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Chemical changes to woody polymers due to high-temperature thermal treatment assessed with near infrared spectroscopy



Jakub Sandak, Anna Sandak* and Ottaviano Allegretti

IVALSA, CNR Trees and Timber Institute, National Research Council, via Biasi 75, 38010 San Michele all Adige, Italy.
E-mail: anna.sandak@ivalsa.cnr.it

Near infrared spectroscopy and an original approach for visualisation of spectra are proposed here for characterisation of vacuum thermally modified samples of eight wood species representing softwoods and hardwoods. Significant changes in absorption bands were observed in conjunction with an increase of treatment temperature. A novel method for visualisation of the degradation patterns (xylograms) is capable of highlighting peculiarities in chemical changes to woody polymers due to the thermal treatment. This method also allows observation of kinetics and permits comparison of thermal stability of investigated species. Such knowledge might be helpful for further optimisation of thermal treatment procedures at an industrial scale. Furthermore, xylograms as a simple and illustrative method might be suitable for visualisation of other modification processes of wood as well as of other materials.

Keywords: chemical changes of wood, xylograms, thermally modified wood, vacuum thermal treatment

Introduction

Fourier transform near infrared (FT-NIR) spectroscopy is a technique with a great potential for non-destructive assessment of organic materials. However, proper spectral presentation and its direct interpretation are challenging. Several pre-processing methods are used for spectral pre-treatment, including baseline correction, normalisation, derivatives, smoothing or scatter correction, amongst others. Selection of the optimal algorithm is case dependent because any pre-processing should eliminate measurement errors, while preserving the information recorded in the spectra thereby highlighting differences related to the chemical state of the materials being investigated. According to Rinnan *et al.*,¹ the reason for pre-processing of NIR data is to remove physical phenomena in the spectra (so called scatter) in order to improve the subsequent multivariate regression, classification model or exploratory analysis. However, most pre-processing methods, especially when used in isolation, might

degrade the data or lose useful information while improving certain qualities of the data.²

An alternative spectral presentation approach as described here was inspired by the work of Tsenkova and her *aquagrams* concept.³ Accordingly, selected NIR bands assigned to functional groups of woody polymers were extracted from the spectra and were used as "information hubs". The distinctive signal pattern, called here a "xylogram", was used for highlighting chemical changes to series of interrelated samples. Thermally modified wood was selected for this research, as various chemical reactions occur to the material during treatment. These include dehydration, depolymerisation, degradation and thermo-oxidation, which take place with different rates depending on the wood species, process duration and treatment temperature.^{4,5} Attempts to understand chemical changes during heat treatment of wood have been made by several authors,^{6–8} using diverse analytical methods. However,

the results reported were usually limited to only a few species or narrow range of treatment conditions. Exact assessment of changes to particular chemical components is rather difficult, since a range of complex chemical reactions occur simultaneously when exposing wood to elevated temperatures. For that reason, sophisticated statistical and chemometric methods are necessary to emphasise chemical changes caused by temperature.^{9,10} It was also demonstrated by analysing isolated wood components that mechanisms of its thermal treatment are considerably different when compared to native wood degradation.^{11,12}

The goal of this research was to exploit the potential of NIR spectroscopy for evaluation of the chemical changes to wood exposed to thermal treatment in vacuum conditions. A new approach of spectral data analysis and representation (xylograms) was developed in order to visualise patterns of chemical degradation noticed for different wood species. Better understanding of the modification kinetics might lead to further adjustment of the current thermal modification procedures in order to optimise industrial processes.

Materials and methods

Experimental samples

Eight wood species, namely Norway spruce (*Picea abies*), silver fir (*Abies alba*), European larch (*Larix decidua*), European beech (*Fagus sylvatica*), sessile oak (*Quercus petraea*), European ash (*Fraxinus excelsior*), wild cherry (*Prunus avium*) and black locust (*Robinia pseudoacacia*), were utilised as experimental samples. Five replicates per treatment (50 mm in length × 40 mm in width × 10 mm in thickness) were cut out from wooden boards (heartwood zone) previously thermally modified with varying process conditions. All samples were conditioned before measurement in a climatic chamber (20 °C, 60% relative humidity) to constant mass. The wood surfaces were refreshed after treatment by sanding with a P240 paper. The border values for the degradation model correspond to the reference samples for each species as either untreated wood, or extensively degraded (torrefied) soft- and hardwoods kept in the reactor for 20 subsequent treatment cycles.

Table 1. Band assignments of wood components according to Schwanninger *et al.*¹³

Band no.	Wavenumber (cm ⁻¹)	Wood component	Functional group
1	4063	Carbohydrate	CH, C–C
2	4195	Lignin	Not assigned
3	4202	Holocellulose	OH
4	4235	Cellulose	OH, CH, CH ₂
5	4268	Cellulose	CH, CH ₂
6	4283	Cellulose, hemicellulose	CH
7	4288	Hemicellulose (xylan)	CH
8	4365	Cellulose	CO, OH, CH ₂
9	4401	Cellulose, hemicellulose	CH, CH ₂ , OH, CO
10	4546	Lignin	CH, C=O
11	4608	Cellulose, hemicellulose	Not assigned
12	4635	Cellulose	OH, CH
13	4686	Hemicellulose/lignin/extractives	CH, C=C, C=O
14	4739	Cellulose	OH
15	4780	Cellulose	OH, CH centre of range
16	4795	Cellulose, hemicellulose (xylan)	OH, CH
17	4808	Cellulose semicrystalline and crystalline	OH, CH
18	5051	Water	OH
19	5198	Water	OH centre of range
20	5236	Hemicellulose	C=O
21	5245	Hemicellulose	C=O
22	5464	Cellulose semicrystalline and crystalline	OH, CO
23	5495	Cellulose	OH, CO
24	5522	Lignin	Not assigned
25	5593	Cellulose semicrystalline and crystalline	CH
26	5618	Cellulose	CH ₂
27	5666	Not assigned	CH, CH ₂

Table 1. Continued

Band no.	Wavenumber (cm ⁻¹)	Wood component	Functional group
28	5692	Not assigned	CH ₂
29	5776	Cellulose	CH
30	5795	Lignin	CH
31	5800	Hemicellulose (furanose/pyranose)	CH
32	5816	Cellulose/hemicellulose/lignin	CH
33	5865	Hemicellulose	CH
34	5872	Cellulose	CH
35	5900	Not assigned	CH
36	5935	Lignin	CH
37	5950	Hemicellulose	CH
38	5963	Lignin	CH
39	5995	Extractives	CH
40	6003	Hemicellulose	CH
41	6126	Cellulose	OH
42	6188	Not assigned	CH
43	6286	Cellulose crystalline	OH
44	6334	Cellulose	OH
45	6450	Cellulose crystalline	OH
46	6472	Cellulose	OH
47	6520	Cellulose	OH
48	6622	Cellulose	OH
49	6660	Cellulose	OH
50	6700	Hemicellulose (glucomannan)	OH
51	6715	Cellulose semicrystalline	OH
52	6740	Cellulose	OH
53	6757	Cellulose	OH
54	6770	Cellulose	OH
55	6790	Cellulose semicrystalline	OH
56	6800	Hemicellulose (glucomannan)	OH
57	6874	Lignin	OH
58	6944	Lignin	CH
59	6974	Not assigned	OH
60	7003	Amorphous cellulose/water	OH
61	7092	Lignin, extractives	OH
62	7215	Not assigned	OH, CH
63	7300	Hemicellulose/all	CH
64	7315	Cellulose	CH beginning
65	7321	Cellulose	CH end
66	7353	All	CH
67	7410	Hemicellulose/all	CH
68	8160	Cellulose	CH beginning
69	8250	Cellulose	CH end
70	8654	Hemicellulose	CH
71	8749	Lignin	CH

Thermal treatment

The thermal treatment was performed under vacuum (250 mbar) for 3 hours in a thermovacuum processor. The treatment temperatures varied from 160 °C to 220 °C, with increments of 20 °C. Additional details regarding the experimental plant, treatment conditions and applied schedule can be found in Sandak *et al.*¹²

FT-NIR measurements

A FT-NIR spectrometer (VECTOR 22-N) produced by Bruker Optics GmbH (Ettlingen, Germany) equipped with a fibre-optic probe was used for spectral collection. The measured spectral range was between 4000 cm⁻¹ and 12,000 cm⁻¹ (2500 nm and 833 nm) with a resolution of 8 cm⁻¹. The spectral wavenumber interval was 3.85 cm⁻¹ and zero-filling = 2. Each spectrum was computed as an average of 32 consecutive internal scans. FT-NIR measurements were performed in a climatic chamber (20 °C, 60% relative humidity), on the radial face, five times for each sample.

Data evaluation

A total of 975 spectra were acquired and evaluated. An average of 25 measurements (5 scans on 5 replicates) was considered as a reference spectrum representing each treatment. Opus QUANT 6.5 (Bruker), PLS_toolbox (Eigenvector Research, Manson, WA, USA, www.eigenvector.com) and LabVIEW 13 (National Instruments, Austin, TX, USA, www.ni.com) software packages were used for spectral pre-processing and data mining. Spectral bands were assigned according to Schwanninger *et al.*¹³ and are summarised in Table 1. The baseline correction was performed with an automatic weighted least squares (Whittaker filter) algorithm of 10th order. Second derivative transformation was computed with a Savitzki-Golay¹⁴ algorithm, second-order polynomial and 21 smoothing points.

Generation of xylogram

Dedicated software for creation of xylograms was developed in LabVIEW. The spectral pre-processing included computation of second derivatives for all treated samples, including both references (untreated and extensively torrefied). The degradation coefficient of thermal treatment c_{tr} was computed according to equation (1):

$$c_{tr}(\lambda) = \frac{s_{nt}(\lambda) - s_{tr}(\lambda)}{s_{nt}(\lambda) - s_{end}(\lambda)} \quad (1)$$

where s_{nt} is the absorbance spectra of reference (untreated wood), s_{tr} the absorbance spectra of treated wood, s_{end} the absorbance spectra of extensively treated wood and λ the wavelength of the infrared light corresponding to the particular functional group.

An example xylogram including details of the assigned bands is presented in Figure 1. It was intended that the reference points were not sorted according to wavenumber value but were grouped according to chemical component and functional group. The outer perimeter corresponds to $c_{tr} = 0$

and indicates negligible changes to the NIR spectra. All the results plotted within the central part of the xylogram indicate significant changes to the NIR spectra and extensive degradation of the corresponding component/functional group. A value of $c_{tr} = 1$ indicates a fully degraded chemical component corresponding to that of wood after extended torrefaction. The expected degradation pattern is that the c_{tr} values gradually change from the outer to the inner part of the xylogram, following the acquired thermal treatment dose.

Results and discussion

The raw result of measurement with an NIR spectrometer is an NIR spectrum. Unfortunately, it is rather impractical to directly interpret it when assessing biological materials. This is due to the fact that anisotropic optical properties of a rough wood surface affect the spectrum by adding a significant signal related to light scatter. Consequently, signal pre-processing is usually applied in order to extract chemical information from a spectrum. It has to be mentioned that the original profile of the NIR spectrum may change after pre-processing, and artificial peaks may be generated. It was observed that the NIR spectra as measured from the thermally modified wood were clearly affected by the treatment intensity. Baseline correction (Whittaker filter) was applied and resulting spectra were plotted for each wood species investigated. Figure 2 presents a general trend of the changes in spectra as related to the treatment intensity. A clear decrease of the absorbance can be noticed with increasing temperature from untreated towards torrefied wood. It was also evident that not all spectral bands changed with the same rate and intensity. However, the approach of analysing the effect of the thermal treatment with spectra which had only baseline correction can be used merely for preliminary analysis. This is due to the fact that the algorithm artificially modifies the outline of the spectrum by zeroing selected spectral points. Therefore the chemical information is still preserved, but extensively distorted. For that reason, the second derivative of NIR spectra, effectively removing the scatter but still preserving spectral features, was selected as a pre-treatment method for xylograms.

Spectral analyses were used for highlighting different mechanisms of thermal decomposition of wood chemical components. Significant changes in absorption bands were observed together with increase in temperature in all wood species investigated (Figure 3). It was noticed that the response of softwoods to the thermal treatment was slightly different from that of hardwoods. Fir seems to be most sensitive to temperature treatment among the investigated softwoods as clear variations in the c_{tr} values were observed in several bands. In particular, absorbance at 4268 cm⁻¹ (5), 4283 cm⁻¹ (6), 4288 cm⁻¹ (7), 4401 cm⁻¹ (9), 5618 cm⁻¹ (26) and 5950 cm⁻¹ (37) linked to CH groups of carbohydrates as well as 6286 cm⁻¹ (43) associated with hydroxyl groups of crystalline cellulose show significant change after treatment at 200 °C. Other bands, e.g. corresponding to lignin at 4564 cm⁻¹ (10), 5935 cm⁻¹ (36), 6874 cm⁻¹

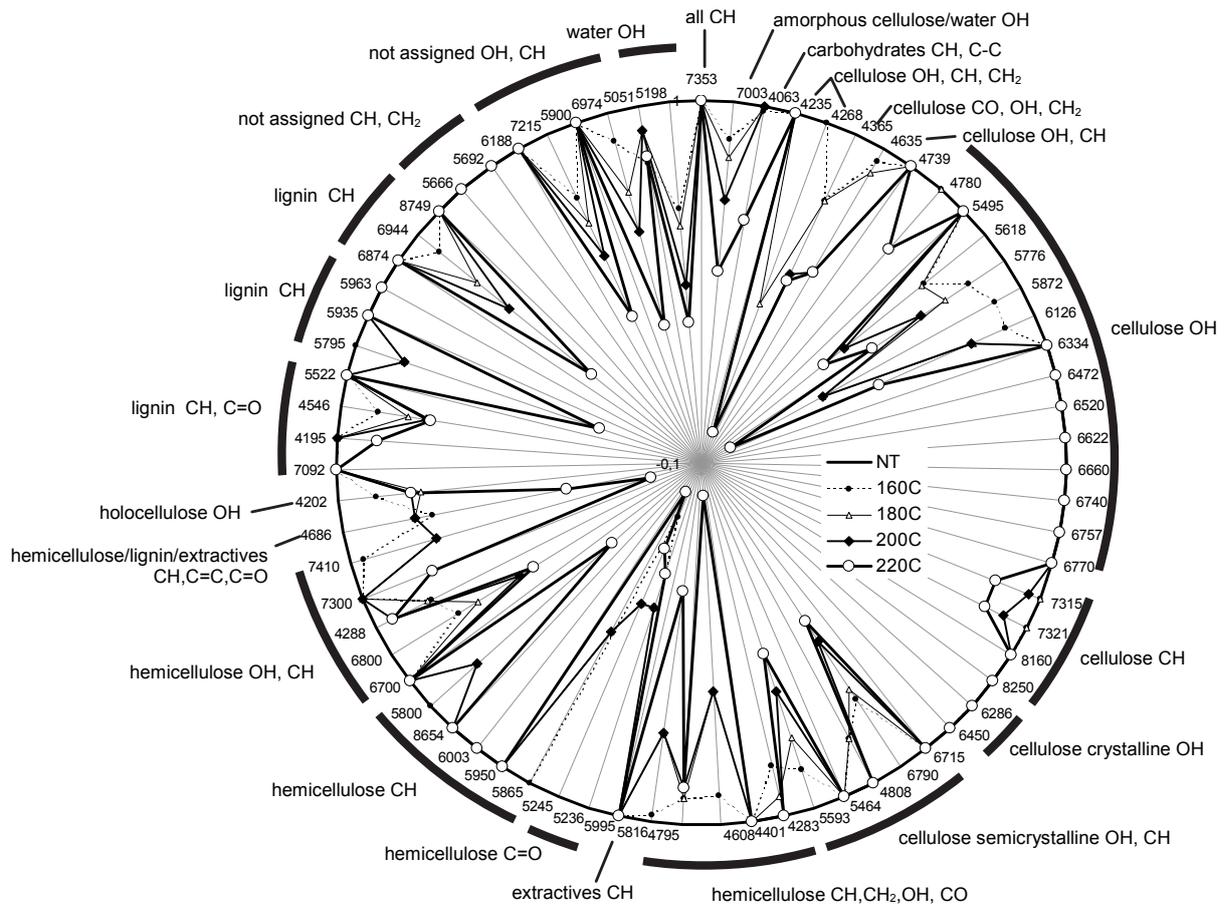


Figure 1. Example of xylogram with band assignments (NT, untreated).

[57] and 6944 cm^{-1} [58], also vary. Conversely, hydroxyl groups of celluloses (right part of xylograms – bands 46–49 and 52–54) exhibit no alteration for all softwoods investigated, especially when comparing with some hardwoods. Closer examination of the xylograms provides additional information regarding kinetics of chemical changes. Degradation progress due to temperature is clearly noticeable in the case of hemicelluloses, e.g. band at 5950 cm^{-1} [37], especially for spruce and fir.

A marked decrease of c_{tr} values for fir wood occurred already at $180\text{ }^{\circ}\text{C}$. On the other hand, only a few bands related to hemicelluloses in larch wood [5236 cm^{-1} [20] and 5245 cm^{-1} [31]] holocellulose [4202 cm^{-1} [3]] and lignin [4195 cm^{-1} [2]] exhibited immediate or marked alterations.

Diffuse porous wood was represented by beech and cherry. Among both species, beech seems to be less sensitive to heat treatment (especially when considering the upper and right

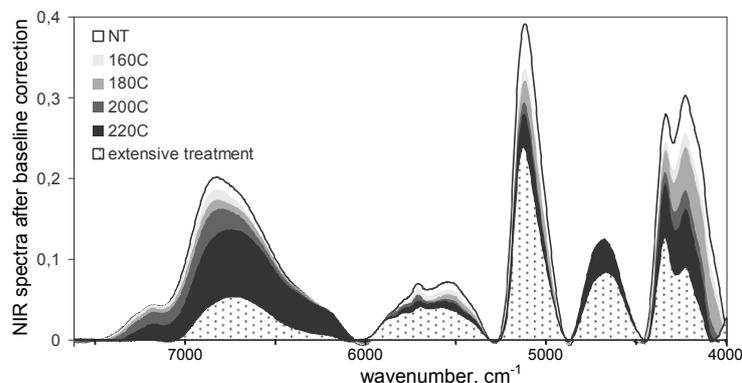
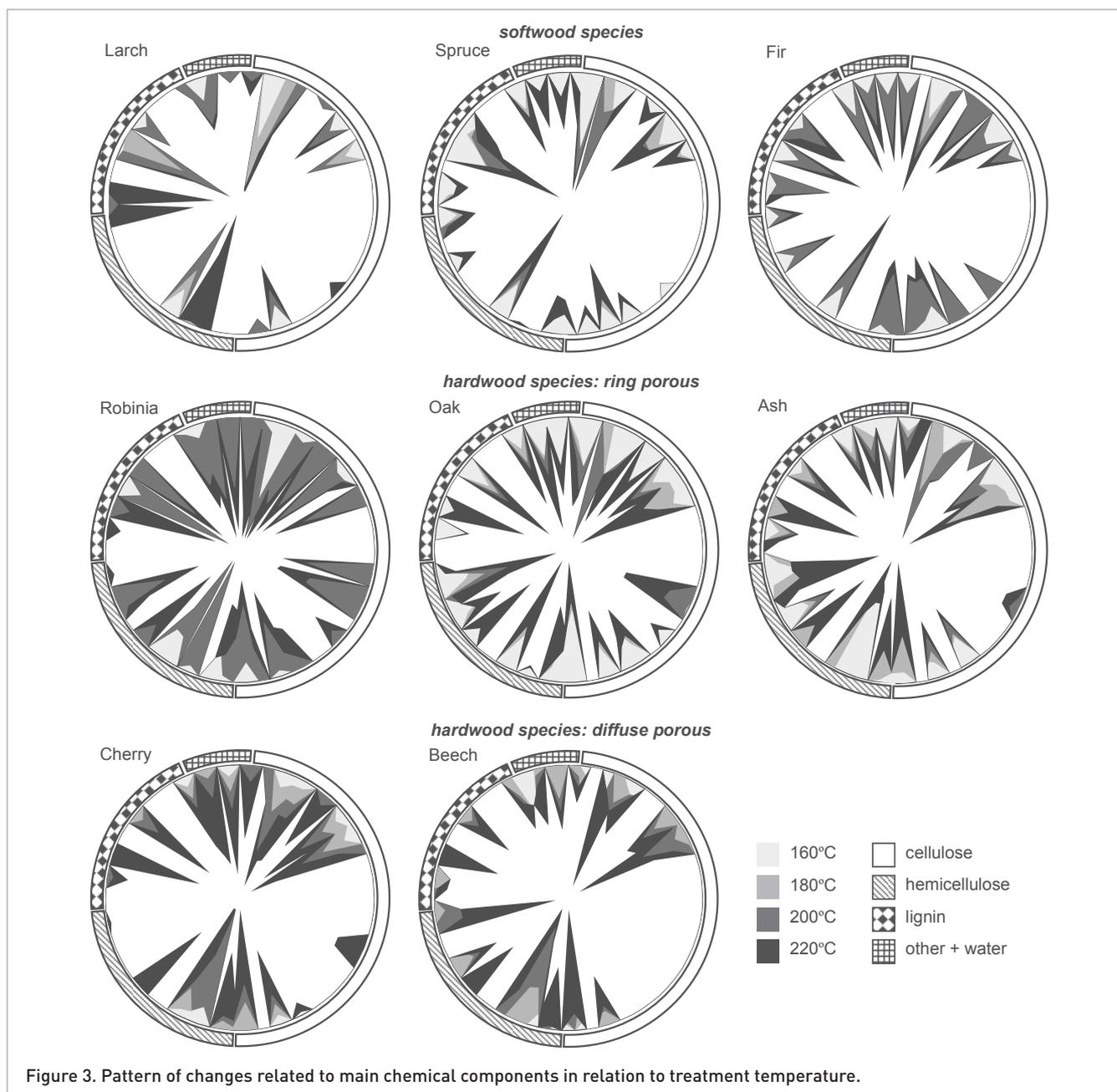


Figure 2. FT-NIR spectra of ash wood (*Fraxinus* sp.) after various intensities of thermal treatment (NT, untreated). The baseline correction was with automatic weighted least squares (Whittaker filter) algorithm of 10th order (PLS_toolbox by Eigenvector).



part of related xylograms). Changes within cherry wood at 220 °C treatment seem to be greater, compared to beech wood. Moreover, some transformation of -CH in cellulose (bands 64 and 65) observed in cherry was not present in the case of beech.

Black locust, among ring porous species, showed the most significant variation in NIR spectra as related to almost all chemical components. It is important to mention that noteworthy chemical changes in black locust were already noticed after treatment at 180 °C. Other ring porous species, such as oak and ash, show evidence of similar degradation kinetics. Only a few bands linked to cellulose (15, 43, 63 and 64) were slightly more degraded in oak than in ash.

It can be assumed that all presented chemical degradation patterns (xylograms) seem to be distinctive for most species, indicating slightly different mechanisms of polymer degradation through thermal treatment. Not all bands assigned to functional groups of woody chemical components were affected by the heat treatment. However, the elevated susceptibility of hemicelluloses to thermal degradation is evidently confirmed in all investigated species, with a particular intensity in hardwoods. This is related to differences in chemical composition of hemicelluloses in soft- and hardwoods. The coniferous hemicelluloses contain mostly galactoglucomannan and arabinoglucuronoxylan. Deciduous wood species contain primarily glucuronoxylan and only low amounts of glucomannan. As a

consequence, thermal stability of softwood hemicellulose is significantly higher than that of hardwood hemicellulose.^{15–18}

All wood species investigated showed slightly varying degradation kinetics. Beech wood seems to be thermally stable up to 200 °C, but significant variations are noticed in the xylograms at the highest treatment temperature. Other species such as oak or ash show more steady change, even if trace evidence of chemical component degradation was already observed at lower temperatures. Knowledge of the degradation kinetics, as summarised in the xylograms, is particularly valuable for optimisation of the thermal treatment intensity. It should enable modification of process parameters considering both the peculiarity of each wood species and the expected pattern of woody polymers resulting from the thermal treatment.¹⁸

Conclusions

Accurate description of final product quality after wood thermal treatment is of interest for both producers and consumers. NIR spectroscopy was proposed here as tool for material characterisation and identification of treatment intensities for thermally modified samples of eight wood species. Considerable changes in absorption bands were observed following increase of the thermal treatment temperature. An original approach for visualisation of the chemical patterns developed within this research (xylograms) allowed identification of differences between degradation kinetics in softwoods and hardwoods. Several spectral bands changed gradually with an increase of the treatment temperature. On the other hand, it was noticed that some functional groups were not affected by the heat treatment. Xylograms allow direct comparison of the thermal stability among all the wood species investigated. Softwoods were in general more stable than hardwoods, where black locust and wild cherry were considered to be the most degraded species. Such knowledge might be helpful for further optimisation of thermal treatment procedures at the industrial scale.

It can be stated that xylograms, as a graphical method for simple and representative visualisation of material chemical changes, might also be used for presentation of other wood degradation/modification processes. They can present kinetics of chemical changes due to synthesis or degradation, weathering, ageing, decay, waterlogging, chemical treatments or densification, among others. Moreover, this method can be also applied for other materials, assuming the availability of detailed band assignments.

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