Characterisation of thermally modified wood: molecular reasons for wood performance improvement

B. F. Tjeerdsma, M. Boonstra, A. Pizzi, P. Tekely, H. Militz

Relatively mild thermal treatments of wood according to a two step process which leads to improved dimensional stability and improved timber performance were investigated by solid phase CP-MAS 13C-NMR to understand at molecular level the reasons for the improvements reported. All the occurrences described appear to be the consequence of reactions which are known in wood chemistry. These are the formation of acetic acid liberated from the hemicelluloses, which further catalyses carbohydrates cleavage, causing a reduction of degree of polymerisation of the carbohydrates. Acid catalysed degradation results in the formation of formaldehyde, furfural and other aldehydes as well as some lignin cleavage at Cα and O4 and believed to cause some aldehyde production from lignin units Cγ, all occurring in the first reaction step. Lignin autocondensation through the cleaved, positively charged benzylic Cα to form some methylene bridges presumably starts already to occur in this first phase. The increase in the number of free reactive sites on the aromatic ring of some lignin units already occurs in this phase but continues into the next.

In the second treatment step completion of the autocondensation of lignin is believed to occur through the formation of methylene bridges connecting aromatic rings. The aromatic nuclei sites are released by demethoxylation and through the cleaved, positively charged benzylic Cα. Reactions of some of the aldehyde groups formed in the first step phase occur with lignin aromatic nuclei sites to connect aromatic rings through methylene bridges.

The extent of these reactions is mild, but nonetheless they lead to an increase in cross-linking with consequent improvement in dimensional stability and decreased hygroscopicity of wood.

Charakterisieren von thermisch behandeltem Holz: Molekulare Ursachen für die Verbesserung der Holzstabilität
Relativ milde thermische Behandlung von Holz nach einem Zwei-Stufen-Verfahren führt zu verbesserter Dimensionsstabilität. Diese verbesserte Schnittholzqualität wurde mit Hilfe der Festphasen NMR untersucht, um die Urachen dafür auf molekularem Niveau zu verstehen. Alle Erscheinungen erweisen sich als Folge von in der Holzchemie bekannten chemischen Reaktionen. Diese sind: Freisetzen von Essigsäure aus den Polyosen, wodurch dann Spaltungen von Polysacchariden katalysiert werden, die zu einer Erniedrigung des Polymerisationsgrades führen. Die Säure-katalysierte Spaltung führt zur Bildung von Formaldehyd, Furfural und anderen Aldehyden sowie zu einigen Ligninspaltungen an Cα und O4. Diese wiederum führen vermutlich zur Bildung einiger Aldehyde aus Lignin-Einheiten (Cχ).
Alle diese Reaktionen laufen innerhalb der ersten Stufe ab. Auch eine weitere Kondensation des Lignins über abgespaltene, positiv geladene Benzyl-Bruchstücke (Cα) und Methylenbrücken findet wahrscheinlich innerhalb der ersten Phase statt. Ebenso der Anstieg von reaktiven Seitengruppen der aromatischen Ringe einiger Lignineinheiten beginnt in dieser ersten Stufen und setzt sich in der nächsten fort.
In der zweiten Behandlungsstufe setzt sich, wie die Autoren annehmen, die Autokondensation des Lignins über Methylenbrücken fort, wobei Seitengruppen der Benzolkerne durch Demethoxylierung abgespalten werden und positiv geladene Benzyleinheiten (Cα) entstehen. Einige der in der ersten Phase freihesetzten Aldehyde vernetzen die aromatischen Ringe des Lignins weiter über Methylenbrücken. Das Ausmaß dieser Reaktionen ist gering, führt aber dennoch zu einer Zunahme der Quervernetzung und infolge davon zu verbesserter Dimensionsstabilität und verringerter hygroskopischer Eigenschaft des Holzes.

A. Pizzi
ENSTIB, University of Nancy 1, B.P. 1041,
F88051 Epinal Cedex: France

B. Tjeerdsma, H. Militz
SHR, Wilde Kamp 1C, 6704 AT, Wageningen, the Netherlands

M. Boonstra
Plato Wood B.V., Wilde Kamp 1B,
6704 AT, Wageningen, the Netherlands

P. Tekely
NMR methodology laboratory, University of Nancy 1,
F 54501 Vandoeuvre, France

Correspondence to: A. Pizzi

1
Introduction
Recent work on heat treatment processes of timber (currently called "torrefied wood" in France and "Plato wood" in the Netherlands) has shown that such types of processes can improve considerably the performance of timber on several aspects (Ruyter 1989; van Zuylen 1995; Holz-Zentralblatt 1996). Heat treatment of wood has been known for long as an effective method to modify the properties of wood (Runkel and Witt, 1953; Seborg et al., 1953; Stamm, 1956; Kollmann and Schneider, 1963; Kollmann and Fengel, 1965; Noack, 1969; Hillis, 1984). The main effect gained by a heat treatment of wood is reduced wood hygroscopicity. Foremost advantages of wood treated in this manner are its increased resistance to different types of biodegradation and its improved dimensional stability. Many methods of thermal modification of wood have been reported in the literature (Seborg et al., 1953; Stamm, 1946; Burmester, 1973, 1975; Burmester and Wille, 1976; Giebeler, 1983). Yet undesired side effects, in particular loss of strength and increased brittleness of the treated

wood have prevented a commercial utilisation of thermal modification so far. Additional to the foregoing processes, the here reported treatment embodies a two-step process (Ruyter, 1989; van Zuylen 1995) rather than a one step one (Armines, 1981a, b; 1985), minimising these disadvantages and hence yielding more noticeable and consistent improvements. The first step consists of a humid step and is followed by a dry step. In order to optimise the process it is of considerable importance to understand which modifications and reactions occur in the wood constituents which result in the environmental and performance advantages outlined above. This article deals with a solid state CP-MAS 13 C NMR study of wood heat-treated according to the two-step process and of modifications introduced in softwoods and hardwoods constituents.

2
Experimental

Beech (*Fagus sylvatica* L.) and Scots Pine (*Pinus sylvestris* L.) sapwood matched wood specimens were treated in a laboratory set-up according to the schedules shown in Table 1. The wood samples were treated in a two-step process; first solid wood blocks saturated in a NaAc buffers solution (10 g/l) were exposed to high temperatures under moist conditions, followed by high temperatures under dry conditions in the second step. Step one was performed in an autoclave heated in an oil bath. Step two was performed in an oven excluding oxygen by flushing with nitrogen gas. The treated, half-treated and non-treated samples were mechanically ground to a fine pow-

Table 1. Schedules used for the two-step heat treatment of Scots Pine and Beech timber
Tabelle 1. Bedingungen für die zweistufige Wärmebehandlung von Kiefern- und Buchen-Schnittholz

	First humid phase	Second dry phase
Control	0	
Half-treated 1	1	0
Half-treated 1	1	2
Half-treated 1a	1	3
Half-treated 2	2	0
Half-treated 2	2	2
Half-treated 2a	2	3
Half-treated 3	3	0

0 = No treatment; 1 = Low temperature treatment; 2 = High temperature treatment; 3 = Extended high temperature treatment

der and made extract-free performing a water extraction followed by a 1:1 (v/v) ethanol:cyclohexane extraction, both executed at elevated temperature in a soxhlet apparatus. The extract free wood samples were then analysed by solid phase CP-MAS ^{13}C NMR.

The solid state CP-MAS ^{13}C NMR spectra of the treated and non-treated timber specimens were obtained with a Bruker MSL 300 FT-NMR spectrometer at a frequency of 75.45 MHz and at sample spin of 4.5 kHz and CP = 1 ms. Chemical shifts were calculated relative to TMS for NMR control. Acquisition time was 0.026 s. with number of transients of about 1000. The spectra were accurate to 1 ppm. The spectra were run with suppression of spinning side bands.

3
Results and discussion

The main effect of heat treatment of wood is a substantial decrease of the hygroscopicity. In the preliminary research on the properties of several wood species treated in a two-step thermal modification process (Tjeerdsma 1998), it has been found that the wood hygroscopicity is influenced by the process conditions. The process temperature appeared to be the most influential parameter. Exploration of a suitable thermal modification of wood in essence comes down to optimise the process for a maximum increase of dimensional stability and durability, while minimising the decrease of strength. It was found that under a severe thermal treatment the equilibrium moisture content (EMC) of wood conditioned in 96% relative humidity (RH) can be decreased from an EMC of approximately 30% of the non-treated wood to an EMC of 10% of the heat-treated wood, and improving the dimensional stability to an anti shrink efficiency (ASE) of 50%. Mild thermal treatment conditions are preferable, with respect to process facility and strength properties of the product, and providing adequate improvement of the wood quality required for many of the applications. The characteristics of wood after a mild thermal treatment are shown in Table 2. From the results it can be concluded that hygroscopicity, dimensional stability and durability are improved substantially accompanying only a minor decrease of the strength.

In order to understand which modifications and reactions occur in wood constituents at the molecular level, samples treated under different conditions were analysed by solid phase CP-MAS ^{13}C NMR. In general the observed

Table 2. Relevant properties of thermal modified wood. Beech and Scots Pine treated in a two-step process under mild conditions
Tabelle 2. Eigenschaften von wärmebehandeltem Buchen- und Kiefernholz nach einem zweistufigen Verfahren unter milden Bedingungen

	Hygroscopicity EMC (%)	Dimensional stability Swelling (%)	Strength MOR (N/mm^2)	Durability Weight loss (%)
Beech				
Non-treated	29.9	7.3	94	31.3
Heat-treated	18.3	5.7	91	3.1
Treatment efficiency (%)	39	22	−3	90
Scots Pine				
Non-treated	27.9	4.7	97	17.7
Heat-treated	18.1	2.8	78	4.9
Treatment efficiency (%)	35	40	−20	72

EMC = Equilibrium Moisture Content of wood conditioned at 96% relative humidity
Swelling = Overall (radial + tangential) swelling of wood; from ovendry to saturated condition
MOR = Modulus of Rupture
Weight loss = weight loss percentage after soil block test (resp. Beech 12 weeks, Scots Pine 16 weeks in soil block test)

final effects appeared stronger in the spectra when the treatment was more extreme. In Figures 1 and 2 the 13 C NMR spectra of the treated wood for some of the treatments lined out in Table 1 are shown. The trends are similar for all the treatments but the modifications observed are more marked after a more extreme treatment. On the total spectrum a noticeable variation is that the level of amorphous carbohydrates increases in the first step and then decreases in the second step but never back to the level before treatment.

As it appears clearly that the major changes occurring could be followed by the region between 100 and 150 ppm, the spectra were expanded in the NMR spectrometer itself, in order to be able to follow the variation of the peaks of interest better. In the Figures 1 and 2 is shown that the heat treatment causes:

1. An increase in the proportion of free sites ortho to the lignin aromatic-OH as a consequence of the increase of the peak at 117 ppm. This can be the result of only two occurrences, namely:

• a greater amount of phenolic-OH groups are present after the treatment as a consequence of demethylation of the methoxy groups of the guaiacyl and syringyl nuclei of lignin, or
• most likely a greater proportion of free ortho sites due to demethoxylation of the same methoxy groups

In both cases this infers that a greater number of aromatic lignin sites are available for reaction and an increased reactivity of the aromatic nuclei of lignin affected by the change as hydroxyl groups activate the aromatic ring more than methoxy or ether groups. This will result in all cases in an increase of the cross-linking level of the material with a concomitant increase in wood dimensional stability.

2. An increase in the proportion of methylene (—CH$_2$)-bridges connecting two phenolic nuclei, and this particularly in the second, dry step of the treatment. This is shown by the noticeable increase in the intensity of the peak at 29 ppm indicating that lignin cross-linking which did not exist at such sites in the non-treated wood has indeed occurred as a consequence of the heat treatment. Detected are more than one type of methylene bridges which are formed as indicated by the number of peaks and shoulders in the 20–37 ppm region of the spectrum. The more intense of them at 29 ppm indicates by its shift to be a ortho-para or ortho-ortho methylene linking two phenolic sites. This infers that the methylene bridge obtained by autocondensation is not only due to reaction of aldehydes on the aromatic nuclei of lignin but is also due to a classical lignin cleavage at the O4 and at the Cα of some lignin units followed by the autocondensation of the reactive —CH2-group formed with a site of negative charge, namely one of the free reactive sites on the phenolic nuclei of another lignin unit.

3. Aldehyde peaks are found present in the 190–220 ppm range. These peaks appear in the spectra before treatment as well as after treatment, however the intensity increases in the first step of the reaction. With respect to the study after the occurrence of the chemical reactions in wood during a thermal treatment it is of interest to examine what sort of aldehydes are represented by the observed peaks. The NMR shifts of the peaks are at 196 ppm and at 191–192 ppm. The first can only be the signal from formaldehyde and the second is the signal from furfuraldehyde. Furfuraldehyde is known to be formed during a heat-treatment of wood under acid conditions and detec-
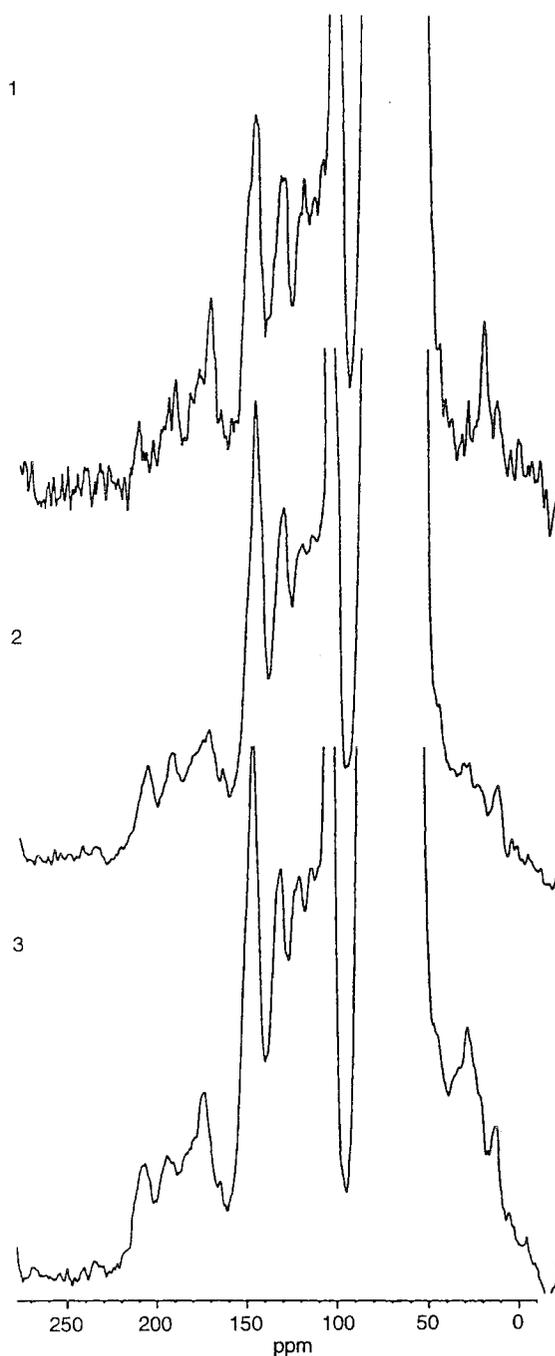
Fig. 1. Expanded to maximize 100–200 ppm region CP-MAS ^{13}C NMR spectra of (1) untreated, (2) first step heat treated (intermediate) and (3) second step heat treated (final) pine wood
Bild 1. Expandierte CP-MAS ^{13}C NMR-Spektren von (1) unbehandeltem Kiefernholz, (2) nach der ersten (Zwischen)-Stufe der Wärmebehandlung, (3) nach zweiten Stufe der Wärmebehandlung

tion of furfuraldehyde on the occasion of different studies after chemical reactions of wood under the influence of temperature has been reported in the literature (Bobleter and Binder, 1980; Fengel and Wegener, 1984; Dietrichs et al., 1978; Burtscher and Bobleter, 1987). Both aldehyde peaks decrease in intensity in the second step of the treatment and thus they are likely contributors to the formation of methylene bridges between lignin aromatic nuclei. The furfural peak increases more markedly in the first step and decreases more markedly in the second step, but both aldehydes decrease. The peak at 207–209 ppm is
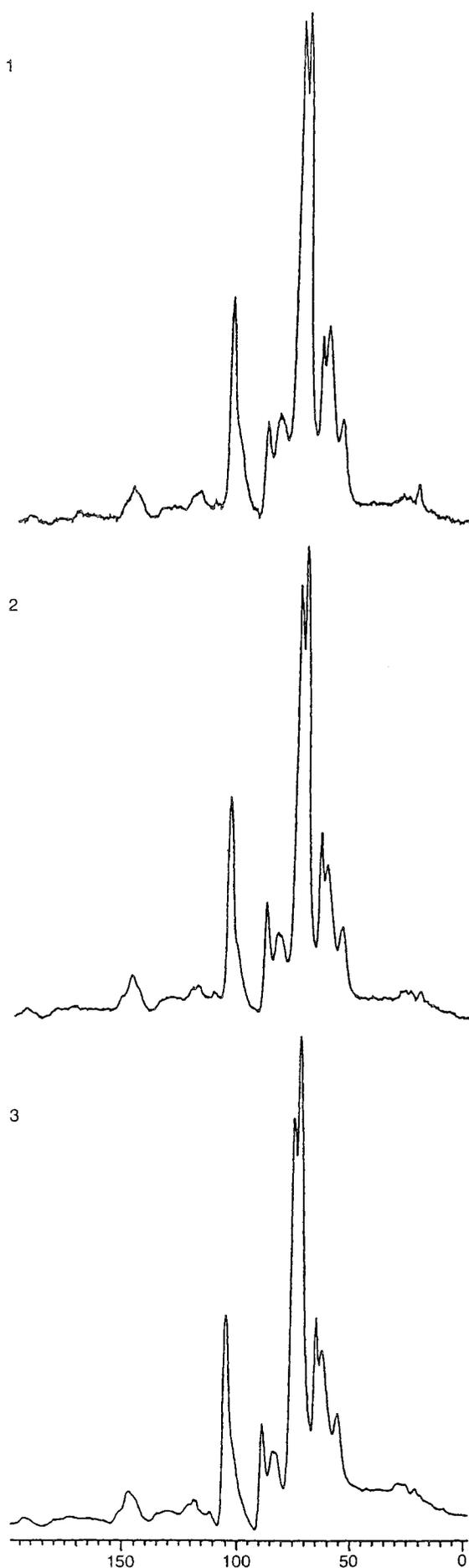
that of a quinone or of a ketone group, were the first is known to darken the wood which also is observed by all the heat-treated wood samples in this research.

4. Strongly connected to the preceding arguments is the appearance in the second step of the treatment of a peak at 127–128 ppm. This appearance of a peak in the region of reacted carbons of phenolic aromatic nuclei indicates condensation on the carbons of the aromatic ring. The same conversion to a more substituted aromatic ring is also confirmed by FTIR analyses of thermal modified wood (Tjeerdsma 1998) by a shift of the aromatic signal at 1510 cm^{-1} in the FTIR spectra. This indicates that indeed lignin aromatic ring sites which were free before the treatment and still free after the first treatment step have reacted after the second step, and are occupied by a methylene group, most likely the same methylene group coming from Cα cleavage of lignin described in point 2 above.

5. The peak at 175 ppm is the signal of the carbon of the carboxyl group (C=O) of acetic acid and its intensity decreases quite noticeably in the first, humid step of the reaction. Its shift value of 175 ppm indicates that this can only be obtained by deacetylation of the hemicelluloses induced by the moisture and heat of the first treatment step. It remains just about constant in the second treatment step. This is also confirmed by the decrease with heat treatment of the methyl group signal of acetic acid at 21–22 ppm. In comparative research using FTIR to study the chemical transformations during a heat treatment of wood, this observation of deacetylation of hemicellulose is also being confirmed by the decrease of the C=O signal for esters at 1740 cm^{-1} in the FTIR spectra. It can therefore be concluded that acetic acid is liberated in the first step of the treatment. It remains just about constant in the second treatment step.

6. Regarding the carbohydrates, the NMR spectra indicate also a decrease in the intensity of the carbohydrates C2 peak at 74–75 ppm particularly in the second, dry phase of the treatment, which might be a consequence of the deacetylation or of the opening of some of the pyranose rings. In this context it is interesting to note that while the crystalline carbohydrates C4 and C6 signals at 89 and 65 ppm respectively slightly increase during the treatment, the amorphous carbohydrates C4 and C6 signals at 84 and 62 ppm decrease markedly as a consequence of the treatment. This indicates that the aldehyde peaks produced are not only likely to be due to formaldehyde but also to a compound of the type of CH_2=CH—CHO (same signal region as formaldehyde) and possibly also due to glycoaldehyde HO—CH_2—CHO which is well known to be produced in the thermal treatments of wood carbohydrates (Fengel and Wegener, 1989).

All the occurrences described above appear to be the consequence of reactions which are not unfamiliar in wood chemistry describing the reactions in wood exposed to high temperatures and moist conditions. Thus the lignin cleavage at O4 and at Cα and its autocondensation reactions (points 1 and 2 above) are occurrences com-

Fig. 2. Standard CP-MAS ^{13}C NMR spectra of (1) untreated, (2) first step heat treated (intermediate) and (3) second step heat-treated (final) pine wood
Bild 2. Standard-CP-MAS ^{13}C NMR-Spektren von (1) unbehandeltem Kiefernholz, (2) nach der ersten (Zwischen)-Stufe der Wärmebehandlung, (3) nach zweiten Stufe der Wärmebehandlung

monly understood in for instance high temperature pulping.(Sjöström, 1981; Goyal and Lora, 1991). The formation of aldehydes and furfural has been established on numerous occasions (Runkel, 1951; Kollmann and Fengel, 1965; Bobleter and Binder, 1980; Ellis and Paszner, 1994.) and the stopping of this reaction at the level of furfural without further degradation can easily be ascribed to the relatively mild temperature and reaction time conditions used in the process. The formation of formaldehyde in acid/neutral conditions is not usual but instances of formaldehyde production from the cleavage of the carbohydrates C6 in wood, as well as from the Cγ of lignin are reported (Fengel and Wegener 1989). It has been recognised that the reaction of aldehydes with phenolic nuclei of lignin (points 2,3 and 4) to form methylene bridges other than those obtained by Cα can occur (Fengel and Wegener 1989). Equally the cleavage of the acetyl groups is known to occur in wood at high temperature and moisture conditions (Kollmann and Fengel, 1965; Dietrichs et al., 1978; Bourgois and Guyonnet, 1988), as well as the carbohydrate reactions outlined in point 6 above (Fengel and Wegener 1989).

Considering all the above described occurrences it is now important to understand how these reactions combine to give the improvement in performance characteristic of heat-treated wood. A possible explanation can be given as follows:

First treatment step
Formation of acetic acid from the hemicellulose, acetic acid which further catalyses carbohydrates cleavage, with some reduction of degree of polymerisation and some degradation to form formaldehyde, furfural and other aldehydes as well as some lignin cleavage at Cα and O4 and some aldehyde production from lignin units Cγ. Lignin autocondensation through the cleaved, positively charged benzylic Cα to form some methylene bridges already starts to occur in the first phase of the process. The increase in the number of free reactive sites on the aromatic ring of some lignin units already occurs in this stage but continues into the next.

Second treatment step
Completion of the autocondensation of lignin to some methylene bridges connecting aromatic nuclei. Reactive sites at the aromatic ring are created by the cleavage at Cα and O4 as well as by the demethoxylation at the aromatic ring of guaiacyl and syringyl units of the lignin complex.

The extent of these reactions is very mild, but nonetheless they result in an increase in cross-linking within the lignin-carbohydrate-complex (LCC) with consequent improvement of the hygroscopicity and the dimensional stability of wood. The formation, or better the reinforcing of a natural phenolic resin based on lignin in the wood network results also in an increase in water repellence of wood, as any synthetic phenolic resin would achieve too. The reduced hygroscopicity and dimensional stability of wood after a heat treatment is explained by the fact that the cellulose microfibrils are surrounded by a firm and more inelastic network due to increased cross-linking within the lignin complex. The cellulose microfibrils present a decreased expansion possibility and therefore less capacity to adsorb water between the cellulose chains, impeding the cell wall to swell. This results in wood with a consequent lower fibre saturation point (FSP), along with a

higher resistance against biological deterioration. Assumed to respond to a lower extent, both effects are also positively influenced by the transformed chemical composition of the wood (substrate). Hemicellulose, the most hydrophilic and easily digested wood component, has been transformed selectively and reacted into a hydrophobic network. The progressively darker wood colour, which becomes more noticeable the more severe are the treatments, is due to oxidation products such as quinones which are observed in the NMR analysis.

4
References

Armines (1981a) French patent 81-16463, No. 2-512-053; 1981b: European patent No. 0-073-714; 1985: USA patent No. 4,553,978

Bobleter O, Binder H (1980) Dynamischer hydrothermaler Abbau von Holz. Holzforschung 34 (2): 48–51

Bourgois J, Guyonnet R (1988) Characterization and analysis of torrified wood. Wood Sci. Technol. 22: 143–155

Burmester A (1973) Einfluß einer Wärme-Druck-Behandlung halbtrockenen Holzes auf seine Formbeständigkeit. Holz Roh-Werkstoff 31: 237–243

Burmester A (1975) Zur Dimensionsstabilisierung von Holz. Holz Roh- Werkstoff 33: 333–335

Burmester A, Wille WE (1976) Quellungsverminderung von Holz in Teilbereichen der relativen Luftfeuchtigkeit. Holz Roh- Werkstoff. 34: 87–90

Burtscher E, Bobleter O (1987) Chromatographic analysis of biomass reaction products produced by hydrothermolysis of Poplar wood. J. Chromat. 390: 410–412

Dietrichs HH, Sinner M, Puls J (1978) Potential of Steaming Hardwoods and Straw for Feed and Food Production. Holzforschung 32(6): 193–199

Ellis S, Paszner L (1994) Activated selfbonding of wood and agricultural residues. Holzforschung 48 (suppl): 82–90

Fengel D, Wegener G (1989) Wood: chemistry, ultrastructure, reactions. W. de Gruyter, Berlijn New York. 613p

Giebeler E (1983) Dimensionsstabilisierung von Holz durch eine Feuchte/Wärme/Druck-Behandlung, Holz Roh- Werkstoff 41: 87–94

Goyal GC, Lora JH (1991) Kinetics of delignification and lignin characteristics in autocatalyzed organosolv pulping of hardwoods. Proc. Int. Symp. Wood Pulp. Chem., Melbourne, Australia, vol. 1: 205–212

Hillis WE (1984) High temperature and chemical effects on wood stability. Wood Sci. Technol. 18: 281–293

Holz-Zentralblatt, 1996, 129, 2034

Kollmann F (1963) Über das Sorptionsverhalten wärmebehandelter Hölzer. Holz Roh- Werkstoff 21: 77–85

Kollmann F, Fengel D (1965) Änderungen der chemischen Zusammensetzung von Holz durch thermische Behandlung. Holz Roh- Werkstoff 23: 461–468

Noack D (1969) Über die Heißwasserbehandlung von Rotbuchenholz im Temperaturbereich von 100 bis 180 °C. Holzforschung Holzverwertung 21: 118–124

Runkel ROH (1951) Zur Kenntnis des thermoplastischen Verhaltens von Holz. Holz Roh- Werkstoff 9: 41–53

Runkel ROH, Witt H (1953) Zur Kenntnis des thermoplastischen Verhaltens von Holz. Holz Roh Werkstoff 11: 457–461

Ruyter HP (1989) European patent Appl. No. 89-203170.9

Seborg RM, Tarkow H, Stamm AJ (1953) Effect of heat upon the dimensional stabilisation of wood. J. For. Prod. Res. Soc. 3(9): 59–67

Sjöström E (1981) Wood chemistry: Fundamentals and Applications. Academic Press, Inc. San Diego. 293p

Stamm AJ (1956) Thermal Degradation of Wood and Cellulose. Ind. Eng. Chem. 48(5): 413–417

Tjeerdsma BF (1998): FTIR characterisation of thermal modified wood. PH.D. Thesis, University of Wageningen, The Netherlands

van Zuylen A (1995) Platonische lifde voor hout. Chemisch magazine 212–213, May