

Comparison of brightening kinetics in the final hydrogen peroxide stage of DE_{OP}DP and OQ(PO)DP bleaching sequences

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Abstract

The main purpose of this work was to study the effect of pulp bleaching history on the brightening kinetics of the final hydrogen peroxide stage in a conventional ECF sequence DE_{OP}DP and in a ECF-light sequence OQ(PO)DP. Two different partially-bleached *Eucalyptus globulus* kraft pulps, DE_{OP}D and OQ(PO)D, were collected before entering the last bleaching stage of two pulp mills. Both industrial pulps were submitted to a laboratorial final P stage using different bleaching conditions in the following ranges: H₂O₂ charge of 0.5-2.0 %odp, NaOH charge of 0.6-0.9 %odp, temperature of 70-90 °C, at 10 % consistency for seven reaction times (0-180 min). A preliminary study was performed to choose the most effective peroxide stabilizing system: the addition to the P stage of EDTA, DTPA, MgSO₄ or a mixture of them. This study has shown the usefulness of DTPA in reducing peroxide consumption and, simultaneously, in minimizing pulp viscosity loss. Therefore, a DTPA charge of 0.05% odp was used to minimize the catalytic effect of transition metals on peroxide decomposition. For both pulps the role of peroxide decomposition reactions was highlighted at higher temperatures, 90°C, especially in the case of the DE_{OP}DP sequence. In addition, the brightening performance of the last P stage was much higher for the OQ(PO)D pulp than for the DE_{OP}D pulp. Therefore, the results clearly show the importance of pulp bleaching history on its bleachability with hydrogen peroxide.

Key Words: Hydrogen Peroxide, Final ECF Stage, Brightening kinetics, Pulp History

Resumo

O principal objectivo deste trabalho foi o estudo do efeito da história da pasta na cinética de branqueamento de um estágio final de peróxido de hidrogénio numa sequência ECF convencional, DE_{OP}DP, e numa sequência ECF-light, OQ(PO)DP. Duas pastas kraft de *Eucalyptus globulus*, parcialmente branqueadas, foram recolhidas em duas fábricas de pasta antes de entrarem no último estágio de branqueamento. Ambas as pastas industriais foram submetidas no laboratório a um estágio final P, utilizando diferentes condições de branqueamento nas seguintes gamas: carga de H₂O₂ de 0.5-2.0% odp, carga de NaOH 0.6-0.9% odp, temperatura de 70-90°C a 10% de consistência para sete tempos de reacção diferentes (0-180 min). Foi realizado um estudo preliminar sobre a escolha do sistema de estabilização mais eficaz: a adição de EDTA, DTPA, MgSO₄ ou a sua mistura no estágio P. Este estudo mostrou a utilidade do DTPA na redução da decomposição do peróxido e, simultaneamente, na minimização da perda da viscosidade da pasta. Assim, foi usada uma carga de 0.05% odp de DTPA para minimizar o efeito catalítico dos metais de transição na decomposição do peróxido. Para ambas as pastas o papel das reacções de decomposição do peróxido foi realçado a temperaturas elevadas, 90°C, sobretudo no caso da sequência DE_{OP}DP. Adicionalmente, o desempenho do estágio P final foi muito superior para a pasta OQ(PO)D do que para a pasta DE_{OP}DP. Assim, os resultados mostram claramente a importância da história de branqueamento da pasta na sua branqueabilidade com o peróxido de hidrogénio.

Palavras Chave: Peróxido de Hidrogénio, Estágio final ECF, Cinética de Branqueamento, História da Pasta

Introduction

The final stage of chemical pulp bleaching sequences is a brightening stage to gain the last difficult brightness points with the destruction of the chromophores still existing in the pulp. Considering this final stage within an ECF bleaching sequence, past research has shown the advantages of replacing the conventional chlorine dioxide stage (acidic) by hydrogen peroxide (alkaline stage). Chlorine dioxide savings [1-3], improved brightness stability [2-5] and higher beatability [5-6] of the pulps bleached with peroxide are the major benefits. Additionally, for a DEDP bleaching sequence (without oxygen delignification) with an ISO brightness target of $90 \pm 0.5\%$, the use of DED pulps with an ISO brightness of at least 87% was recommended by Carvalho et al. [5] in order to achieve superior papermaking properties in spite of the lower pulp intrinsic viscosity observed.

The higher beatability and tensile strength of the pulps bleached with a final P stage (compared to the final D stage) was assigned by Loureiro et al. [7] to the better fibre swelling capacity, which in turn is caused by a greater amount of carboxyl groups (ionized form) and by the osmotic pressure increase inside the fiber wall due to carboxylate counter-ions. Moreover, the brightness efficiency of a final P stage in destroying chromophoric structures is dependent on the ability of the previous stage to act as a pre-activation of the subsequent P-stage [8]. In addition, as proposed by Eiras et al. [9], the use of electrophilic oxidants, such as chlorine dioxide to remove pulp hexenuronic acids, and a final nucleophilic oxidation stage, such as peroxide to extract the remaining reducing unknown substances and to oxidize potential chromophores, benefits the brightness stability of eucalyptus bleached pulps. For instance, as shown by Rosenau et al. [10], the peroxide resistant 2-hydroxy-[1-4]benzoquinone structures can be chlorinated in the D stage (especially a D_{HT} stage), rendering the subsequent final P stage effective in destroying them and preventing the formation of new chromophores during ageing.

In a P-stage, not only occurs pulp brightening but also hydrogen peroxide decomposition. The latter's reaction mechanisms and effective control practices have been investigated for a long time. These reactions are rather complex involving different catalysts and pathways [11-12], being water, oxygen and the intermediates hydroxyl ($HO\cdot$) and superoxide anion ($O_2^{\cdot-}$) radicals the decomposition products. Based on the above, it is essential to minimize hydrogen peroxide decomposition because it leads to a wasteful loss of chemicals and to the production of unselective radicals that can attack polysaccharides, resulting in a reduced bleached pulp yield, an increased chemical oxygen demand (COD) of the effluent and a lower pulp viscosity.

The hydrogen peroxide anion (HOO^-) is considered to be the active brightening agent, formed according to Eq. (1) ($pK_a = 11.6$, $25^\circ C$). This anion is a strong nucleophile that reacts preferentially with carbonyl and conjugated carbonyl groups, for instance quinone structures formed in previous bleaching stages, such as chlorine dioxide and oxygen stages [13]. Since the nature of many of the remaining chromophores in almost full bleached pulps are of the quinone type [10] the suitability of hydrogen peroxide as a final brightening agent is confirmed.



Peroxide decomposition can be considered as base catalysed and metal catalysed reactions and depends on the local chemical environment. While, on the one hand, a higher pH favours the hydrogen peroxide dissociation into HOO^- , on the other hand it promotes alkali induced decomposition reaction [13], Eqs. (2-3):



In addition, the presence of transition metals, such as manganese, iron and copper, present as impurities in the bleaching chemicals, process waters and unbleached pulps, have a tremendous impact on peroxide decomposition. Although not having a general agreement, some possible mechanistic pathways are shown on Eqs. (4-6) where M means the transition metal ion [13, 14]. Another peroxide catalytic decomposition model, proposed by Vuorinen and Heikkilä, considers the effect of reducing sugars and oxygen on the decomposition rate [15-16].



Therefore, a maximum peroxide bleaching response demands a previous metal control in the bleach plant. The most commonly used practices are a selective metal chelation (Q stage) and an

unselective acid wash (A stage) both run in separated towers and followed by standard washing. These treatments can significantly improve the brightening achieved in a P stage [17]. The use of MgSO₄, as an additive in the P stage, is also common, especially in acid treated pulps to restore the appropriate level of magnesium, which is an important stabilizer of peroxide bleaching solutions. The addition of chelating agents (e.g., EDTA and DTPA), acting as transition metals scavengers in the P stage, is also efficient in minimizing peroxide decomposition. In some cases, combinations of both additives may be the most efficient stabilizing system as well, though cost may be prohibitive [11].

Although it is now well recognized the advantages of the final DP stages on the overall bleached pulp properties, little attention has been given to the effect of pulp bleaching history/type on the performance of the final brightening stages. The understanding of the upstream factors that contribute to the final pulp brightening is needed to better control bleached pulp properties as early as possible. In this sense, the effect of pulp bleaching history was assessed in the present work by comparing the brightening response of a final alkaline hydrogen peroxide stage applied to two partially-bleached kraft pulps from pulp mills that use distinct ECF bleaching sequences (DE_{OP}D and OQ(PO)D). This was accomplished by means of laboratorial kinetic studies being the development of mathematical kinetic models our ultimate goal. Their importance relies on ensuring efficient process control and optimization and, whenever possible, in providing some mechanistic insights on chemical reactions.

Experimental

Two industrial samples of *Eucalyptus globulus* kraft pulps partially bleached with the sequences DE_{OP}D (conventional ECF) and OQ(PO)D (ECF-light) were used in this work. They were thoroughly washed in the laboratory. In the preliminary laboratory experiments, these pulps were further bleached with hydrogen peroxide in order to find the best stabilizing system to use henceforward in the kinetic studies. The sodium salt of diethylenetriaminepentaacetate (DTPA) and ethylenediaminetetraacetate (EDTA) and MgSO₄ were added as stabilizers in the ranges presented in Table 1, and using 20 g of pulp (on a dry basis).

For the kinetic studies, the pulps were bleached with hydrogen peroxide at the selected conditions summarized in Table 1, and at the reaction times of 1, 5, 15, 30, 60, 120 and 180 min. All components of the bleaching system were pre-heated to the desired temperature as follows: the pulp was mixed with DTPA and NaOH solutions at 13% consistency in a polyethylene bag; the H₂O₂ solution was added to the equivalent amount of water needed to attain a final consistency of 10% in a glass flask. After the pre-heating period in an agitated thermostatic water bath, the hydrogen peroxide solution was added to the pulp suspension, setting the beginning of the reaction.

Table 1. Ranges of bleaching conditions used in the final P stage*.

Bleaching variable	Preliminary studies	Kinetic studies
H ₂ O ₂ (% odp)	DE _{OP} DP: 1.0 OQ(PO)DP: 0.5	0.5 – 2.0
NaOH (% odp)	0.60	0.6 – 0.9
DTPA (% odp)	0.05-0.20	0.05
EDTA (% odp)	0.05-0.20	---
MgSO ₄ (% odp)	0.025-0.100	---
Temperature (°C)	70	70 – 90
Time (min)	30	0 – 180
Consistency (%)	10	10

* - odp: oven dried pulp.

After each batch experiment, the pulp was vacuum filtered and the collected filtrate was used for the determination of chemicals residual after its cooling in an ice bath. The pulp was also cooled with distilled water (~4°C) and then washed with three litres of distilled water (~35°C) divided into three equal portions. Hydrogen peroxide residual was determined by iodometric titration with standardized sodium thiosulphate solution while sodium hydroxide residual was determined by titration until pH 8.6 with standardized hydrochloric acid solution after barium chloride addition and filtration. All the experimental procedures were performed twice.

The ISO brightness and intrinsic viscosity were measured according to ISO 2470 and ISO 5351, respectively. The corresponding values for the industrial pulps used in this study are shown in Table 2.

Handsheets for optical properties determination were prepared using the standard procedure described in ISO 3688.

Table 2. ISO brightness and intrinsic viscosity of the industrial DE_{OP}D and OQ(PO)D pulps.

Pulp	ISO brightness (%)	Intrinsic viscosity (dm ³ /Kg)
DE _{OP} D	87.5	1066
OQ(PO)D	87.4	988

Results and Discussion

Preliminary experiments were performed prior to the kinetic studies to find an efficient peroxide stabilizing system that could minimize competitive reactions catalyzed by transition metals. Accordingly, the most common additives used in the pulp and paper industry (DTPA, EDTA and MgSO₄) were used separately and combined in different proportions (Table 3), being the choice of the best system based on peroxide consumption, pulp ISO brightness and pulp intrinsic viscosity.

The positive effects of these additives on the performance of the final P stage are unequivocal translated by the results presented in Table 3. Regarding peroxide consumption, DTPA is the most effective in reducing it, being a small charge of 0.05% odp quite enough to stabilize hydrogen peroxide bleaching of DE_{OP}D pulps. Consequently, with the use of DTPA, lower hydrogen peroxide charge is wasted due to its decomposition. Moreover, the production of unselective radicals that can attack polysaccharides is minimized. In fact, when no additives are added the drop in intrinsic viscosity is significant compared to the stabilized systems due to the detrimental effects of the transition metals on peroxide decomposition. For the DE_{OP}D pulp, EDTA is not as effective as DTPA or MgSO₄ is from the intrinsic viscosity point of view. For this pulp, the highest charge of MgSO₄ did not reduce the peroxide consumption, doing the opposite by raising it. These results clearly show that the amount of Mg must be optimized, in accordance with the results of Bouchard et al. [17]. The different combinations of additives do not show improved results compared to DTPA alone.

Table 3. Effect of different stabilizing systems on the performance of the final P stage of the DE_{OP}DP and OQ(PO)DP bleaching sequences.

Stabilizer charge (% odp)			DE _{OP} DP (1.0% odp H ₂ O ₂ charge)			OQ(PO)DP (0.5% odp H ₂ O ₂ charge)		
MgSO ₄	DTPA	EDTA	H ₂ O ₂ consumed (%)	ISO brightness (%)	Intrinsic viscosity (dm ³ /kg)	H ₂ O ₂ consumed (%)	ISO brightness (%)	Intrinsic viscosity (dm ³ /kg)
---	---	---	31	90.2	989	57	90.9	912
0.025	---	---	21	89.9	1002	30	90.4	951
0.100	---	---	43	90.0	1041	23	90.5	973
---	0.050	---	9	90.1	1051	19	90.5	961
---	0.200	---	9	89.8	1055	22	90.2	974
0.025	0.050	---	15	89.9	1018	17	90.5	957
0.100	0.100	---	28	89.9	1053	12	90.1	986
---	---	0.050	22	90.0	1000	39	90.5	941
---	---	0.200	15	89.7	1001	14	90.4	963
0.025	---	0.050	14	89.9	1050	20	90.3	975
0.100	---	0.100	19	89.7	1035	20	90.3	982

As for OQ(PO)D pulp the positive impact of the additives on peroxide consumption and pulp intrinsic viscosity is also seen. The different metal profile of the two pulps and the chemical nature of the last chromophores are certainly responsible for the distinct bleaching response of the two pulps. In fact, a more pronounced brightness gain is observed for the OQ(PO)D pulp. Moreover, for this pulp,

the most effective system in reducing peroxide consumption and in preserving intrinsic viscosity is the mixture of 0.1% DTPA with 0.1% MgSO₄, but the difference between this mixture and the use of DTPA alone is not significant enough to offset the higher cost of the former. In addition, the higher brightness gain of the OQ(PO)DP pulp without additives, reaching an ISO brightness near 91%, in comparison with the experiments with additives, suggests that the peroxide decomposition products (radicals) have also participated in brightening reactions besides lowering pulp viscosity.

Being the main purpose of this work to establish a comparison between the brightening kinetics of both pulps, it is important to guarantee the most similar bleaching conditions under which the kinetic trials will occur. Therefore, a charge of 0.05% odp of DTPA was chosen for both pulps based on the results discussed above.

The importance of pulp bleaching history on the brightening kinetics of the final hydrogen peroxide bleaching stage is clearly shown in the results depicted on Figures 1-8. Although the ISO brightness of the OQ(PO)D pulp decreased slightly in the pre-heating period (alkali darkening not happened with the DE_{OP}D pulp), the OQ(PO)D pulp has a faster brightening response to the hydrogen peroxide than the more conventional DE_{OP}D pulp whatever the operating conditions. In fact, regarding the brightness gain in the final P stage, the difference between the bleached pulps is quite pronounced (Figures 1-2) and a much lower time, temperature or H₂O₂ charge, is needed for the OQ(PO)DP pulp to reach the same final brightness compared to the DE_{OP}DP pulp. The effect of temperature is noteworthy: even with 90°C the DE_{OP}D pulp shows worst brightening response than the OQ(PO)D pulp at 70°C. In addition, the increase of temperature accelerates the brightness development for the DE_{OP}D pulp in the first 60 minutes, but after this time of reaction at 90°C, a brightness ceiling is achieved alongside with a total consumption of hydrogen peroxide (Figures 3-4). A slight darkening even occurs for long times due to the depletion of H₂O₂. A similar trend has been found by Méndez and Area [18] in the E_P stage brightening kinetics of a pine kraft pulp bleached with a DE_ODE_PD sequence. On the contrary, for the OQ(PO)DP pulp the brightness development slows down after 60 min of reaction but the peroxide consumption does not reach 100%.

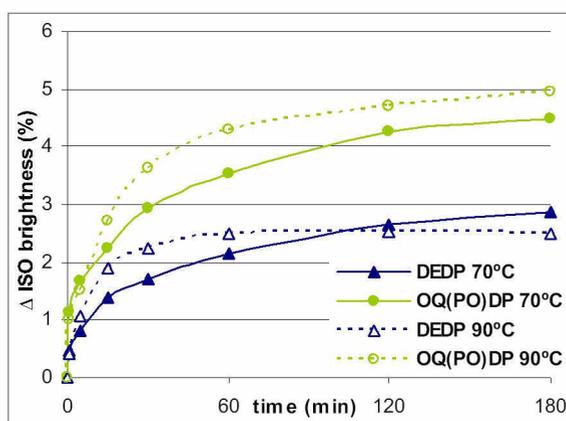


Figure 1. ISO brightness gain kinetics in the final P stage of the sequences DE_{OP}DP and OQ(PO)DP with 0.5% odp H₂O₂ at 70 and 90°C.

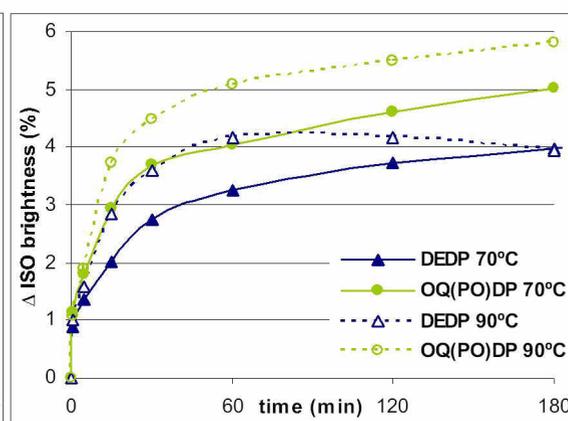


Figure 2. ISO brightness gain kinetics in the final P stage of the sequences DE_{OP}DP and OQ(PO)DP with 2.0% odp H₂O₂ at 70 and 90°C.

These significant differences are likely related with the nature and amount of chromophores that can react with hydrogen peroxide and are dependent on the preceding stages. For instance, the oxygen delignification used in the OQ(PO)D pulp may have a great impact on pulp bleachability with hydrogen peroxide stages. Comparing the H₂O₂ charges reported in the literature for eucalyptus, a greater amount is needed in the final P stage to bleach DE_{OP}D pulps than ODE_{OP}D pulps to achieve the same brightness level [2, 5]. Moreover, as previously reported [19-20], the chlorine dioxide delignification, as in the case of DE_{OP}D pulp, raises dramatically the amount of quinones, which are known to have a negative impact on the pulp ECF bleachability [21]. On the other hand, Jiang et al. [22] demonstrated the benefit of adding oxygen delignification to achieve a higher brightness ceiling (ODE_ODED versus DE_ODED). Being both unbleached kraft pulps from the same hardwood species, it is wise to attribute these differences to the bleaching sequence. Parthasarathy and Colodette [6] have also found that the final brightness of DD and DP pulps (ODE_PDP) was dictated by the first chlorine dioxide stage, D₀ versus D_{HT}, with the D_{HT} pulps having higher brightness at lower chemicals

consumption. In addition, Röst et al. [23] found that the total charge of hydrogen peroxide to reach full brightness was highly dependent on the pulp brightness after the oxygen stage, thus supporting the chromophores effect on the pulp bleachability using hydrogen peroxide.

Regarding sodium hydroxide consumption, the ECF-light pulp shows greater values whatever the temperature and H₂O₂ charge are (Figures 5-6). However, this consumption is highly affected by the temperature, especially for the DE_{OP}D pulp. At the moderate temperature of 70°C the NaOH consumption profile is by floors, while at 90°C a more continuous increase is established. The negative effect of high NaOH consumption and temperature on decreasing pulp yield and intrinsic viscosity is also expected [24].

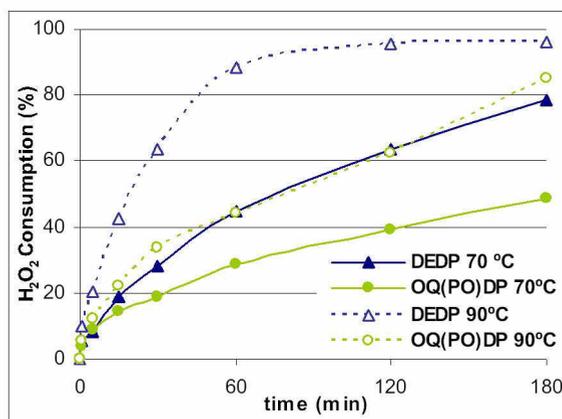


Figure 3. Hydrogen peroxide consumption kinetics in the final P stage of the sequences DE_{OP}DP and OQ(PO)DP with 0.5% odp H₂O₂ at 70 and 90°C.

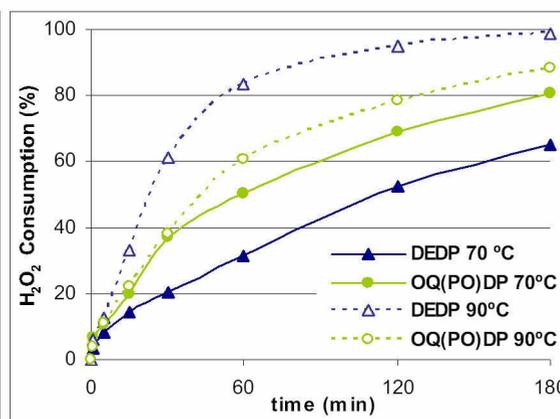


Figure 4. Hydrogen peroxide consumption kinetics in the final P stage of the sequences DE_{OP}DP and OQ(PO)DP with 2.0% odp H₂O₂ at 70 and 90°C.

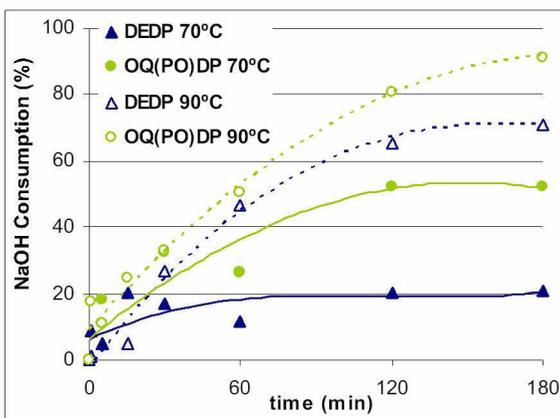


Figure 5. Sodium hydroxide consumption kinetics in the final P stage of the sequences DE_{OP}DP and OQ(PO)DP with 0.5% odp H₂O₂ at 70 and 90°C.

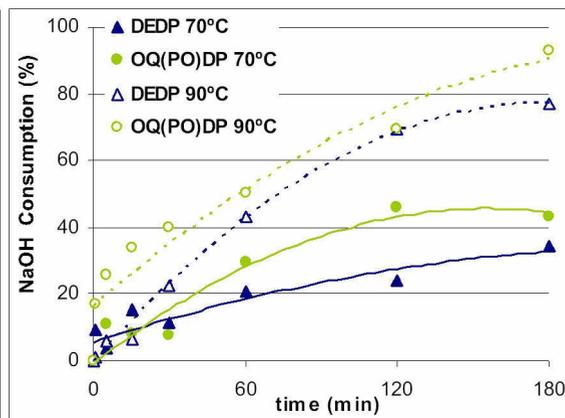


Figure 6. Sodium hydroxide consumption kinetics in the final P stage of the sequences DE_{OP}DP and OQ(PO)DP with 2.0% odp H₂O₂ at 70 and 90°C.

Since hydrogen peroxide is consumed to a greater extent with the DE_{OP}D pulp, not corresponding to a higher rate of chromophores removal, the bleachability of this pulp (defined as the brightness gain per unit of the amount of hydrogen peroxide consumed) is lower than that of OQ(PO)D pulp as depicted in Figures 7-8. The impact of temperature on this pulp property is dependent, however, on the pulp and the H₂O₂ charge used: the highest temperature is only positive for OQ(PO)D pulp using the higher peroxide charge. In fact, at 70°C for a H₂O₂ charge of 2% odp (Figure 4), a higher peroxide consumption for the OQ(PO)DP pulp is observed, but, as the brightness is also higher, the peroxide is usefully consumed in brightening reactions (Figure 8). Therefore, for the conventional ECF sequence,

it can be concluded that hydrogen peroxide is wasted in larger amounts in side reactions in comparison with the OQ(PO)D pulp. The raise of temperature over 70°C is detrimental in terms of peroxide decomposition for the DE_{OP}D pulp. Although DTPA was added to the P stage, its effectiveness in deactivating metal-catalysed decomposition reactions may be impaired at the highest temperature (90°C). Higher peroxide decomposition may also be related with the nature and amount of transition metals in both pulps, but this specific analysis was not yet performed. Since the ECF-light sequence has a chelation stage (Q) it is expected lower metals content which favours a higher brightening performance.

All these aspects are the result of different kinetics and will be clarified with the development of the mathematical models (including brightening and decomposition reactions) and with the analysis of the respective kinetic parameters.

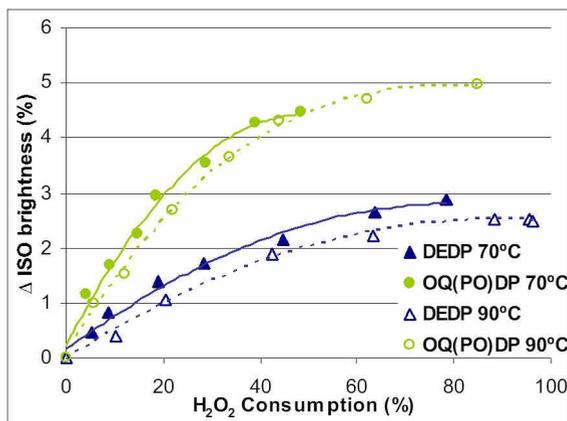


Figure 7. Bleachability of the final P stage for the sequences DE_{OP}DP and OQ(PO)DP with 0.5% odp H₂O₂ at 70 and 90°C.

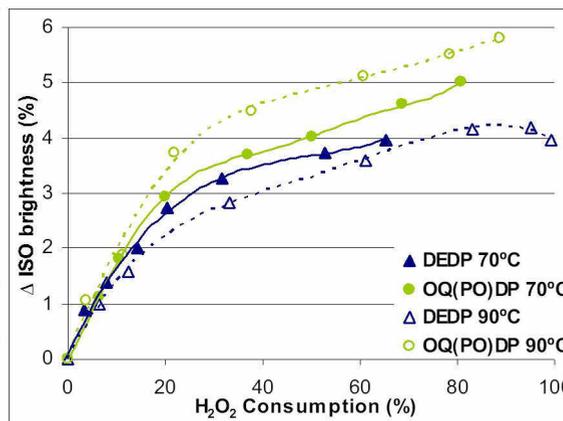


Figure 8. Bleachability of the final P stage for the sequences DE_{OP}DP and OQ(PO)DP with 2.0% odp H₂O₂ at 70 and 90°C.

Conclusions

Two industrial *Eucalyptus globulus* pulps partially bleached using different sequences (DE_{OP}D and OQ(PO)D), but exhibiting the same brightness level, were further bleached in this work with a final P stage.

In the preliminary experiments the usefulness of DTPA in reducing peroxide consumption and, simultaneously, in minimizing pulp viscosity loss was shown especially in the case of DE_{OP}D pulp. The best stabilizing system for the OQ(PO)D was a mixture of DTPA+MgSO₄. A DTPA charge of 0.05% odp was used in the kinetic studies of both pulps.

It can be concluded that the chromophoric structures in the OQ(PO)D pulp are more readily destroyed than in the DE_{OP}D pulp, having the former a greater bleachability towards hydrogen peroxide. Nevertheless, a higher sodium hydroxide was observed in comparison with the conventional ECF pulp (DE_{OP}D).

The efficiency of accelerating brightening reactions by raising the temperature above 70°C in the final P stage strongly depends on pulp history. After 60 min at 90°C, peroxide is almost depleted in the case of DE_{OP}D pulp and therefore no further brightness increase is achieved. On the contrary, with the OQ(PO)D pulp it is possible to reach a retention time of 180 min with a continuous brightening evolution. This clearly expresses the great impact that the peroxide decomposition reactions can have, especially at high temperature in the case of DE_{OP}D sequence, even with the addition of DTPA in the P stage. It thus follows that for the DE_{OP}D pulp longer times than 60 min at 90°C are not advisable while for the OQ(PO)D pulp wider time and temperature ranges are possible. The best option for the last P stage applied to the DE_{OP}D pulp is to choose a lower temperature (70°C) although longer reaction times. In the case of OQ(PO)D pulp, higher temperatures may be suitable to achieve very high brightness levels without spending too much chemicals.

The reasons of these dissimilar behaviours are likely related with the nature and the amount of chromophores that can react with hydrogen peroxide which depend on the pulp bleaching history. A further study on the transition metals profiles, on the papermaking potential and on the development of kinetic models will remain for the future.

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