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Heat-treated timber: potentially toxic byproducts presence and extent of wood cell wall degradation

D. P. Kamdem, A. Pizzi, M. C. Triboulot

Wood which underwent a relatively mild thermal treatment according to a one-step process leading to improved dimensional stability and improved timber performance was extracted with organic solvents to determine the presence of potentially toxic compounds produced by the thermal treatment. The extractives were examined by GC-Mass spectrometry as well as by ^{13}C NMR to determine which type of loose chemical compounds were produced by the thermal treatment. The formation of some toxic polynuclear aromatic hydrocarbons derivatives of phenantrene as well as other classes of polyaromatics compounds was detected. It is most likely that the presence of all such compounds contributes, perhaps to a relatively substantial extent, to the reported resistance of heat treated timber to fungal and other biological attack. Other allegedly non-toxic compounds due to wood constituents degradation were also found, mainly the by-products of lignin pyrolysis. The extent of toxic and non-toxic compounds in the heat treated wood were not quantified, but it can be stated that their proportion appears to be quite small. The lack of quantification of the concentration of these products does not allow to ascertain if the final product is toxic or not, and to what extent. Nonetheless, the amount of polynuclear aromatic hydrocarbon-type derivatives should be quantified and related to the type of heat treatment process undertaken before assigning to this type of wood treatment a completely clean health safety label.

Hitzebehandeltes Holz: Mögliche toxische Nebenprodukte und Ausmaß des Zellwandabbaus

Relativ milde Hitzebehandlung mit einem Ein-Schritt-Verfahren führte zu verbesserter Dimensionsstabilität und verbessertem Schnittverhalten. Dieses Holz wurde mit organischen Lösemitteln extrahiert um mögliche toxische Nebenprodukte des Verfahrens zu bestimmen. Zu diesem Zweck wurden die Extrakte mittels GC-MS und ^{13}C NMR untersucht. Einige toxische polykondensierte Aromaten vom Phenantrentyp und andere Polyaromaten wurden gefunden. Es ist möglich, daß diese zur bekannten Widerstandsfähigkeit des hitzebhandelten Holzes gegen Pilze und andere Mikroorganismen beitragen. Gefunden wurden auch andere, vorgeblich nicht-toxische Aubbauprodukte der Holzkomponenten, insbesondere aufgrund der Ligninpyrolyse. Die Substanzen wurden nicht quantitativ bestimmt; ihr Anteil ist jedoch sehr gering. Daraus kann man allerdings nicht schließen, ob diese Produkte tatsächlich toxisch sind oder nicht. Denn dazu müßten diese Abbauprodukte quantifiziert werden und den verschiedenen Methoden der Hitzebehandlung zugeordnet werden, bevor ein Gesundheitsrisiko ausgeschlossen werden kann.

1
Introduction

Recent work on the heat treatment processes of timber to prepare what is currently called torrefied wood in France, plato wood in the Netherlands and retified wood in the USA has shown that such types of processes can improve the performance of timber in several aspects (Ruyter 1989; van Zuylen 1995; Holz-Zentralblatt 1996). Foremost advantages of wood treated in this manner are its resistance to fungal decay (Ruyter 1989; van Zuylen 1995) without the need to use wood preservatives, with consequent environmental advantages, notably improved water repellancy, and improved dimensional stability to moisture variations. One-step (Armines 1981a, b, 1985) and two-steps (Ruyter 1989; van Zuylen 1995) heat treatment processes have been reported. The chemistry of the modification of the polymeric wood constituents induced by such heat treatments and leading to all such improvements has recently been investigated by CP MAS ^{13}C NMR, elucidated and reported (Tjierdsma et al 1998). However, the somewhat dark appearance of the heat-treated wood, as well as its very characteristic and persistent odour indicated that derivatives of extractives, lignin, hemicellulose and cellulose are generated. These byproducts might further react to form polynuclear aromatic hydrocarbons. As the issue of toxicity of any consumer products is to-day a very topical one, it was necessary to investigate the decomposition compounds produced.

This article deals with the extraction, isolation and characterization by GC-Mass spectrometry and by ^{13}C NMR of the byproducts found in wood heat-treated from a one-step process.

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Experimental

Maritime pine and poplar samples of dimensions 50 × 100 × 2000 mm were heat treated during 6 h at

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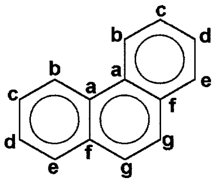
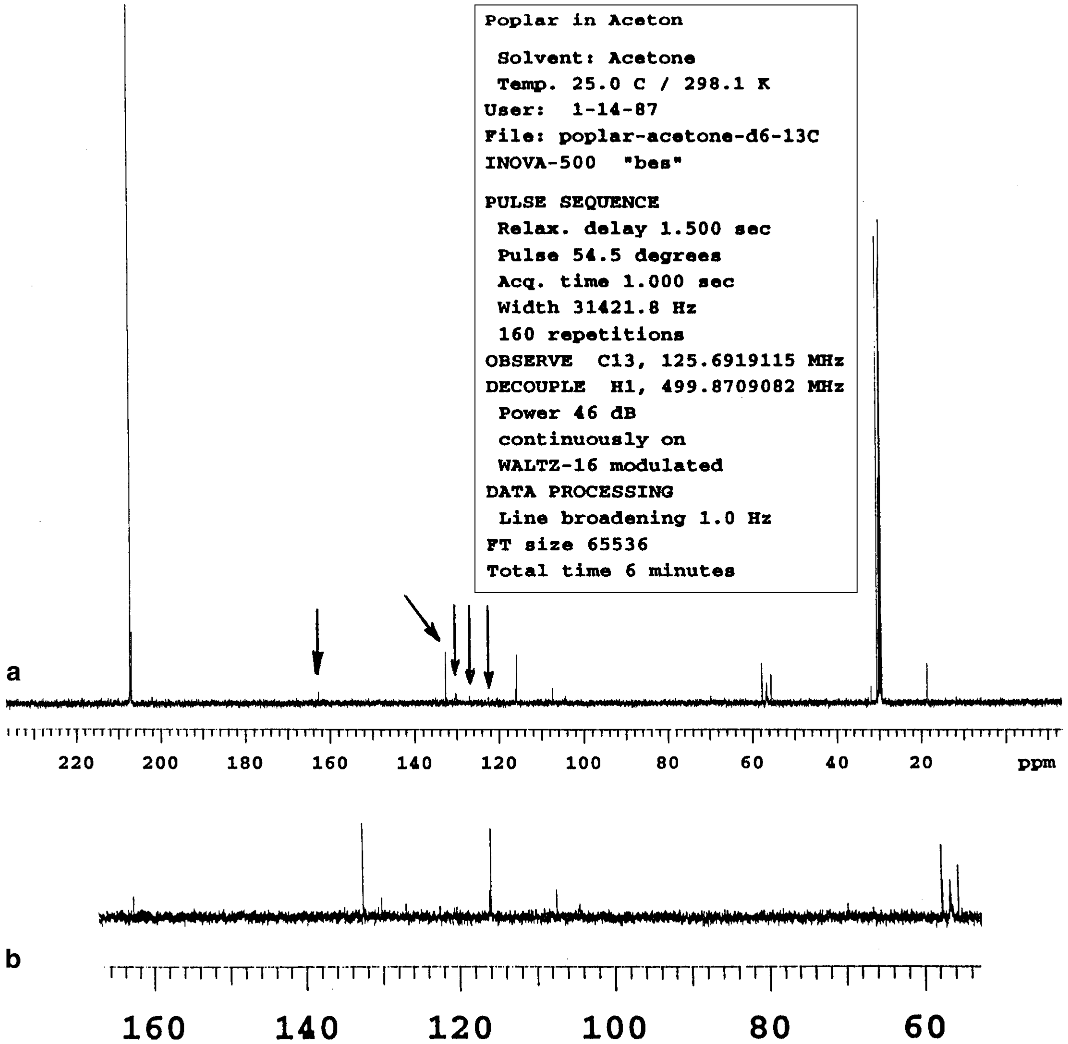
temperature varying from 200 to 250 °C depending on species (Avat 1993). About 10 g of each species were ground and soxhlet extracted for 8 h with either acetone or diclhoromethane. The extractives were roto-evaporated to remove the extra solvent and increase the concentration of the extracted compounds. The extracted materials were further dissolved in acetone and analyzed with GC/MS and NMR. An HP5890 FID gas chromatography fitted with 30 m by 0.25 mm (0.25Fm film thickness) DB 5 and DBwax fused silica capillary columns from J&W which was programmed and used as follows: 40 °C for 5 min, from 40 °C to 300 °C at 5 °C per min and at 300 °C for 15 min. The injector and the detector were set at 300 °C and the flowrate of the helium carrier gas was 1 ml per minute and a split at 80 to 1. Compounds were identified using the HP5970msd in the EI mode at 200 °C and 70 eV. About 5 ml of the extracted products diluted in acetone at a ratio of 1:10 was injected in the GC/MS. CP/MAS C^{13} NMR spectra were obtained at 100.6 MHz on a Brüker DPX 400 equipped with a 6 mm diameter solid probe. Acquisition time was 0.068 s. The pulse repetition time was 4 s and the cross polarization contact time was 1.5 ms. The data points were close to 4 K. The rotation spinning of the sample was 4500 Hz. Chemical shifts were measured with respect to TMS. A total of 5000 to 10000 scans were accumulated for each sample. The spectral width was 30000 Hz (−300 ppm).

Industrially heat treated wood samples of dimensions 20 × 100 × 300 mm treated according to the Armine patents was examined by scanning electron microscopy using a Hitachi 520 scanning electron microscope.

3
Results and discussion

The first indication of the presence of polynuclear aromatic hydrocarbons derived by a phenantrene derivative subpattern present almost in its pure state in the acetone extract of poplar wood. The spectrum in Fig. 1a and its detail in Fig. 1b illustrate well this case.





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Poplar in Aceton

 Solvent: Acetone
 Temp. 25.0 C / 298.1 K
User:  1-14-87
File: poplar-acetone-d6-13C
INOVA-500  "bes"

PULSE SEQUENCE
 Relax. delay 1.500 sec
 Pulse 54.5 degrees
 Acq. time 1.000 sec
 Width 31421.8 Hz
 160 repetitions
OBSERVE  C13, 125.6919115 MHz
DECOUPLE  H1, 499.8709082 MHz
 Power 46 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 6 minutes
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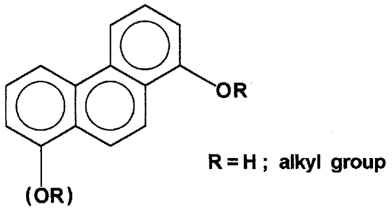
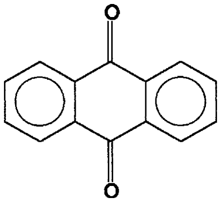
Fig. 1a, b. ^{13}C NMR spectrum of acetone extract of heat treated poplar wood: **a** full spectrum, **b** detail of the phenantrene-type pattern
Bild 1a, b. ^{13}C NMR Spectrum des Acetonextrakts von hitzebehandeltem Pappelholz. **a** gesamtes Spektrum; **b** Detail der Phenantrene-Strukturen

The following signal of the sub-pattern can be clearly assigned for the phenantrene structure in the above Figure: (a) observed 132.2 ppm (theoretical 131.9 ppm); (b) observed 122.4 ppm (theoretical 122.4 ppm); (c) and (d) observed 127 ppm (theoretical 126.3 ppm); (f) observed 130.0 ppm (theoretical 130.1 ppm); (g) observed 126.3 ppm (theoretical 126.6 ppm). The only carbon of the structure of phenantrene, whose signal cannot be found, is that of the two (e) carbon, a signal which theoretically should be found at 128.3 ppm. No such signal is present in the spectrum. However, the aromatic carbon of a phenolic -OH, or to the aromatic carbon of a ether $(Ar)\underline{C}-O-$, is present at 162 ppm and from its relative intensity definetely belongs to the pattern of the phenantrene structure. The phenantrene derivative structure which is proposed is then as follows:



On the base of this experiment, the presence of a potentially toxic polynuclear aromatic derivative structure appears to be characteristic only of poplar wood having undergone heat treatment. In the spectrum in Fig. 1, the peaks characteristic of the acetone solvent used for the extraction are clearly visible at 207.2 and 30.5 ppm and constitute the primary, dominant pattern of the spectrum. However, in this dominant pattern a series of very evident peaks in the range 29.3–30.3 ppm indicate the presence of methyl (CH_3-) and mainly methylene (-CH_2-) groups characteristic of long aliphatic saturated hydrocarbon-type chains, whose methylene groups are generally found between 29.5 and 32.4 ppm. They constitute the majority of the compounds extracted with acetone from heat-treated poplar wood. A series of even smaller peaks, a tertiary pattern, is also present in the acetone extract of poplar, namely peaks at 124.9 ppm, 122.5 ppm, 115.8 ppm (this characteristic of a lignan), at 107.2 ppm, 70 ppm, 56–58 ppm and 19 ppm. These are likely to belong to traces of different compounds, and it is not possible to interpret exactly what they represent.

The presence of polyaromatic phenantrene-type structures in acetone extract of treated wood appears to be confirmed by GC-Mass spectrometry from one of the mass spectra obtained (Fig. 2) for treated pine wood extract (elution time 10 min 15 s). A phenantrene with a phenolic -OH in the (e) site would give a parent peak at 194 and a fragmentation pattern where characteristic peaks should appear at 91 (a tropylium cation); 79 ($C_6H_7^+$), 78 ($C_6H_6^+$),77 ($C_6H_5^+$); 66, 65 (by elimination of an acetylene molecule from the tropylium ion). All these peaks do indeed appear in the mass spectra in Fig. 2. However, other fragmentation peaks characteristic of other compounds also occur indicating that the compound is impure. In Fig. 3 from the poplar acetone extract the characteristic decomposition pattern of athracenedione is evident.



In the case of poplar, other compounds definetely nontoxic were also present in the same extract – all identified by GC-MS – mainly vanillin, as well as a compound having the same parent peak of vanillin which could not be properly identified but which appeared to be acenaphtylene.

Equal NMR experiments on acetone extracts on spruce and pine timber do not yield a phenantrene pattern, indicating that polyaromatics are likely to be present in too low a concentration to be detectable by NMR. Conversely, the acetone extracts of both heat-treated spruce and pine timber clearly present an equally intense pattern of methylene (-CH_2-) groups characteristic of long aliphatic saturated hydrocarbon-type chains as observed for poplar.

In the case of heat treated pine acetone extract, several compounds were identified by GC-mass spectrometry, namely a compound that at first was thought to be vanillin (elution time 7 min 25 s) but which then proved to be acenaphtylene, 2-methoxy-4-(1-propenyl)-phenol acetate

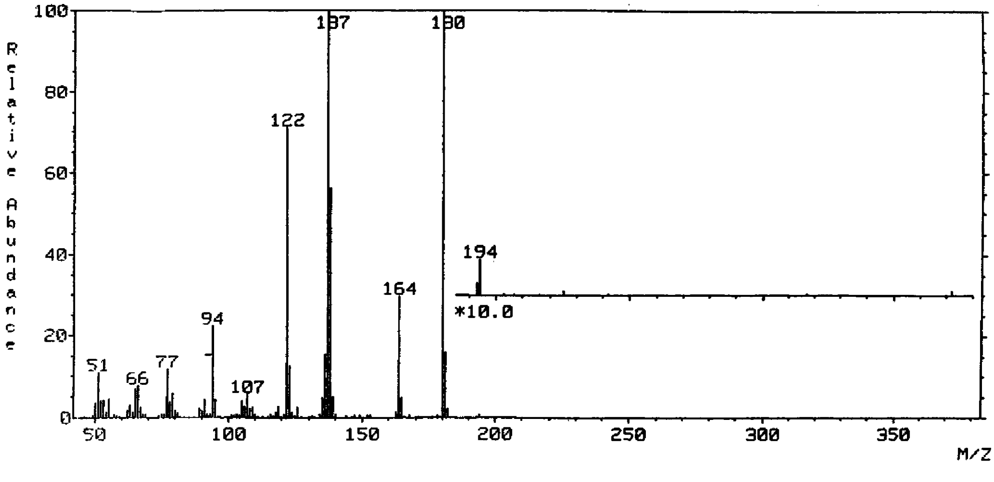


Fig. 2. Mass spectrum of compound obtained at elution time 10 min 15 s from the acetone extract of heat treated pine wood
Bild 2. Massenspektrum der Komponente, die nach 10 Min. und 15 Sek. aus dem Acetonextrakt von hitzebehandeltem Kiefernholz eluiert wird

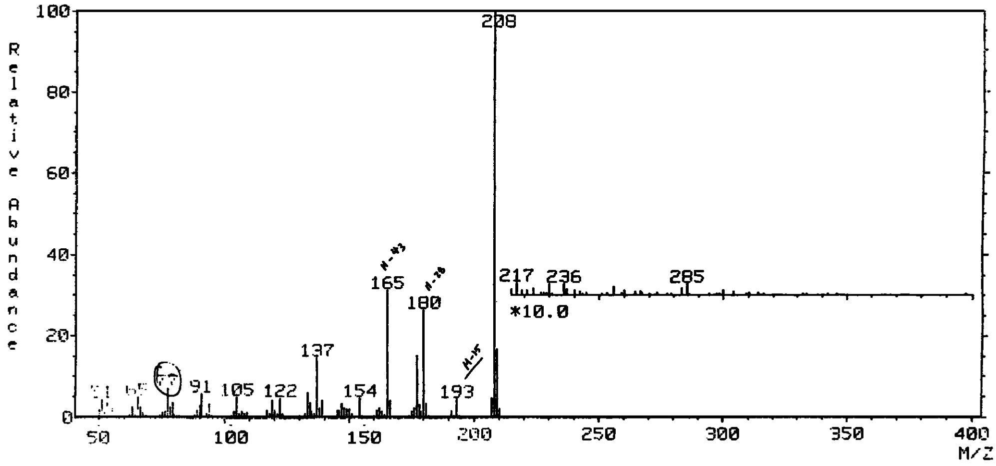


Fig. 3. Mass spectrum of a compound (anthracenedione) obtained from the acetone extract of heat treated poplar wood

Bild 3. Massenspektrum einer Komponente (Anthracendione) aus dem Acetonexktrakt von hitzebehandeltem Pappelholz

(elution time 8 min 15 s), acenaphtylenoic acid (elution time 9 min 6 s) and a complex compound at 28 min 54 s elution time which was identified as dehydroabietic acid. Thus, two compounds of acenaphtylene structure were found, the most definite being, shown in Fig. 4, whose mass decomposition pattern is $m^+ = 196$, 179 (-OH), 164/163 (- -O-), 131, 121(-CO_2 from the 165/163 peak), 103 (the methyl tropylium cation which is the general precursor of the 91 peak), 91 (a tropylium cation due to the presence of the 65 peak is most likely, or $C_6H_5CH_2^+$), 77 ($C_6H_5^+$); 66, 65 (by elimination of an acetylene molecule from the tropylium ion), 55, 51.

Heat treated poplar and heat treated acetone were also extracted with methylene chloride and the extracts examined by ^{13}C NMR without separation of the mixture to try to get confirmation of some of the other findings. In both extracts the considerable amount of methylene groups coming from aliphatic saturated hydrocarbon-type chains is again observed. In the case of the treated pine extract, the signals of several polyaromatic hydrocarbon structures are noticeable in the 120–130 ppm region. The signals pertaining to the peaks of the acenaphtylene, but also of other similar structures, are visible, but the mix not being separated, it is impossible to identify all the polyaromatics transmitting in this region. The same is valid for the poplar extract, again in the case of the methylene chloride extract the mixture being unresolved.

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Conclusions

Wood which has undergone a relatively mild thermal treatment according to a one step process leading to improved dimensional stability and improved timber performance and extracted with organic solvents, showed the presence of polyaromatic compounds produced by the thermal treatment degradation of wood constituents. The leachates were examined by GC-Mass spectrometry as well as by ^{13}C NMR to determine which type of chemical compounds were produced by the thermal treatment. Polynuclear aromatic hydrocarbons derivatives of phenantrene and acenaphtylene as well as other classes of polyaromatics compounds appeared to be present. It is most likely that the presence of all such compounds contributes, perhaps to a relatively substantial extent, to the reported resistance of heat treated timber to fungal and other biological attack. Other non-toxic compounds due to wood constituents degradation were also found. The extent of toxic and non-toxic compounds in the heat treated wood were not quantified, but their proportion appears to be quite low. The lack of quantification of the concentration of these products does not allow to decide whether the final product is toxic or not, and if it is, to what extent. Nonetheless, both quantifications related to the type of heat treatment as well as optimization at lower temperature, perhaps by the use of appropriate catalysts, should be

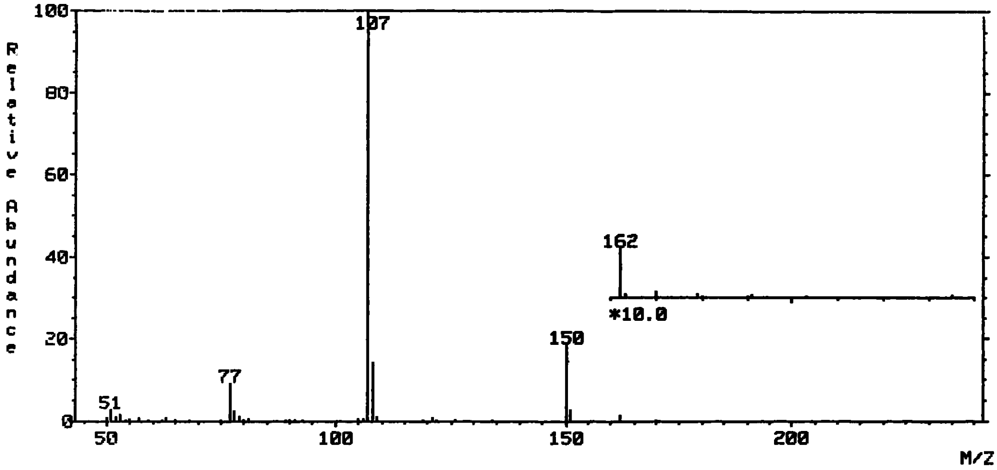

Fig. 4. Mass spectrum of a compound obtained from the acetone extract of heat treated pine wood

Bild 4. Massenspektrum einer Komponente aus dem Acetonextrakt von hitzebehandeltem Kiefernholz undertaken before assigning to this type of wood treatment a completely clean health safety label.

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