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In-situ X-ray diffraction investigation of thermal decomposition of wood cellulose

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Abstract

The kinetics of thermal decomposition of crystalline cellulose in spruce wood (*Picea abies* [L.] Karst.) was studied by *in-situ* X-ray diffraction using synchrotron radiation. Fiber diffraction patterns resulting from the crystal lattice of native cellulose arranged in oriented microfibrils were collected as a function of heat treatment time for various temperatures from 300 to 360°C. Sample heating was performed using a specially designed *in-situ* pyrolysis furnace based on halogen lamps with elliptical-shaped reflectors. The variations of the cellulose microfibril size were analyzed by calculating the Scherrer size from equatorial and

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meridional diffraction peaks. By quantitatively analyzing the kinetics for different temperatures it is found that thermal decomposition of crystalline cellulose in wood occurs mainly via a thermally activated decrease of the fibril diameter and an estimate for the activation energy is obtained. A simple scheme about the structural degradation of cellulose is presented.

Keywords: Wood pyrolysis; Cellulose degradation; X-ray diffraction

1. Introduction

The hierarchical organization of wood is known to provide a biomaterial with excellent mechanical properties in spite of its low density. The structure of wood can be described in different terms, depending on the level of hierarchy taken into consideration [1]. On the micrometer or cell level wood is a cellular porous solid, built up of tracheids, which are hollow tube-shaped cells with diameters of several micrometers and lengths in the order of millimeters. The cell wall is organized in layers, where the secondary cell wall layer S2 is by far the thickest one [1, 2]. On the nanometer scale, an analogy can be made with a unidirectional fiber-reinforced composite material, in which the crystalline cellulose microfibrils represent the fiber reinforcement and the amorphous hemicelluloses and lignin represent the composite matrix. The elementary cellulose microfibrils are aligned parallel to each other and wind around the wood cell in a helical manner at a characteristic microfibril angle with respect to the cell axis [1, 3, 4].

Native crystalline cellulose (cellulose I) has been intensively studied in polymer science for almost one century [5-10]. Two polymorphs of cellulose I exist, triclinic cellulose I α and monoclinic cellulose I β . Cellulose produced by primitive organisms were said to have the I α component dominant, while those produced by the higher plants have the I β form dominant

(see the review article by O'Sullivan [10] and references therein). Some attention was paid to the relationship between thermal treatment and changes of structure. In particular, thermal expansion of the cellulose crystal lattice up to temperatures of about 250°C [10-14] and changes of crystallinity of various types of cellulose in the same temperature range was reported [15-19]. It was shown that annealing at temperatures of 270°C transform most of the cellulose I α to the I β form [10].

The conversion of plant tissues into carbon at high temperatures (> 600°C), has been comprehensively studied from a chemical point of view, since the understanding of pyrolytic processes is particularly important for improving the production of carbonaceous materials (see [20-22] for an overview and references therein). The thermal degradation of biomass was investigated in numerous studies using in particular thermogravimetric analysis and differential thermal analysis [20, 23-28]. Besides fuel applications, the use of wood as template for novel inorganic or organic/inorganic ceramic materials has attracted considerable attention over the recent years [29, 30]. Carbon char from wooden materials is of particular interest due to the potential use of cellular carbon templates in advanced ceramics manufacturing for structural applications [31-33]. One goal is the replication of the cellular structure of wood into SiC ceramics, for instance, implying potential applications such as catalysts and filters. Consequently, a series of recent investigations were focused on the transformation of the hierarchical structure of wood into monolithic carbon [34-39].

In contrast to low- (< 250°C) and high-temperature studies (> 600°C), structural investigations of wood at intermediate temperatures, where degradation of the biopolymers takes place, are scarce in the literature. In early X-ray diffraction investigations, Taniguchi and Nakato [40] and Chow and Pickles [24] reported a study of thermal decomposition of wood cellulose but the detailed pathways of degradation were not clarified. In a recent *in-situ* study, Kim *et al.* performed X-ray investigations at 320°C and proposed an anisotropic

decomposition mechanism of wood cellulose under isothermal conditions [41], which was confirmed by Kawamoto and Saka [42].

The aim of the present study is the investigation of the kinetics of wood cellulose degradation at different temperatures. A custom-made heating cell mounted at a high-brilliance synchrotron radiation source offers a powerful tool to elucidate the fast reaction kinetics of cellulose degradation *in situ* for different temperatures. The work focuses on the changes of the crystallite size in the course of isothermal decomposition in an inert gas atmosphere in the temperature range from 300 to 360°C. Therefore, it closes the gap between thermal modifications of wood well below 300°C and the field of charcoal formation at higher temperatures. A general kinetics law on the level of nanometer-sized microfibrils is provided and a simple structural scheme for the mechanism of cellulose degradation is proposed.

2. Experimental

Spruce wood (*Picea abies* [L.] Karst.) from the stem of an eighty-year old tree with annual rings of regular intervals containing normal wood with small microfibril angle was selected for the investigation of softwood pyrolysis. Tangential slices of 0.25 mm thickness from latewood regions of the annual rings were cut by using a Leica RM225 (Leica, Germany) sledge microtome.

For measuring *in-situ* X-ray diffraction (XRD) patterns in transmission geometry, a special custom-made furnace with mirror heaters was designed (Fig. 1). The concept of mirror heating offers the advantage of a non-contact heating to generate a 'hot zone' in free space [43, 44]. Low power consumption, no demand for cooling systems, and in particular extremely fast heating and cooling rates of small sample volumes are advantages of mirror heaters. Commercially available Osram Xenophot HLX 64635 (Osram, Germany) halogen photo optic lamps with elliptical-shaped gold-coated glass mirror reflectors were used. Three

mirror lamps were positioned in a copper block of the shape of an equilateral triangle. The wood slice was mounted between two rings of quartz glass and it was positioned at the common focus point of the lamps. The focusing arrangement of the three lamps assured a homogeneous radiation spot of about 5 mm in diameter at the sample position. The temperature was measured by a Ni-Cr/Ni-Al thermocouple, which was assembled in a quartz glass ring of the specimen holder, less than 1 mm away from the X-ray beam position at the sample. A Eurotherm 2408 (Eurotherm, Germany) PID controller was used to control the temperature of the specimen. The *in-situ* furnace was enclosed in a steel tube covered with Kapton X-ray windows. Continuous flow of helium gas provided a non-oxidizing atmosphere in the furnace chamber, with an additional advantage of low X-ray absorption and background scattering as compared to nitrogen.

In-situ XRD measurements were performed at the beamline A2 [45] at Hamburger Synchrotronstrahlungslabor (HASYLAB), Deutsches Elektronen-Synchrotron (DESY) in Hamburg, Germany. Synchrotron radiation was monochromatized by a germanium 111 crystal to an energy E of 8.27 keV ($\Delta E/E = 10^{-3}$), focused by a single mirror, and the beam cross section was defined by aperture slits to $250 \times 250 \mu\text{m}^2$. An X-ray area detector (MarCCD 165, Marresearch, USA) with 2048×2048 pixels (pixel size: $79 \times 79 \mu\text{m}^2$) was used to detect the scattered photons. The sample-to-detector distance of 158.2 mm was determined by calibration with a standard sample of silver behenate. The X-ray diffraction patterns covered a total range of the scattering vector q of $4 \text{ nm}^{-1} < q < 19 \text{ nm}^{-1}$. The length of the scattering vector is given by $q = (4\pi/\lambda) \sin\theta$, with 2θ being the scattering angle and λ the wavelength. The transmission of the sample at each pyrolysis state was determined *in situ* by using an ionization chamber in front of the heating chamber to monitor the primary synchrotron X-ray flux and a photodiode mounted in the beamstop to measure the transmitted photons.

Before the start of an experiment, the furnace was flooded with helium gas and the wood slice was dried at 105°C for 10 min. After this initial drying procedure, the specimen was heated to the final temperature at a rate of 10°C s⁻¹ and was kept at constant temperature to study the kinetics of structural changes *in situ*. The samples were pyrolyzed at temperatures of 300, 310, 320, 330, 340, 350, and 360°C, respectively. The possibility of X-ray radiation damage was investigated by exposing a wood specimen for one hour without heating, but no significant changes in the scattering patterns were observed.

An exposure time of 60 s yielded a scattering pattern with excellent counting statistics. The scattering patterns were corrected for background scattering, electronic noise, transmission, and polarization by using the data reduction program Fit2D [46].

3. Results

Fig. 2 displays a typical two-dimensional XRD pattern of native spruce wood. Markings denote the Miller indices of the diffraction peaks following the notation of Fengel and Wegener [1]. The pattern is typical for cellulose I and shows the strong equatorial diffraction peaks 002 and the overlapping peak doublet indexed 101 and 10 $\bar{1}$. Meridional diffraction peaks 020 and a quartet of mixed-indices diffraction peaks of the type 021 are clearly visible. Furthermore, a streak-like small-angle scattering signal, which is due to the difference in electron density between the cellulose fibrils and the matrix of polyoses and lignin, is observed close to the primary beam.

No changes in the azimuthal intensity distribution of the two-dimensional XRD pattern could be detected during thermal treatment. Therefore, for further analysis the diffraction peaks were azimuthally integrated for equal radial distances from the central beam by integrating narrow sectors ($\pm 10^\circ$) of the two-dimensional XRD patterns, yielding the scattering intensity as function of the length of the scattering vector q . Fig. 3 shows the time dependence of the

different diffraction peaks at 330°C, together with the curves from the native and the dried sample. Drying at 105°C caused a small shift of the maximum position to lower scattering vectors due to thermal expansion of the cellulose. The rapid heating of the specimen to 330°C caused further shift of the peak position and subsequently the peak intensities started to decrease gradually from the state of crystalline cellulose to an amorphous state. The XRD data were quantitatively analyzed by performing least-square fitting of the diffraction peaks (except for the 020 diffraction peak, see below). Although the literature reports several different functions to analyze these diffraction peaks, it was shown in a comparative study that peak fitting with *pseudo*-Voigt functions yielded best fits with the observed diffraction intensities for native cellulose materials [47]. *Pseudo*-Voigt $I_{pv}(q)$ functions are defined by

$$I_{pv}(q) = A [\eta I_L(q) + (1 - \eta) I_G(q)] \quad (1)$$

with $I_L(q)$ being a Lorentzian function

$$I_L(q) = \frac{2}{\pi w} \left[1 + 4 \left(\frac{q - q_0}{w} \right)^2 \right]^{-1} \quad (1a)$$

and $I_G(q)$ a Gaussian function

$$I_G(q) = \frac{2}{w} \sqrt{\frac{\ln 2}{\pi}} \exp \left[-4 \ln 2 \left(\frac{q - q_0}{w} \right)^2 \right]. \quad (1b)$$

Positions of the diffraction peaks q_0 , full widths at half peak maximum w , peak areas A , and coupling-parameters η , were fitting parameters. An additional linear background was chosen, taking into account the diffuse scattering from amorphous components. A custom written least-square fitting program based on the free software Python (Python Software Foundation) and Gnuplot (T. Williams and C. Kelley) was used to fit and separate each peak from its background. As can be seen in Figs. 2 and 3a, the 101/10 $\bar{1}$ doublet is not clearly separated. Therefore, these two peaks were not taken into account for further data analysis. From the positions of the diffraction peaks, the lattice spacings d were determined by $d = 2\pi / q_0$. The

dried specimen gave the following averaged values of d -spacing: $d_{002} = 0.395$ nm, $d_{021} = 0.430$ nm, and $d_{020} = 0.510$ nm. After heating to the final pyrolysis temperature, the d -spacings shifted to higher values, due to thermal expansion of the cellulose crystal lattice (see e.g. [12-14, 41]) and then further increased slightly with increasing pyrolysis time. The Scherrer sizes of the cellulose microfibrils L_{hkl} , also referred to as widths of the crystallites in the respective crystallographic directions hkl , were estimated by applying the Scherrer equation [48]

$$L_{hkl} = K \frac{2\pi}{\beta_{hkl}}, \quad (2)$$

where K is a shape-dependent constant that varies typically between 0.85 and 1. K was set to one as the absolute value of the fibril size is not of importance here. The integral width $\beta_{hkl} = A_{hkl} / H_{hkl}$ was calculated from the ratio of peak area A_{hkl} and maximum peak height H_{hkl} . As can be seen in Fig. 3c, a pronounced shoulder at the high- q edge of the 020 diffraction peak is visible, which does not allow simple least-square fitting of this peak. The reason for the appearance of the shoulder just after reaching the final temperature could be due to a partial phase change of cellulose I α to I β [10] or due to inhomogeneous strains along the chain axis. However, the integral width of the 020 diffraction peaks could be determined numerically and the corresponding Scherrer size was calculated by equation (2). In particular, in the case of strains the interpretation of this parameter as fibril length is somehow problematic. Nonetheless, it provides a coherence length that is closely related to a meridional coherence length of the fibrils. For dried spruce wood, the following averaged values of L_{hkl} were obtained from the corresponding diffraction peaks: $L_{002} \approx 2.0$ nm and $L_{020} \approx 13$ nm. Even though the width of the 020 diffraction peak is much smaller than the one of the equatorial peaks, the width is still well above the instrumental resolution function of the setup, which was controlled by measuring a reference sample of corundum.

Fig. 4 shows the results for L_{hkl} derived from the 002 (Fig. 4a), 021 (Fig. 4b), and 020 (Fig. 4c) diffraction peaks as function of time for pyrolysis temperatures from 300 to 360°C. Data points in Fig. 4 are displayed only as long as the peaks were clearly visible and significantly above the scattering level of the diffuse background scattering. As can be seen in Fig. 4, there is hardly any decline of L_{hkl} at 300°C, but a decrease of L_{002} and L_{021} is clearly visible and accelerated with increasing heat treatment temperature. L_{020} also decreases for temperatures above 300°C, but does not show such pronounced temperature dependence.

The simplest model for describing the cellulose degradation is by means of a global one-step reaction. A first-order reaction kinetics law, which was primarily designed for the description of macroscopic weight loss, was adapted from the literature [23] to describe the change of the Scherrer size of the cellulose microfibrils:

$$\frac{dL}{dt} = -k (L - L_{\infty}), \quad (3)$$

where k is the rate constant, t is the pyrolysis time, and L_{∞} is the crystallite size at the final steady-state at a certain heat treatment temperature. Integration of equation (3) yields

$$\frac{L - L_{\infty}}{L_i - L_{\infty}} = \exp(-k t), \quad (4)$$

where L_i is the initial crystallite size. The decay of L with time was least-square fitted with equation (4), where L_i , L_{∞} , and k were free fit parameters and no constraints were set. The values of L_{∞} are not zero due to a remaining short range order of the molecules after decomposition. For all, the 002, 021, and 020 crystallographic directions L_{∞} decreases towards zero for increasing temperature, which is consistent with the diminishing of short range order with increasing temperature. The values of the rate constant in the equatorial (k_{002}) and meridional (k_{020}) directions are displayed in an Arrhenius representation in Fig. 5. Even though there is statistical scatter of the data for the equatorial direction, there is a clear trend of k_{002} to decrease with decreasing temperature in the range from 310 to 360°C. A linear

regression provides an estimate of the activation energy of $E_{002} = 112 \pm 17 \text{ kJ mol}^{-1}$ from the slope of the Arrhenius plot (Fig. 5a). Such apparent temperature dependence is obviously not seen in Fig. 5b for k_{020} and therefore no activation energy could be estimated.

4. Discussion and conclusions

In the present work, thermal degradation of cellulose crystallites was investigated in the temperature range from 300 to 360°C. At temperatures below 310°C, the kinetics was very slow and wood cellulose was hardly degraded. Above 360°C, the reaction kinetics was too fast to allow *in-situ* measurements. Within this temperature interval, the thermal degradation mechanisms of cellulose were found different along and across the cellulose fibrils (Fig. 4). The Scherrer size in the equatorial 002 direction decreased with time according to a first-order kinetics law. The temperature dependence of the corresponding rate constant was consistent with a thermally activated process with an activation energy of $E \approx 112 \text{ kJ mol}^{-1}$. This value lies well within the range of the literature data for macroscopic weight loss during wood pyrolysis, which varies roughly between 60 and 170 kJ mol^{-1} [23, 26]. In the meridional 020 direction, the decrease of the Scherrer size with temperature was also consistent with a first-order kinetics law. In contrast to the equatorial direction, however, the rate constant in meridional direction seems to be rather independent of temperature (Fig. 4d), and consequently, it cannot be ascribed to a thermally activated process (Fig. 5b).

In a recent *in-situ* study, Kim *et al.* discussed three possible models for thermal decomposition of wood cellulose crystallites [41]. Their model A was based on a homogeneous radial and axial degradation of the cellulose microfibrils, whereas model B suggests that the decomposition preferentially proceeds along the microfibril axes, and model C is such that a crystallite that once started to decompose undergoes rapid decomposition while others remain largely intact. Kim *et al.* dismissed model A due to the rapid decrease of

the peak intensities as compared to the crystallite size. The models B or C were favored, but were not based on experimental evidence, since no data were available for axial fibril size. The ideas of Kim *et al.* [41] were taken as the basis for an advanced degradation model, summarized in the sketch in Fig. 6. Compared to their studies, additionally to the equatorial diffraction peaks, the meridional 020 peaks were analyzed in the present work to obtain information also on the decomposition along the cellulose fibril axis. Both the axial and the radial Scherrer sizes decrease with time at a given temperature with corresponding rate constants being of the same order of magnitude, supporting model A from Kim *et al.* [41]. Our data further suggest a thermally activated reduction of the microfibril diameter (Figs. 4a, and 5a), however, the decrease of the microfibril length seems to be controlled by another mechanism (Fig. 4c and 5b). We propose an anisotropic degradation mechanism starting from the equatorial surfaces, where initial degradation occurs at the boundaries between the crystalline cellulose microfibrils and the surrounding hemicelluloses. The anisotropic thermal degradation among the different crystallographic directions is ascribed to the crystal structure of cellulose. Anisotropic thermal expansion of the cellulose crystal lattice at temperatures up to 250°C was proven already by other authors [14]. The cellulose molecules run parallel along the meridional *b*-axis of the monoclinic unit cell, and thus merely degrade along this covalently-bonded direction at these low temperatures. Thus the decrease of the Scherrer size in meridional fibril direction might be a consequence of random piecewise breaking up of the crystalline order along the fibrils due to local narrowing down of the fibril diameter. In contrast, the decrease of *L* in equatorial direction is much more sensitive to temperature, because no intermolecular bonds need to be broken. Not much can be said at this point on the influence of the amorphous cell wall polymers (i.e., lignin and hemicelluloses) on the course of cellulose decomposition. Since their glass transition temperatures T_g are in a similar range as the temperatures of the present investigation [2], it can, however, be speculated that

enhanced mobility of the amorphous polymers above T_g might strongly influence the details of cellulose decomposition.

In conclusion, the thermal decomposition of crystalline cellulose fibrils in wood is found to occur mainly via a thermally activated decrease of the fibril diameter and may be accompanied by a random breaking of the fibrils into pieces of shorter length. This is a consequence of the extremely anisotropic nature of the equatorial and meridional bonding forces in cellulose crystallites.

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References

- [1] D. Fengel and G. Wegener, *Wood – Chemistry, Ultrastructure, Reactions*, de Gruyter, Berlin, New York, 1989.
- [2] J. Fahlén and L. Salmén, *J. Mater. Sci.*, 38 (2003) 119.
- [3] H. Lichtenegger, A. Reiterer, S. E. Stanzl-Tschegg, P. Fratzl, *J. Struct. Biology*, 128 (1999) 257.
- [4] M.-P. Sarén and R. Serimaa, *Wood Sci. Technol.*, 40 (2006) 445.
- [5] K. H. Meyer and L. Misch, *Helv. Chim. Acta*, 20 (1937) 232.
- [6] R. H. Atalla and D. L. VanderHart, *Science*, 20 (1984) 283.
- [7] Y. Nishiyama, P. Langan, H. Chanzy, *J. Am. Chem. Soc.*, 124 (2002) 9074.
- [8] Y. Nishiyama, J. Sugiyama, H. Chanzy, P. Langan, *J. Am. Chem. Soc.*, 125 (2003) 14300.
- [9] T. Imai and J. Sugiyama, *Macromolecules*, 31 (1998) 6275.
- [10] A. C. O’Sullivan, *Cellulose*, 4 (1997) 173.
- [11] J. H. Wakelin, A. Sutherland, L. R. Beck Jr., *J. Polym. Sci.*, 42 (1960) 278.
- [12] S. Seitsonen and I. Mikkonen, *Polym. J.*, 5 (1973) 263.
- [13] M. Takahashi and H. Takenaka, *Polym. J.*, 14 (1982) 675.
- [14] R. Hori and M. Wada, *Cellulose*, 12 (2005) 479.
- [15] C. M. Conrad and J. J. Creely, *J. Polym. Sci.*, 58 (1962) 781.
- [16] E. Roffael and K. Schaller, *Holz Roh. Werkst.*, 29 (1971) 275.
- [17] N. Hirai, N. Sobue, I. Asano, *Mokuzai Gakkaishi*, 18 (1972) 535.
- [18] M. T. R. Bhuiyan, N. Hirai, N. Sobue, *J. Wood Sci.*, 47 (2001) 336.
- [19] S. Andersson, R. Serimaa, T. Väänänen, T. Paakkari, S. Jämsä, P. Viitaniemi, *Holzforschung*, 59 (2005) 422.
- [20] M. J. Antal Jr. and G. Varhegyi, *Ind. Eng. Chem. Res.*, 34 (1995) 703.
- [21] D. Meier and O. Faix, *Bioresource Technol.*, 68 (1999) 71.

- [22] M. J. Antal Jr. and M. Grønli, *Ind. Eng. Chem. Res.*, 42 (2003) 1619.
- [23] M. V. Ramiah, *J. Appl. Polym. Sci.*, 14 (1970) 1323.
- [24] S.-Z. Chow and K. J. Pickles, *Wood Fiber Sci.*, 3 (1971) 166.
- [25] J. Hayashi, T. Horikawa, I. Takeda, K. Muroyama, F. N. Ani, *Carbon*, 40 (2002) 2381.
- [26] C. Branca and C. Di Blasi, *J. Anal. Appl. Pyrolysis*, 67 (2003) 207.
- [27] C. J. Gómez, G. Várhegyi, L. Puigjaner, *Ind. Eng. Chem. Res.*, 44 (2005) 6650.
- [28] N. Grioui, K. Halouani, A. Zoulalian, F. Halouani, *Thermochim. Acta*, 440 (2006) 23.
- [29] Y. Shin, J. Liu, J. H. Chang, Z. Nie, G. J. Exarhos, *Adv. Mater.* 13 (2001) 728.
- [30] A. S. Deshpande, I. Burgert, O. Paris, *Small*, 2 (2006) 994.
- [31] P. Greil, *J. Eur. Ceram. Soc.*, 21 (2001) 105.
- [32] E. Vogli, H. Sieber, P. Greil, *J. Eur. Ceram. Soc.*, 22 (2002) 2663.
- [33] C. Zollfrank, R. Kladny, H. Sieber, P. Greil, *J. Eur. Ceram. Soc.*, 24 (2004) 479.
- [34] C. E. Byrne and D. C. Nagle, *Mat. Res. Innovat.*, 1 (1997) 137.
- [35] H. Iizuka, M. Fushitani, T. Okabe, K. Saito, *J. Porous Mater.*, 6 (1999) 175.
- [36] M. Kumar, B. B. Verma, R. C. Gupta, *Energy Sources*, 21 (1999) 675.
- [37] A. K. Kercher and D. C. Nagle, *Carbon*, 41 (2003) 3.
- [38] O. Paris, C. Zollfrank, G. A. Zickler, *Carbon*, 43 (2005) 53.
- [39] G. A. Zickler, T. Schöberl, O. Paris, *Phil. Mag.*, 86 (2006) 1373.
- [40] T. Taniguchi and K. Nakato, *Bull. Kyoto Univ. For.*, 38 (1966) 192.
- [41] D.-Y. Kim, Y. Nishiyama, M. Wada, S. Kuga, T. Okano, *Holzforschung*, 55 (2001) 521.
- [42] H. Kawamoto and S. Saka, *J. Anal. Appl. Pyrolysis*, 76 (2006) 280.
- [43] J. Schneider, in J. V. Gilfrich *et al.* (Eds.), *Advances in X-ray Analysis*, Plenum Press, New York, Vol. 36, 1993, p. 397.
- [44] T. Proffen, F. Frey, H. Plöckl, H. G. Krane, *J. Synchrotron Rad.*, 2 (1995) 229.
- [45] G. Elsner, C. Riekel, H. G. Zachmann, *Adv. Polym. Sci.*, 67 (1985) 1.

[46] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, D. Häusermann, High Press. Res., 14 (1996) 235.

[47] M. Wada, T. Okano, J. Sugiyama, Cellulose, 4 (1997) 221.

[48] B. D. Cullity and S. R. Stock, Elements of X-ray Diffraction, Pentice-Hall, Upper Saddle River, 2001.

Figure captions

Fig.1. Schematic cross-sectional view of the custom-made furnace for *in-situ* X-ray diffraction measurements of wood pyrolysis. The direction of the X-ray beam is perpendicular to the paper plane.

Fig. 2. Two-dimensional X-ray diffraction pattern of native spruce wood dried at 105°C for 10 min, covering a maximal scattering vector q of 19 nm^{-1} . The wood fiber axis is horizontal. Scattered intensity is displayed as inverse gray-scale, i.e. high intensities are dark and low intensities are bright. Markings denote the Miller indices of the observed diffraction peaks.

Fig. 3. Integrated X-ray scattering profiles: (a) equatorial diffraction peaks 101, $10\bar{1}$, and 002, (b) mixed-indices diffraction peaks 021, and (c) meridional diffraction peaks 020. Dash-dotted lines represent the native sample, dashed lines display the scattering signal after drying at 105°C, and solid lines show various states of pyrolysis at 330°C. The numbers given in the Figures refer to the pyrolysis times.

Fig. 4. The change of the Scherrer size L_{hkl} of the cellulose microfibrils of the 002 (a), 021 (b), and 020 (c) diffraction peaks as function of heat treatment time for pyrolysis temperatures of 300 (squares), 320 (circles), 340 (triangles), and 360°C (diamonds). The solid lines denote data fitting with equation (4).

Fig. 5. Arrhenius plots of the rate constant k from the time dependence of the 002 (a) and 020 (b) Scherrer sizes of the cellulose microfibrils. The vertical error bars denote standard deviations due to evaluation of several pyrolysis series and the horizontal error bars denote an

error of $\pm 5^{\circ}\text{C}$ of temperature determination. The solid line represents a fitted curve of the data in the temperature range from 310 to 360°C .

Fig. 6. Schematic representation of the thermal degradation of cellulose microfibrils in wood.

Figure1, Zickler *et al*

Figure 2, Zickler *et al*.

Figure 3, Zickler *et al.*

Figure 5, Zickler *et al.*

Figure 6, Zickler *et al.*