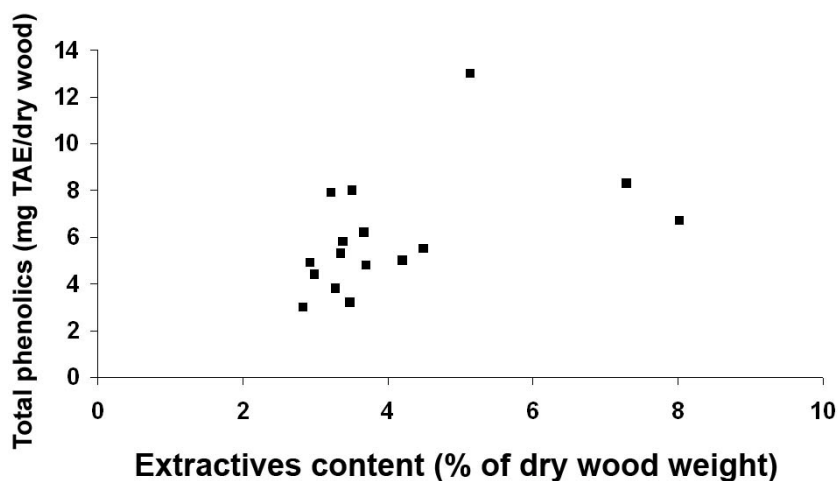


Fig. 9. Concentration of total phenolics (mg TAE/g dry wood) measured by the FC assay as a function of extractives content (% of dry wood weight) in pine heartwood in samples dried at various temperatures in series A–F. Linear correlation coefficient $r = 0.46$.

Concentration of Total Phenolics in Heated Green Sawdust

The mass losses in this study showed large variations, and the investigated parameters phenolic content, density, and extractives content explained only parts of the variation in mass loss in test material deriving from batches of sawn lumber from normal sawmill production with its variation of wood properties. Since one main issue with this work has been to investigate the influence of drying parameters such as temperature level on the phenolic concentration, a supplementary study on heating of mixed wood sawdust was performed in order to minimize the influence of natural variation in various wood properties.

The results from the study on heated, mixed sawdust from pine heartwood with varying extractives content are presented in Fig. 10. The average extractives content according to the Soxhlet extraction with acetone in series I was 8.2%, and in series II–III 23.4%, given in % of dry weight of the extractives-free sawdust.

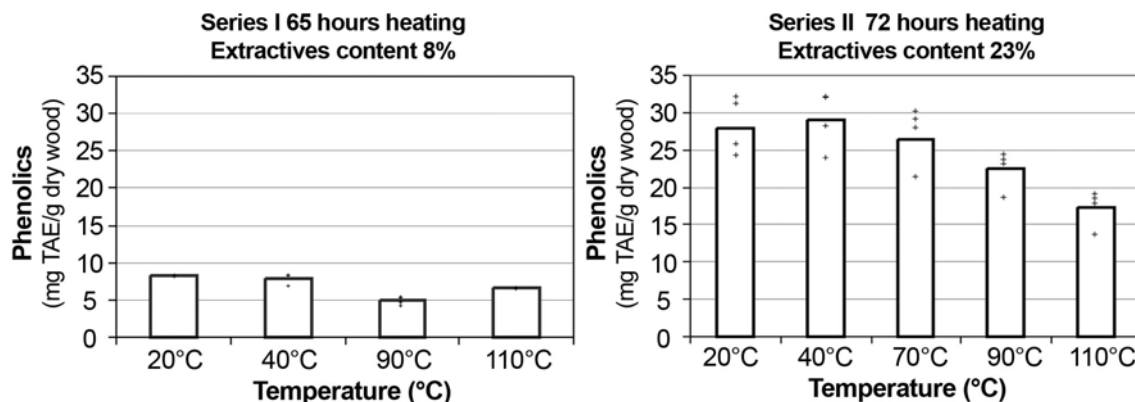


Fig. 10. Concentration of total phenolics (mg TAE/g dry wood) measured by the FC assay in pine heartwood with normal extractives content (series I) and high extractives content (series II) heated at various temperatures during 65 and 72 hours respectively. Each bar is an average of 4 measurements.

The concentration of total phenolics was, as expected, found to be substantially higher in heartwood with high extractives content (series II) than in heartwood with normal extractives content (series I). The ratio between phenolics in series I and II was approximately of the same magnitude (≈ 3) as the ratio between extractives contents. Thus, the concentration of total phenolics content was roughly related to the concentration of extractives. Heartwood with high extractives content, such as in series II with its high concentrations of total phenolics, is expected to show high durability with low mass loss according to Fig. 3.

The effect of heating temperature was found to be more marked in series II than in series I. In series II, a continuous decrease of the concentration of total phenolics was found at heating temperatures exceeding 70°C.

In Fig. 11, the results from heating at higher temperatures during 3 hours are presented. When comparing the concentration of total phenolics in series II (Fig. 10) and series III (Fig. 11) at 110°C, it is obvious that the duration of heating had an impact on the content of total phenolics; heating during 72 hours reduced the phenolics considerably more than heating during 3 hours. Pinosylvin is the dominant component of phenol extractives in pine heartwood and has been reported to have antioxidative (Zulaica-Villagomez *et al.* 2005) abilities and to reduce the activity of brown rot fungi (Rennerfelt and Nacht 1955). Oxidation of pinosylvin can lead to formation of dark-coloured compounds (Morgan and Orsler 1968), and condensation with lignin may take place under certain conditions (Erdtmann 1949; Migita *et al.* 1953).

An indication of reduction of phenolic content in extract from heated wood at heating temperatures exceeding 160°C was found in series III (Fig. 11). Thus, the concentration of phenolics seems to decrease with a combination of temperature and time during heating in moist conditions. However, analysis of phenols in extracts from heat-

treated spruce using the FC method showed that phenols started to increase at temperature higher than 235°C (Ahajji *et al.* 2009). Formation of phenols during heat-treatment has also been shown (Fengel and Przyklenk 1970; Wikberg and Maunu 2004; Windeisen *et al.* 2007) probably as a consequence of degradation of lignin (Sano 1975; Westermark *et al.* 1997). Julkunen-Titto (1985) found that the FC response was dependent on the structure of phenols, and further work is necessary to evaluate formation of phenols at higher temperatures.

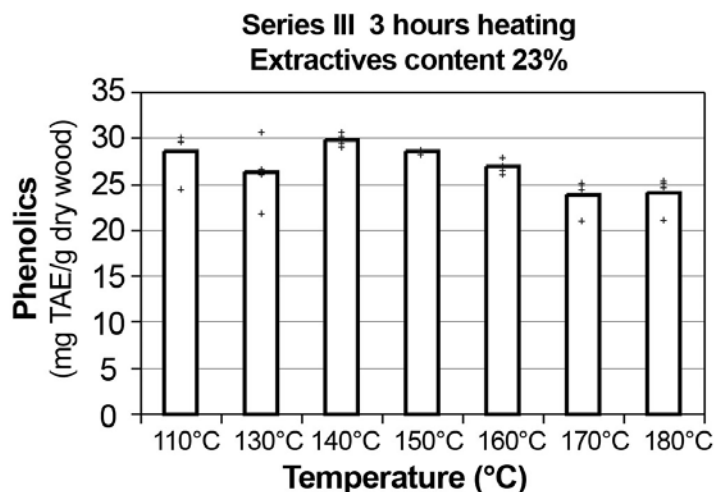


Fig. 11. Concentration of total phenolics (mg TAE/g dry wood) measured by the FC assay in pine heartwood with high extractives content heated at various temperatures (series III) during 3 hours. Each bar is an average of 4 measurements.

CONCLUSIONS

The durability of wooden products for outdoor applications is an urgent issue for the future utilization of wood as a competitive construction material. During recent years there has been some indication that the drying process may have negative effects on the natural durability of wood, such as, for example, high-temperature-dried pine poles in playgrounds that have become seriously decomposed after just a few years usage (Wamming 2005). Durability of Scots pine heartwood in sawn lumber has in a previous study Sehlstedt-Persson M, and Wamming, T. (2010) been shown to be affected by the industrial drying process at elevated temperatures, with highest durability in air-dried heartwood.

The aim with this study has been to investigate how the industrial drying process of sawn lumber at different temperature levels affects the concentration of total phenolics – compounds known to contribute to the natural durability in Scots pine heartwood. Furthermore, the relation between mass loss and total phenolics in industrially dried Scots pine heartwood has been studied and compared with a similar study on Scots pine heartwood in standing trees (Harju and Venäläinen 2006b) in which a fairly strong negative correlation was found.

In order to minimize the influence of variation in various wood properties which is inevitable when studying sawn lumber from normal productions at sawmills, a study with heating of green mixed and sieved sawdust was also done.

The findings are summarized as follows:

- Lower levels of total phenolics measured according to the FC assay were found in industrially dried heartwood than in the study on juvenile heartwood in standing trees (Harju and Venäläinen 2006b).
- The results in this study on industrially dried heartwood do not show the same apparent relation between mass loss and concentration of total phenolics as the study on heartwood in standing trees (Harju and Venäläinen 2006b). A weak negative correlation was found for heartwood dried at various maximum temperatures between 20°C and 110°C, with a linear correlation coefficient $r = -0.52$ ($p < 0.05$). In heartwood dried at maximum temperature 90°C, the linear correlation coefficient was $r = -0.42$ ($p < 0.2$). These correlation coefficients are weaker than those of the study on Scots pine heartwood in standing trees (Harju and Venäläinen 2006b) with $r = -0.82$ ($p < 0.001$).
- The concentration of total phenolics in heated, mixed, green sawdust was higher in extractives-rich Scots pine heartwood than in heartwood with a normal extractives content.
- Heating of mixed, green sawdust from Scots pine heartwood with high extractives content decreased the concentration of phenolics with a combination of temperature and time. Heating in moist conditions
 - at 110°C during 72 hours reduced the concentration of total phenolics substantially compared to 3 hours heating.
 - tended to reduce the concentration of total phenolics at temperatures exceeding 70°C during 72 hours of heating.
 - resulted in a small reduction of the concentration of total phenolics at temperatures exceeding 160°C up to 180°C during 3 hours of heating.
- A weak negative correlation was found between mass loss and density, with a linear correlation coefficient $r = -0.62$ ($p < 0.02$), thus somewhat stronger than the correlation between mass loss and phenolics.
- The FC-method has frequently been used to study the presence of phenolic extractives in wood materials. We found that industrial drying and heating of heartwood results in a decrease of levels of total phenolics content as determined by using the FC-method. Furthermore, degradation of phenolics during heating could be a reason for the lowered correlation of mass loss to phenolics during brown rot decay of wood dried at 90°C. Thus, the FC-method cannot be strongly recommended as a quick method to predict stability against brown rot fungi *Coniophora puteana* when wood is industrially dried at elevated temperatures or thermally modified.

REFERENCES CITED

- Ahajji, A., Diouf, P. N., Aloui, F., Elbakali, I., Perrin, D., Merlin, A., and George, B. (2009). "Influence of heat treatment on antioxidant properties and colour stability of beech and spruce wood and their extractives," *Wood Sci. Technol.* 43, 69-83.
- Bergström, B. (2003). "Chemical and structural changes during heartwood formation in *Pinus sylvestris*," *Forestry* 76(1), 45-53.
- Bergström, M., Rydell, Å., and Elowson, T. (2004). "Durability of untreated Norway spruce (*Picea abies*) exposed outdoors above ground for nine years," *Holzforschung* 58, 167-172.
- Boutelje, J. B., and Nilsson, T. (1985). "The effects of felling time and felling area, wet storage, tree species and wood density on the durability of wood. Part I: Durability against fungal decay," (In Swedish) The Swedish Institute for Wood Technology Research, Report 73, pp. 1-31.
- Chubinsky, M. A. (2003). "Durability of larch wood," Summary of the dissertation (In Russian). Forest Technical Academy, St. Petersburg.
- Eberhardt, T. L., Han, J. S., Micales, J. A., and Young, R. A. (1994). "Decay resistance in conifer seed cones: Role of resin acids as inhibitors of decomposition by white rot fungi," *Holzforschung* 48, 278-284.
- Erdtmann, H. (1949). "Compounds inhibiting the sulfite cook," *Tappi* 32, 303-304.
- European Committee for Standardization Central Secretariat (1994) European Standard EN 350-2. Durability of wood and wood-based products. Natural durability of solid wood. Part 2: Guide to natural durability and treatability of selected wood species of importance in Europe. European Committee for Standardization Central Secretariat, Brussels
- Fengel, D. and Przyklenk, M. (1970). "On changes in wood and its components at temperatures up to 200 °C – Part V: Influence of thermal treatment on lignin in sprucewood," *Holz Roh-Werkst.* 28, 254-263.
- Fries, A., Ericsson, T., and Gref, R. (2000). "High heritability of wood extractives in *Pinus sylvestris* progeny tests," *Can. J. Forest Res.* 30(11), 1707-1713.
- Harju, A., and Venäläinen, M. (2006 a) "Variation in natural durability of scots pine heartwood," ECOWOOD 2nd International Conference on Environmentally-Compatible Forest Products Fernando Pessoa University, O Porto, Portugal, 20-22 September.
- Harju, A. M., and Venäläinen, M. (2006 b) "Measuring the decay resistance of Scots pine heartwood indirectly by the Folin-Ciocalteu assay," *Can. J. Forest Res.* 36, 1797-1804.
- Harju, A. M., Kainulainen, P., Venäläinen, M., Tiitta, M., and Viitanen, H. (2002). "Differences in resin acid concentration between brown-rot resistant and susceptible scots pine heartwood," *Holzforschung* 56(5), 479-486.
- Hillis, W. E. (1987). *Heartwood and Tree Exudates*, Springer Verlag, Berlin
- Julkunen-Titto, R. (1985). "Phenolic constituents in the leaves of northern willows: Methods for the analysis of certain phenolics," *J. Agric. Food Chem.* 33, 213-217.
- Lange, W., Kubel, H., and Weißman, G. (1989). "Die Verteilung der Extraktstoffe im Stammholz von *Pinus sylvestris* L.," *Holz Roh. Werkst.* 47, 487-489.

- Lindgren, B., and Norin, T. (1969). *Hartsets Kemi*, Hartskompendium. Svenska Pappers och Cellulosaingenjörsföreningen, Stockholm, pp 20-29.
- Martínez-Inigo, M. J. M., Immerzeel, P., Gutierrez, A., del Río, J. C., and Sierra-Alvarez, R. (1999). "Biodegradability of extractives in sapwood and heartwood from Scots pine by sapstain and white-rot fungi," *Holzforschung* 53(3), 247-252.
- Micales, J. A., Han, J. S., Davis, J. L., and Young, R. A. (1994). "Chemical composition and fungitoxic activities of pine cone extractives," *Biodeterioration Research* 4, G. C. Llewellyn *et al.* (eds.), Plenum Press, New York, pp. 317-332.
- Migita, N., Nakano, J., Ichino, M., and Mikawa, H. (1953). "Studies on lignin (XXI). The condensation product of pinosylvin with vanillyl alcohol, as a model compound of lignin," *J. Jap. Forestry Soc.* 35(10), 313-315.
- Morgan, J. W. W., and Orsler, R. J. (1968). "The chemistry of colour changes in wood. I. The significance of stilbenes," *Holzforschung* 22, 11-15.
- Nilsson, T. and Daniel, G. (1992) "On the use of % weight loss as a measure for expressing results of laboratory decay experiments," *International Research group on Wood Preservation Document No: IRG/WP 2394-9, IRG Secretariat, Sweden.*
- Rennerfelt, E., and Nacht, G. (1955). "The fungicidal activity of some constituents from heartwood of conifers," *Sven. Bot. Tidskr.* 49, 419-432.
- Rydell, Å., Bergström, M., and Elowson, T. (2005). "Mass loss and moisture dynamics of Scots pine (*Pinus sylvestris* L.) exposed outdoors above ground in Sweden," *Holzforschung* 59, 183-189.
- Sano Y. (1975). "Hydrolysis of lignin with dioxane and water. XV. Hydrolysis of 1-guaiacyl-2-guaiacoxyl-1-propane-3-ol and guaiacylglycerol- β -guaiacyl ether," *Mokuzai Gakkaishi.* 21(9), 508-519.
- Scheffer, T. C., and Cowling, E. B. (1966). "Natural resistance of wood to microbial deterioration," *Ann. Rev. Phytopath.* 4, 147-170.
- Sehlstedt-Persson, M. (2001). "The effect of extractive content on moisture diffusion properties for Scots pine and Norway spruce," COST action E15 Advances in the drying of wood (1999-2003) Proceedings 3rd Workshop on SOFTWOOD DRYING TO SPECIFIC END-USES, 11–13 June, Helsinki.
- Sehlstedt-Persson M, and Wamming, T. (2010). "Wood drying process – Impact on Scots pine lumber usability," *J. Wood Sci.* 56, 25-32.
- Taylor, A. M., Gartner, B. L., and Morrell, J. J. (2002). "Heartwood formation and natural durability - A review," *Wood Fiber Sci.* 34(4), 587-611.
- Wamming, T. (2005). "Besiktning av nedmonterat klättertorn (in Swedish)," SP Träteknik Uppdragsrapport, P504194.
- Windeisen, E., Strobel, C., and Wegener G. (2007). "Chemical changes during the production of thermo-treated beech wood," *Wood Sci. Technol.* 41, 523-536.
- Venäläinen, M., Harju, A. M., Terziev, N., Laakso, T., and Saranpää, P. (2006). "Decay resistance, extractive content, and water sorption capacity of Siberian larch (*Larix sibirica* Lebed.) heartwood timber," *Holzforschung* 60, 99-103.
- Westermarck, U., Samuelsson B., and Lundquist K. (1997). "Homolytic cleavage of the β -ether bond in phenolic β -O-4 structures and its significance in high-yield pulps and lignin," *Nordic Pulp and Paper Research Journal* 12(3), 150-154.

- Wikberg, H., and Maunu, S. L. (2004). "Characterisation of thermally modified hard- and softwoods by ^{13}C CPMAS NMR," *Carbohydrate Polymers* 58, 461-466.
- Zulaica-Villagomez, H., Peterson, D. M., Herrib, L., and Young, R. A. (2005). "Antioxidant activity of different components of pine species," *Holzforschung* 59(2), 156-162.

Article submitted: May 19, 2009; Peer review completed: June 19, 2009; Revised version received and accepted: April 14, 2010; Published: April 16, 2010.