ELEMENTAL CHLORINE-FREE BLEACHING OF SODA RAPESEED PULP

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Abstract
Soda pulp cooked from rapeseed straw (*Brassica napus* L. convar. *napus*, in our case winter line genotype Labrador) was subjected to a four-stage elemental chlorine-free bleaching under laboratory conditions. Chlorine dioxide and hydrogen peroxide were used as bleaching chemicals. For comparison, kraft pulp cooked from a blend of spruce and pine was subjected to the same bleaching sequence $D_0E_PD_1P$. The initial kappa number of both pulps was 18.8. After each bleaching step, the optical and strength properties were measured. The preliminary results showed that bleachability of soda rapeseed pulp was lower in comparison with kraft softwood pulp for $D_0E_PD_1P$ bleaching sequence. The brightness increment of 43.2 % ISO and 48.5 % ISO was achieved for soda and kraft pulps, respectively. However, the bleaching had a negative impact on the zero-span breaking length which decreased from 3.9 km for unbleached soda pulp to 3.6 km for bleached soda pulp.

Keywords: soda rapeseed pulp, ECF bleaching, brightness, zero-span breaking length

Introduction
Unbleached chemical pulps contain a residual lignin. While lignin in native wood is coloured only slightly, residual lignin of a pulp after cooking is highly coloured. Moreover, unbleached pulps also contain other coloured impurities originating from wood (resin compounds, shives, bark), from cooking process (carbon specks, rust), and from external sources (grease, sand). A continuation of cooking to further reduce the noncarbohydrate impurities would inevitably lead to a significant impairment of pulp quality due to enhanced cellulose degradation. Therefore, alternative concepts must be applied to selectively remove chromophore structures and impurities present in the unbleached pulp[1].
Bleaching of chemical pulps consists in delignification and removal of the residual chromophores. Various chlorine- and oxygen-based oxidants have proven to be efficient bleaching chemicals. Nowadays, the most common bleaching agents in the bleached chemical pulp production are mainly oxygen (O), ozone (Z), chlorine dioxide (D), hydrogen peroxide (P), and peracetic acid (Paa). However, each bleaching chemical develops its own chemistry with residual lignin. Some of them are acting in alkaline conditions, others in acid ones[2]. Hence, 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. 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 high selectivity towards the oxidation of chromophoric structures, chlorine dioxide was applied not only for delignification in the first bleaching stage but also for its capability for pulp brightness 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, the various chemicals are used in bleaching sequences to reach higher brightness of pulps. In contrast to chlorine dioxide which reacts as an electrophilic agent, hydrogen peroxide is nucleophilic agent. Although the oxidation potential for hydrogen peroxide is significantly higher under acidic conditions, typical bleaching reactions are 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. Since some transition metal ions such as copper, manganese, and iron accelerate the catalytic decomposition of the active perhydroxyl ion (hydroperoxide anion), presumably through a free-radical mechanism, it is necessary to decrease transition metal ions concentration before peroxide stage using a chelation step (Q)[8–14]. Hydrogen peroxide is usually used to brighten pulps during the final bleaching stages to prevent the pulp from losing brightness over time.

In this paper, soda pulp cooked from rapeseed straw was subjected to a four-stage elemental chlorine-free (ECF) bleaching under laboratory conditions. Bleaching sequence consisted of chlorine dioxide step in combination with subsequent alkaline extraction followed by another chlorine dioxide and hydrogen peroxide stages. Optical and strength properties of pulp measured after each bleaching step were compared with those obtained for kraft pulp cooked from softwoods.

Experimental

Rapeseed straw (*Brassica napus* L. convar. *napus*, in our case winter line genotype Labrador) collected 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 total amount were valves of siliques. After removing natural dirt and silique valves, the stalks were manually cut to 1 to 2 cm pieces which were used for laboratory soda pulping. Chemical composition of both basic components of rapeseed straw, stalks and silique valves, was reported in our previous paper[15].

Batch soda-AQ pulping of rapeseed straw was carried out in a laboratory rotary digester comprising six autoclaves of 750 cm^3 capacity, 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 Na_2O per oven-dried raw material, and the anthraquinone charge of 0.1 %, based on oven-dried raw material.

On the basis of pulping experiments performed earlier[15], the temperature regime consisted of four periods, *i. e*., at first heating from a room temperature to 105 ^{o}C for 45 min, then dwelling at 105 ^{o}C for 30 min, followed by heating to 160 ^{o}C for 30 min, and finally dwelling at cooking temperature. The batch cooks were ended as soon as the H-factor reached a value of 1,600 h. After the cooking process, the cooked pulp was refined, thoroughly washed with tap water, and screened to remove rejects using 10 mesh sieve. The soda pulp was stored cold at a temperature of 6 °C before bleaching experiments. The kappa number of unbleached soda pulp was determined according to standard method ISO 302.

Unbleached pulp was subjected to a $D_0E_PD_1P$ bleaching sequence. Chlorine dioxide (ClO_2) solution and hydrogen peroxide (H_2O_2) were applied as bleaching chemicals. The chlorine dioxide solution was prepared by acidification of a sodium chlorite ($NaClO_2$) solution under laboratory conditions. Commercial product of hydrogen peroxide having a concentration of 30 mass % was used as another bleaching chemical. Water solutions of sodium hydroxide and/or sulphuric acid were added to 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 oven-dried tonne of pulp to protect cellulose in the pulp samples from degradation was added in the E_P and P stages.

The bleaching stages were performed in sealed polyethylene bags immersed in a tap water bath preheated to the required temperatures. The pulp samples were hand-kneaded before and during bleaching steps. The pulp consistency, *i. e*., mass fraction of moisture-free fibres in suspension expressed in mass %, in each stage was maintained at a value of 10 %. The bleaching sequence $D_0E_PD_1P$ is illustrated in Fig. 1 in which one can find the charge of bleaching agents, for chlorine dioxide expressed as active chlorine aCl_2, retention time (τ), pH value, and temperature (t) which characterize operating conditions of each bleaching stage.

After each bleaching stage a multi-stage washing based on dilution at 4 % pulp consistency followed by thickening was performed with distilled water until neutral effluent was achieved.

Pulp handsheets of 80 g/m^2 were prepared using a standard handsheet former as described in TAPPI test method T 205 sp-2. Using an L&W Elrepho SE 071/070R instrument, the brightness of soda pulp was measured for handsheet samples obtained in each bleaching step. The zero-span breaking length was determined according to TAPPI test method T273 by means of a TIRA test instrument. Before strength measuring, the handsheets were air-conditioned in the conditioning room under a constant temperature of (23±1) °C and relative humidity of (50±2) %. All the strength measurements were performed at least on 20 replicates per each tested sample.

Results and discussion

The soda pulp cooked from the stalks of rapeseed straw under laboratory conditions was undergone a four-stage bleaching sequence using chlorine dioxide and hydrogen peroxide as bleaching chemicals. A simplified flowsheet of the $D_0E_PD_1P$ sequence is illustrated in Fig. 1. The kappa number of unbleached soda pulp cooked up to H-factor of 1,600 h had a value of 18.8. For comparison, the unbleached kraft pulp cooked industrially

from a blend of spruce and pine having the kappa number of 18.8 was undergone the same bleaching steps simultaneously. The initial brightness of soda and kraft pulps was 28.7 % ISO and 33.6 % ISO, respectively.

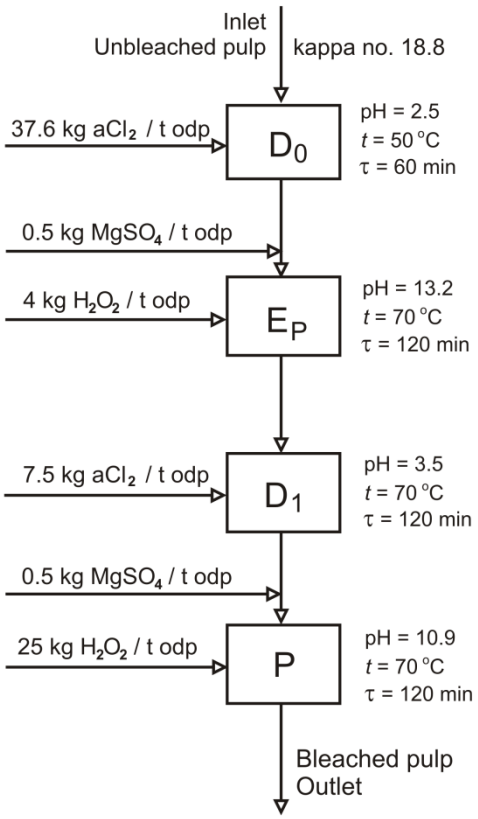

Figure 1. Simplified flowsheet of $D_0E_PD_1P$ bleaching sequence.

The pulp brightness attained after bleaching steps is shown in Fig. 2. After last bleaching stage, the final brightness of soda and kraft pulps was 71.9 % ISO and 82.1 % ISO, respectively. Thus, the difference in brightness between both pulps increased from 4.9 % ISO for unbleached pulps to 10.2 % ISO for bleached pulps. The reason may be that the brightness increment in the D_0 stage, where delignification is the primary goal, was too low for soda pulp comparing with kraft pulp. Figure 3 illustrates the brightness increments attained in each bleaching step for soda and kraft pulps. While the brightness increment of 13.2 % ISO was reached for soda pulp, an increase in brightness was 27.7 % ISO in the D_0 bleaching step for kraft pulp. It was confirmed that the D_0 chlorine dioxide bleaching step has predominant influence upon the final brightness of pulp treated by the ECF bleaching.

Chlorine dioxide oxidizes lignin via a number of reaction pathways, highly depending on pH value. The optimum pH for hardwood pulps is between 2.8 and 3.5 (ref.[5]). Moreover, the pH governs the proportion of each reactive component (ClO_2, $HClO_2$, $HClO/Cl_2$) present in the solution[7]. However, during the bleaching of pulp with chlorine dioxide, part of the chlorine dioxide is converted into chlorate. Since chlorate is an ineffective delignification chemical, its formation represents waste of the oxidizing power of chlorine dioxide[6]. It was found that a lower pH results in less chlorate formation. Thus, lower pH of 2.5 in the D_0 stage may result in a slight loss in delignification efficiency, but, on the other hand, may result in a substantial removal of non-process metals. This improved metals removal may reduce peroxide decomposition in the subsequent E_P stage[5]. Nevertheless, the difference in bleachability between various pulps is not easy rationalised particularly when they have approximately the same kappa numbers and brightnesses.

In the following steps, alkaline E_P and chlorine dioxide D_1, the brightness increment of soda pulp was greater than that of kraft pulp while the hydrogen peroxide step brought the same brightness increment for both pulps (Fig. 3). It is worth mentioning that the final brightness measured for soda and kraft pulps was much greater than that reached for oxygen-predelignified kraft softwood pulp with the initial kappa number of 9.7 when the

final brightness did not exceed 65 % ISO in the case of totally chlorine-free bleaching with hydrogen peroxide and peracetic acids[11].

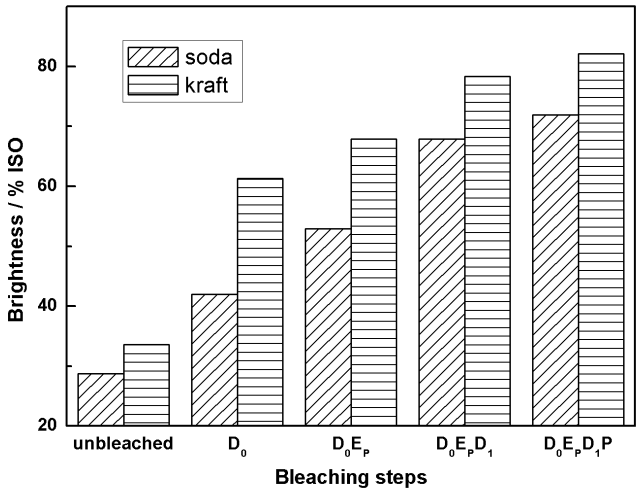

Figure 2. Pulp brightness after bleaching stages for soda and kraft pulps.

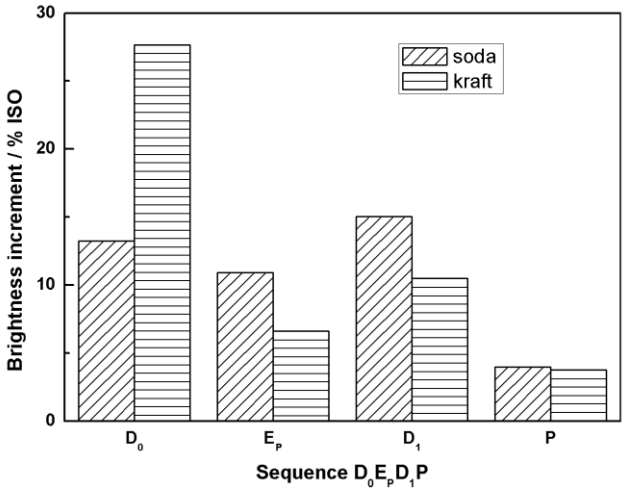

Figure 3. Brightness increments in bleaching stages for soda and kraft pulps.

For comparison, Enayati *et al.*[16] report 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 $D_0E_PD_1$, the final brightness was found to be 78.4 % ISO. The total brightness increment of 41.9 % ISO reported by Enayati *et al.*[16] for the three-step sequence is in good agreement with that of 43.2 % ISO measured in our work. It should be noted that one of possible reasons why lower final brightness was reached under our laboratory conditions is that pulp washing with distilled water was performed after each bleaching stage while, in bleaching plants, the wash liquor and pulp are flowing in the opposite directions as countercurrent flows.

During sequential bleaching operations, pulp fibre properties are gradually changed due to mechanical and chemical treatment. Hence, besides brightness, the strength of pulp was measured as well. The evaluation of pulp strength properties by conventional methods is not suitable for detailed specifications of pulps or fibre line, as the measured tensile strength is a combination of tensile strength of fibres and fibre-to-fibre bond strength. Therefore, 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. In the zero-span test, the tested sheet strips and, consequently, a given fibre is clamped at zero span of the tester jaws[17].

The influence of the bleaching steps on the zero-span breaking length (ZSBL) of soda and kraft pulps is shown in Fig. 4. It is evident that the first three bleaching stages, D_0, E_P, and D_1, brought down the zero-span breaking length of both pulps. A decrease in the zero-span breaking length after alkaline extraction step means that besides the alkali-soluble lignin fragments, degraded hemicelluloses are also lost in the extraction stage[10]. However, in the final hydrogen peroxide step, an increase in the zero-span breaking length, mainly for soda pulp, was reached. Comparing unbleached and bleached pulps after final bleaching step, a decrease in the zero-span breaking length was found to be 0.29 km and 0.52 km for soda and kraft pulps, respectively. For comparison, Enayati *et al*.[16] report for unrefined unbleached and bleached canola stalks soda pulps, the tensile index of 24 N m/g and 23.1 N m/g, respectively, measured by a convectional tensile strength method. It seems that, for soda pulps from canola and rapeseed, a decrease in the tensile strength was not substantial.

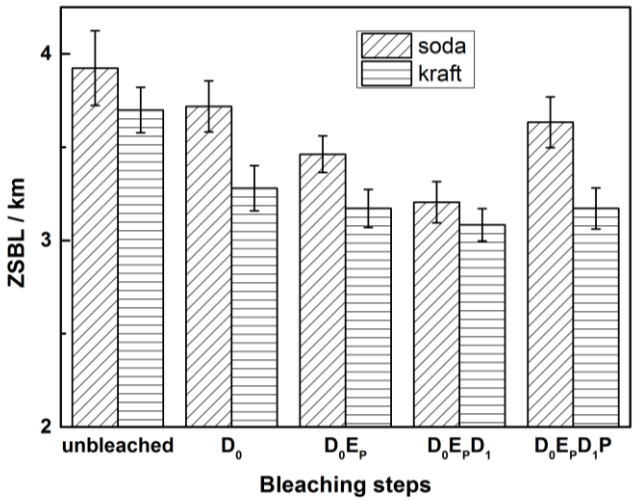

Figure 4. Influence of bleaching steps on zero-span breaking length for soda and kraft pulps. Error bars – 95% confidence limits.

It could be surprising that the zero-span breaking length of soda pulp from rapeseed straw is greater than that of kraft pulp cooked from softwoods. However, it must be noted that soda pulp was never dried while the air-dried kraft pulp was used in bleaching experiments. The reason for lower strength of kraft pulp fibres may be a phenomenon known as hornification which refers to the stiffening of the polymer structure that takes place in lignocellulosic materials upon drying or water removal. When pulp fibres are dried, the internal fibre volume shrinks, because of structural changes in pulp fibres. For comparison, the zero-span breaking length of 3.92 km was determined for never dried unbleached kraft pulp cooked from a blend of spruce and pine, having the kappa number of 9.7 after oxygen bleaching[11].

Conclusions

In conclusion, the brightness of soda pulp with the initial kappa number of 18.8 and the initial brightness of 28.7 % ISO subjected to the four-stage $D_0E_PD_1P$ sequence was found to be 71.9 % ISO. The total brightness increment of 43.2 % ISO was lower than that of 48.5 % ISO attained for kraft softwood pulp having the same initial kappa number. A total decrease in the zero-span breaking length of 0.29 km seems to be acceptable with respect to strength characteristics of soda rapeseed pulp attained after each bleaching step. It can be concluded that chlorine dioxide is certainly the most important bleaching chemical with high oxidation power mainly in a D_0 stage, having a substantial impact upon the final pulp brightness, mainly in combination with a subsequent alkaline extraction. This fact confirms the important role of chloride dioxide in bleaching process and its impact on the pulp brightness in elemental chlorine-free bleaching.

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