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# Spectral and photophysical properties of thermomechanical pulps bleached with the use of acidified and alkaline hydrogen peroxide

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## Abstract

We characterized spruce thermomechanical high-yield pulps subject to a variety of non-delignifying hydrogen peroxide treatments. Apart from standard technological analysis, spectral and photophysical properties of the sample pulps were evaluated using steady-state diffuse reflectance spectroscopy and time-resolved emission and diffuse reflectance spectroscopy with sub-microsecond time resolution. The steady-state diffuse reflectance spectra allow to obtain a more complete information as compared to standard brightness measurements, as they include the data from the UV-A zone, crucially determining the yellowing rates of the respective paper products. Time-resolved emission and diffuse reflectance results provide additional information on the amount and reactivity of photoactive groups present in the pulp, which also affect the yellowing rates of the paper products. The best characteristics were registered for the pulp sample prepared using a two-stage hydrogen peroxide brightening, with the preliminary acidic and the final alkaline treatment, which can be recommended for industrial implementation.

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**Keywords:** Thermomechanical pulps; Laser induced emission; Paper photoyellowing; Phenoxyl radicals methoxy-substituted; Diffuse reflectance laser flash photolysis

## 1. Introduction

A wide range of pulps that differ in their chemical composition is produced for different end-users. Thermomechanical pulp (TMP) as a typical high-yield fibrous raw material, containing most of the structural wood constituents namely cellulose, hemicelluloses, lignin and even residual extractives (tannins and waxes). Although all of these constituents influence to some extent the optical properties of the pulp, it is the presence of lignin chromophores that is mainly responsible for its final brightness or rather for the lack of it. The removal of lignin chromophores from TMP during the bleaching stage is essential from the commercial point of view if the pulp is to be used for production of high-grade paper. Hydrogen peroxide is widely used for non-delignifying bleaching of high-yield pulps under alka-

line conditions. Because of the relatively high treatment costs, many attempts have been made in order to improve peroxide bleaching by varying the process conditions, including the use of acidic medium at the first stage. Two-stage bleaching of spruce TMP with hydrogen peroxide under acidic and alkaline conditions has beneficial effect both on peroxide consumption and on the final brightness, at the same time conserving the pulp yields [1]. However, the high content of lignin after non-delignifying two-stage peroxide bleaching of TMP may cause pulp yellowing upon exposure to daylight, especially to its near-ultraviolet portion. To obtain a better understanding of the mechanism of pulp yellowing, the interaction of light with lignin and/or lignin chromophores has been intensively examined [2–6]. It is generally accepted that light with the wavelengths shorter than 396 nm leads to yellowing of the high-yield pulp and its paper products; in contrast, light with wavelengths longer than 396 nm leads to bleaching of the same materials [2]. Photoyellowing and photo-bleaching processes are both very complex, depending strongly on structure and composition of the pulp. Chromophores and

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chemical species responsible for the photochemical instability of pulp can exist either in the starting pulp, or may be newly formed during the subsequent stages of paper making. Therefore, the studies of the effective removal of chromophores from pulp during bleaching stages, and the stability of brightness, are equally essential from the technological and commercial points of view.

Identification of the transient species formed during the lignin photodegradation processes responsible for yellowing of the lignin-rich papers is the key problem in such studies [7–10]. Prevention of coloration is more likely to succeed if the phenoxy and/or ketyl radicals derived from alcohol groups and produced during the photodegradation of lignin could be targeted for scavenging before they undergo oxidative processes that promote yellowing.

Earlier studies have shown that the use of the ground-state reflectance and steady-state luminescence spectroscopy, together with the diffuse reflectance laser flash photolysis, leads to better understanding of the process of delignifying peroxide bleaching of kraft pulps [11], providing a good example of the practical impact of the diffuse reflectance spectroscopy [12,13]. In this work we were focused on application of the spectroscopic methods to describe the consequences of the non-delignifying hydrogen peroxide treatment of TMP under acidic and alkaline conditions.

## 2. Experimental

### 2.1. Sample preparation

Spruce thermomechanical pulp (TMP) obtained from the International Paper – Kwidzyn/Poland mill was used in all experiments, with 28.3% initial lignin content, and 49.92% ISO brightness. Content of lignin's methoxyl groups was 4.54% on o.d. (oven dry) pulp (determined following the Viebock-Schwappach method).

All experiments on the TMP bleaching were made in zip-lock PET bags placed in a thermostatic water bath. After bleaching or additional chemical treatment the pulps were washed with distilled water to neutral reaction and dried at room temperature.

Standard one-stage alkaline peroxide bleaching was carried out at pH 10.8 regulated with NaOH, at 10% pulp concentration, at 70 °C, for 2 h, using 3% H<sub>2</sub>O<sub>2</sub> charge on o.d. pulp and peroxide stabilizers (MgSO<sub>4</sub>·7H<sub>2</sub>O, 1% on o.d. pulp and Na<sub>2</sub>SiO<sub>3</sub>, 3% on o.d. pulp). This sample is labelled as Pap-6 in Table 1.

Six more samples were prepared for the spectroscopic studies, labelled Pap-0 to Pap-5. The sample Pap-0 was used for reference with no additional treatment. Pap-1 was treated with hydrogen peroxide in acidic conditions, with pH 4.5 at the starting point. Other parameters of the sample preparation were as follows: pulp concentration 10%, H<sub>2</sub>O<sub>2</sub> charge 5% on o.d. pulp, temperature 70 °C, and 1 h treatment time. In preparing the sample labelled as Pap-2 two stages of hydrogen peroxide bleaching were used. The first acidic stage at pH 4.5 in the beginning, used 10% pulp concentration, H<sub>2</sub>O<sub>2</sub> charge 5% on o.d. pulp, temperature 70 °C, and 30 min treatment time. The second, alkaline stage at pH 11 (regulation with NaOH) went on for 2 h, pulp concentration, peroxide charge and temperature were the same as in the first (acidic) stage. Two-stage hydrogen peroxide bleaching was used for sample Pap-3 in the same treatment conditions as Pap-2, with additional reduction of carbonyl groups with NaBH<sub>4</sub> after peroxide stages (pulp concentration 1%, 3% NaBH<sub>4</sub> on o.d. pulp, pH 10.0, time of treatment 18 h, room temp.). The same two-stage hydrogen peroxide brightening was applied for Pap-4, with subsequent methylation of phenolic hydroxyl groups with methyl sulphate at pH > 11 [14]. Methoxyl content was 5.31% on o.d. pulp. This treatment yielded additional chromophores, causing a decrease of brightness to 36.64%. The last sample labelled as Pap-5 was also prepared using the two-stage hydrogen peroxide brightening, with the acidic stage at pH 2.5 using CuSO<sub>4</sub> as a catalyst, time of treatment 1 h, 80 °C, 3% H<sub>2</sub>O<sub>2</sub> on o.d. pulp, pulp concentration 10% (pH regulation with H<sub>2</sub>SO<sub>4</sub>). The alkaline stage was run at pH 10.8 (regulated with NaOH), stabilizers: 0.1% MgSO<sub>4</sub> and 3% Na<sub>2</sub>SiO<sub>3</sub> on o.d. pulp, time of treatment 1 h.

### 2.2. Equipment and measurement methods

Standard technological and chemical indices were determined after the pulp treatment: hydrogen peroxide consumption by iodometric titration using saturated ammonium molybdate as a catalyst, pulp yield was defined on the basis of humidity

Table 1

Results of the standard technological analysis applied to spruce thermomechanical pulps, Pap-0 to Pap-6—see Section 2 for the detailed sample preparation procedures

Sample	ISO brightness (%)	ISO brightness after UV irradiation (%)	Lignin (%)	H <sub>2</sub> O <sub>2</sub> consumption (%)	Yield (%)
Pap-0: reference	54.8	49.3	28.3	—	—
Pap-1: acidic treatment with hydrogen peroxide	51.7	36.7	27.1	27.0	97.9
Pap-2: two-stage hydrogen peroxide bleaching	54.1	37.5	As above	81.7	81.7
Pap-3: two-stage hydrogen peroxide bleaching, with subsequent reduction of carbonyl groups with NaBH <sub>4</sub>	58.8	38.9	As above	As above	As above
Pap-4: two-stage hydrogen peroxide bleaching, with subsequent methylation of phenolic hydroxyl groups with methyl sulphate at pH > 11	36.6	31.5	As above	As above	As above
Pap-5: two-stage hydrogen peroxide bleaching with acidic stage at pH 2.5 using CuSO <sub>4</sub> as a catalyst	61.2	40.3	As above	53.5	94.4
Pap-6: standard one-stage alkaline peroxide bleaching	57.7	—	28.0	83.0	94.4

measurements by drying samples to constant weight, Klason lignin content following TAPPI T-222-os-74 method [15], brightness of the paper sheets was tested by L and W ELREPHO 2000 spectrophotometer following ISO 2470 standard method (R457 with C-illuminant) [16].

UV aging experiments on the same pulp samples were conducted at 70 °C with UV radiation (280 nm, 300 W/m<sup>2</sup>), 18 h irradiation time.

Time-resolved diffuse reflectance laser flash photolysis (DRLFP) experiments and laser induced emission (LIE) emission measurements were made using the systems available in Lisbon, and were performed at room temperature, in the front-face arrangement. A diagram of the system is presented in reference [17]. The system uses the 337.1 nm pulse of a N<sub>2</sub> laser (Photon Technology Instruments, Model 2000, ca. 600 ps FWHM, ~1.3 mJ/pulse) as the excitation source. The light arising from the irradiation of solid samples by the laser pulse is collected by a collimating beam probe coupled to a fused silica optical fibre and detected by a gated intensified charge coupled device (ICCD, Oriel Model Instaspec V). The ICCD is coupled to a fixed imaging compact spectrograph (Oriel, Model FICS 77441). The system can be used either by integrating all light emitted by the sample or in the time-resolved mode by using a delay box (Stanford Research Systems, Model D6535) and a suitable gate width. The ICCD has high-speed (2.2 ns) gating electronics and an intensifier, and covers the 200–900 nm spectral range. Time-resolved absorption and emission spectra are available in the nanosecond to second time range [17,18].

Steady-state fluorescence spectra were obtained with a Jobin Yvon-Spex Fluorolog 3-11 spectrofluorometer, and UV-vis absorption spectra on a Varian Cary 5E spectrophotometer.

### 3. Results and discussion

In this paper we describe spruce thermomechanical pulps that underwent different chemical treatments. The results of standard technological analysis applied to seven spruce thermomechanical pulps, samples Pap-0 to Pap-6, are presented in Table 1. As can be seen from these results, the two-stage hydrogen peroxide pulp treatment with the use of Cu<sup>2+</sup> ions as a catalyst and the stabilizers (Pap-5) gives generally better results than traditional one-stage alkaline brightening (Pap-6). The ISO brightness number determined for this pulp was the highest among all of the studied samples — 61.2%. The yield was also suitable for high-yield mechanical pulping (94.4%) and the peroxide consumption (53.5%) much lower than the standard one-stage alkaline peroxide brightening. The lignin content determined in all of the peroxide treated pulps (Pap-1 to Pap-6) generally confirms the non-delignifying character of the treatment. Note that the lignin decrease by about 1% in comparison to the untreated pulp (Pap-0) is insignificant from the technological point of view. The results of this study show that the two-stage bleaching of the spruce TMP with hydrogen peroxide under acidic and alkaline conditions could be a viable alternative to the standard one-stage process. The treatment carried out in two bleaching towers configuration with recirculation of the acidified peroxide solution allows to reuse the peroxide after

replenishing of the chemical losses and facilitates alkaline treatment carried out in a separate tower [19].

However, the chemistry of the acidic and alkaline treatments is different. In acidic medium and in the presence of metal catalysts hydrogen peroxide decomposes by a free-radical mechanism [20]. In alkaline medium the peroxide anion (OOH<sup>-</sup>) is the species most reactive towards pulp chromophores [21]. The brightness after the acidic stage is not much higher than the reference value, and incidentally may even get lower (Pap-1). The two-stage treatment without catalyst in acidic medium and stabilizers in alkaline one (Pap-2) gives a slightly higher ISO brightness, but is still commercially unsuitable. Reduction of the carbonyl groups increases the pulp brightness (Pap-3) but not as much as in Pap-5; besides, this kind of pulp treatment does not improve its stability upon exposure to sunlight (Table 1). Taking everything into consideration, we conclude that it is essential to characterize the spectral differences in the pulp chromophores depending on the changes in acidic/alkaline treatment.

The opaque character of the samples makes the diffuse reflectance method one of the best to study the effect of the interaction of light with solid materials. The measured remission spectra of six samples are presented in Fig. 1.

Ground-state diffuse reflectance spectra were recorded on a Varian Cary 5E spectrophotometer with a Labsphere diffuse reflectance attachment. These spectra are presented in the form of the Kubelka–Munk remission function  $F(R)$  [22]. In the Kubelka–Munk theory the remission function for an ideal diffuse scatterer, which is optically thick at the wavelength of measurement, and for a homogeneous distribution of absorbers throughout the sample, is given by the Kubelka–Munk function:

$$F(R) = \frac{(1 - R^2)}{2R} = \frac{K}{S} \quad (1)$$

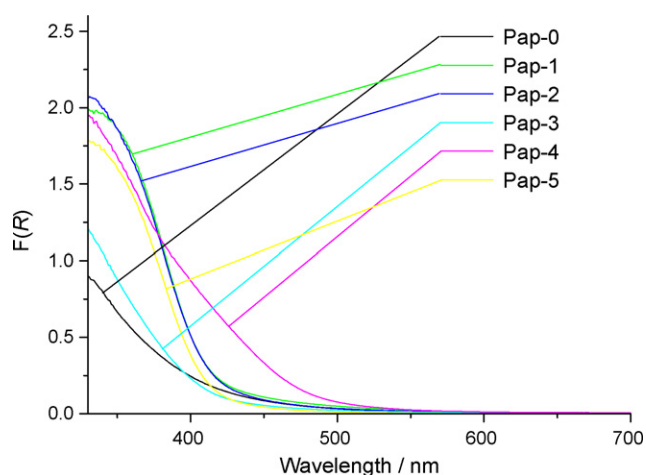


Fig. 1. The remission spectra of spruce thermomechanical pulps after different treatments: Pap-0, reference; Pap-1, acidic treatment with hydrogen peroxide; Pap-2, two-stage hydrogen peroxide brightening; Pap-3, two-stage hydrogen peroxide brightening, with subsequent reduction of carbonyl groups with NaBH<sub>4</sub>; Pap-4, two-stage hydrogen peroxide brightening, with subsequent methylation of phenolic hydroxyl groups with methyl sulphate at pH > 11; Pap-5, two-stage hydrogen peroxide brightening with acidic stage at pH 2.5 using CuSO<sub>4</sub> as a catalyst.

where  $R$  represents the observed diffuse reflectance from the surface of the sample,  $K$  and  $S$  are absorption and scattering coefficients, respectively, measured in  $(\text{length})^{-1}$  units. It is important to note that the use of  $F(R)$  provides a more adequate measure of the chromophore concentration in the pulp than the usual ISO brightness method, which also relies on light scattering data [23].

As seen in Fig. 1, the UV–vis spectra of the ground state show that the  $F(R)$  values for the untreated sample and those treated with hydrogen peroxide are different. The increase in the  $F(R)$  values in the range below 400 nm of all the treated samples suggests changes in the chromophore system of the pulp. The  $F(R)$  values in the UV range are generally higher if compared to the reference sample, Pap-0. However, in the borhydride-reduced sample, Pap-3, the  $F(R)$  values are only slightly higher in comparison to the reference sample, whereas in all the other samples the  $F(R)$  values below 400 nm are almost twice those of the reference sample. Note that in pulps the high absorption in the 300–400 nm range is generally attributed to lignin's  $\alpha$ -carbonyls [24]. The sample after borhydride reduction, Pap-3, and the sample with the two-stage treatment with stabilizers, Pap-5, have lower  $F(R)$  values than the reference sample in the visible range above 400 nm. For Pap-4, the sample subject to two-stage hydrogen peroxide bleaching treatment and then methylation of the phenolic hydroxyl groups, the  $F(R)$  values are significantly higher in the visible range if compared to all the other samples. The results of spectral measurements are quite consistent with the brightness measurement results of spruce thermomechanical

pulps presented in Table 1. However, these results also confirm that the usage of  $F(R)$  instead of ISO brightness gives more information about the pulp sample, allowing observation of two important spectral regions with the wavelengths of absorption lower and higher than 400 nm, whereas brightness accounts for the visible spectral range only, and ignores the UV part. Similarly to natural yellowing of paper, the oxidative treatment applied to samples Pap-1, Pap-2, Pap-4 and Pap-5 increased their absorption and  $F(R)$  in the UV and, excluding Pap-5, in the visible range as well. On the other hand, the subsequent reductive treatment applied to the sample Pap-3 almost restored the original  $F(R)$  values in the UV and simultaneously improved its reflectance in the visible and, correspondingly, its whiteness, as compared to the untreated Pap-0 pulp sample. Indeed, the reduction step eliminates the carboxyl groups present in the oxidised lignin, thus reducing optical absorbance and improving the reflectance characteristics of the pulp.

We have performed steady-state and time-resolved emission measurements, the latter with a pulsed laser excitation, obtaining similar results in the two approaches, despite the steady-state results being more difficult to obtain because of the less intense excitation source. In Fig. 2 we present emission measurements in the nanosecond time range for all of the samples obtained in the laser-pulse excitation experiments. The spectra obtained by the time-resolved method, with their maxima at 440 nm (Fig. 2) showed only small differences in either position of the fluorescence maxima or the fluorescence band shape. The only exception is once more the sample Pap-4, for which the observed

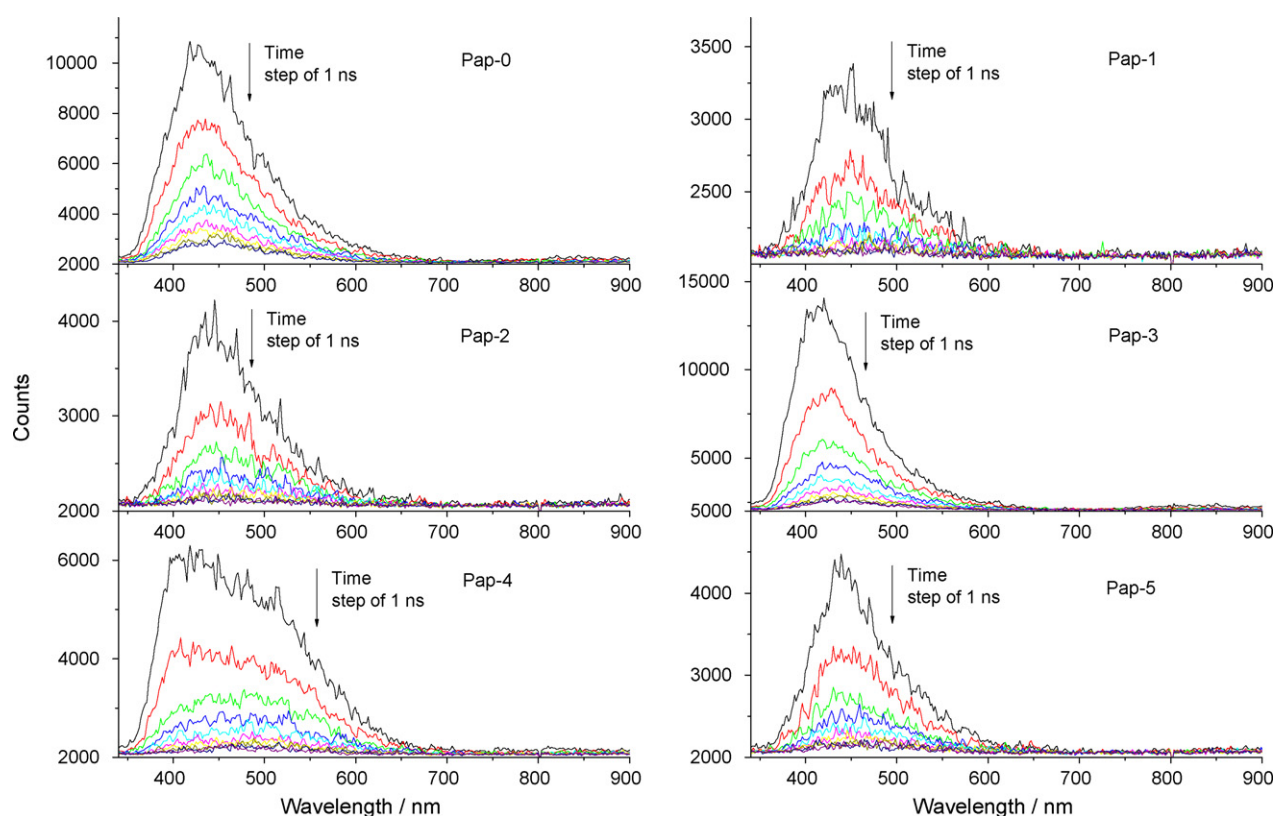


Fig. 2. Time-resolved fluorescence spectra of spruce thermomechanical pulps, Pap-0 to Pap-5. Excitation was at 337 nm in all samples, the spectra were recorded with the time step of 1 ns.



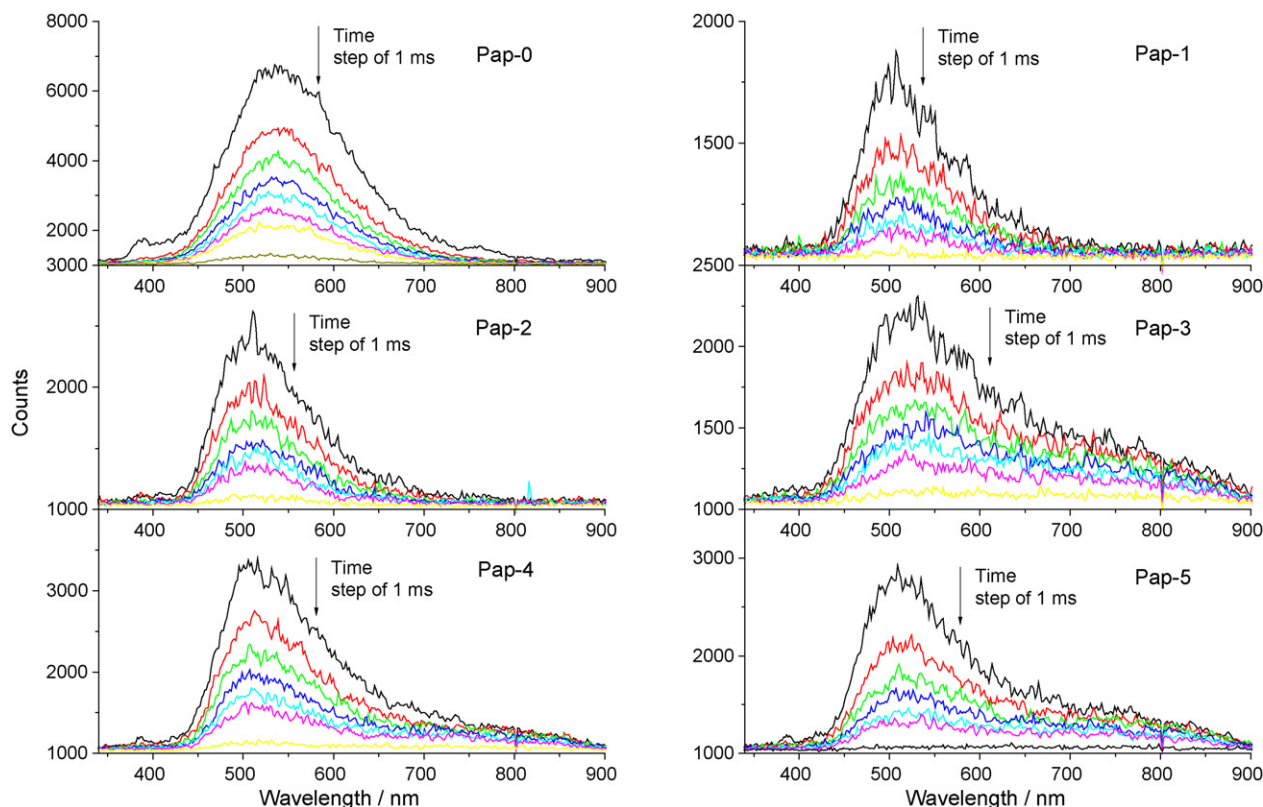


Fig. 3. Time-resolved emission spectra of spruce thermomechanical pulps, Pap-0 to Pap-5. Excitation was at 337 nm in all samples, the spectra were recorded with the time step of 1 ms.

fluorescence is broad and has the band shape suggesting at least two emissive species, one similar to that present in all of the other samples, and a new one with the maximum at ca. 510 nm. This new band may result from the phenolic hydroxyl groups methylation and formation of new fluorescent products in the pulp; in any case, further studies would be required to confirm this hypothesis. The time evolution of the fluorescence spectra suggests that all of the respective fluorescence lifetimes are very similar. However, it is interesting to note that the intensity of fluorescence observed is the highest in Pap-0 and Pap-3, and the lowest in Pap-1, Pap-2 and Pap-5. It is well known that the luminescence of the wood pulps is mainly caused by the lignin fluorescence. The intense fluorescent emission of the reference samples (Pap-0) may be attributed to such lignin structural motifs as coniferyl, biphenyl or stilbene groups. However, both the samples Pap-0 and Pap-3 that contain either “native” lignin or lignin that was at first oxidised with peroxide and then reduced with sodium borohydride, are characterized by low carbonyl groups content. The intense fluorescence after the borohydride reduction (Pap-3) is in agreement with the results by Machado et al. [4] and is probably caused by elimination of carbonyl groups that are basically non-fluorescent and creation of more strongly fluorescent reduced species. It is worth to note that the intensity of the fluorescence of the samples treated with peroxide only though at varied conditions (Pap-1, Pap-2 and Pap-5) differs from sample to sample, which suggests changes in the chromophoric system due to the treatments.

In addition to fluorescence measurements in the nanosecond time range we also performed luminescence measurements in the millisecond time range for all samples. All samples show such long-lived luminescence, and their time-resolved luminescence spectra are presented in Fig. 3. The spectra of pulp samples recorded with the time step of 1 ms show less distinct differences than those observed in the nanosecond time range. The spectra of all of the samples after chemical treatment have luminescence maxima at about 500 nm (Fig. 3), in some cases having also a tail extending to the near-infrared, suggesting an emission maximum at longer wavelengths. This happens especially in the case of Pap-3 and may be explained as above by formation of new more fluorescent species after reduction of the carbonyl groups. A similar broad structureless tail is to some extent observed in Pap-4 and Pap-5. Interestingly, the luminescence in Pap-0 has the maximum at ca. 545 nm. The luminescence intensity and the lifetimes are very similar for all the six samples. The only exception is the higher luminescence intensity of the reference sample Pap-0.

Fig. 4 shows diffuse reflectance laser transient absorption spectra recorded in a very wide time range from 1  $\mu$ s to 20 ms after the excitation pulse. These spectra present larger sample-to-sample variability. For the reference sample Pap-0, transient species with the maximum at about 430 nm and a broad structureless tail extending beyond 750 nm are observed, with both bands decaying. However, build-up of a new species is noticeable after ca. 100  $\mu$ s with an absorption maximum at ca. 400 nm.

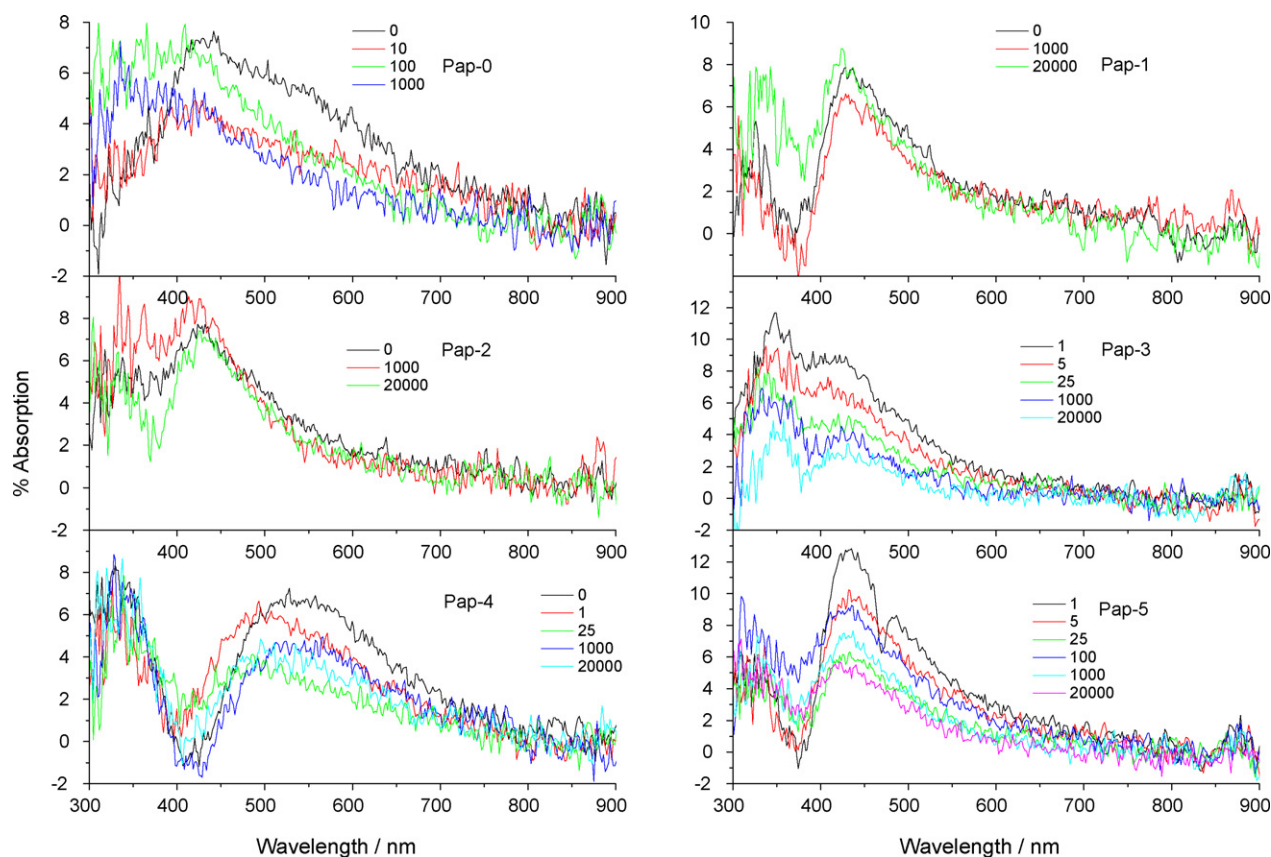


Fig. 4. Diffuse reflectance laser flash photolysis spectra of spruce thermomechanical pulps, Pap-0 to Pap-5. For all samples the excitation was at 266 nm, the spectra were recorded after the time delay shown in microseconds.

At the 10 ms delay time the transient absorption maximum shifts to about 340 nm, retaining a relatively high intensity. As compared to the reference, the transient spectra of the Pap-1 and Pap-2 show differences of the photochemical behaviour that reflect the changes of the chromophoric system due to peroxide treatment. In Pap-1 and Pap-2 the initial transients are similar to each other, and have the maximum at about 430 nm, like the reference sample. However, in contrast to the reference sample, the transient species observed in Pap-1 and Pap-2 have lower absorption in the 500–700 nm range; the presence of the respective absorption in the reference sample indicates existence of a distinct transient species absent in Pap-1 and Pap-2. In contrast to the reference sample, no spectral shift is observed in these two samples. However, comparing the spectra taken immediately after excitation to those after millisecond delays indicate that after the fast decay of the initial transient, another transient is built up, strongly absorbing in the same spectral region. It is important to note that the used DRLFP system discovered differences between short-lived intermediates observed in untreated TMP (Pap-0) and that bleaching in acidic peroxide (Pap-1). The changes of chromophores caused by peroxide under acidic conditions are difficult to observe, as the free radicals formed during the treatment modify the chromophores without eliminating them completely. The consumption of hydrogen peroxide is low, and the results of ISO brightness measurements may be confusing after the short preliminary pulp treatment (Table 1). The observed differences in transient absorption between the

reference sample and the peroxide treated pulp (Pap-1, Pap-2 and Pap-5) together with the analysis of the standard chemical and technological indices (Table 1) suggest that modification of the chromophoric system during the acidic stage facilitates the removal of these chromophores at the alkaline stage of bleaching, which is essential from the technological point of view.

The transient decay of Pap-3 is one of the simplest: after the initial formation of a transient with the maximums at about 350 and 420 nm it is slowly decaying. It should be noticed that after ca. 1000  $\mu$ s the transient absorption of the borohydride-reduced pulp is lower as compared to other peroxide-only treated samples (Pap-1, Pap-2 and Pap-5). Similar behaviour but observed at zero time after the laser pulse had been reported by Schmidt et al. as an evidence that the transient is caused by the absorption of light by lignin's conjugated carbonyl groups [14]. Finally, Pap-5 is somewhat similar to Pap-3, with a continuous decay observed. However, in contrast to Pap-3, here the maximum at ca. 430 nm is dominant, whereas the second maximum does not appear.

Pap-4 representing TMP sample after phenolic hydroxyl group methylation exhibits a broader initial band with its maximum at about 550 nm and another maximum at about 336 nm. The band with the initial absorption at 550 nm indicates some complexity of the system. Shortly after excitation, a new species with a maximum at ca. 500 nm is formed, with long-lived species formed after the initial fast decay. However, methylation that has blocked the phenolic hydroxyl groups did not increase the amount of transient species as would be expected. Such

a phenomenon had been noticed by Schmidt et al. as a proof of quenching of carbonyl triplets by phenolic hydroxyls [14]. The possible explanation is that presently the methylation was limited to the phenolic hydroxyl groups of lignin, having left intact the acidic hydroxyl groups of polysaccharides (note the relatively low content of methoxyl after methylation—5.31%). Since the high-yield pulp contains nearly all of the original wood chemical constituents, the excited carbonyl triplets may abstract hydrogen both from the phenolic hydroxyls and from carbon atoms of secondary alcohols such as cellulose and hemicelluloses, which would explain the efficient quenching of the carbonyl triplets [14].

The spectra and kinetics recorded by us are very similar to the transient spectra recorded previously for black spruce thermo-mechanical pulp [14], for example, the maximum wavelength of the transient spectra had previously been reported to be around 450 nm [25]. Our transient absorption spectra are similar to others published for the lignin model compounds with methoxy substituents in the para position [10,26,27]. The comparison and similarity of the spectroscopic data lead to the suggestion that in our case the transient observed can also be assigned as a triplet excited state localized at aromatic carbonyls, probably the electronic triplet excited state of the aryl ketone group in lignin [11].

The results presented demonstrate that the techniques proposed may especially help in better understanding of the photochemistry of different pulps and papers, and of the different stages of the technological processes of papermaking. Because of its high efficiency, low cost and reliability, the method of diffuse reflectance spectroscopy can be an interesting alternative to time-consuming and expensive wet chemistry analytic techniques at different phases of the paper technology. Additionally, the proposed two-stage treatment may be recommended for industrial implementation, as it provides higher quality of the final product at a significantly reduced consumption of the chemicals.

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