HOW TO EVALUATE THE KRAFT PULP BRIGHTNESS STABILITY?

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ABSTRACT

Proper accelerated ageing methods (dry vs. humid heat) and applicability of UV-Vis reflectance spectroscopy for brightness stability studies of kraft pulps were considered. It was shown that UV-Vis reflectance spectroscopy can be used as a very sensitive and simple method to follow the degradation of HexA during thermal ageing treatments of kraft pulps. It was confirmed that the dry heat treatment (105°C, 4h), often used for eucalyptus kraft pulps, does not fully reveal the contribution of HexA to brightness reversion, and may thus lead to erroneous conclusions regarding the factors affecting brightness stability. According to UV-Vis measurements, dry heat treatment with prolonged reaction time leads to the degradation of HexA, but the actual color forming reactions of HexA's degradation products probably do not take place in dry conditions.

INTRODUCTION

Brightness is one of the most important quality parameters of commercial pulps, and it should be maintained also after transportation and storage. Especially for high brightness eucalyptus market pulp, the brightness stability is a significant issue, and lot of research has been carried out recently in order to optimize the pulping process also in this respect.

Brightness reversion is, however, a complex phenomenon affected by several factors. For better control of kraft pulp brightness stability, it is important to identify all the fiber components and their substructures responsible for brightness reversion. Especially the detrimental effect of hexenuronic acid (HexA) and its degradation products has been highlighted recently (1, 2). Still it is only one factor among others, and in some studies no correlation between pulp HexA content and brightness reversion tendency has been observed (3, 4). Residual lignin remaining in bleached pulp, oxidized carbohydrate structures formed during pulp production, metals, some extractives as well as chlorinated structures also enhance kraft pulp brightness reversion (5, 6, 7, 8). Due to the numerous contributors, detailed chemical characterization is required to understand the phenomena.

Besides the pulp composition, also the prevailing conditions affect brightness reversion. It is well known that the chemical pulps are more prone to heat than light induced brightness reversion. Some of the thermally induced discoloration reactions require humidity, whereas high temperature alone may convert some of the leucochromophores to colored structures. Recent results suggest that the detrimental effect of HexA on brightness stability cannot be seen in dry heat treatment, but only in moist conditions (9). To identify the true factors responsible for brightness reversion, it is important to select proper accelerated ageing method. Dry heat treatment is often used to evaluate the brightness stability of eucalyptus pulps (3, 8, 10), but in practice, *e.g.* at drying machine, or during shipping and storage, both moisture and temperature affect.

The aim of this paper is to clarify the importance of proper accelerated ageing method, as well as analytical methods for reliable evaluation of kraft pulp brightness reversion tendency. Therefore, the contribution of HexA to brightness reversion was investigated using both dry and humid heat treatments. As a fast and simple tool to follow the degradation of HexA during accelerated ageing, the applicability of very sensitive UV-Vis reflectance spectroscopy was introduced. Methods and general phenomena affecting brightness reversion were investigated using eucalyptus (*E. globulus* and *E. grandis*), birch and pine kraft pulps.

EXPERIMENTAL

Pulps investigated

ECF bleached Eucalyptus kraft pulps were obtained from mills for brightness stability analyses. *Eucalyptus globulus* pulp (ISO Br. 90.2 %) was provided by a South European mill, and *Eucalyptus grandis* pulp (ISO Br. 91.1 %) by a South American mill. Those were compared with an ECF bleached Birch (*Betula verrucosa/pubescens*) kraft pulp (ISO Br. 89.5) from a Finnish mill.

Birch pulps were also prepared in laboratory, using DEDED and (O/O)Q(Paa/Q)(PO)/(PO) bleaching sequences. Final brightness of ECF and TCF pulps was 89.7 % and 88.0 %, respectively.

Pine (*Pinus sylvestris*) kraft pulps were prepared in laboratory by two-stage cooking using profiled alkalinity (PA) and low sulphidity (LS) to produce pulps with clearly different properties, and also different HexA content (5). Both pulps were cooked to kappa level 30, and they were bleached after oxygen delignification using several ECF (DEDD, DEDDPaa, DEDP, DEZ/QP) and TCF (QPPaaP and QPZ/QP) sequences. The final brightness target was the same for all pine pulps (88-89% for ECF and 83-84% for TCF pulps).

Accelerated ageing methods

Humid heat treatment was performed according to ISO 5630-3 standard at temperature of 80°C and 65% relative humidity for 48 h. Dry heat treatment was performed according to Tappi UM-200 at 105°C for 4 h, and also for 48 h to better justify the comparison with humid heat treatment.

UV-VIS spectroscopy

The UV-Vis reflectance spectra were recorded at constant 50% relative humidity at 23°C by Perkin Elmer Lambda 900 spectrometer equipped with integrating sphere. The whole spectral region (200-800 nm) was measured before and after thermal ageing using either thick handsheets of 184 g/m^2 or thin handsheets of 20 g/m^2, with adjusted pH 5.0-5.2. In case of thin sheets, the reflectance measurements were performed against white (R_{wb}) and black (R_0) reference backgrounds, and the reflectance of a hypothetical infinitely thick sample (R_∞) was calculated from those as described in (11, 12). In all cases, the reflectance spectra were converted to absorbance spectra (*k/s*) using the Kubelka-Munk equation (1) to follow changes in pulp chromophores during ageing.

$$\frac{k}{s}=\frac{(1-R_\infty)^2}{2R_\infty} \qquad (1)$$

The *k* and *s* values were not determined separately, but the ratio *k/s* as such was considered to represent absorption spectra well enough for semi-quantitative evaluations.

The extent of brightness reversion was evaluated by PC-numbers, which were determined using reflectance (R_∞) values measured before and after thermally induced ageing at 457 nm, according to equations (1) and (2).

$$PC=100\cdot\left[\left(\frac{k}{s}\right)_{after}-\left(\frac{k}{s}\right)_{before}\right] \qquad (2)$$

Other pulp analyses

Pulp brightness (ISO 2470), kappa number (ISO 302) and viscosity (ISO 5351-1) were determined using standard methods. Lignin kappa was calculated by subtracting the contribution of hexenuronic acids (HexA) to the kappa number (kappa – 0.085 x HexA) (13). The HexA content was determined by HPAEC-PAD after enzymatic hydrolysis (14). Carbonyl group contents were determined using the hydroxylamine method (15). Extractive content was determined gravimetrically after acetone extraction.

Lignin contents of the pine pulps were determined by pyrolysis GC/MS using the external calibration method from handsheet samples washed with tap water (16). Samples were pyrolyzed at 580ºC using a Pyrola2000 filament pulse pyrolyzer (PyrolAB, Sweden). For birch and eucalyptus pulps, total lignin content was determined as Klason lignin and acid soluble lignin (modified Tappi T 222 method).

RESULTS AND DISCUSSION

Applicability of UV-Vis reflectance spectroscopy for brightness stability studies

UV-Vis reflectance spectroscopy is an efficient method for brightness stability studies. Contrary to ordinary brightness measurements, the entire spectral region of UV and visible light can be covered by the reflectance measurements, and valuable information on reasons leading to the brightness reversion can be obtained in addition to the actual brightness drop or PC number. Together with more detailed chemical charcterization methods – or in some cases maybe even instead of those – UV-Vis reflectance spectroscopy can be used as a fast and simple method to reveal mechanisms behind yellowing.

Visible spectral region and reflectance spectra as such are sensitive to the changes in colored pulp components determining pulp brightness. After conversion of reflectance spectra into absorbance (*k* or *k/s*) spectra by Kubelka-Munk equation, also changes in UV-active structures can be followed. This is important, because the colorless UV-active structures (like HexA, carbonyl groups and some lignin units) are known precursors to the colored structures formed during yellowing. This way it is possible to obtain some information directly from pulp handsheets on chemical changes leading to the brightness reversion without laborious chemical analyses. In earlier works, *k/s* spectra have been used to follow delignification and removal of HexA during bleaching according to specific absorption maxima of lignin (280± 5 nm) and HexA (235 ± 5 nm) (12, 17). Those wavelengths were shown to correlate reasonably well with changes in pulp lignin and HexA content during bleaching (12). Similarly changes for example in HexA can be followed after accelerated ageing treatments, as shown in this paper.

According to the PC numbers given in Table 1 for the laboratory birch pulps studied, the TCF bleached pulp has significantly higher tendency towards yellowing compared to the ECF bleached pulp. Carbonyl content of the pulps was not determined, but due to peroxide and peracetic acid stages, it should be relatively low in

TCF pulp. Lignin and extractives contents were relatively similar, and chlorinated structures should not exist in TCF pulp. Thereby, the poor brightness stability of TCF pulp was suggested to be largely due to the exceptionally high HexA content. This was confirmed with UV-Vis reflectance measurements.

Table 1. Chemical composition and pulp properties of TCF and ECF bleached birch pulps.

	ECF Birch	TCF Birch
Brightness, %	89.7	88
Kappa number	1.0	4.7
Lignin kappa	1.0	1.6
Total lignin, %	1.5	1.1
Viscosity, ml/g	1240	700
Extractives, %	0.5	0.5
HexA, mmol/kg	*	36
PC number	2.0	8.7
R457 before, %	92.5	89.5
R457 after, %	80.6	65.1

**Below reliable detection limit of HexA (4.5 mmol/kg)*

The high HexA content of TCF bleached birch pulp can be seen as a strong signal at 240 nm in *k/s* spectrum (curve 1) given in Figure 1. As a result of humid heat treatment, the signal intensity decreases as HexA degrades during ageing, and a new absorption band at 285 nm is formed (curve 2). For ECF bleached pulp with HexA content below detection limit, only slight increase in absorbance at 285 nm is detected (curves 3 and 4).

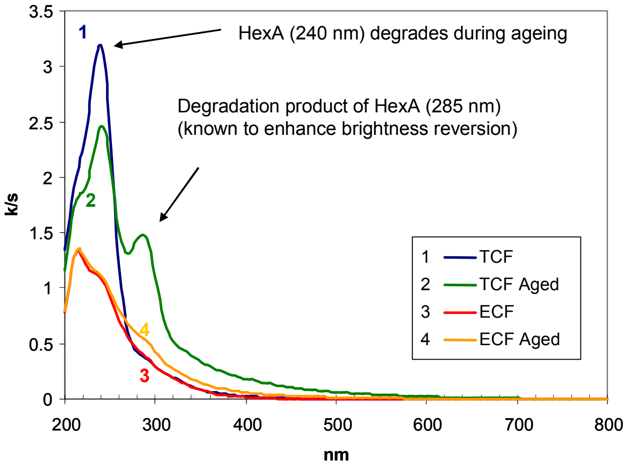

Figure 1. Absorbance (k/s) spectra of TCF and ECF bleached birch pulps as such and after humid heat treatment (80°C, 65% RH, 48h).

The difference between TCF and ECF bleached pulps can be seen even better in the difference absorbance spectra, shown in Figure 2. The positive absorption bands indicate structures formed during thermal treatment, whereas negative bands indicate structures removed. According to the representative absorption maximum of 285 nm, the new structure formed during thermal treatment was identified to be 5-formyl-2-furancarboxylic acid (FFA), which in addition to 2-furancarboxylic acid, is known to be formed in acid hydrolysis of HexA (18).

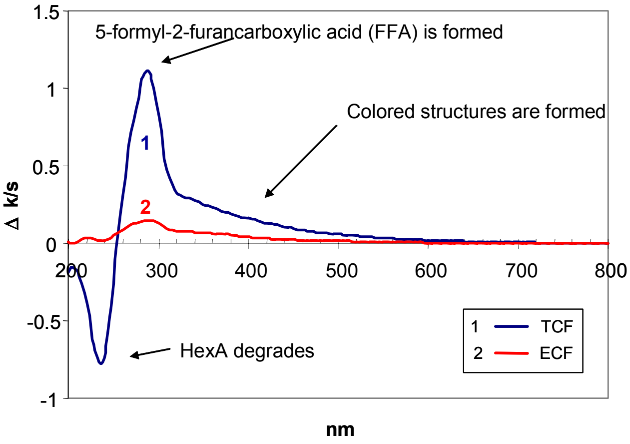

Figure 2 Difference absorbance (Δ k/s) spectra of TCF and ECF bleached birch pulps, describing reactions taking place during humid heat treatment (80°C, 65% RH, 48h).

The assignment was confirmed by FFA model compound impregnated on filter paper. As an UV-active compound, the FFA itself is colorless, but during humid heat treatment it reacts further forming colored structures, as shown in Figure 3. The brightness reversion enhancing effect of FFA has been observed also previously (1).

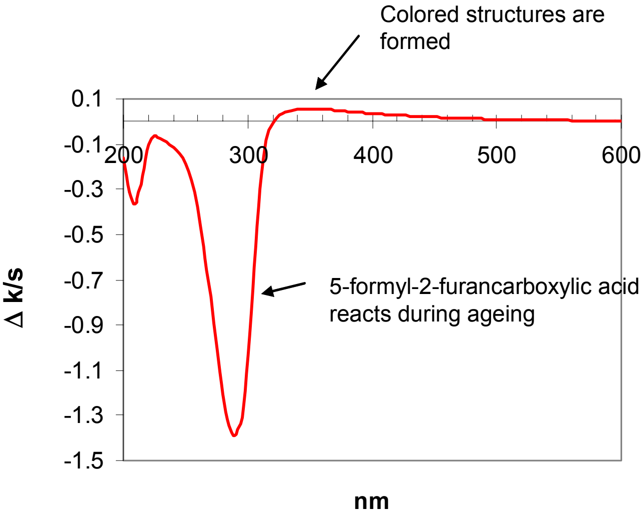

Figure 3 Difference absorbance (Δ k/s) spectrum of 5-formyl-2-furancarboxylic acid (FFA) model compound impregnated on filter paper, showing reactions taking place during humid heat treatment (80°C, 65% RH, 48h).

Since the formation of FFA can be easily detected by UV-Vis reflectance measurements, it can be considered as an indicator of the involvement of HexA to brightness reversion. For example, in another study where properties of a birch mill pulp were compared with the properties of two eucalyptus mill pulps, the brightness reversion of the pulps increased in following order: *E.grandis* < Birch < *E. globulus*. Observed differences could not, however, be explained by their chemical composition (Table 2).

Table 2. Chemical composition and pulp properties of ECF bleached birch and eucalyptus mill pulps.

	Birch	**E. grandis**	**E. globulus**
Brightness, %	89.5	91.1	90.2
Total lignin, %	0.4	0.4	0.4
Extractives, %	0.12	0.06	0.06
Monosaccharide composition:			
Glucose, %	74.8	84.8	80.2
Xylose, %	25.2	15.2	19.8
HexA, mmol/kg	*	*	*
PC number	1.2	0.4	1.7

**Below reliable detection limit of HexA (4.5 mmol/kg)*

Although the HexA content was below the detection limit of HPAEC method in all the pulps, the UV-Vis measurements suggest that HexA content of pulps increases in the same order as their brightness reversion tendency (Figure 4).

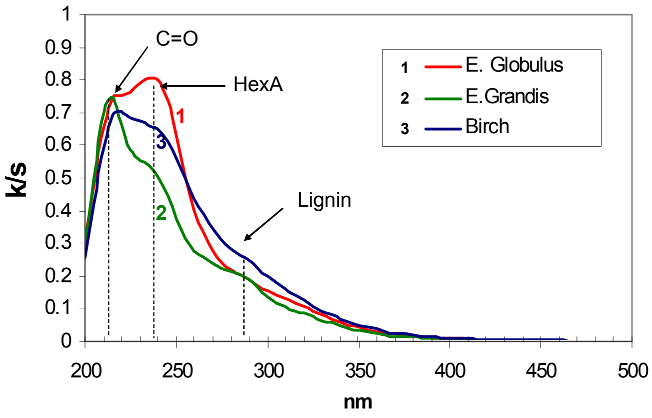

Figure 4. Absorbance (k/s) spectra of ECF bleached birch and eucalyptus pulps.

Figure 5 clearly shows the typical signal of FFA in difference spectrum of *Eucalyptus globulus,* indicating degradation of HexA. The reactions of HexA and its effect on brightness stability can thus be detected even in very low amounts by very sensitive UV-Vis reflectance measurements.

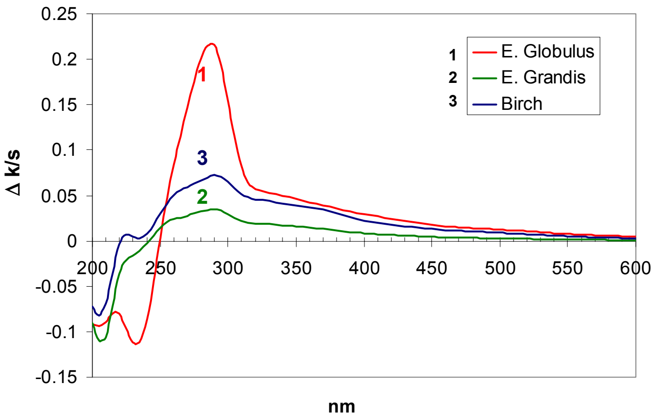

Figure 5. Difference absorbance (Δ k/s) spectra of ECF bleached birch and eucalyptus pulps, describing reactions taking place during humid heat treatment (80°C, 65% RH, 48h).

Effect of ageing method and HexA content on brightness stability results

Brightness stability results obtained in different studies are not comparable as such, since there is a large variety of accelerated ageing methods commonly used. Different conditions do not only affect the level of PC-numbers, but may also emphasize factors affecting brightness reversion differently. Recent results suggest that the detrimental effect of HexA on brightness stability cannot be seen in dry heat treatment, but only in moist conditions (9). However, in most studies dry heat treatment is used to the brightness stability evaluation of eucalyptus pulps (8, 3, 10).

To investigate the effect of humidity on brightness reversion tendency, some well characterized softwood kraft pulps (Table 3) were now ageid in dry conditions (105°C, 4h and 48h), and results were compared to those obtained previously after humid heat treatment (80°C, 65% RH, 48h) (5). Especially the contribution of moisture to the HexA related brightness reversion was investigated using pulps with different HexA contents after cooking, and also after ECF and TCF bleaching.

It is reasonable to believe that the behaviour of HexA is similar in softwood and hardwood pulps, although the impact is more severe in hardwood pulps due to their higher HexA content. Due to different cooking conditions, the profiled alkalinity (PA) pulp had significantly higher HexA content (42 mmol/kg) compared to the low-sulphidity (LS) pulp (15 mmol/kg). The former is comparable to the HexA level of most hardwood kraft pulps.

Table 3. Properties of ECF and TCF bleached profiled-alkalinity (PA) and low-sulfidity (LS) pulps.

Sample	**ISO Br.** (%)	**Lignin kappa**	**HexA** (mmol /kg)	**Py-lignin** (%)	**C=O** (mmol /kg)
ECF:					
PA-pulp:					
ODEZ/QP	87.5	0.6	*	0.20	10
ODEDP	87.6	0.5	*	0.20	6
ODEDD	85.4	0.6	*	0.18	10
ODEDDPaa	88.8	0.5	*	0.16	8
LS-pulp:					
ODEZ/QP	87.2	0.4	*	0.08	10
ODEDP	87.1	0.6	*	0.15	6
ODEDD	87.2	0.6	*	0.09	10
ODEDDPaa	88.8	0.5	*	0.08	9
TCF:					
PA-pulp:					
OQPPaaP	82.2	3.3	4.1*	0.76	6
OQPZ/QP	81.7	2.3	11	0.40	7
LS-pulp:					
OQPPaaP	82.7	2.1	1.8*	0.86	7
OQPZ/QP	83.0	1.3	3.9*	0.46	8

**Below reliable detection limit of HexA (4.5 mmol/kg)*

Humid heat treatment

In our previous study, the combined effect of cooking and bleaching sequence on brightness stability of softwood kraft pulps was investigated after humid heat treatment (80°C, 65% RH, 48h) (5). According to results shown in Figure 6, the LS pulp with low initial HexA content had better brightness stability than the PA pulp, especially after TCF bleaching.

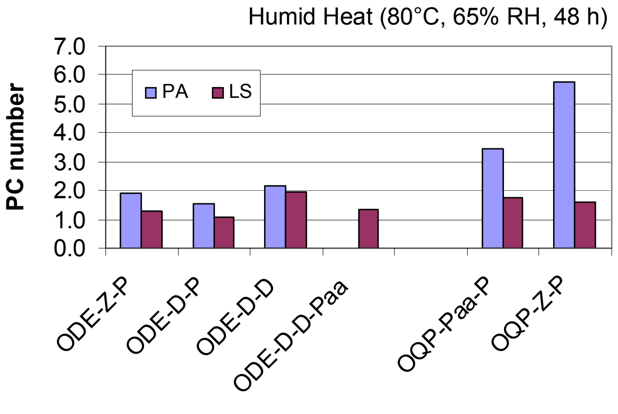

Fig. 6. Brightness reversion of ECF and TCF bleached pine kraft pulps after humid heat treatment (80°C, 65% RH, 48h .

In all ECF bleached pulps, the HexA content was below reliable detection limit, and no clear sign on formation of FFA during humid heat treatment could be seen in *k/s* spectra either. HexA had thus no impact on brightness reversion of the ECF pulps, and the differences observed between sequences were largely explained by carbonyl contents of the pulps. Ozone increased carbonyl content, reducing brightness stability compared to D1 stage. It was beneficial to use peroxide as a final bleaching stage instead of chlorine dioxide. Hydrogen peroxide diminishes the carbonyl content by oxidative reactions, whereas chlorine dioxide as a final stage rather generates new carbonyl structures, *e.g.* quinones. Paa stage performed after the D2 stage also diminishes the carbonyl content and improves brightness stability, although not as effectively as peroxide.

All HexA or residual lignin could not be removed as efficiently by TCF bleaching. Thereby, the higher initial HexA content of PA pulp remains also after TCF bleaching and results in significantly lower brightness stability compared to ECF pulps or TCF bleached LS pulps. In TCF sequences, Paa removes HexA more efficiently, whereas lower lignin contents were achieved with ozone (Table 3). Better brightness stability was thus obtained for profiled alkalinity PA pulp with peracetic acid than with ozone. For the low-sulphidity LS pulp, nearly same brightness stability was obtained with both chemicals.

Dry heat treatment

The PC-numbers obtained after the commonly used dry ageing method (105°C, 4h, Tappi UM-200) are shown in Figure 7 for the same pulps. The PC numbers are significantly lower in all pulps, and almost at the same level in both TCF and ECF bleached pulps. After dry heat treatment, the detrimental effect of the higher HexA content of TCF-bleached PA pulps cannot be seen at all. This was the case also after the prolonged treatment time of 48 h, which corresponds to the time used in humid heat treatments (Figure 8). This is in accordance with the results of Björklund *et al.* (9), supporting that HexA related brightness reversion takes place only with humid heat.

For ECF pulps, similar results were obtained by both dry and humid heat, only the level of PC-numbers was lower. Effect of carbonyl structures can thus be seen similarly by both methods.

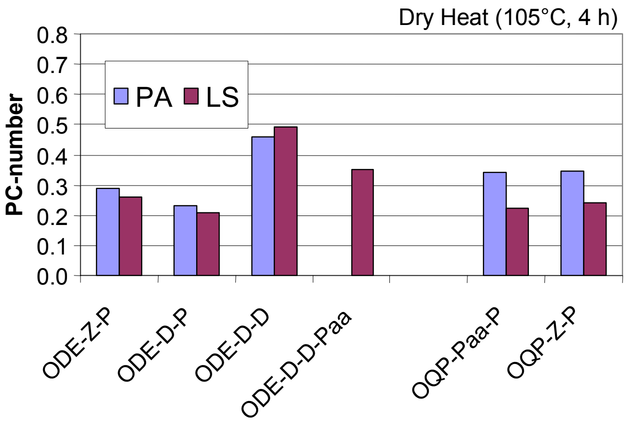

Figure 7. Brightness reversion of ECF and TCF bleached pine kraft pulps after dry heat treatment (105°C, 4h) .

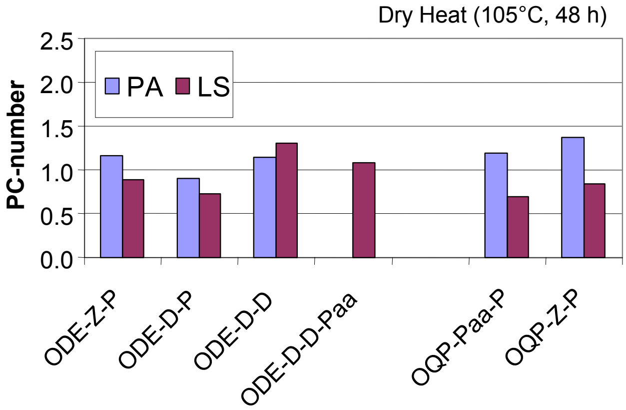

Figure 8. Brightness reversion of ECF and TCF bleached pine kraft pulps after prolonged dry heat treatment (105°C, 48h) .

According to UV-Vis measurements of OQPZP bleached PA pulp (Figure 9) with the highest HexA content, some FFA (at 285 nm) is formed also in dry conditions. After 4 h dry heat treatment, the formation of FFA is minor, supporting that the effect of HexA cannot be seen by the most commonly used dry heat treatment method (curve 1).

After 48h dry heat treatment (Figure 9, curve 2) the signal of FFA is comparable to that after humid heat treatment (curve 3), although the color formation above wavelengths of 350 nm is still minor compared to the humid heat treatment. This suggests that HexA is degraded also in dry conditions, but the further reactions of FFA that are responsible for the actual color formation probably do not take place. Since FFA is formed and removed in humid heat treatment, the lower signal intensity after humid heat treatment (curve 3) does not necessarily indicate that FFA is formed in lower extent, but rather that the further reactions take place in higher extent in presence of moisture. The behavior of FFA in dry heat treatment, however, needs to be confirmed by model compound experiments.

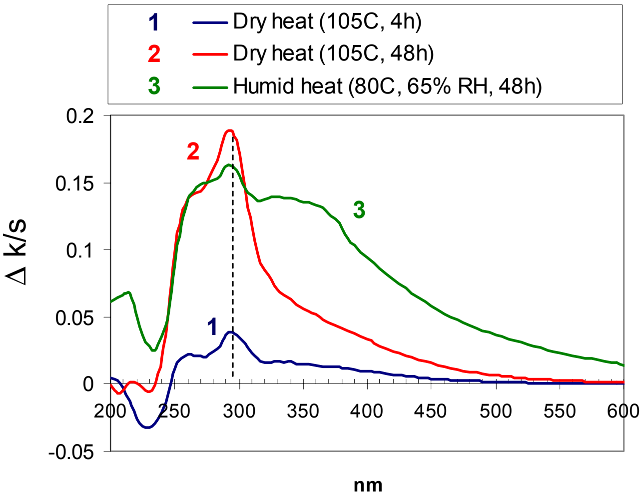

Figure 9. Difference absorbance (Δ k/s) spectra of OQPZP bleached PA pulp, describing reactions taking place during dry heat treatment of 4h and 48 h, as well as during humid heat treatment (80°C, 65% RH, 48h).

CONCLUSIONS

According to our results, the UV-Vis reflectance spectroscopy can be used as a very fast and simple method to follow the degradation of HexA during thermal ageing treatments for brightness stability studies of kraft pulps. Owing to the sensitivity of UV-Vis method, the 5-formyl-2-furancarboxylic acid (FFA) formed as a degradation product of HexA could be detected even in cases where HexA content of pulp was below detection limit of HPAEC method.

It was also confirmed that the contribution of HexA to brightness reversion cannot be fully revealed by dry heat treatment, which may lead to erroneous conclusions regarding factors affecting brightness reversion. According to UV-Vis measurements and FFA formation, no significant degradation of HexA takes place in conditions of the commonly used dry heat treatment (105 °C, 4h). Dry heat treatment with prolonged reaction time of 48 h results in degradation of HexA, but the actual color forming reactions of HexA’s degradation products probably do not take place in dry conditions.

The selection of proper accelerated ageing method depends on conditions we want to simulate. In practice, however, both moisture and temperature affect in most cases simultaneously, *e.g.* at drying machine, or during shipping and storage. Therefore, humid heat treatment is more reliable method for evaluation of kraft pulp brightness stability.

ACKNOWLEDGEMENTS

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