

Ultraviolet Resonance Raman Spectroscopy Analysis of Carbonyl Groups Present after Different Bleaching Stages for Various Bleach Sequences

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Different bleaching reagents have different efficiencies of removing chromophore groups from chemical pulps. The objective of this work was to evaluate the effect of different bleaching sequences on the removal of chromophore groups, especially carbonyls, which are suspected to cause brightness reversion. The bleaching sequences analyzed comprise the stages: chlorine dioxide, acid hydrolysis at high temperature, alkaline extraction with hydrogen peroxide, pressurized hydrogen peroxide, and hydrogen peroxide. After bleaching an oxygen-delignified eucalypt kraft pulp with these sequences, the pulps were analyzed for their final brightness, brightness reversion, and pulp viscosity; the bleached pulps were also analyzed using ultraviolet resonance Raman spectroscopy in the infrared region. The infrared analysis indicated that bleaching stages that used hydrogen peroxide, such as pressurized hydrogen peroxide or hydrogen peroxide, in the terminal position reduced the amount of carbonyl groups in the bleached pulp as measured by the absorption band intensity. This study observed that the inclusion of a hot acid hydrolysis stage in the bleach sequence improved the final brightness and brightness stability of the bleached eucalyptus pulp. The replacement of a chlorine dioxide brightening stage by a hydrogen peroxide stage at the end of a bleach sequence yielded higher pulp brightness, and less brightness reversion. The use of pressurized hydrogen peroxide with oxygen resulted in less brightness reversion.

Keywords: Chromophoric groups; Infrared spectroscopy; Carbonyl groups

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INTRODUCTION

The production of bleached pulp is of great economic importance in the country, and it is the subject of studies to improve the properties of the final product. Both brightness and brightness stability are important parameters for qualifying pulp in the market.

Bleaching removes the chromophoric groups present in the cellulosic pulp, such as lignin, extractives, carbonyl and carboxyl groups, carbohydrate and lignin complexes, and metals, aiming to achieve the brightness and brightness stability required for pulp marketing (Eiras and Colodette 2005; Oliveira *et al.* 2006). Carbonyl groups tend to be the main organic functional group that intensifies brightness reversion.

The bleaching process utilizes different combinations of bleaching reagents in individual stages to ensure the effective and efficient removal of chromophoric groups in chemical pulp, and it is the final bleaching stage that ensures removal of the carbonyl groups, as well as ensures final pulp brightness stability. Nevertheless, precautions are taken with the bleaching stages, such that there are minimum reductions in the pulp viscosity due to non-optimum bleaching conditions (Colodette and Gomes 2015), but it is the final bleaching stage that determines the purity stability of the pulp according to its efficiency in the removal of the carbonyl groups.

Brightness reversion is an aggravating factor in the bleached pulp quality criterion because it is the reduction of brightness already achieved during the bleaching process, which is intensified by the presence of remaining chromophore groups in the bleached pulp.

According to Peak (2005) and Zhihua and Moore (2015), infrared spectroscopy is a form of vibrational spectroscopy in the study of a variety chemical processes, as well as being a fast, economical, immune to water interference, non-destructive technique and which does not require sample preparation. According to Dudek et al. (2019) and Herrero (2008), individual molecular spectra are the result of Raman scattering effects and molecular vibrations. Such spectra can serve as fingerprints for compounds and mixtures.

Ultraviolet resonance Raman (UVRR) spectroscopy can analyze residual chromophores in the pulp even at very low concentrations. By applying a suitable UV excitation wavelength, these structures can be analyzed *via* Raman scattering (Loureiro *et al.* 2010). According to Silverstein *et al.* (1980), it is possible to identify the presence of chemical compounds present in the sample through comparing the spectra in the infrared region of the sample with a standard.

The amount of carbonyl groups (C=O) in the pulp has been correlated to the degree of brightness reversion (Oliveira *et al.* 2006; Barbosa *et al.* 2013). Therefore, spectrometry in the infrared region (at specified wavenumbers) is used in this investigation to study this functional group in bleached pulp.

The stretching frequency of the carbon-oxygen double bond of the carbonyl group exhibits a strong peak between 1630 and 1850 cm^{-1} . This moiety is found in aldehydes, ketones, esters, carboxylates, amides, and other organic functional groups, so the exact wavenumber value depends on the particular functional group and adjacent functional groups (Silverstein *et al.* 1980).

In this context, infrared analysis is a very important tool, because according to the intensity of the absorption bands it is possible to evaluate the presence of the carbonyl groups in the pulp and consequently to verify the efficiency of the bleaching stages in the removal or transformation of these groups.

EXPERIMENTAL

Materials

An oxygen-delignified eucalypt kraft pulp was obtained from a Brazilian pulp mill (Itapeva, Brazil). The initial characteristics of the eucalypt pulp are: Kappa number of 8, brightness of 65.2% ISO, and pulp viscosity of 27.3 cP.

In this study, the reference bleach sequence $D_0(E+P)D_1D_2$ has been modified by the addition and/or replacement of bleaching stages, such as A_{HT} , (PO) and P. The modified bleach sequences examined were $A_{HT}D_0(E+P)D_1D_2$, $D_0(E+P)D_1P$, $A_{HT}D_0(E+P)D_1P$,

$A_{HT}D_0(PO)$, and $A_{HT}D_0(PO)D_1$. The abbreviations for the individual bleaching stages of D, A_{HT} , (E+P), (PO), and P refer to chlorine dioxide, acid hydrolysis at high temperature, alkaline extraction reinforced with hydrogen peroxide, pressurized hydrogen peroxide, and atmospheric hydrogen peroxide, respectively.

The bleaching stages were conducted in polyethylene bags, where the chemical reagents were manually mixed with the pulp, and afterwards the bags were sealed. The bags were then placed into a heated water bath at the prescribed reaction temperature for a predetermined time. The stage with pressurized peroxide (PO) was performed in a digester with four individual stainless steel reactors, each with a capacity of 1.5 L, with temperature and pressure adjustment. The specific conditions of the individual bleaching stages are shown in Table 1.

Table 1. General Conditions of the Bleaching Process

Conditions	Bleaching Stages							
	D ₀	D ₀ [*]	A _{HT}	P	(E + P)	D ₁ [*]	D ₂ [*]	(PO)
Consistency (%)	10	10	10	10	10	10	10	10
Time (min)	30	120	120	120	60	180	180	60
Temperature (°C)	60	70	95	95	70	70	70	105
Pressure (kPa)	-	-	-	-	-	-	-	500
Final pH	2.7	3.8	2.0	11	11.2	3.8	4.1	10.5
NaOH (kg/t)	-	Optim.	-	Optim.	8.0	-	-	6.0
H ₂ SO ₄ (kg/t)	Optim.	-	Optim.	6.0	-	-	0.3	-
ClO ₂ , (kg/t as Cl ₂)	KF ¹ =0.2	20.0	-	-	-	8.0	2.0	-
H ₂ O ₂ (kg/t)	-	-	-	3.0	3.0	-	-	3.0

¹ KF is Kappa factor charge (% ClO₂ on pulp (as act. Cl₂)/Kappa no. of entering pulp); *D₀ is chlorine dioxide delignification stage, D₁ is first chlorine dioxide brightening stage, and D₂ is the second chlorine dioxide brightening stage

For each bleaching stage, constant operating conditions were adopted, according to Table 1. The operational conditions were established to ensure the minimum brightness in each of the analyzed sequences (90 ± 0.5 % ISO). The bleaching conditions of stage D₀^{*} were adequate with prior experimental study, so that the bleaching sequence $A_{HT}D_0(PO)$ reached 90% ISO brightness as the others. All bleaching stages were replicated twice.

The pulps were analyzed using the following TAPPI standard methods or Useful Methods (UM): forming handsheets according to TAPPI T205 sp-12 (2015), Kappa number according to TAPPI T236 om-13 (2015), pulp viscosity according to TAPPI T230 om-13 (2015), brightness of pulp according to TAPPI T525 om-12 (2015), and the brightness loss according to TAPPI UM 200 (2015).

Methods

Spectroscopic analysis in the medium infrared region attenuated total reflection ultraviolet (ATR-UV)

Spectrometric analyses in the infrared region can detect the presence of carbonyl groups that can be detrimental to the final brightness stability.

The influence of the acid hydrolysis stages, pressurized peroxide with oxygen, chlorine dioxide, and final hydrogen peroxide in the carbonyl groups was observed in the

infrared ATR. The analyses were performed on a Platinum ATR equipment with an infrared microscope (Hyperion 2000; Bruker, Araraquara, Brazil) of the absorption spectrometer in the middle infrared region with a Raman coupled laser (1064 nm with a power of 1000 mW), at the 400 to 4000 cm^{-1} wavenumber range at a resolution of 4 cm^{-1} ; 64 scans were performed for each spectra recorded for a given pulp handsheet (made by TAPPI T205 sp-12 (2015)).

The focus of the study was in the spectral range of 1630 cm^{-1} to 1850 cm^{-1} of the carbonyl groups.

Statistical analyses

Statistical analyses of the results were determined at the 95% confidence level ($\alpha = 0.05$). Tukey's statistical test was used for the paired comparison among treatments with an α of 0.05. To show the differences among treatments, the principle letters for the comparison among means by the Tukey test was adopted: means accompanied by the same letter do not differ statistically among themselves at the 5% probability level. The analyses were performed using the R Project for Statistical Computing (R Foundation, version 3.5.1, Vienna, Austria).

RESULTS AND DISCUSSION

Results from Various Bleaching Sequences

The results from the bleaching of the oxygen-delignified eucalypt pulp by the various bleach sequences are presented in Table 2.

Table 2. Results from the Bleaching of Oxygen-delignified Eucalypt Pulp with Various Bleaching Sequences

Pulp Property	D ₀ (E + P)D ₁ D ₂	A _{HT} D ₀ (E + P)D ₁ D ₂	A _{HT} D ₀ (E + P)D ₁ P	A _{HT} D ₀ (PO)	A _{HT} D ₀ (PO)D ₁
Brightness reversion ($\Delta\%$ ISO)	2.1 a* (0.0548)	1.8 b (0.0548)	1.1 c (0.0816)	1.0 d (0.0983)	1.0 d (0.1033)
Viscosity (cp)	22.77 a (0.9309)	21.75 a (1.4828)	19.8 b (0.3213)	17.63 c (0.0924)	19.8 b (0.0658)
Final brightness (% ISO)	91.0 a (0.1643)	91.0 a (0.0408)	92.0 b (0.1169)	90.0 c (0.0837)	89.6 d (0.0894)
Reverted brightness (% ISO)	88.9 (0.1673)	89.3 (0.0516)	90.9 (0.1169)	89.0 (0.1506)	88.6 (0.1366)

*Means followed by the same letters do not present statistical differences in paired comparisons (Tukey's test, $\alpha = 0.05$); mean values listed are followed by their standard deviations in parentheses

The use of the A_{HT} stage in the A_{HT}D₀(E + P)D₁D₂ sequence improved the brightness stability of the pulp when compared to the control D₀(E + P)D₁D₂ sequence. This result is attributed to the removal of hexenuronic acids and transitional metal ions from the pulp, as is generally described in the bleaching literature (Forsström and Greschik 2007). Replacing the D₂ stage with a P stage increased the final brightness and brightness stability of the pulp bleached by the A_{HT}D₀(E + P)D₁P sequence *versus* the A_{HT}D₀(E + P)D₁D₂ sequence. However, this substitution resulted in a significant drop in pulp viscosity.

Minor brightness reversion was observed with the A_{HT}D₀(PO)D₁ and A_{HT}D₀(PO) sequences due to the efficiency of the (PO) stage to eliminate the carbonyl groups.

However, pulp viscosity losses were noted when using bleach sequences that contained (PO) stages.

To evaluate the effects of bleaching stages on brightness reversion, a statistical analysis was performed to compare $D_0(E + P)D_1D_2$, $A_{HT}D_0(E + P)D_1D_2$, $A_{HT}D_0(E + P)D_1P$, $A_{HT}D_0(PO)D_1$, and $A_{HT}D_0(PO)$ bleaching sequences. The calculated p -values among the bleach sequences were less than 0.05, which indicated that there were statistical differences among the sequences at the 95% level or higher. Tukey's tests indicated statistical differences among the paired comparisons. The $A_{HT}D_0(PO)D_1$ and $A_{HT}D_0(PO)$ sequences did not differ with respect to the brightness reversion; nevertheless, the other sequences did differ from these two sequences and from each other.

Infrared (IR) Spectroscopy Analysis

The effect of the last bleaching stage on the chemical composition of the pulp was evaluated. The IR spectra observed at the various stages of each of the various bleach sequences were similar, which varied from one another in their absorption intensity depending on the bleaching stages that were used.

A wide band relative to OH stretching, which is indicative of alcohols and carboxylic acids (Silverstein *et al.* 1980), was observed between 3000 to 3500 cm^{-1} . The characteristic absorption band for aromatic and heteroaromatic skeletons was observed at the 1300 to 1500 cm^{-1} ; bands absorptions at 1085 to 1150 cm^{-1} are associated with the asymmetric axial deformations of the C-O-C structures of aliphatic esters. The angular deformation of C-C structures was observed in the region of 500 cm^{-1} , while at 800 to 1000 cm^{-1} there were axial vibrations of the C-C bond. The intense absorptions at 2840 to 3000 cm^{-1} are attributed to C-H bonds, and the absorption band at 1024 cm^{-1} suggested the presence of silicone, due to defoamers used in the mill. The absorption bands at 1033 to 1060 cm^{-1} correspond to the axial deformations of C-O structures in primary and secondary alcohols. Absorptions at 2850 to 2955 cm^{-1} indicated the presence of aliphatic structures, which are typical of long-chained hydrocarbons. The band located around 1429 cm^{-1} is attributed to the axial deformation of C=C bonds. The observed absorption bands of most interest of this study, 1630 and 1750 cm^{-1} , are assigned to the C=O stretching of carbonyl groups. The infrared spectra obtained after the D_1 and D_2 stages of the $D_0(E + P)D_1D_2$ and the $A_{HT}D_0(E + P)D_1D_2$ bleach sequences are shown in Figs. 1 and 2, respectively.

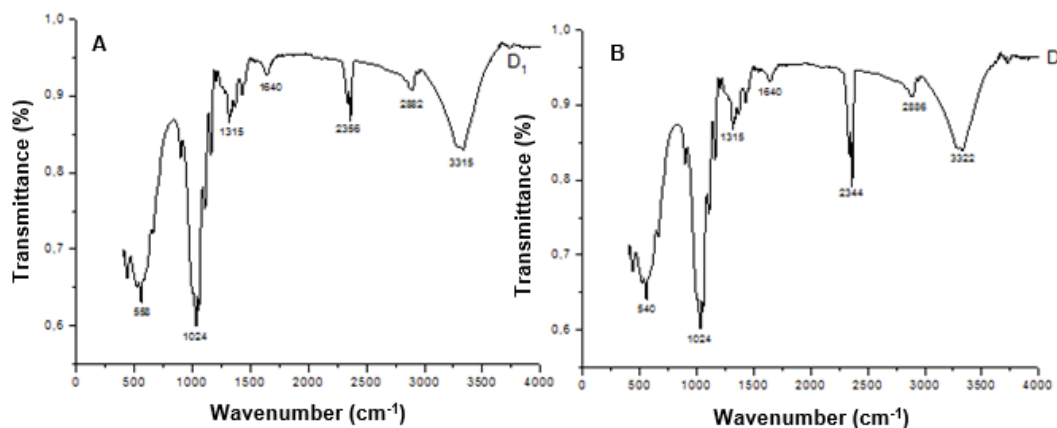


Fig. 1. Infrared spectra of the sequence $D_0(E + P)D_1D_2$: A – after the D_1 stage, and B – after the final D_2 stage

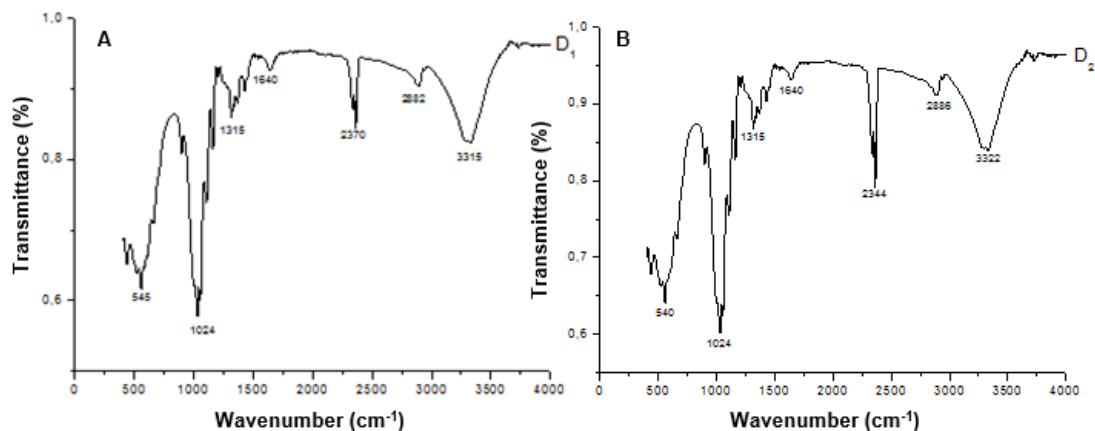


Fig. 2. Infrared spectra of the sequence $A_{HT}D_0(E + P)D_1D_2$: A – after the D_1 stage, and B – after the final D_2 stage

The recorded infrared spectra obtained after the D_1 stage and after the P stage for the $A_{HT}D_0(E + P)D_1P$ sequence are shown in Fig 3. The infrared spectra recorded after the D_0 stage and after the (PO) stage for the $A_{HT}D_0(PO)$ bleach sequence are shown in Fig 4.

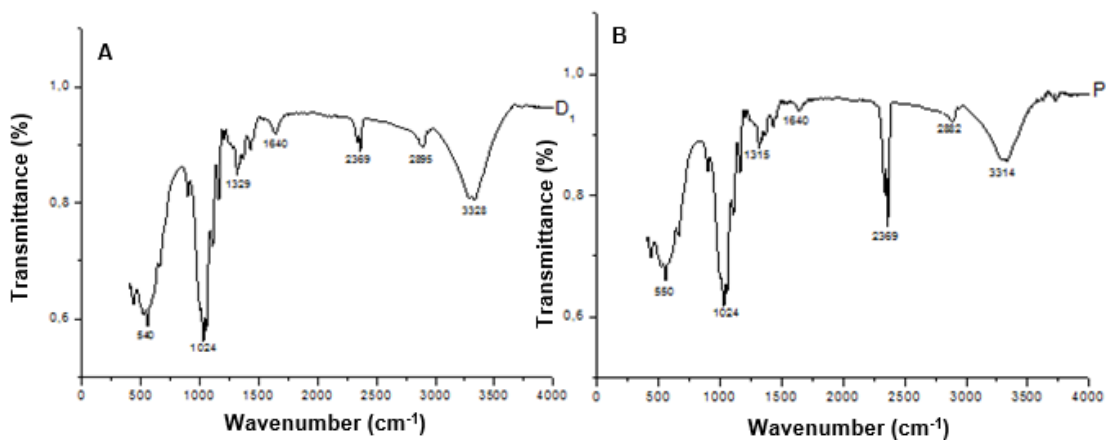


Fig. 3. Infrared spectra of the sequence $A_{HT}D_0(E + P)D_1P$: A – after the D_1 stage, and B – after the final P stage

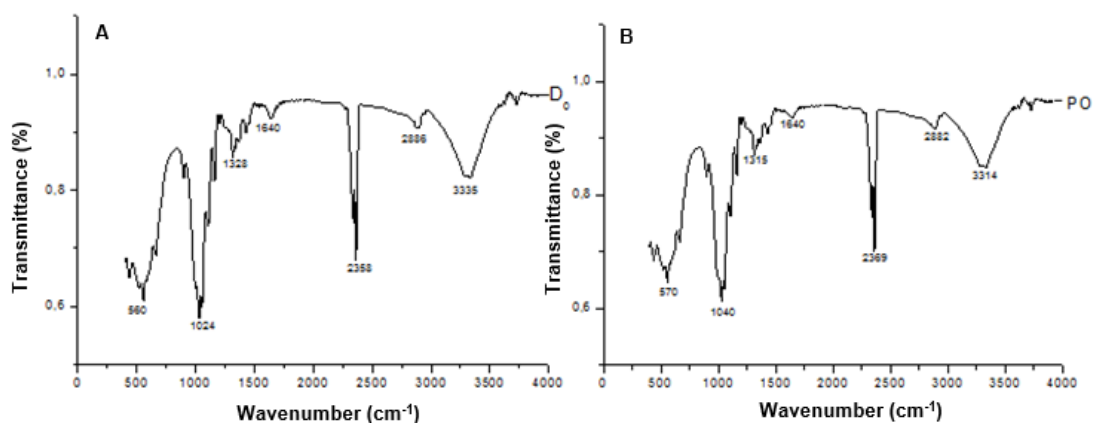


Fig. 4. Infrared spectra of the sequence $A_{HT}D_0(PO)$: A – after the D_0 stage, and B – after the final (PO) stage

The infrared spectra recorded after the D₀, (PO), and D₁ stages of the A_{HT}D₀(PO)D₁ bleach sequence are shown in Fig. 5. The spectra after each of these bleaching stages were similar to one another. It was necessary to evaluate all three bleaching stages because the final stage and its preceding stages are important in this bleaching sequence. However, the D₀ stage that preceded the (PO) stage is of utmost interest due to the observed intensity of the carbonyl absorption band.

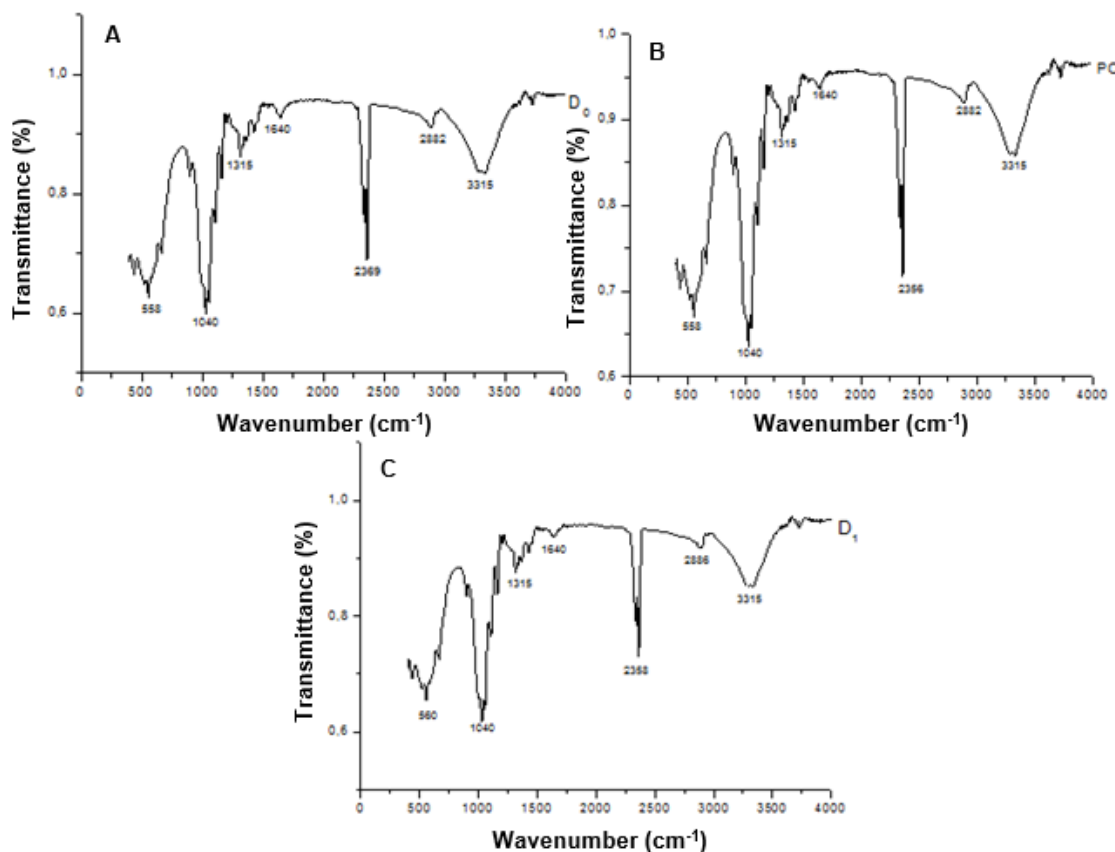


Fig. 5. Infrared spectra of the sequence A_{HT}D₀(PO)D₁: A – after the D₀ stage, B – after the (PO) stage, and C –after the final D₁ stage

Carbonyl Spectral Analysis of D₀(E + P)D₁D₂ Bleach Sequence

The infrared absorption intensity in the spectral region of 1630 to 1750 cm⁻¹ was analyzed to evaluate the efficiency of the final D₂ stage in the D₀(E + P)D₁D₂ sequence to remove carbonyl groups, as shown in Fig. 6. This figure compares the spectra after the final D₂ stage to that of the previous D₁ stage to see how the C=O stretch absorption bands were affected.

Comparing the two stages, D₁ and D₂, it was observed that there was no difference in the absorption band intensities in the region examined. In this bleach sequence case, it appeared that chlorine dioxide did not affect the amount of carbonyl groups in the pulp. It was shown earlier that the D₀(E + P)D₁D₂ sequence had the greatest brightness reversion (Δ 2.1% ISO), which was attributed to the negligible change in the amount of carbonyl groups during the D₂ stage treatment. Loureiro *et al.* (2012a) and Boas (2005) reported similar observations.

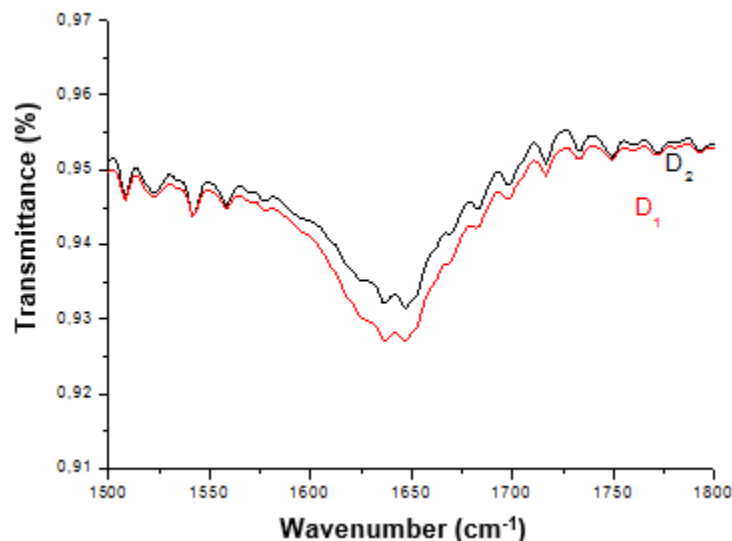


Fig. 6. Carbonyl absorption bands after D_1 and D_2 for $D_0(E + P)D_1D_2$ bleach sequence

Carbonyl Spectral Analysis of $A_{HT}D_0(E + P)D_1D_2$ Bleach Sequence

The carbonyl removal efficiency of the final D_2 stage in the $A_{HT}D_0(E + P)D_1D_2$ sequence was also evaluated (Fig. 7), where the spectra after the final D_2 stage was compared to that immediately after the D_1 stage.

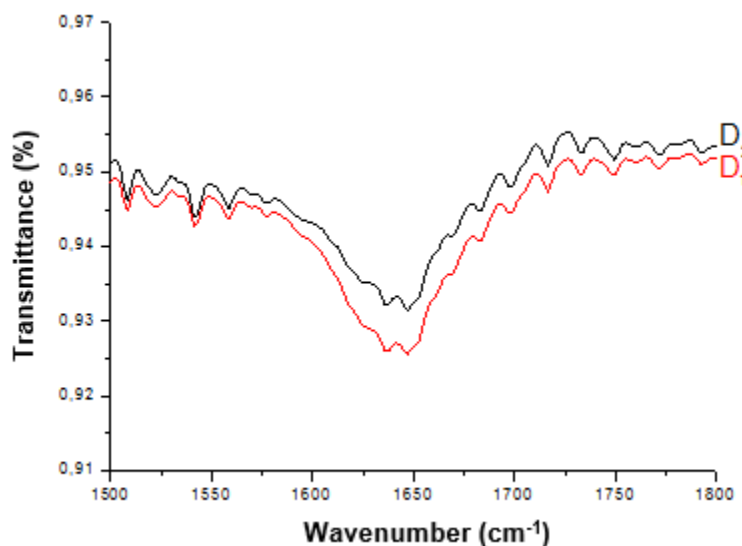


Fig. 7. Carbonyl absorption band after D_1 and D_2 for $A_{HT}D_0(E + P)D_1D_2$ bleach sequence

In this comparison, the absorption intensities of the two spectra were nearly identical, which suggested that the D_2 stage did not affect the amount of carbonyl groups *versus* the D_1 stage. This observation reaffirmed the hypothesis that the chlorine dioxide does not remove the carbonyl groups.

It should be emphasized that the introduction of a hot acid hydrolysis stage in this bleaching sequence resulted in a brightness reversion of $\Delta 1.8\%$ ISO, which was slightly lower than the corresponding $D_0(E + P)D_1D_2$ sequence ($\Delta 2.1\%$ ISO). This observation suggested that the inclusion of the A_{HT} stage reduced final brightness reversion with this

bleach sequence regardless of the removal of carbonyl groups by chlorine dioxide. This indicated that there are other factors that also affected brightness reversion. Eiras and Colodette (2005), Forsström and Greschik (2007), and Ventorim *et al.* (2009) reported higher brightness stabilities when the bleach sequence included a high temperature acid hydrolysis stage. The authors attributed this positive effect of the elimination of hexenuronic acids by acid hydrolysis. Additionally, Sevastyanova *et al.* (2006) has also suggested that the improved brightness stability can also be related to the removal of transition metal ions by the hot acid hydrolysis stage.

Carbonyl Spectral Analysis of A_{HT}D₀(E + P)D₁P Bleach Sequence

The carbonyl removal efficiency of the final P stage in the A_{HT}D₀(E + P)D₁P bleaching sequence was determined by comparing the spectra of the D₁ stage to that of the P stage (Fig. 8).

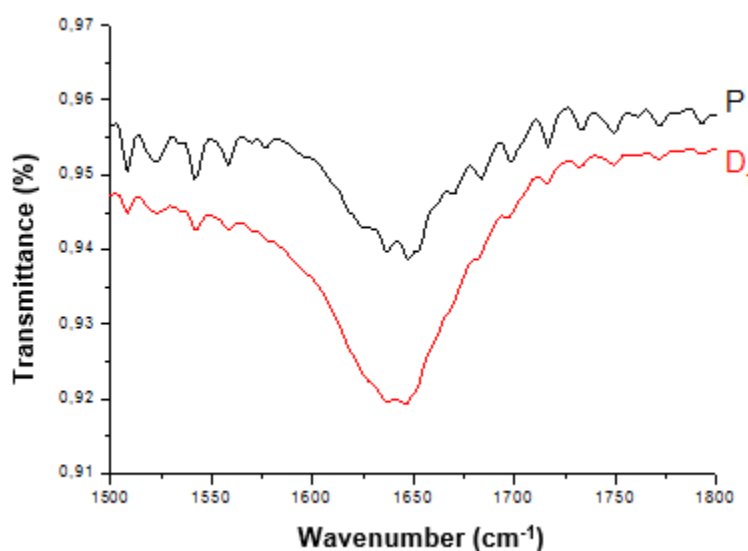


Fig. 8. Carbonyl absorption band after D₁ and P for A_{HT}D₀(E + P)D₁P bleach sequence

The intensity of the carbonyl band was reduced after the final P stage when compared to the preceding D₁ stage. Hydrogen peroxide reacted with the aldehydes and ketones (that contain carbonyl groups) to convert them into carboxylates; the ionized carboxylates were more soluble in alkaline media, and were removed from the pulp. This resulted in a reduction in the absorption band intensity in the region of carbonyl groups.

The A_{HT}D₀(E + P)D₁P sequence had low brightness reversion (Δ 1.1% ISO) when compared to the bleach sequences that had a final D₂ stage, such as D₀(E + P)D₁D₂ (Δ 2.1% ISO) or A_{HT}D₀(E + P)D₁D₂ (Δ 1.8% ISO). From these observations, it was concluded that the final P stage removed carbonyl groups (Fig. 8), which had a positive effect on the final brightness stability. Eiras and Colodette (2005), Ventorim *et al.* (2009), and Loureiro *et al.* (2012b) also showed that a P stage caused a decrease in the carbonyl levels in the pulps that had been previously bleached with chlorine dioxide stages. Loureiro *et al.* (2005), Boas (2005), and Pinheiro (2005) indicated that hydrogen peroxide is effective at the removal of carbonyls groups during bleaching through examining various spectra analyses.

Carbonyl Spectral Analysis of A_{HT}D₀(PO) Bleach Sequence

The efficiency of a final (PO) stage to remove carbonyl groups with the A_{HT}D₀(PO) sequence was evaluated by comparing the D₀ spectra to that of the (PO) spectra in the carbonyl absorption band region (Fig. 9).

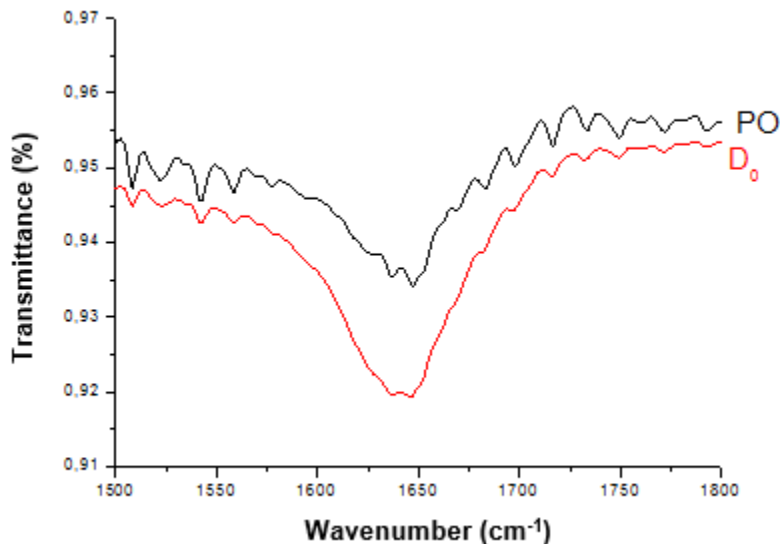


Fig. 9. Carbonyl absorption band after D₀ and (PO) for A_{HT}D₀(PO) bleach sequence

The absorption band of the carbonyl groups after the final (PO) stage was reduced when compared to the D₀ stage. Hence, it was concluded that the (PO) stage efficiently removed carbonyl groups, which impacted final brightness stability (Δ 1.0% ISO) of the A_{HT}D₀(PO) sequence. Eiras and Colodette (2005) reported that sequences with a (PO) stage resulted in pulps with low brightness reversion. Pinheiro (2005) and Boas (2005) observed that the (PO) stage was effective at the removal of carbonyl groups in bleached pulps.

Carbonyl Spectral Analysis of A_{HT}D₀(PO)D₁ Bleach Sequence

It has been shown earlier in this study that chlorine dioxide did not reduce the level of carbonyls in the bleached pulp when the pulp was analyzed by IR spectroscopy. However, it is necessary to evaluate how a final D₁ stage of the A_{HT}D₀(PO)D₁ affects the amount of carbonyl groups. Because this bleach sequence had a (PO) stage that preceded the D₁ stage, it was necessary to examine the carbonyl absorption band spectra (1630 to 1750 cm⁻¹) of these three stages, D₀, (PO), and D₁, to determine their carbonyl removal efficiencies. The comparisons of these spectra are shown in Fig. 10.

Based on the spectra absorption intensities for the carbonyl absorption band of the final D₁ stage *versus* the preceding (PO) stage, there were no differences observed. This indicated that chlorine dioxide did not affect the levels of carbonyl groups in the bleached pulp. However, the reduction in absorption intensity after the stage (PO) when compared to the preceding D₀ stage reaffirmed the hypothesis that the (PO) stage was effective at removing carbonyl groups. Pinheiro (2005) indicated that a terminal chlorine dioxide brightening stage that was preceded by a (PO) stage did not affect the carbonyl absorption band intensity of the pulp. This observation by Pinheiro (2005) is reaffirmed by the results obtained in this study.

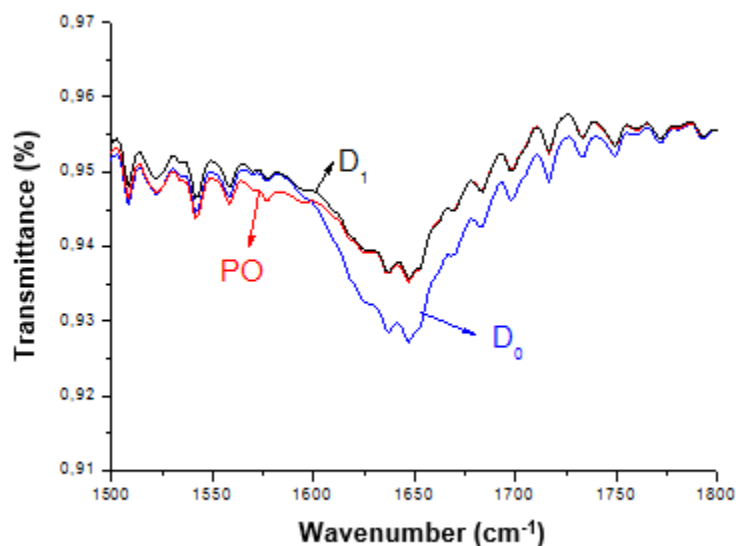


Fig. 10. Carbonyl absorption band after D_0 , after (PO), and after D_1 for $A_{HT}D_0(PO)D_1$ bleach sequence

CONCLUSIONS

The following statements can be concluded from the observations made in this study:

1. The $D_0(E + P)D_1D_2$ sequence resulted in a bleached pulp with the lowest brightness stability of all the bleach sequences examined, with a brightness reversion of 2.1 %ISO.
2. The inclusion of an A_{HT} stage in the bleach sequence increased the brightness stability of the oxygen-delignified eucalypt kraft pulp.
3. The replacement of the terminal chlorine dioxide brightening stage with a hydrogen peroxide stage, P, yielded a pulp with higher brightness and higher brightness stability. The final peroxidation sequence, $A_{HT}D_0(E+P)D_1P$, promoted lower brightness reversion, 1.1 %ISO compared to the sequences terminated with chlorine dioxide, $D_0(E+P)D_1D_2$ and $A_{HT}D_0(E+P)D_1D_2$, 2.1 and 1.8 %ISO, respectively, but caused a decrease in viscosity.
4. Low brightness reversion, 1 %ISO was observed with bleach sequences that used pressurized peroxide, (PO), stages but caused a decrease in viscosity.
5. Examination of the infrared spectra absorption bands from the bleached pulps indicated that a terminal chlorine dioxide brightening stage was inefficient at removing carbonyl groups when compared to bleached pulps that had a terminal P or (PO) stage.
6. The final peroxidation and pressurized peroxide was more efficient at removing carbonyl groups, which afforded greater brightness stability

ACKNOWLEDGMENTS

The authors would like to thank Capes (Coordination of Improvement of Higher Level Personnel) for their financial support for this study.

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Article submitted: October 9, 2018; Peer review completed: December 30, 2018; Revised version received and accepted: January 15, 2019; Published: January 23, 2019.
DOI: 10.15376/biores.14.1.1915-1927