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Characterisation of thermally modified hard- and softwoods by ^{13}C CPMAS NMR

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Abstract

The changes induced by thermal modification in the chemical structure of spruce [*Picea abies* (L.) Karst.], birch (*Betula pendula*), aspen (*Populus tremula*) and oak (*Quercus robur*) were studied by ^{13}C CPMAS NMR spectroscopy. Spruce, birch and aspen were thermally modified at ~195 °C and oak at ~160 °C, under steam, according to an industrial-scale heat treatment process. In both hard- and softwood samples, ^{13}C CPMAS NMR measurements revealed a degradation of less ordered carbohydrates (i.e. hemicelluloses and amorphous cellulose) in the thermally modified wood, which resulted in an increase in the cellulose crystallinity. Furthermore, thermal modification induced changes in the lignin structure by a cleavage of the β-O-4 linkages. In the softwood lignin, a decrease also occurred in the methoxyl group content leading to a more condensed lignin structure.

Keywords: 13C CPMAS NMR; Thermal modification; Softwood; Hardwood; Crystallinity of cellulose; Lignin content

1. Introduction

Wood is a complex composite material, which consists mainly of cellulose (40–45%), hemicelluloses (20–30%) and lignin (20–30%). Cellulose represents the crystalline part of wood, while the structures of hemicelluloses and lignin are amorphous. The main mechanical function of hemicelluloses and lignin is to buttress the cellulose fibrils.

Heating of wood modifies the cell wall components. Several modifications are reported to result from high temperature and steam (Alén, Kotilainen, & Zaman, 2002; Haw, 1985; Haw, Maicel, & Biermann, 1984; Hemmingson & Newman, 1985; Kotilainen, Alén, & Toivanen, 2003; Nuopponen, Vuorinen, Jämsä, & Viitaniemi, 2004; Sivonen, Maunu, Sundholm, Jämsä, & Viitaniemi, 2002; Sudo, Shimizu, & Sakurai, 1985; Tekely & Vignon, 1987; Tjeerdsma, Boonstra, Pizzi, Tekely, & Militz, 1998; Zaman, Alén, & Kotilainen, 2000). Hemicelluloses and less ordered cellulose deteriorate and as a consequence, the degree of cellulose crystallinity increases. Changes in the aromatic structures involve cleavage of the aryl-ether linkages between the lignin phenylpropane units as well as lignin demethoxylation in high temperatures. Most studies on the thermal modification of wood have been done on laboratory scale and the results are of limited value at industrial scale. The wood samples investigated in this study were thermally modified in an industrial-scale heat treatment process developed at the Technical Research Centre of Finland (VTT). The process is carried out under normal pressure, using water vapour as a shielding gas (Viitaniemi, Ranta-Maunus, Jämsä, & Ek, 1995).

The chemical modifications in wood structure occurring at high temperature are accompanied by several favourable changes in physical structure: reduced shrinkage and swelling, low equilibrium moisture content, better decay resistance, enhanced weather resistance and decorative, dark colour (Nuopponen, Wikberg et al., 2004; Santos, 2000; Sivonen, Nuopponen, Maunu, Sundholm, & Vuorinen, 2003; Viitaniemi, 2000). Thermally modified wood finds use in outdoor furniture, claddings on wooden

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buildings, floor material, musical instruments and a diversity of other outdoor and indoor applications. Unfortunately, the mechanical properties, e.g. strength, hardness and stiffness are reduced at the same time. The relationship between mechanical properties and the structural variables such as cellulose crystallinity has not been fully clarified.

In earlier work we carried out thermal investigations on pine (*Pinus sylvestris*) (Sivonen et al., 2002). We now investigate four other European wood species, birch (*Betula pendula*), aspen (*Populus tremula*), oak (*Quercus robur*) and spruce [*Picea abies* (L.) Karst.], by ^{13}C CPMAS NMR spectroscopy, with the aim of clarifying the changes in chemical structure caused by industrial-scale heat treatment. The changes induced in the structure of these wood species by industrial treatment have not been reported extensively elsewhere.

2. Experimental

2.1. Wood samples

The thermally modified wood samples were obtained from VTT, where an industrial-scale heat treatment process has been developed (Viitaniemi et al., 1995). Spruce was heat treated at about 195 °C under steam. The total time of the heat treatment was 44 h and the actual time at this high temperature was 188 min. Birch and aspen were heat treated at about 195 °C under steam. The total time of the heat treatment was 56 h and the actual time at this high temperature was 130 min. Oak was heat treated at 160 °C under steam.

Only one untreated sample and one thermally modified sample of each species were measured because of the long measuring times required. The thermally modified and untreated samples of each species were from the same tree trunk.

2.2. NMR spectroscopy

^{13}C CPMAS NMR measurements were done with a Varian ^{UNITY}INOVA 300 MHz spectrometer operating at 75.47 MHz for carbon. For all the wood samples, the spinning speed was 5000 Hz, contact time 1 ms, acquisition time 20 ms and delay between pulses 2 s. Samples were moistened before the measurements in order to achieve better signal-to-noise ratio (Horii, Hirai, Kitamaru, & Sakurada, 1985; Willis & Herring, 1987). The chemical shifts were referenced to the cellulose C-1 signal (105 ppm) in CPMAS spectra and to the methoxyl signal (56 ppm) in dipolar dephased (DD) spectra.

The crystallinity of cellulose, measured as the crystallinity index (CrI), was determined using a spin-locking technique in which there is a delay between the proton preparation pulse and cross-polarization to allow the relaxation of certain of the components (Newman & Hemmingson, 1990, 1995). The difference in proton relaxation times allows the subspectra of the more ordered part (e.g. cellulose) and amorphous matrix (lignin and hemicelluloses) to be separated by taking the linear combination of spectra measured with different delay times (t_{sl} = 6, 8, 10 ms). For each sample, subspectra were separated by linear combination of two spectra and the CrI values are reported as an average of the values determined from each subspectrum. CrI values were calculated from the areas of the (a) crystalline (86–92 ppm) and (b) amorphous (79–86 ppm) cellulose C-4 signals by deconvolution using Lorenzian line shapes according to Teeäär, Serimaa, and Paakkari (1987); $\mathrm{CrI} = a/(a+b)$.

In dipolar dephasing (DD) measurements, the high-power decoupler was turned off for 50 μs before the data acquisition. During the delay, the dipolar interactions cause dephasing of the protonated carbons. The DD pulse sequence selectively reduces the intensity of the signals from the protonated carbons so that there is less interference in the aromatic lignin region of the spectrum (Gerasimowicz, Hicks, & Pfeffer, 1984; Hatcher, 1987).

3. Results and discussion

3.1. Chemical shifts

The signal assignments for the ^{13}C CPMAS NMR spectra are presented in Table 1. In brief, cellulose gives signals in the region between 50 and 105 ppm. The signal at 89 ppm corresponds to C-4 of the highly ordered cellulose of the crystallite interiors, whereas the broader upfield signal at 84 ppm is assigned to the C-4 of disordered cellulose (Atalla & VanderHart, 1999; VanderHart & Atalla, 1984). The signals at 65 and 62 ppm are assigned to C-6 of ordered

Table 1
Signal assignments for ^{13}C CPMAS spectra of wood

Chemical shift (ppm)	Assignment
173	COOH in acetyl groups
153	S 3/5e, G 4e
148	S 3/5f, G 3
146	G 4f
136	S 1/4e, G1e
133	S 1/4f, G1f
120	G 6
116	G 5
112	G 2
105	C-1 of cellulose
102	C-1 of hemicelluloses
89	C-4 of crystalline cellulose
84	C-4 of amorphous cellulose
72–75	C-2/C-3/C-5 of cellulose
65	C-6 of crystalline cellulose
62	C-6 of amorphous cellulose
56	methoxyl groups in lignin
21	CH_3 in acetyl groups

S, syringyl; G, guaiacyl; e, etherified C-4; f, free phenolic C-4.

and disordered cellulose, respectively, and the signals at 72–75 ppm to C-2,3,5 of cellulose. The cellulose signals overlap the signals of the aliphatic carbons of lignin and, in part, those of hemicelluloses (Haw et al., 1984; Hawkes, Smith, Utley, Vargas, & Viertler, 1993; Leary, Newman, & Morgan, 1986). The small shoulder at 102 ppm on the C-1 cellulose signal (105 ppm) belongs to the hemicelluloses. In addition, the signals of the methyl and carboxylic carbons of acetyl groups attached to hemicelluloses resonate at 21 and 173 ppm, respectively. The lignin methoxyl groups give a signal at 56 ppm. The region between 125 and 160 ppm is specific to the aromatic carbons of lignin. The main unit in softwood lignin is guaiacyl (G), while hardwood lignin contains both guaiacyl and syringyl (S) units (Fig. 1). The signal at 153 ppm is assigned to C-3 and C-5 of S units that are etherified at C-4. The signal at 148 ppm is also assigned to C-3 and C-5 of S units, but for those with free phenolic groups at C-4. Additionally, the signal at 148 ppm is assigned to C-3 and C-4 of G units. The signal at 136 ppm is assigned to C-1 and C-4 of S and G units that are etherified at C-4. No internal standard was used in the measurements, which means that the absolute intensities of signals in different spectra cannot be compared, only the relative intensities.

3.2. Carbohydrates

It is apparent from the ^{13}C CPMAS NMR spectra of hardwoods (birch, aspen and oak, Fig. 2a–f) and softwood spruce, Fig. 2g and h) that some degradation of carbohydrates has occurred during the thermal modification. The shoulder at 102 ppm on the signal of cellulose C-1, assigned to hemicelluloses, is diminished in the thermally modified softwood spectrum indicating some degradation of hemicelluloses. The shoulder is poorly seen in the spectra of hardwoods. Softwoods and hardwoods differ in the percentage and the composition of hemicelluloses: softwoods contain abundant mannose units and more galactose units than hardwoods, while hardwoods contain abundant xylose units and more acetyl groups than softwoods (Fengel & Wegener, 1989). The shoulder at 102 ppm is thus probably due to glucomannans rather than xylans because it is more apparent in the spectra of softwoods than hardwoods. In addition, the relative intensity of the signals of methyl (21 ppm) and carboxylic carbons (173 ppm) of acetyl groups attached to hemicelluloses are decreased in every spectrum after thermal modification. The higher content of acetyl groups in untreated hardwood than in untreated softwood is clearly seen in the more prominent signals at 21 and 173 ppm in the spectra of the hardwoods (Fig. 2b, d, f). Softwood xylans differ from hardwood xylans in the lack of acetyl groups (Fengel & Wegener, 1989). Softwood acetyl groups are attached to the glucomannan backbone. Deacetylation of hemicelluloses causes liberation of acetic acid, which further catalyses depolymerisation of the less ordered carbohydrates, i.e. less ordered cellulose.

In the spectra in Fig. 2 the ratio of the relative intensities of the signals at 84 ppm assigned to the C-4 of disordered cellulose and the signal at 89 ppm assigned to the highly ordered cellulose C-4 is smaller in the thermally modified samples. The crystallinity indices for cellulose (CrI), presented in Table 2, were determined by the spin-locking technique (Newman & Hemmingson, 1990, 1995). With this technique the subspectra of cellulose and the lignin-hemicelluloses-matrix can be separated spectroscopically, and all chemical changes in the structure that might occur in chemical treatment are thereby avoided. The CrI values are

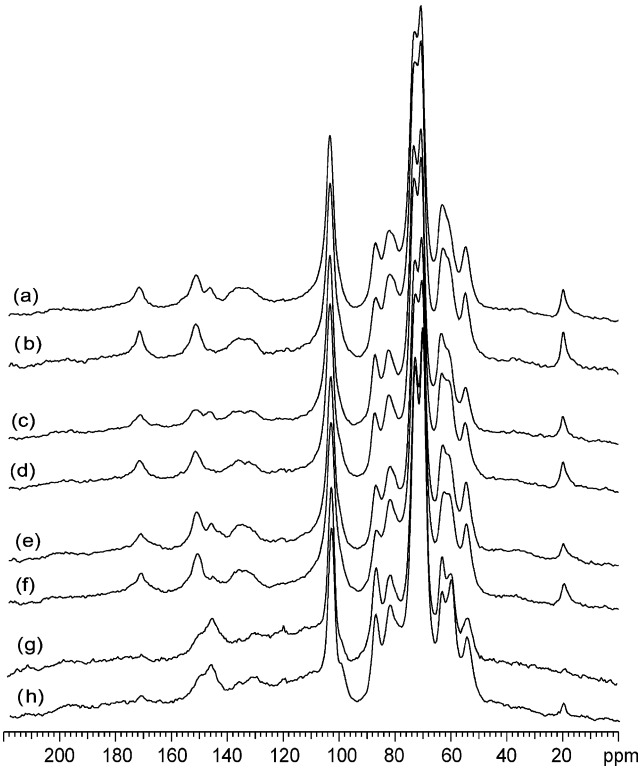

Fig. 2. ^{13}C CPMAS NMR spectra of (a) thermally modified birch, (b) untreated birch, (c) thermally modified aspen, (d) untreated aspen, (e) thermally modified oak, (f) untreated oak, (g) thermally modified spruce and (h) untreated spruce samples.

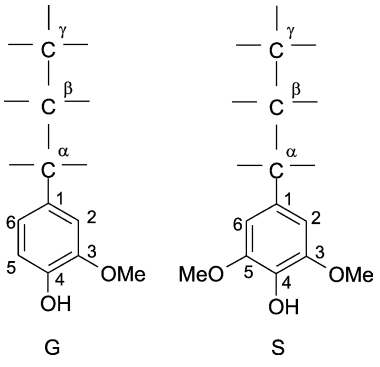

Fig. 1. Chemical structures of guaiacyl (G) and syringyl (S) units in lignin.

Table 2
Cellulose crystallinity indices (CrI) for wood samples

Sample	CrI (%)
Ref birch	41
Tm birch	52
Ref aspen	48
Tm aspen	54
Ref oak	46
Tm oak	53
Ref spruce	54
Tm spruce	65

Ref refers to the untreated reference sample and Tm to the thermally modified sample.

calculated from the cellulose subspectrum. Here, only the highly ordered cellulose in the interior of the crystallites is considered to be crystalline cellulose, while the less ordered cellulose, including the fibril surfaces, is considered to be amorphous (Atalla & VanderHart, 1999; VanderHart & Atalla, 1984). The CrI of every wood sample increased in thermal modification, as can be seen in Table 2. This is probably due to the degradation of the less ordered chains during the thermal treatment rather than to any increase in the amount of more ordered cellulose. The crystallinity index was highest for the thermally modified spruce (65%) while the crystallinities of thermally modified hardwoods were of similar magnitude (52–54%). The accuracy of the crystallinity values was estimated to be $\pm 3\%$ based on processing of the spectra.

The original crystallinity of spruce (54%) was higher than the original crystallinities of birch (41%), aspen (48%) and oak (46%). Newman and Hemmingson (1990) reported mean values 54 and 57% for cellulose crystallinity in hardwoods and softwoods, respectively. These observations indicate that there are differences in the original cellulose crystallinity between softwood and hardwood as well as between different hardwoods. Wood is a heterogeneous material and its chemical structure varies even in the trunk of a single tree. Variations exist in the structure of cells and pores as well as in the amount and distribution of different cell wall components. Further, the fibre structures as well as the cellulose morphology within a fibre differ. These factors, at least, affect the degree of cellulose crystallinity. In order to avoid unnecessary differences in the structure of the thermally modified wood and its untreated reference, we took sample pairs from the trunk of the same tree. In our previous study we observed that the variations in cellulose crystallinity between samples taken from different parts of the same tree are minor (Andersson, Wikberg, Pesonen, Maunu, & Serimaa, 2004).

Degradation of hemicelluloses and less ordered cellulose, not the increase in the cellulose crystallinity, is probably the main cause of the reduced strength of thermally modified wood. Even though hardwoods have lower cellulose crystallinities, their strength properties are reported to decrease more in the thermal modification (Möller & Otranen, 1999).

3.3. Lignin

In the DD spectra in Fig. 3, the signals from protonated aromatic carbons are relaxed during the delay allowing the signals from the quaternary carbons of lignin to be analysed more reliably. The spectra of the untreated hardwoods (Fig. 3b, d and f) show signal at 153 ppm assigned to C-3/5 of syringyl (S) units that are etherified at C-4 and signal at 136 ppm assigned to C-1/4 of S units that are etherified. There is a signal at 148 ppm due to S 3/5 carbons in non-etherified units and to guaiacyl (G) 3/4 carbons in the spectra of untreated oak (Fig. 3f) and aspen (Fig. 3d), but the signal is scarcely seen in the spectrum of untreated birch (Fig. 3b). Evidently, the lignin in untreated oak and aspen contains more guaiacyl units and probably more non-etherified syringyl units than the lignin in untreated birch. The content of guaiacyl units appears to be highest in the oak lignin and lowest in the birch lignin, which suggests greatest predominance of guaiacyl units in untreated oak. Manders (1987) determined the syringyl/guaiacyl ratio for several hardwoods using solid state ^{13}C NMR and he, like us, obtained higher S/G ratio for birch than for oak.

After the thermal modification, a reduction in the relative intensity of the signal at 153 ppm and an increase in

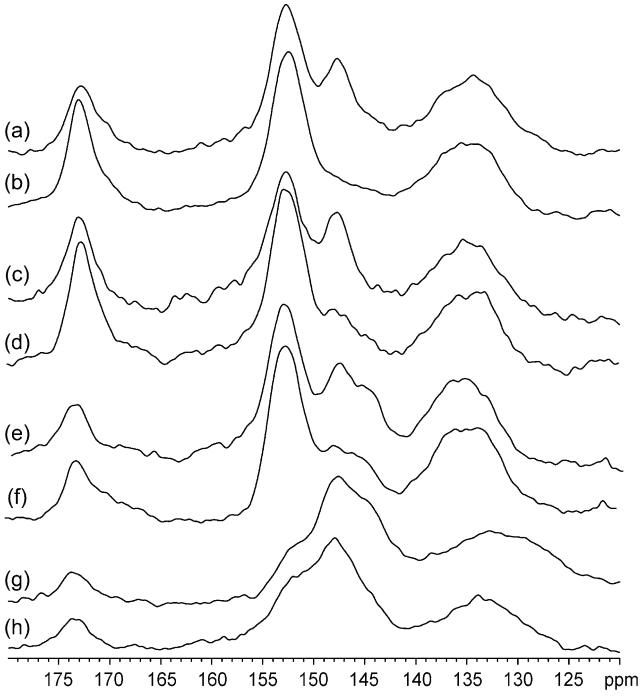

Fig. 3. Dipolar dephased (DD) NMR spectra of (a) thermally modified birch, (b) untreated birch, (c) thermally modified aspen, (d) untreated aspen, (e) thermally modified oak, (f) untreated oak, (g) thermally modified spruce and (h) untreated spruce samples.

the relative intensity of the signal at 148 ppm were seen in every hardwood spectrum (Fig. 3a, c and e). The relative intensities of these two signals in the heat treated and untreated wood spectra can be used as a measure of the degree to which β-O-4 linkages in lignin are cleaved during the thermal modification (Haw, 1985, Haw et al., 1984). According to this, the majority of the syringyl units in hardwoods included β-O-4 linkages before the thermal modification while after the thermal modification a substantial part of the β-O-4 linkages were cleaved. This extensive aryl-ether bond cleavage is probably due to the steam used in the heat treatment process (Haw, 1985; Haw et al.; Sudo et al., 1985). Thermal modification and steam partially depolymerise wood lignin by hydrolysing the aryl-ether linkages involving C-4 of syringyl and guaiacyl units, which leads to the formation of free hydroxyl phenolic groups and α- and β-carbonyl groups. However, no signs of new carbonyl groups were seen in the NMR spectra. Probably at least part of the volatile and water-soluble products, like depolymerised hemicelluloses and lignin, were leached out of the wood structure with steam during the modification process and the amount that remained was too low to be detected by solid state NMR.

The shoulder at 146 ppm, assigned to the G units that are non-etherified at C-4, is observed in the spectra of oak before (Fig. 3f) and especially after the thermal modification (Fig. 3e). Part of the guaiacyl phenolic units in oak was probably originally non-etherified at C-4, and after treatment even more of these units were free. The NMR spectra show no clear sign of this kind of cleavage in the guaiacyl units of aspen or birch. However, the shoulder at 145 ppm in the spectra of oak due to the condensed tannins may interfere with the interpretation of the signal at 146 ppm (Leary et al., 1986; Martínez, Almendros, González-Vila, & Fründ, 1999; Morgan & Newman, 1987). Finnish hardwoods, like birch and aspen, do not contain tannins, as observed from the spectra.

Thermal modification caused a reduction in the relative intensity of the shoulder at 153 ppm for C-4 of G units that are etherified, and an increase in the shoulder at 146 ppm for C-4 of non-etherified S units in the DD spectrum of spruce (Fig. 3 g and h). These changes are an indication of cleavage of β-O-4 linkages in the lignin guaiacyl units. In addition, a broad shoulder appears in the DD spectrum at 128 ppm after thermal modification. This shoulder is assumed to arise from lignin C-5-substituted structures, such as biphenyl (5–5) or diphenylmethane. Its appearance suggests that guaiacyl units are linked by carbon-carbon bonds and hence the content of condensed guaiacyl structures (120–140 ppm) is increased in the thermal modification relative to guaiacyl groups (140–160 ppm) (Liitiä, Maunu, Sipilä, & Hortling, 2002). This increase is further supported by the slight decrease in relative intensity of the methoxyl signal at 56 ppm in the CPMAS spectrum (Fig. 2 g and h). A similar increase was observed for Scots pine (Sivonen et al., 2002). Demethoxylation of lignin makes more lignin sites available for reaction. A more condensed lignin structure is achieved as a result. Neither condensation nor demethoxylation is observed in the DD spectra of hardwood samples (Fig. 3a–f), which indicates that only guaiacyl units are condensed by the formation of carbon-carbon bonds at C-5 and C-3 positions in the thermal modification. These bonds cannot be formed between syringyl units because a methoxyl group occupies the C-5 and C-3 positions. The lignin condensation probably improves the strength of thermally modified softwoods compared to hardwoods.

The most notable differences between the DD spectra of untreated hard- and softwoods are the signals at 153 and 148 ppm (Fig. 3). The signal at 153 ppm, assigned principally to syringyl units, is the major signal in the spectrum of hardwoods (Fig. 3b, d and f) and only a small shoulder in the spectrum of the softwood (Fig. 3 h) (Martínez et al., 1999). The signal at 148 ppm, in turn, which arises mainly from guaiacyl units, is of greater relative intensity in the softwood spectrum than the hardwood spectra because softwood lignin contains mainly guaiacyl units while hardwood lignin contains both guaiacyl and syringyl units. From the differences in the relative signal intensities in the NMR spectra, it appears that the cleavage of the β-O-4 bonds during thermal modification is more extensive in hardwoods than in softwoods. Hardwood syringyl lignin is reported to depolymerise to a greater extent than softwood guaicyl lignin when exposed to steam treatment (Sudo et al., 1985).

4. Conclusions

An industrial-scale heat treatment process was applied to softwood and three hardwoods and the changes occurring in the chemical structure were studied by ^{13}C CPMAS NMR spectroscopy. The carbohydrate fraction of every wood sample was altered by the degradation of hemicelluloses and amorphous cellulose. The crystallinity index of cellulose increased as a consequence. Hardwood lignin was broken down by extensive cleavage of β-O-4 linkages. Softwood lignin, in turn, was altered by the cleavage of β-O-4 linkages and demethoxylation that led to a more condensed lignin structure.

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