Correlation of ^{13}C-NMR Analysis with Fungal Decay Tests of Polymeric Structural Wood Constituents. II. Ground Contact Tests

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ABSTRACT: Heat treatment at relatively high temperatures (ranging from 150°C to 260°C) appear to be an effective method to improve the durability of wood. This study investigated the reasons for the decay resistance of heat-treated and untreated wood as composed of polymeric structural constituents by solid-state CP-MAS ^{13}C-NMR analysis after fungal exposure in ground contact. An industrially used two-stage heat treatment method under relatively mild conditions (<200°C) was used to treat the samples. Fungal exposure in ground contact resulted in strong degradation of the carbohydrates (cellulose and hemicellulose) of treated and untreated Scots pine, Radiata pine, and Simaruba. Fungal attack of the carbohydrates appeared to occur mainly at C4, resulting in cleavage and eventually depolymerization of cellulose and hemicellulose. The CP-MAS ^{13}C-NMR spectra of the heat-treated wood revealed similarities but also clear differences after fungal exposure in ground contact with the untreated wood. In ground contact fungi appeared to attack the carbohydrates of heat-treated wood at C1 and possibly at C4 in order to cleave and eventually depolymerize cellulose and hemicellulose. An attack on the out-of-the-ring alcoholic group, —CH_2OH, of the carbohydrates of the heat-treated wood was observed (particularly in treated Radiata pine). The fungus possibly tried to cleave the out-of-the-ring CH2—OH group on the main H-bond fixing sites of the crystalline cellulose structure in order to open the cellulose crystalline structure to an amorphous structure to decrease its water repellency and facilitate enzymatic cellulose degradation; this was also observed, but to a lesser extent, in untreated Radiata pine and untreated Scots pine. The opening of the glucose pyranose ring in heat-treated Simaruba after fungal exposure, not observed in the untreated wood, was remarkable, and the thermal degradation of alpha-arabinofuranose during heat treatment indicated more extensive decay. Demethoxylation and ring opening of the aromatic structure of lignin were observed, especially in the heat-treated Radiata pine, Douglas fir, and Simaruba. J Appl Polym Sci 102: 616–622, 2006

Key words: degradation; biopolymers; polysaccharides; NMR

INTRODUCTION

Wood can be colonized and degraded by a variety of fungi including brown rot, white rot, and soft rot. Fungal decay is a very complex process and depends on the fungus and the wood species involved, wood structures, (micro)environments, as well as interactive competition. During decay the major wood components (cellulose, hemicellulose, and lignin) are depolymerized and/or modified in order to provide energy and metabolites for fungal synthesis. Heat treatment at relatively high temperatures (ranging from 150°C to 260°C) appears to be an effective method for improving the durability of wood under non-ground-contact conditions.[1–7] Similarities but also clear differences in the degradation of the main wood components (cellulose, hemicellulose, and lignin) were observed after exposure of heat-treated and untreated wood to brown rot and white rot fungi.[8] In ground contact decay of wood can be caused not only by basidiomycetes (brown and white rot fungi), but also by soft rot fungi (*Fungi imperfecti* and ascomycetes) and bacteria.[9–12] The preferences of these decay organisms might differ according to the wood species involved.

This study used CP-MAS ^{13}C-NMR analysis to investigate in more detail the reasons why the resistance to decay was greater in heat-treated wood than in untreated wood after fungal exposure in ground contact. A previous study investigated decay after exposure to a single fungal species under controlled laboratory conditions.[8] A ground contact study under standard controlled conditions (EN 252)[17] such as the present one was deemed necessary to reproduce the real situation of heat-treated timber in service. A well-established industrial process in current use,[13] based on a two-stage heat treatment method under relatively

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mild conditions (<200°C), was used to treat the wood samples. The results of ^{13}C-NMR, FTIR, and chemical analyses of similar heat-treated wood before any decay tests have been reported previously.[14–16] Although several previous studies investigated wood decay by NMR,[19–25] the focus of the present study was different because it addressed the decay of heat-treated wood, a material already shown to be rather different and to possess characteristics very different from those of normal wood.[6,14]

EXPERIMENTAL

Materials

Scots pine (*Pinus sylvestris* L.), Norway spruce (*Picea abies* KARST), Douglas fir (*Pseudotsuga menziesii*), Radiata pine (*Pinus radiata* D.), and Simaruba (*Simaruba amara* AUBL.) specimens were used for heat treatment and chemical analyses. Untreated specimens were used as references. Boards with standard cross-section sizes (thickness: 32–38 mm; width: 150 mm) and a length of at least 3.0 m were used for heat treatment. The moisture content before treatment was 16%–20% ("shipping dry").

Heat treatment

The heat treatment was performed in two stages. In the first stage the wood boards were treated in an aqueous environment at superatmospheric pressure (6–8 bar) using liquid water as the heating medium to increase the temperature of the boards. This so-called liquid full hydrothermolysis treatment was done in a 600-L reactor at an effective treatment temperature of 165°C. A heat exchanger was used to heat and cool the process water in the reactor, and NaOH was added to control the pH. The wood samples were then dried using a conventional drying process at 50°C–60°C. After drying, the wood samples were heat-treated again in a special curing kiln (the second stage) under dry and atmospheric conditions, the so-called curing treatment (at 170°C–180°C). During this stage, the superheated steam was used as a sheltering gas to exclude oxygen (reducing fire risks and preventing undesired oxidation reactions).

Fungal testing

Thirty treated and 30 untreated specimens (each 25 × 50 × 600 mm) of each wood species tested were prepared and exposed to soil according to the graveyard test (EN 252)[17] in Wageningen, The Netherlands. Each year the test specimens were inspected, and the failed stakes were removed, dried, and stored.

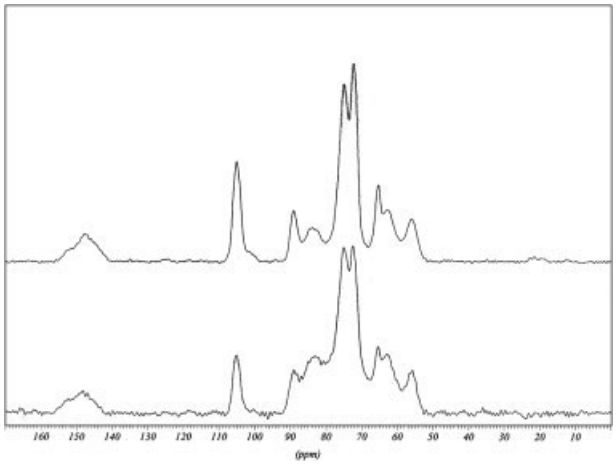

Figure 1 CP-MAS ^{13}C-NMR spectra after fungal exposure in ground contact (EN 252) of untreated and heat-treated Scots pine.

Solid-state CP-MAS ^{13}C-NMR analysis

Failed stakes from the EN 252 graveyard test were selected to prepare the NMR samples. Small slices (25 × 50 × 10 mm) with a clearly visible decayed surface (brown, white, and/or soft rot) were sawn near the soil-air level. The samples were grinded before analysis. Treated and untreated wood specimens were used for NMR analysis.

The treated and untreated timber specimens were analyzed by solid-state CP-MAS ^{13}C-NMR. Spectra were obtained on a Bruker MSL 300 FT-NMR spectrometer at a frequency of 75.47 MHz and at a sample spin of 4.0 kHz. The impulse duration at 90° was 4.2 ms, contact time was 1 ms, number of transients was about 1000, and the decoupling field was 59.5 kHz. Chemical shifts were determined relative to tetramethyl silane (TMS), which was used as the control. The spectra were accurate to 1 ppm. The spectra were run with suppression of spinning side bands.

RESULTS AND DISCUSSION

Characterization of wood after fungal exposure

Figures 1–5 show the CP-MAS ^{13}C-NMR spectra of the heat-treated and untreated Scots pine, Radiata pine, Norway spruce, Douglas fir, and Simaruba specimens after fungal exposure in ground contact. The major changes from fungal degradation are described below.

Untreated wood

Fungal exposure in ground contact resulted in a strong attack on the carbohydrates (cellulose and hemicellulose) of the untreated Scots pine (Fig. 1). The crystalline peak (89 ppm) and especially the amorphous peak (82 ppm) of the C4 of the carbohydrates

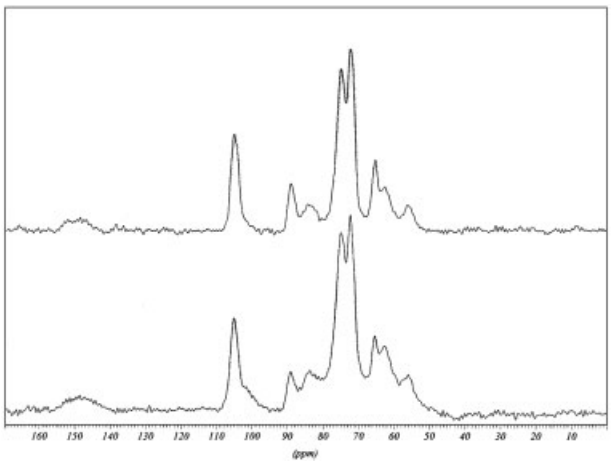

Figure 2 CP-MAS ^{13}C-NMR spectra after fungal exposure in ground contact (EN 252) of untreated and heat-treated Radiata pine.

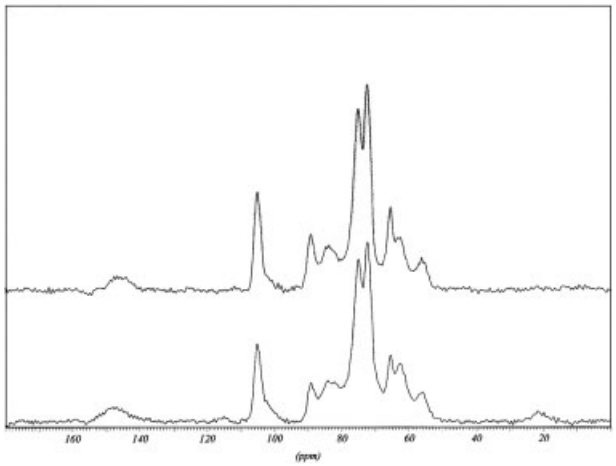

Figure 4 CP-MAS ^{13}C-NMR spectra after fungal exposure in ground contact (EN 252) of untreated and heat-treated Douglas fir.

decreased after fungal exposure. The high peak at 105 ppm showed a clear decrease, and the shoulder on the right side of this peak almost disappeared. This peak and its shoulder belong to the C1 of the carbohydrates. Fungal attack at C1 and C4 was believed to cause cleavage of hemicellulose and cellulose, decreasing the degree of polymerization. A decrease in the crystalline (65 ppm) and amorphous (62 ppm) peaks of the carbohydrate C6 band was found after fungal exposure. It was also found after fungal exposure to basidiomycetes.[8] It was suggested that the fungus tries to cleave this out-of-the-ring CH_2—OH group to open the cellulose crystalline structure to an amorphous structure, both to facilitate cellulose degradation and to decrease the water repellence of the (crystalline) structure.[8] This is the first time that attack at this site has been observed. It was not observed on untreated wood by any of the previous NMR studies of normal timber decay.[22–24]

The C2 (75 ppm) and C3,C5 (72 ppm) carbohydrate peaks also appeared to be badly affected, implying a relatively small but observable opening of the glucose pyranose ring. The acetyl group ($\underline{C}H_3COO$—) peak of hemicellulose (at 23 ppm) disappeared, indicating marked degradation of hemicellulose (Fig. 1).

The attack on lignin of untreated Scots pine after fungal exposure was rather limited. There was a slight decrease in the —OCH_3 peak (56 ppm), which means some but not too extensive demethoxylation of lignin. Ring opening of the aromatic structure of lignin probably did not occur since the Ar$\underline{C}$—OH peak at 148 ppm and the Ar$\underline{C}$—OCH_3 peak at 145 ppm did not change after fungal exposure (Fig. 1).

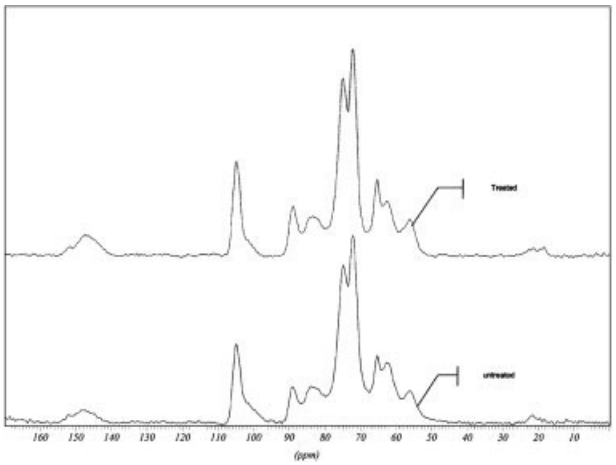

Figure 3 CP-MAS ^{13}C-NMR spectra after fungal exposure in ground contact (EN 252) of untreated and heat-treated Norway spruce.

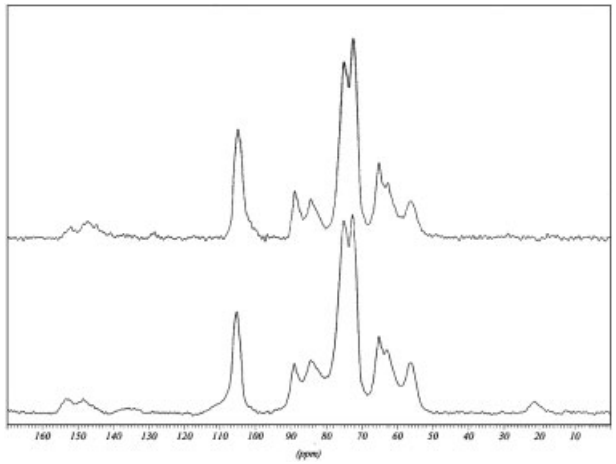

Figure 5 CP-MAS ^{13}C-NMR spectra after fungal exposure in ground contact (EN 252) of untreated and heat-treated Simaruba.

A serious attack on the amorphous carbohydrates of untreated Radiata pine was observed because the amorphous C4 (82 ppm) and C6 (62 ppm) peaks were clearly decreased after fungal exposure in ground contact (Fig. 2). There was a slight decrease in the crystalline C6 (65 ppm) and C4 (89 ppm) peaks, and the C1 peak (105 ppm) appeared to be unchanged. Therefore, fungal attack of the carbohydrates mainly occurred at the amorphous C4, causing cleavage of hemicellulose and cellulose decreasing the degree of polymerization. The acetyl group ($\underline{C}H_3COO$—) peak of hemicellulose (at 23 ppm) disappeared, indicating marked degradation of hemicellulose (Fig. 2). The NMR spectra also show a clear attack on the lignin of the untreated Radiata pine after fungal exposure in ground contact. Although the —OCH_3 peak decreased (56 ppm), meaning there was some demethoxylation of lignin, but still rather limited, the Ar$\underline{C}$—OH peak at 148 ppm and the Ar$\underline{C}$—OCH_3 peak at 145 ppm were clearly decreased, indicating ring opening and degradation of the aromatic nuclei (Fig. 2).

Degradation of the carbohydrates of untreated Douglas fir and Norway spruce revealed similarities and was less marked after fungal attack than in the other species (Figs. 3 and 4). A decrease in the C6 peak at 62 ppm revealed some attack on the amorphous carbohydrates. The C4 peaks at 82 (amorphous) and 89 (crystalline) ppm and the C1 peak appeared to be unchanged, indicating no or low cleavage/depolymerization of the carbohydrates. The $\underline{C}H_3COO$— hemicellulose peak (23 ppm) was still visible, indicating the presence of some hemicellulose (Figs. 3 and 4). The ^{13}C-NMR spectra of untreated Douglas fir revealed a slight decrease in the —OCH_3 peak (56 ppm) after fungal exposure, which means some demethoxylation of lignin occurred. This was not observed in the ^{13}C-NMR spectra of the untreated Norway spruce. There appears to have been some ring opening of the aromatic structure of lignin because the Ar$\underline{C}$—OH peak at 148 ppm and the Ar$\underline{C}$—OCH_3 peak at 145 ppm were slightly decreased after Norway spruce and Douglas fir were subjected to fungal exposure (Figs. 3 and 4).

The ^{13}C-NMR spectra of untreated Simaruba revealed a decreased level of amorphous carbohydrates after fungal exposure in ground contact because the amorphous C4 peak (82 ppm) and especially the amorphous C6 peak (62 ppm) were decreased (Fig. 5). The crystalline C6 (65 ppm) and C4 (89 ppm) peaks and the C1 peak at 105 ppm appeared to be unchanged, although the shoulder on the right side of the C1 peak disappeared. Therefore, cleavage of hemicellulose and cellulose, which caused a decreased degree of polymerization, mainly occurred at the amorphous C4. The C2 (75 ppm) and the C3,C5 (72 ppm) peaks of the carbohydrates were unchanged, meaning there was no pyranose ring opening. The $\underline{C}H_3COO$— hemicellulose peak (23 ppm) was still visible, indicating the presence of some hemicellulose (Fig. 5). The low shoulder at 108—110 ppm in the untreated Simaruba was the C1 of an alpha-arabinofuranose; hence, it was a pectic substance. This means that amorphous carbohydrates such as pectic substances are rather difficult to degrade. It is not known why this is so. Possible explanations include that they have a much higher degree of polymerization in Simaruba than in other wood species, that they could have been treated with water repellents or anti–blue stains, or that they could have slightly different structures.

No or low demethoxylation of lignin occurred because the decrease in the —OCH_3 peak (56 ppm) was rather limited. The presence of the broad peak at 133–140 ppm (aromatic C-1 of guaiacyl and syringyl lignin), the Ar$\underline{C}$—OCH_3 peak at 145 ppm, the Ar$\underline{C}$—OH peak at 148 ppm, and the peak at 153 ppm (aromatic C-3, C-5, or C-4e of guaiacyl and syringyl lignin) indicate no or little ring opening of the aromatic nuclei (Fig. 5).

Heat-treated wood

Heat treatment modified and changed compositions of the main components of the wood (cellulose, hemicellulose, and lignin).[14–16,18] The most important changes found were:

1. degradation of the hemicellulose;
2. increase in the relative proportion of the crystalline cellulose; and
3. further crosslinking of the lignin network because of polycondensation reactions.

In the spectra of the heat-treated wood (Figs. 1, 2, 4, and 5) the acetyl group ($\underline{C}H_3COO$—) peak of hemicellulose (at 23 ppm) disappeared. This could have been a result of fungal decay, but it has been found that heat treatment causes thermal degradation of hemicellulose including cleavage of the acetyl group.[8,14] A clear decrease in the amorphous C4 (83 ppm) and C6 (62 ppm) peaks of the carbohydrates also was found after heat treatment because of thermal degradation of hemicellulose and amorphous cellulose.[8,14,18]

The ^{13}C-NMR spectra of heat-treated Scots pine revealed an attack on the carbohydrates (cellulose and hemicellulose) after fungal exposure in ground contact (Fig. 1). The amorphous C6 (62 ppm) and C4 (83 ppm) peaks decreased, which could have been a result of fungal decay and/or thermal degradation during heat treatment. The 105 ppm peak of C1 did not changed, although its shoulder on the right side disappeared. Therefore, an attack on the carbohydrates of heat-treated Scots pine in ground contact occurred at C1 and possibly at C4 in order to cleave and eventually depolymerize cellulose and hemicellulose. The C2

(75 ppm) and C3,C5 (72 ppm) carbohydrate peaks appeared to be unchanged, indicating no or little opening of the glucose pyranose ring.

A slight decrease in the —OCH_3 peak (56 ppm) was observed after fungal exposure, which means there was some demethoxylation of lignin. The same has been observed in previous studies of untreated wood.[19–25] The Ar$\underline{C}$—OCH_3 peak at 145 ppm and the Ar$\underline{C}$—OH peak at 148 ppm appeared to be unchanged, indicating no or only a slight attack on the aromatic structure of lignin (Fig. 1).

Fungal exposure in ground contact caused a clear attack on the carbohydrates of heat-treated Radiata pine (Fig. 2). The amorphous C6 (62 ppm) and C4 (83 ppm) peaks decreased, which could have been a result of fungal decay and/or thermal degradation during heat treatment. The crystalline C4 peak (89 ppm) appeared to be unchanged, but the crystalline C6 peak (65 ppm) was slightly decreased, indicating some attack on the out-of-the-ring CH_2OH group at the C6 of the carbohydrates. The C1 peak (105 ppm) was decreased, and its shoulder on the right side had disappeared. In ground contact fungi appeared to have attacked the carbohydrates of heat-treated Radiata pine at C1 and possibly at C4 in order to cleave and eventually depolymerize cellulose and hemicellulose. The C2 (75 ppm) and C3,C5 (72 ppm) carbohydrate peaks appeared unchanged, indicating no or little opening of the glucose pyranose ring.

Similar to in untreated wood, demethoxylation and ring opening of the aromatic nuclei were observed when heat-treated Radiata pine was exposed to fungi in ground contact because the —OCH_3 peak (56 ppm), the Ar$\underline{C}$—OCH_3 peak at 145 ppm, and the Ar$\underline{C}$—OH peak at 148 ppm were clearly decreased (Fig. 2).

The attack on the wood components of heat-treated Norway spruce during exposure in ground contact was rather limited (Fig. 3). The amorphous carbohydrate C6 (62 ppm) and C4 (83 ppm) peaks decreased. This could have been a result of fungal decay but also to thermal degradation during heat treatment. The crystalline carbohydrate C6 (65 ppm) and C4 (89 ppm) peaks appeared unchanged. Some attack on the carbohydrate's C1 was observed because its shoulder on the right side was slightly decreased. It was remarkable that the $\underline{C}H_3COO$— peak of hemicellulose at 23 ppm was present (Fig. 3); this was not visible after exposure to *C. puteana*, *G. trabeum*, *P. placenta,* and *C. versicolor*.[8] The CH_3COO— side group must be present after heat treatment, and it is not degraded during exposure in ground contact. Furthermore, the ^{13}C-NMR spectra of Norway spruce showed a small peak at 18 ppm belonging to the CH_3— group, indicating that hemicellulose was less degraded in this type of timber. The —OCH3 peak at 56 ppm, the Ar$\underline{C}$—OCH_3 peak at 145 ppm, and the Ar$\underline{C}$—OH peak at 148 ppm appeared to be unchanged, indicating no or only a slight attack on lignin (Fig. 3).

The main difference between the ^{13}C-NMR spectra of the treated and untreated Douglas fir specimens was the decrease in the amorphous C4 (82 ppm) and C6 (62 ppm) peaks and the absence of the $\underline{C}H_3COO$— peak of hemicellulose (23 ppm) in the heat-treated Douglas fir spectra (Fig. 4). This could have been a result of fungal degradation, but it more probably resulted from thermal degradation of the carbohydrates during heat treatment. Therefore, it appears that the Fungal attack on the carbohydrates during exposure in ground contact was rather limited under EN 252 standard test conditions,[18] although some attack on the carbohydrate's C1 was observed because its shoulder on the right side was slightly decreased.

It appears that an attack on the lignin component of the heat-treated Douglas fir occurred during fungal exposure in ground contact. A slight decrease in the —OCH_3 peak (56 ppm), meaning some demethoxylation of lignin occurred, and a decrease in the Ar$\underline{C}$—OH peak at 148 ppm and the Ar$\underline{C}$—OCH_3 peak at 145 ppm, indicating ring opening of the aromatic nuclei, were observed (Fig. 4).

A strong decrease in the amount of the amorphous carbohydrates of heat-treated Simaruba was observed, because the amorphous C4 peak (82 ppm) and especially the C6 peak (62 ppm) decreased after fungal exposure in ground contact (Fig. 5). This could have been caused by fungal attack, but was more probably a result of degradation of the carbohydrates during heat treatment. The C1 peak (105 ppm) was clearly decreased, and its shoulder on the right side partially disappeared. The attack on the carbohydrates of heat-treated Simaruba in ground contact appeared to occur mainly at C1 in order to cleave and eventually depolymerize cellulose and hemicellulose. Furthermore, there is a clearly visible decrease in the C2 peak (75 ppm), indicating glucose pyranose ring opening of the carbohydrates.

The low shoulder at 108–110 ppm, reflecting the C1 of an alpha-arabinofuranose, almost disappeared in heat-treated Simaruba after fungal exposure in ground contact. Because this peak was still clearly visible in the NMR spectra of untreated Simaruba (Fig. 5), heat treatment must have cleaved these pectic substances extremely easily.

Lignin of heat-treated Simaruba seems to have been more affected than untreated wood after fungal exposure in ground contact (Fig. 5). A clear decrease in the —OCH_3 peak (56 ppm) indicated strong demethoxylation of lignin. The broad peak at 133–140 ppm (aromatic C-1 of guaiacyl and syringyl lignin) had almost disappeared, and the 153 ppm peak (aromatic C-3, C-5, or C-4e of guaiacyl and syringyl lignin) was strongly decreased, indicating ring opening and degradation of the aromatic nuclei. However, the

Ar$\underline{C}$—OCH_3 peak at 145 ppm and the Ar$\underline{C}$—OH peak at 148 ppm appeared unchanged after fungal exposure. The 148 ppm peak could have been a result of the production of furfural.

A comparison of the ^{13}C-NMR spectra of the different wood species used in this study (Figs. 1–5) showed similarities but also clear differences in the way the wood polymeric structural constituents were degraded during exposure in ground contact (the toughest type of exposure). In general, there were similarities in the way wood-degrading fungi attacked wood (treated and untreated), such as hemicellulose degradation and demethoxylation of lignin, also revealed in other ^{13}C-NMR studies.[19–25] This article does not pretend to evaluate the relative extent of decay of treated and untreated wood, only its differences and similarities at a molecular level. The differences can have been caused by the wood species involved, softwood (Scots pine, Radiata pine, Norway spruce, and Douglas fir) versus hardwood species (Simaruba), sapwood versus heartwood, the level of decay (Norway spruce and Douglas fir appeared less degraded than the Scots pine and Radiata pine), and the fungi involved on the location of the EN 252 stakes (brown rot, white rot, and soft rot fungi and/or bacteria). Although a soil test method is subject to several unknown variables, especially when compared to the basidiomycetes lab test under controlled conditions already done,[8] this study revealed useful information about the degradation of untreated and heat-treated wood species in ground contact in a "real" work situation, reflecting as closely as possible the real performance of heat-treated wood in service conditions.

CONCLUSIONS

CP-MAS ^{13}C-NMR spectra revealed similarities but also clear differences in the polymeric structural wood constituents between heat-treated and untreated wood after fungal exposure.

Fungal exposure in ground contact resulted in strong degradation of the carbohydrates (cellulose and hemicellulose) of untreated Scots pine, Radiata pine, and Simaruba. Fungal attack of the carbohydrates appeared to occur mainly at C4, resulting in cleavage and eventually depolymerization of cellulose and hemicellulose. In untreated Scots pine, which appeared to be strongly degraded, the C1 of the carbohydrates also was attacked during fungal exposure in ground contact. Furthermore, the C2 and C3,C5 carbohydrate peaks of untreated Scots pine appeared also to be badly affected, suggesting there was a relatively small but observable ring opening of the glucose units.

Attack on the out-of-the-ring alcoholic group —CH_2OH of the carbohydrates of heat-treated wood was observed. It is possible that the fungus tried to cleave this out-of-the-ring CH_2—OH group to open the cellulose crystalline structure to an amorphous structure in order to decrease its water repellency to facilitate enzymatic cellulose degradation. Such a fungal attack strategy implies considerable decay under EN 252 conditions and supports the validity of this type of standard ground-contact test. A considerable attack on the acetyl group of the hemicellulose occurs during fungal exposure of untreated Scots pine and Radiata pine in ground contact. This hemicellulose degradation was less marked for untreated Simaruba.

It was remarkable that alpha-arabinofuranose, a pectic substance, appeared in the untreated Simaruba, which appeared not to be degraded during fungal exposure in ground contact. This means that amorphous carbohydrates such as pectic substances are rather difficult to degrade. The reasons for this are not known. Possible explanations include that they could have a much higher degree of polymerization than in other wood species, that they could have been treated with water repellents or anti–blue stains, or that they could have slightly different structures.

Degradation of the carbohydrates of untreated Norway spruce and Douglas fir was less marked after fungal attack than in the other wood species. However, it appears that the lignin component of untreated Douglas fir was attacked during fungal exposure, as there was an indication of ring opening of the aromatic structure. This also occurred in untreated Radiata pine but to a lesser extent or not at all in untreated Scots pine and Simaruba.

In ground contact fungi appeared to attack the carbohydrates of heat-treated wood at C1 and possibly at C4 in order to cleave and eventually depolymerize cellulose and hemicellulose. An attack on the out-of-the-ring alcoholic group was observed (in treated Radiata pine). The opening of the glucose pyranose ring in heat-treated Simaruba after fungal exposure, suggesting noticeable decay, not observed in the untreated wood, and the thermal degradation of alpha-arabinofuranose during heat treatment were remarkable. Demethoxylation and ring opening of the aromatic structure of lignin was observed, especially in heat-treated Radiata pine, Douglas fir, and Simaruba.

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