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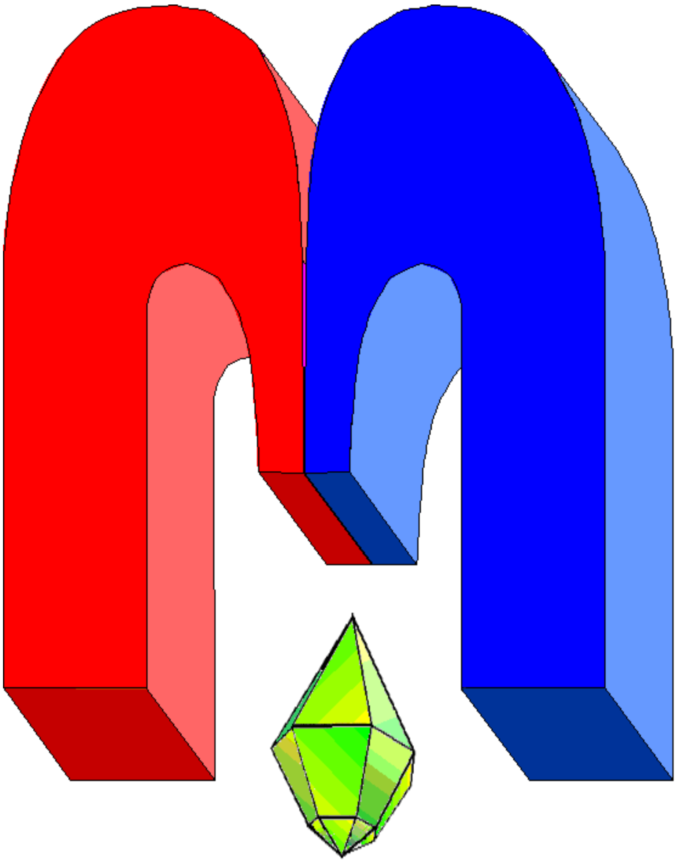

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Electron paramagnetic resonance and quantitative color investigations of various vacuum heat treated wood species[†]

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The effect of the heat treatment duration on the electron paramagnetic resonance signal amplitude of free radicals for various wood species was observed. It was found that the amplitude of the electron paramagnetic resonance signal grows linearly with the vacuum heat treatment duration. The quantitative measurements of color changes for various wood species (pine, spruce, larch, birch and small-leaved lime) were performed. It is found that results of EPR experiments and color measurements of heat treated samples correlate with each other.

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1. Introduction

Vacuum heat treatment is an effective method to improve some of wood properties such as dimensional stability, durability and other mechanical properties [1]. Electron paramagnetic resonance (EPR) method is a non-invasive method that allows to provide information about changes in the structure of the wood as well as control or assess the quality of heat treatment wood. For example, in 1980 Hon et al. [2] reported that free radicals have been easily obtained by exposing the samples to the daylight, sunlight and artificial ultraviolet light. A high amount of free radical concentration was registered from wood specimens treated with sunlight, but most of the free radicals were relatively unstable. Alternatively, a low amount of free radicals was created from specimens treated with fluorescent light and these radicals were relatively stable at ambient temperature. In 2006 Humar et al. [3] investigated the effect of the moisture content of the wood on the intensity of free radical EPR signal and found that intensity of the free radicals EPR signal significantly correlates with wood moisture content.

Wood discoloration depends on several factors such as chemical composition, role of phenolic compounds, heat, the presence of microorganisms, exposure to light, drying, etc [4]. Tannins and resinous substances in the cavities of the cells also influence on the color of the wood. Natural wood has a different color: from white (spruce, linden, etc) to black (ebon), which first of all depends on various climatic conditions. Vacuum heat treatment influences the initial color of the wood as well.

In 2003 Bekhta et al. [5] investigated the effect of high temperature on mechanical properties, stability of the size and change in color of spruce wood which were subjected to heat treatment at 200°C for 2, 4, 8, 10 and 24 h and at 100, 150 and 200°C for 24 h. Their results show that

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heat treatment resulted in a darkening of wood tissues, improvement of the dimensional stability of wood and reduction of its mechanical properties. In 2007 Bruno Esteves et al. [6] the heat treatment of Pinus pinaster and Eucalyptus globulus wood were carried out by hot air in an oven for 2–24 h at 170–200°C and by steam in an autoclave for 2–12 h at 190–210°C and the color parameters L^*, a^* and b^* were determined. The lightness (L^*) decrease was related to chemical changes with good correlations with glucose (coefficient of multiple correlation $R^2 = 0.96$), hemicelluloses ($R^2 = 0.92$) and lignin ($R^2 = 0.86$) and the contribution of red (a^*) and yellow (b^*) colors decreased with heat treatment. Mottonen et al 2008 [7] study the effects of drying force timber thickness, and initial moisture content on the color of high-temperature-dried birch wood. They found that at increase in drying force increased the lightness and decreased the redness and the yellowness of wood but color difference was observed between the sample surface and the interior. Pretreatment of timber with water soaking decreased the difference in color between the surface layer and the interior of boards when low drying force was used.

In 2010 Gunduz [8] studied samples of Uludag Fir wood to a heat treatment at 170, 190, and 210°C for 4, 8, and 12 h treatment temperature had a more significant effect on color changes than did treatment time. The color space CIE 1976 L^*, a^* and b^* parameters did not change significantly between 8 and 12 h treatment and it was determined that mechanical and technological properties were negatively affected at higher temperatures. For quantitative color measurements the colorimetry is widely used. In this method the color is represented by color parameters X, Y and Z (color space CIE 1931 XYZ) which are red, green-yellow, and blue part contributions, respectively. Values of the color space CIE XYZ parameters we can convert into the color space CIE $L^*a^*b^*$ parameters [9].

In $L^*a^*b^*$ color space a lightness is set by coordinate L^* ($0 < L^* < 100$) and chromatic components are represented by two coordinates a^* and b^*. The parameter a^* indicates the position in the color range from green to red and coordinate b^* is position in the color range from blue to yellow.

The purpose of this work was to study the dependence of EPR signal amplitude and the quantitative characteristics of the color on vacuum heat treatment duration, and to assess the possible relationship between results of both experiments. In this paper we present results of EPR experiments that reveal some changes in wood samples induced by vacuum heat treatment at 220°C temperature. The duration of the treatment varies from 40 minutes to 8 hours. The results of color changes measurements after the treatment are reported and their connection with the changes of wood polymer structures are discussed.

2. Materials and methods

In this work various species of wood as a Scots pine (*Pinus sylvestris*), Birch (*Betula pendula*), Russian larch (*Larix sibirica*), Norway spruce (*Picea abies*), Small-leaved Lime (*Tilia cordata*) from Kirov region, Russia, were investigated. Sapwood of these species logs was cut to have parallelepiped shape and $3 \times 3 \times 5$ cm^3 dimensions before the vacuum thermal treatment.

A special vacuum oven Aktan VTSh-K24-25 equipped with VRO 5/21 rotary vane vacuum pump were used for the vacuum heat treatment of wood samples at the temperature 220°C. The duration of processing was varied in the range from 40 minutes to 8 hours. The wood samples moisture content values were measured by the special Hydro Condtrol device and also obtained through the weight measurements with laboratory scales.

The electron paramagnetic resonance (EPR) experiments were carried out on the Varian

E-12 X-band spectrometer at 9.3 GHz frequency and at the room temperature. During the experiments special reference sample has been used to qualitatively and quantitatively compare the obtained EPR spectra of different samples. Microwave power of 1 mW and 100 kHz modulation frequency were used during all EPR spectra measurements. The samples were cut to the $0.35 \times 0.35 \times 5$ cm^3 dimensions.

Images of untreated and heat treated samples were obtained by a Canon 350D photo camera under the daylight source that corresponds to CIE standard illuminant D65. Image of a special white reference sample was also obtained under the same conditions. Initial RGB color presentation of images at first was converted to CIE XYZ color space using standard equations [10]. The CIE LAB color space is known to be independent of illumination values and allows to compare color measurements performed under various conditions at different research groups. The CIE LAB color space coordinates were calculated from the CIE XYZ values using specific X_n, Y_n, Z_n values of the white point and following equations [11]:

$$L^* = 116 \times f(\frac{Y}{Y_n}) - 16, \tag{1}$$

$$a^* = 500 \times \left[f(\frac{X}{X_n}) - f(\frac{Y}{Y_n}) \right], \tag{2}$$

$$b^* = 200 \times \left[f(\frac{Y}{Y_n}) - f(\frac{Z}{Z_n}) \right], \tag{3}$$

$$f(t) = \begin{cases} t^{\frac{1}{3}}, & t > (\frac{6}{29})^3 \\ \frac{1}{3} \times (\frac{29}{6})^2 t + \frac{4}{29}, & t \le (\frac{6}{29})^3 \end{cases} \tag{4}$$

These L^*, a^* and b^* color parameters were determined for all used heat treatment durations of investigated wood species. The L^* parameter is known to describe the lightness and can vary from 0 (dark) to 100 (light). Parameters a^* and b^* describe redness and yellowness, correspondingly, and vary from -100 to 100.

The color variation ΔE of wood samples were calculated from the CIE $L^*a^*b^*$ values using the following equation:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}. \tag{5}$$

3. Results and Discussion

The measured EPR spectra of wood samples contain a single free radicals line near $g = 2.002$. Since the amplitude of the EPR signal of free radicals in wood strongly depends on the moisture content of samples, all of them were conditioned to have the same moisture content before EPR experiments. Experimentally obtained dependences of free radicals signal amplitude on duration of vacuum heat treatment at 220°C of wood samples are presented in Fig. 1.

The linear correlation between the free radicals signal amplitude and the vacuum heat treatment duration is observed for all wood samples. This means that chemical bonds in wood polymers constantly break during the heat treatment and free radicals appear at these locations. It was detected by other methods that hemicellulose degrades more than cellulose and lignin with heat treatment of wood [6]. Also it is known that water molecules leave some cellulose molecules leading to their depolymerization.

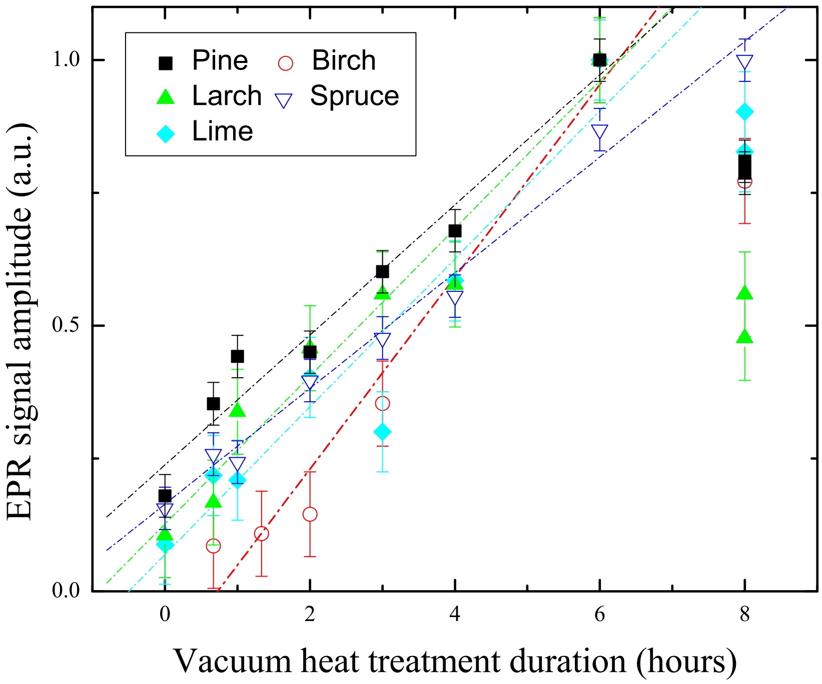

Figure 1. The normalized EPR signal amplitude of birch, lime, larch, spruce and pine samples as a function of the vacuum heat treatment duration at 220°C. Dash-dot line represents the linear behaviour of the obtained data from 0 h to 6 h.

A long vacuum heat treatment introduces a severe damage to the internal structure of wood samples. In our experiments free radicals signal amplitude values drastically decrease in birch, lime, larch and pine samples after 8 h vacuum heat treatment (see Fig. 1). This is likely connected with the destructive changes occurring in a sample.

The obtained lightness L^* values for untreated wood samples were close for all observed wood species. Lightness $L^* = 85 \pm 11$ while a^* and b^* parameters vary depending on wood species. Thus a^* values for spruce, pine and lime samples are within a range of 5.4 ± 1.5, and $a^* = 12.5\pm2.2$ for birch and larch samples. Obtained b^* parameter of untreated samples is responsible for yellow tones of samples and its values are $b^* = 12.7 \pm 2.9$ for birch, 5.4 ± 3.0 for spruce, 19.2 ± 3.0 for pine, 5.3 ± 3.4 for lime and 20.0 ± 5.7 for larch. These results are in a good agreement with $L^*a^*b^*$ values that were observed for untreated spruce in [4, 12], pine [6, 13] and birch [7].

Fig. 2 displays the change of the lightness L^* color parameter of our wood samples after a 220°C vacuum heat treatment. The lightness L^* of used wood samples decays exponentially with the vacuum heat treatment duration. For some species as spruce and birch the lightness decays relatively slowly during the treatment. After 8 h treatment values of L^* reduce by 17% for spruce samples while the decrease of lightness reaches 60% and 85% for larch and lime samples correspondingly.

A monotonous decrease of lightness in pine samples was observed after traditional heat treatment at 170–200°C temperature range in [6]. A strong correlation between the lightness L^* decrease and relation between hemicellulose, glucose and lignin in pine was found out. The less hemicellulose contents in pine samples, the lower lightness value was measured. A similar decrease of lightness after heat treatment was also observed in spruce samples at 190–245°C [5,12, 13]. The authors report on the correlation between the lightness decrease and samples mass loss.

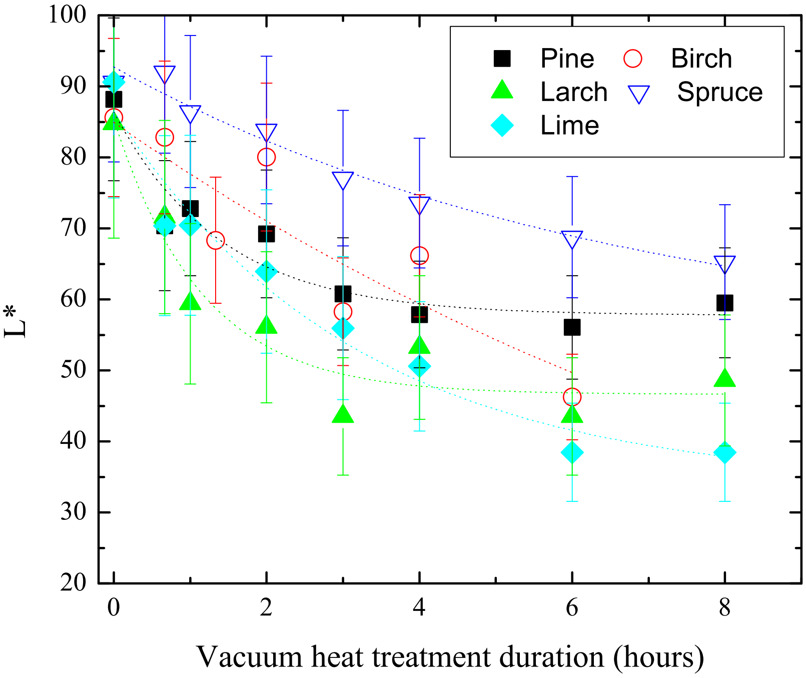

Figure 2. Evolution of L^* parameter values as a function of the vacuum heat treatment duration for spruce, lime, pine, birch and larch samples. The temperature of heat treatment is 220°C. Dotted lines represent envelope curves.

The vacuum heat induced changes of a^* and b^* parameters of pine, birch, larch, spruce and lime samples are presented in Fig. 3, 4. The a^* values that are responsible for red tones increase during first two hours of treatment for all studied species. And a^* values do not change with further heat processing of pine, larch and spruce samples. However a^* parameter decreases to its initial values in birch and lime samples after 6–8 h treatment. At first parameter b^* values increase and then decrease with the heat treatment in our samples. Behavior of a^* and b^* parameters during the reported plain heat treatment of spruce and pine wood [5, 13] is qualitatively similar. It was also noted [13] that Δa usually has the lowest correlation with any chemical constituent of the wood. While the relationship between Δb and wood polymers was found. It was strongly correlated with hemicellulose changes in beech samples, with lignin in pine, and with glucose in spruce samples. Amount of cellulose in studied samples do not make effect on color parameters. Relationship between hemicellulose contents and lightness L^* of various wood samples and its behaviour during heat treatment is also in agreement with results of our EPR experiments that point out on the degradation processes of some wood polymers as hemicellulose in our samples during a heat treatment.

Fig. 5 displays the correlation between the color change ΔE and the EPR signal amplitude during the vacuum heat treatment. The linear behaviour is observed for lime with the coefficient of multiple correlation $R^2 = 0.862$, pine ($R^2 = 0.808$) and birch ($R^2 = 0.756$). The less linear correlation is obtained for spruce ($R^2 = 0.566$) and larch ($R^2 = 0.624$). These results are in agreement with studies of Ahajji et al. [14], the authors also observed linear relationship between the color variations ΔE and EPR signal intensity for beech and spruce samples heat treated for 1 h at 210–250°C. However Altgen et al. [15] report on logarithmic correlation function between the ΔE values and EPR signal amplitude for their heat treated beech and spruce samples.

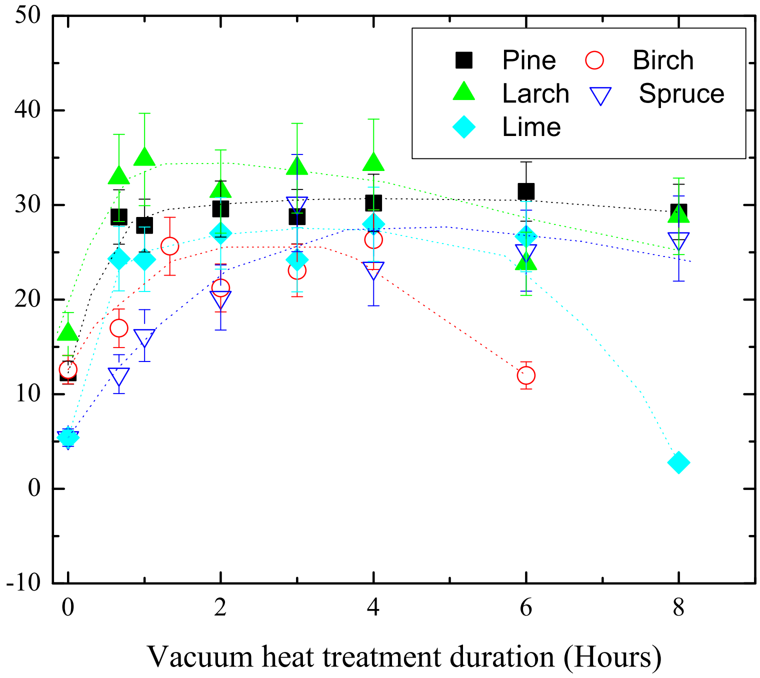

Figure 3. Evolution of a^* parameter values as a function of the vacuum heat treatment duration for spruce, lime, pine, birch and larch samples. The temperature of heat treatment is 220°C. Dotted lines represent envelope curves.

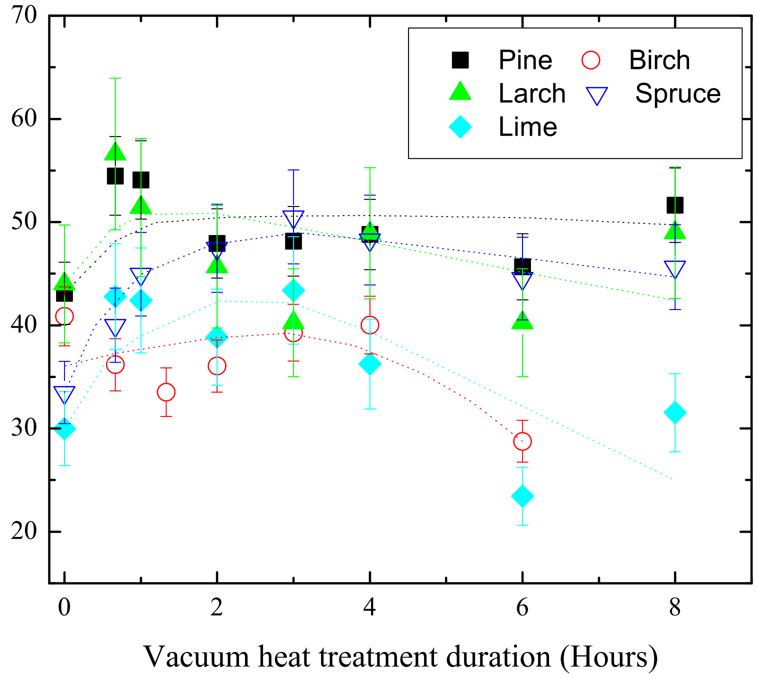

Figure 4. Evolution of b^* parameter values as a function of the vacuum heat treatment duration for spruce, lime, pine, birch and larch samples. The temperature of heat treatment is 220°C. Dotted lines represent envelope curves.

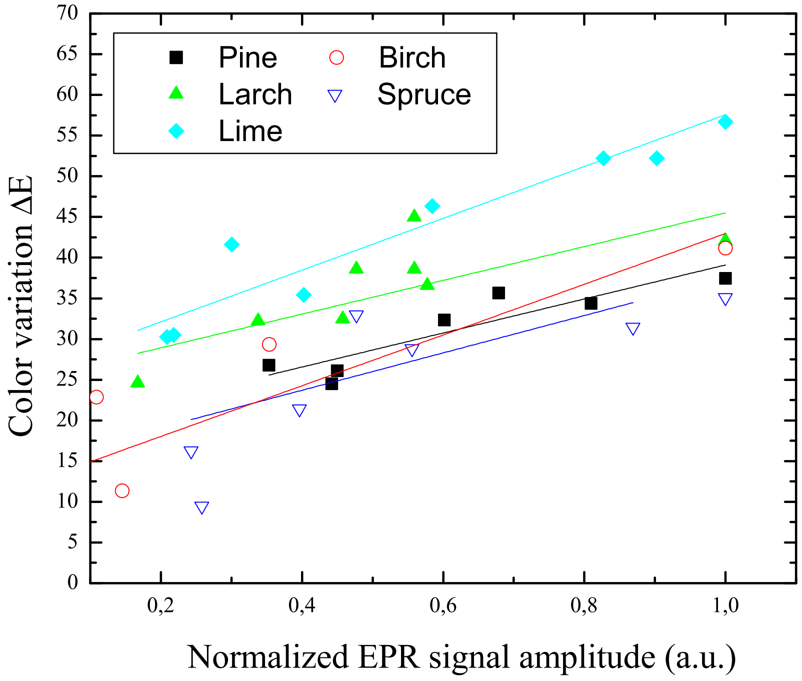

Figure 5. Correlation between the color variation ΔE and the normalized EPR signal amplitude of heat-treated spruce, lime, pine, birch and larch samples. Solid lines represent the linear correlation. The temperature of heat treatment is 220°C.

4. Summary

Results of quantitative wood color measurements in this work confirm earlier reports on color changes in pine, spruce and birch samples after heat treatment, and expand them for other wood species as larch and small-leaved lime. Vacuum heat modification of wood species significantly changes their color. It is found that lightness L^* in CIE $L^*a^*b^*$ color space decreases exponentially with the vacuum heat treatment duration while the effect on a^* and b^* parameters is nonlinear. Observed changes in L^* and b^* values are connected with the hemicellulose and lignin contents in wood samples. This is in agreement with results of our EPR experiments. The close to linear correlation between the color variation ΔE and the EPR signal amplitude of heat-treated spruce, lime, pine, birch and larch sample is observed. It is found that the amplitude of free radicals signal grows linearly with the vacuum heat treatment duration. The changes in the free radicals signal amplitude in wood samples are attributed to destruction of chemical bonds in some wood polymers as hemicellulose and lignin that appear during a heat treatment at 220°C.

Acknowledgments

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