

ELEMENTAL CHLORINE-FREE BLEACHING OF SODA RAPESEED PULP

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*Dedicated to the memory of
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Soda rapeseed pulps delignified to kappa numbers of 21.4 and 16.4 underwent elemental chlorine-free bleaching using chlorine dioxide, hydrogen peroxide, and peracetic acid as bleaching agents under laboratory conditions. Three four-stage bleaching sequences, DE_pPPaa, D₀E_pD₁P and D₀E_pD₁D₂, were applied to investigate the properties of bleached soda pulps, namely their brightness, zero-span breaking length and degree of polymerisation. For comparison, an oxygen-predelignified kraft softwood pulp with an initial kappa number of 10.5 was bleached under the same conditions. Soda pulps subjected to bleaching processes comprising two or three D stages were found to have a final brightness of 83.1 to 83.8% ISO, which was lower than that of 87.6 to 87.9% ISO obtained for kraft softwood pulp. The decrease in fibre strength was of only 7-9% for soda pulps, slightly greater than that of kraft softwood pulp. In contrast to fibre strength, the loss in the degree of polymerisation was considerable, roughly of 35% for soda pulps and 40 to 47% for kraft softwood pulp, depending on the bleaching sequence.

Keywords: soda rapeseed pulp, elemental chlorine-free bleaching, brightness, zero-span breaking length, degree of polymerisation

INTRODUCTION

Nowadays, bleaching of chemical pulps is achieved by two processes, *i.e.*, the elemental chlorine-free (ECF) process and/or the total chlorine-free (TCF) one, in which bleaching is carried out essentially by using oxygen compounds.¹ Which concept is preferred depends mainly on the desired final brightness of the pulp to be bleached, its properties, capital costs of bleaching chemicals, and concentration of chlorine-containing components in the effluent. Bleaching to full brightness, greater than 88% ISO, requires multi-stage application of bleaching chemicals.

Since elemental chlorine is no longer used in modern pulp mills because of environmental reasons, chlorine dioxide has become the most important bleaching chemical.² At first, chlorine dioxide in combination with subsequent alkaline extraction was used as a first bleaching stage after cooking or oxygen-delignification. Later, owing to its high selectivity towards the oxidation of chromophoric structures, chlorine dioxide was applied for delignification not only in the first bleaching stage, but also in the final bleaching stage of elemental chlorine-free sequences to produce chemical pulps with sufficient strength properties.³⁻⁷

As some reaction products are generally resistant to further oxidation by chlorine dioxide, various chemicals are used in the bleaching sequences to reach higher brightness of the pulps. In contrast to chlorine dioxide, which reacts as an electrophilic agent, hydrogen peroxide is a nucleophilic agent.² Although the oxidation potential for hydrogen peroxide is significantly higher under acidic conditions, bleaching reactions are typically conducted under alkaline conditions. The reason is that hydrogen peroxide reacts only slowly with organic compounds under acidic conditions. Decomposition of hydrogen peroxide is necessary to delignify pulp, but the rate of decomposition into reactive intermediates must be controlled to achieve all the goals of peroxide bleaching. Transition metals, such as copper, manganese, and iron, can induce severe peroxide decomposition.² The decomposition

of peroxide can be controlled by using mildly alkaline conditions, stabilizing the hydrogen peroxide by adding magnesium salts, and removing transition metals by prior acid washing or chelation.⁸⁻¹⁴ Hydrogen peroxide is usually used to brighten pulps during the final bleaching stages to prevent the pulp from losing brightness over time.

Compared with hydrogen peroxide, the reaction of peracids with lignin, following mainly an electrophilic pathway, is both more rapid and more selective under weak acidic conditions. Hence, peracids, such as peracetic acid, are preferred for elemental chlorine-free sequences, as well as for totally chlorine-free bleaching with a final peracetic acid step.^{11,12,15-18}

In countries with limited forest resources, the use of agricultural residues for pulp manufacturing offers a possibility to solve the lack of wood. With respect to the lower bleaching efficiency of pulps from annual plants because of anatomical and chemical characteristics,¹⁹ as well as the relatively high ash content,²⁰ totally chlorine-free bleaching procedures do not confer an adequate brightness level to this type of pulp.²¹ Therefore, elementary chlorine-free bleaching sequences seem to be more suitable for pulps from agricultural residues. Using chlorine dioxide and hydrogen peroxide, three-stage bleaching sequences have been applied for bleaching of pulp cooked from wheat straw,^{1,22,23} corn stalks,^{22,24} cotton stalks,¹ kash,²⁴ bagasse,¹ and canola stalks.²⁵

In this paper, soda pulp cooked from rapeseed straw was subjected to four-stage elemental chlorine-free bleaching under laboratory conditions. The soda pulp with two various delignification degrees was bleached using the DE_pPPaa, D₀E_pD₁P, and D₀E_pD₁D₂ sequences. Pulp properties, *viz.* brightness, zero-span breaking length, and polymerisation degree, were determined after each bleaching stage of these sequences in order to examine their changes during the bleaching process. For comparison, kraft softwood pulp from an industrial source after oxygen-delignification was bleached under the same laboratory conditions using the same ECF sequences.

EXPERIMENTAL

Rapeseed straw (*Brassica napus* L. convar. *napus*, in our case winter line genotype Labrador), harvested from the field in Polabian lowlands near the city of Pardubice (Czech Republic), was used for the pulping process. Raw materials consisted mainly of stalks, but approximately one third of the total amount represented valves of siliques. After removing the leaves, roots, soil and silique valves, the stalks were manually chopped into 1 to 2 cm pieces, which were used for laboratory soda pulping. The chemical composition of both basic components of rapeseed straw, stalks and silique valves, was reported in our previous paper.²⁶

Batch soda-AQ pulping of rapeseed straw was carried out in a laboratory rotary digester comprising six autoclaves, immersed in an oil bath. Batch cooks were performed at the liquor-to-raw material ratio of 5:1, alkali charge of 19% expressed as Na₂O per oven-dried raw material, and the anthraquinone charge of 0.1%, based on oven-dried raw material. The pulping process, including the temperature regime, was described in detail earlier.²⁷ The soda pulps with kappa numbers of 21.4 and 16.4 were cold stored at a temperature of 6 °C until the bleaching experiments. The kappa number of unbleached soda pulps was determined according to the standard TAPPI test method T 236 om-99. Using an atomic absorption spectrophotometry method, the concentrations of transition metals, Fe, Mn and Cu, in the soda pulps were determined as well.

Samples of unbleached pulp comprising 22 g of o.d. pulp were subjected to the DE_pPPaa, D₀E_pD₁P and D₀E_pD₁D₂ bleaching sequences. Chlorine dioxide (ClO₂), hydrogen peroxide (H₂O₂) and peracetic acid (CH₃COOOH) were applied as bleaching chemicals. The chlorine dioxide solution was prepared by acidification of a sodium chlorite (NaClO₂) solution under laboratory conditions. Commercial products of hydrogen peroxide with a concentration of 30 wt% and of peracetic acid as a 34 wt% equilibrium solution of peracetic acid, as well as hydrogen peroxide and water were used as further bleaching chemicals. The bleaching stages were conducted in sealed polyethylene bags immersed in a tap water bath preheated to the required temperatures. The pulp samples were occasionally hand-kneaded during the bleaching steps. The pulp consistency, *i.e.*, mass fraction of moisture-free fibres in suspension expressed in wt%, in each stage was kept at a value of 10%.

The first chlorine dioxide stage, D₀, was performed at a temperature of 60 °C for 60 min. A volume of the chloride dioxide solution was added to obtain a dose of the active chlorine equal to twice the kappa number of the pulp to be bleached. Then, the pH value was adjusted to 2.2. The following alkaline extraction stage, E_p, was carried out at a temperature of 70 °C for 120 min. This stage was enhanced by hydrogen peroxide addition in the amount of 4 kg per 1 tonne of o.d. pulp. The NaOH charge was 0.7% on the basis of oven-dried pulp. Then, the pH value was adjusted to 10.8. The following D₁ and D₂ stages were performed at 80 °C with active chlorine doses of 26 kg and of 8 kg per 1 tonne of o.d. pulp and at pH values of 4.0 and 4.5, respectively, for 180 min. The hydrogen peroxide stage, P, was carried out at a temperature of 70 °C and at the pH value of 10.9 for 120 min. The hydrogen peroxide dose was 25 kg per 1 tonne of o.d. pulp. The peracetic acid charge of 10 kg per 1 tonne of o.d. pulp was applied in the Paa stage carried out at 65 °C and a pH level of around 4.4 for 90 min.

Water solutions of sodium hydroxide and/or sulphuric acid were added to the pulp samples to achieve a desired pH value. A solution of magnesium sulphate in the amount corresponding to 0.5 kg of $MgSO_4$ per 1 tonne of o.d. pulp to protect cellulose in the pulp samples from degradation was added in the E_p and P stages. The samples were thereafter washed repeatedly with distilled water until a washing solution with a neutral pH was obtained. For comparison, the oxygen-prebleached kraft softwood pulp (kappa number of 10.5) produced at industrial scale underwent the same complete ECF bleaching sequences.

Pulp handsheets of about 80 g/m^2 basis weight were prepared after each bleaching stage using a standard handsheet former, as described in TAPPI test method T 205 sp-2. Treated pulp samples were characterized in terms of brightness, zero-span breaking length, and degree of polymerization. Using an L&W Elrepho SE 071/070R instrument, the brightness of the soda pulp was measured on handsheet samples obtained after each bleaching step. The zero-span breaking length was determined according to TAPPI test method T 273 by means of a TIRA test instrument. Before strength measurements, the handsheets were air-conditioned in the conditioning room under a constant temperature of $23 \pm 1 \text{ }^\circ\text{C}$ and relative humidity of $50 \pm 2\%$, according to standard ISO 187. All the strength measurements were performed on at least 20 replicates per each tested specimen.

The average degree of polymerisation was determined by a viscosity test using a FeTNa solution (iron (III) sodium tartrate complex) as a solvent for the soda pulps, according to ISO 5351/2-1981. The average degree of polymerisation, DP , was evaluated from the following relationship:

$$DP = K_m^{-1} \frac{\tau - \tau_0}{\rho \tau_0 \left[1 + k \left(\frac{\tau - \tau_0}{\tau_0} \right) \right]} \quad (1)$$

where τ is the efflux time of solution (s), τ_0 is the efflux time of solvent (s), ρ is the pulp concentration (g/L), k and K_m are empirical constants equal to 0.3 and $8.14 \times 10^{-4} \text{ L/g}$, respectively.²⁸

RESULTS AND DISCUSSION

Soda rapeseed pulps delignified to the two levels of the kappa number, 21.4 and 16.4, having starting brightness of 27.7 and 28.7% ISO, respectively, underwent four-stage ECF bleaching sequences. Simultaneously, oxygen pre-bleached kraft softwood pulp with a kappa number of 10.5 and 40.7% ISO brightness was bleached under the same bleaching conditions, generally recommended for kraft pulps.²

For the DE_pPPaa bleaching sequence, the final brightness values of the soda pulps with kappa numbers of 21.4 and 16.4 were of 80.7, and 75.4% ISO, respectively, and, for comparison, the softwood kraft pulp achieved 83.4% ISO brightness (*cf.* Fig. 1). However, the further bleaching sequences, $D_0E_pD_1P$ and $D_0E_pD_1D_2$, brought final brightness of 83.1 to 83.8% ISO without apparent dependence on the starting kappa number (*cf.* Figs. 2 and 3). Moreover, the substitution of the last chlorine dioxide stage in an ECF bleaching sequence by a final peroxide stage P can have a positive effect on brightness stability.¹⁰

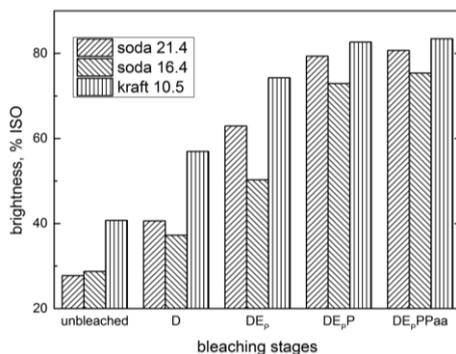


Figure 1: Variation of brightness during bleaching stages of DE_pPPaa sequence

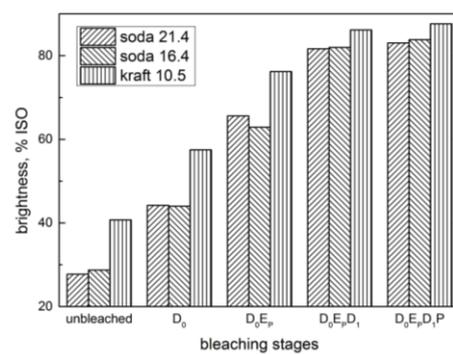


Figure 2: Variation of brightness during bleaching stages of $D_0E_pD_1P$ sequence

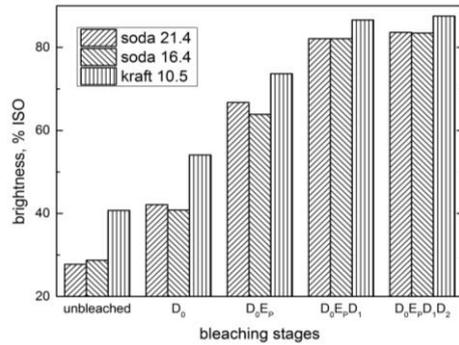


Figure 3: Variation of brightness during bleaching stages of D₀E_pD₁D₂ sequence

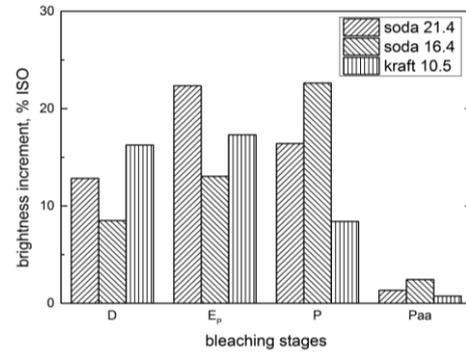


Figure 4: Brightness increment in bleaching stages of DE_pPPaa sequence

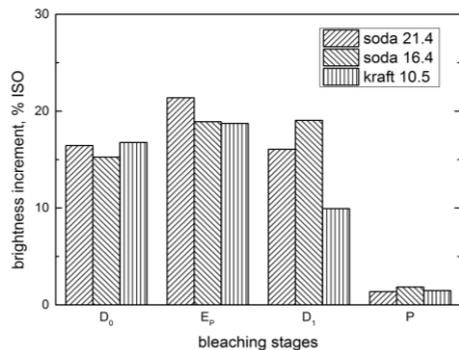


Figure 5: Brightness increment in bleaching stages of D₀E_pD₁P sequence

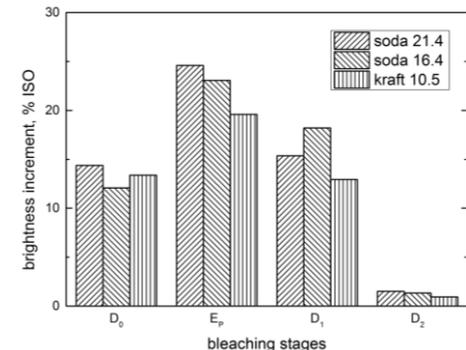


Figure 6: Brightness increment in bleaching stages of D₀E_pD₁D₂ sequence

In the case of the kraft softwood pulp, the bleaching sequences comprising two or three chlorine dioxide stages produced pulps with the final brightness ranging from 87.6 to 87.9% ISO. Of course, the total brightness increment of 55% ISO achieved for the soda pulps was greater than that of 47% ISO reached for the kraft softwood pulp. It is worth mentioning that, in our previous study,¹¹ when the totally chlorine-free bleaching with hydrogen peroxide and peracetic acids was applied on oxygen-predelignified kraft softwood pulp with the initial kappa number of 9.7, the final brightness did not exceed 65% ISO.

For comparison, Enayati *et al.*²⁵ reported the bleaching results of canola stalks soda pulp with the initial kappa number of 23.8 and brightness of 36.5% ISO. Using the three-stage bleaching sequence, D₀E_pD₁, they achieved a final brightness of 78.4% ISO. For the same three-stage bleaching sequence, Jimenéz *et al.*²³ and Tschirner *et al.*²² reported final brightness values for wheat straw pulp of about 80% ISO and 87.5% ISO, respectively, while for corn stalks, Tschirner *et al.*²² and Jahan and Rahman²⁴ achieved brightness values of 88.9 and 85.4% ISO, respectively.

For a more synoptical comparison, the brightness increments achieved in each bleaching stage are illustrated in Figs. 4-6. For soda rapeseed pulp, the brightness increment in the first D₀ stage as a delignifying stage is lower than that in the second alkaline stage E_p, in which lignin compounds formed by preceding acidic treatment are solubilised and removed under alkaline extraction enhanced by the addition of hydrogen peroxide. For soda pulps with the starting kappa number of 21.4 and 16.4, the average brightness increment was 8.5-16.5% ISO in the D₀ stage, and 13.0 and 24.6% ISO in the E_p stage. In all ECF bleaching sequences, the chlorine dioxide charge based on active chlorine equal to twice the starting kappa number of pulp was applied. Chlorine dioxide oxidizes lignin *via* a number of reaction pathways, highly depending on the pH value. Moreover, the pH governs the proportion of each reactive component (ClO₂, HClO₂, HClO/Cl₂) present in the solution.⁷ Low pH values (below 2.5) in the D₀ stage may result in less chlorate formation, which contributes to the loss in delignification efficiency, and in a substantial removal of non-process metals, reducing peroxide decomposition in the subsequent E_p stage.^{5,6} Presumably, the relatively low levels of transition metals, Fe, Mn and Cu, in the unbleached soda pulp measured as 22.7, 14.4, and 4.7 mg per kg of oven-dried

pulp, respectively, together with the acid conditions in the D_0 stage resulted in relatively good bleachability in the E_p stage.

A similar bleaching impact in the D_0 and E_p stages was found for oxygen-prebleached kraft softwood pulp when the average brightness increments were of 15.1 and 19.0% ISO, respectively. Thus, the brightness increments achieved for the soda and kraft pulps confirmed that the D_0 chloride dioxide step, followed by the extraction step, had a predominant influence upon the final brightness of the kraft pulp treated by ECF bleaching.

For the soda pulps, the D_1 chlorine dioxide stage produced a higher brightness increment, of 15.4 to 19.1% ISO, compared with the D_0 stage. The third bleaching stage, D_1 , narrowed the brightness difference between soda pulps. In the case of the kraft softwood pulps, however, the third bleaching step did not produce as much effect as for the soda pulps. The contribution of the last bleaching stage, P and D_2 , lower than 2.5% ISO, led to nearly the same brightness of the soda pulps treated by the bleaching sequences comprising two and three chlorine dioxide stages, irrespective of the starting kappa number.

During multi-stage bleaching, changes in fibre strength and pulp viscosity gradually occur. Therefore, the pulp was characterized after each bleaching stage as to zero-span breaking length (*cf.* Figs. 7-9) and average degree of polymerisation (*cf.* Figs. 10-12). The zero-span tensile test is a widely used method for evaluating the average strength of individual fibre rather than the strength of the paper itself. It is worth mentioning that, in unbleached pulps, similarly to brightness, zero-span breaking length and degree of polymerisation are greater for lower kappa number of soda pulp, but both parameters are lower than those measured for the softwood kraft pulp after oxygen delignification. This tendency is also obvious for the bleached soda pulps after the final bleaching step of the sequences comprising two or three chlorine dioxide steps, except for the degree of polymerisation. The loss in zero-span tensile strength of the bleached pulps has been attributed to weakening or deterioration of the fibre matrix by the removal of lignin and the degradation of carbohydrates.²⁹

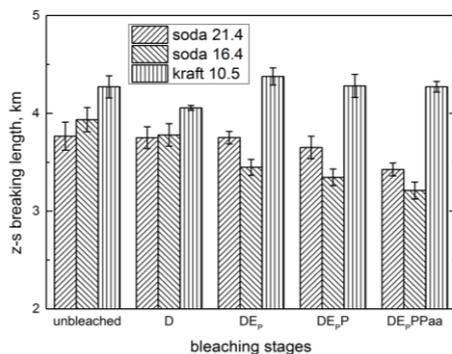


Figure 7: Variation of zero-span breaking length during bleaching stages of DE_pPPaa sequence (error bars: 95% confidence limits)

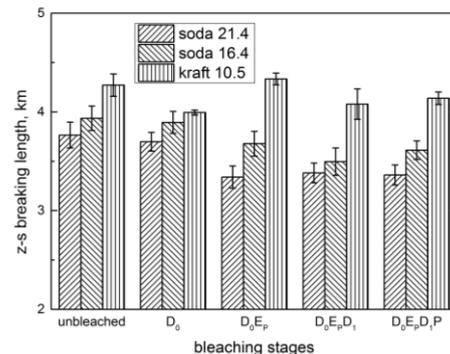


Figure 8: Variation of zero-span breaking length during bleaching stages of $D_0E_pD_1P$ sequence (error bars: 95% confidence limits)

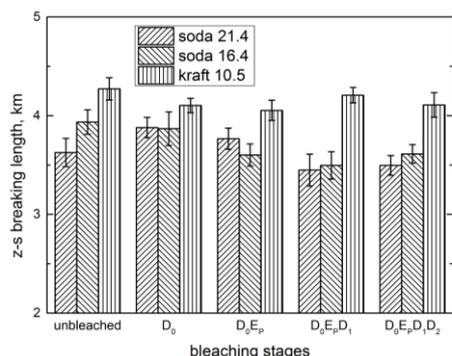


Figure 9: Variation of zero-span breaking length during bleaching stages of $D_0E_pD_1D_2$ sequence (error bars: 95% confidence limits)

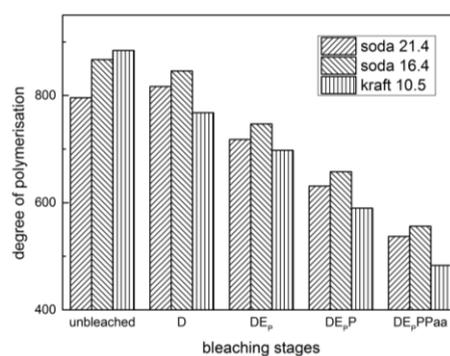


Figure 10: Variation of degree of polymerisation during bleaching stages of DE_pPPaa sequence

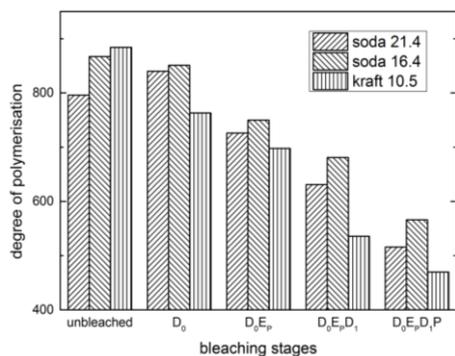


Figure 11: Variation of degree of polymerisation during bleaching stages of D₀E_pD₁P sequence

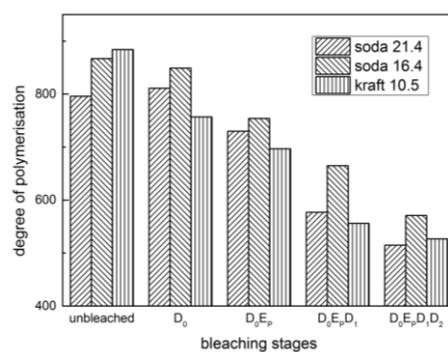


Figure 12: Variation of degree of polymerisation during bleaching stages of D₀E_pD₁D₂ sequence

Furthermore, the fibre strength and pulp degree of polymerisation gradually changed in different manners during the ECF bleaching sequences, as shown in Figs. 7-12. In the case of the softwood kraft pulp with the initial zero-span breaking length of 4.27 km, the changes in the strength are within the experimental errors, so that the zero-span breaking length achieved values above 4.1 km after all bleaching sequences. However, for the soda pulps, the loss in zero-span breaking length was of approximately 9% and 7% of the initial strength for D₀E_pD₁P and D₀E_pD₁D₂ bleaching sequences, respectively. Of course, soda rapeseed fibres are short, predominantly below 1 mm.²⁶ Their use in paper production will be based on their contribution to surface smoothness and optical properties of the paper sheet. It should be also noted that a decrease in the zero-span breaking length of the soda pulps was much lower than that of 10 to 15% measured after the TCF bleaching sequences comprising hydrogen peroxide, peracetic acid, extraction and chelation stages for oxygen-predelignified softwood pulp with the initial zero-span breaking length of 3.92 km found in our previous papers.^{11,12}

In contrast to the fibre strength, the average degree of polymerisation decreases almost linearly during the bleaching processes for all the pulps tested. The initial degree of polymerisation of 793 and 867 dropped to 515 and 570 for the soda pulps with the kappa numbers of 21.4 and 16.4, respectively, treated by the bleaching sequences with two and three D stages. The unbleached softwood kraft pulp had a degree of polymerisation of 884 and 47% and 40% of the initial value was lost during the D₀E_pD₁P and D₀E_pD₁D₂ bleaching sequences, respectively. While for the soda pulps, the lowest loss in the degree of polymerisation was found to be in the D₀ stage, the decrease in the degree of polymerisation in the E_p stage was greater for the soda pulps in comparison with the kraft pulp. The loss of degree of polymerisation in the D₁ and D₂ stages can be ascribed to the higher pH values in these stages in agreement with some authors,³⁰ who tested oxygen-predelignified softwood kraft pulp. It should be also noted that the loss in the degree of polymerisation achieved at an ECF bleaching of soda and kraft pulps was comparable to that ranging from 31 to 50% after TCF bleaching sequences using hydrogen peroxide and peracetic acid for oxygen-predelignified kraft softwood pulp with the intrinsic viscosity of 867 mL/g, as discussed in our preceding papers.^{11,12} For comparison, Enayati *et al.*²⁵ reported an average degree of polymerisation ranging from 1408 to 1579 for soda pulp cooked from canola stalks using cupriethylenediamine (CED) as a solvent. The considerable differences between our results and those obtained in their study²⁵ can be due to the different solvents used for the viscometric measurements of the degree of polymerisation, as mentioned by Kačik *et al.*²⁸

CONCLUSION

Soda rapeseed pulps with kappa numbers of 21.4 and 16.4 were bleached using three four-stage bleaching sequences, DE_pPPaa, D₀E_pD₁P and D₀E_pD₁D₂, in each stage, under conditions of pulp consistency, chemical dose, pH, temperature, and retention time similar to those common for kraft pulp bleaching. The results obtained enabled drawing some conclusions valid within the framework of our study, as detailed below.

(i) The soda pulp cooked from rapeseed straw seems to be more difficult to bleach in comparison with kraft softwood pulp. Hence, a bleaching sequence comprising at least two D stages is necessary to obtain pulp with a brightness value above 83% ISO. The final brightness achieved by the D₀E_pD₁P

and D₀E_pD₁D₂ bleaching was between 83.1 and 83.8% ISO, while for kraft softwood pulp a higher value by 4% ISO was measured.

(ii) The fibre strength of soda pulp expressed by the zero-span breaking length decreased after the final bleaching stage only by 7-9% and was greater than 3.4 km. This decrease in fibre strength seems to be acceptable for using soda rapeseed bleached pulp for paper production.

(iii) All ECF bleaching sequences brought relatively great loss in the degree of polymerisation for both soda and kraft pulps tested in this work.

(iv) While the final brightness of soda pulp was approximately the same for the D₀E_pD₁P and D₀E_pD₁D₂ sequences, the fibre strength, as well as the degree of polymerisation, was found to be slightly higher for soda pulp bleached by the ECF sequence without a peroxide step in comparison with that comprising hydrogen peroxide as bleaching agent.

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