CHLORINE DIOXIDE BLEACHING OF SODA RAPESEED PULP

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Abstract

Soda pulp cooked from rapeseed straw (*Brassica napus* L. convar. *napus*, winter line genotype Labrador) was subjected to a four-stage elemental chlorine-free bleaching under laboratory conditions. The bleaching sequence comprised three chlorine dioxide stages. The alkali extraction enhanced with hydrogen peroxide addition followed the first chlorine dioxide delignification. For comparison, kraft pulp cooked from a blend of spruce and pine was subjected to the same bleaching sequence $D_0E_PD_1D_2$. 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 final brightness of 83.5 % ISO and 87.8 % ISO was achieved for soda and kraft pulps, respectively. However, the bleaching had a negative impact on the strength of soda rapeseed fibres. The zero-span breaking length decreased from 4.0 km to 3.3 km for unbleached and bleached soda pulps, respectively, while, for kraft softwood pulp, a decrease in fibre strength was not found.

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

Introduction

Bleaching is a chemical purification and modification process in which the optical properties of pulp fibres are changed either by removing components capable of absorbing visible light or by reducing their light absorption capability. Bleaching reactions can be grouped according to their principal mode of operation. Electrophilic reactions (oxidative) typically initiate lignin-degrading bleaching processes, frequently in acidic conditions, and involve cations and also radicals generated from used bleaching chemicals. Nucleophilic reactions (reductive) typically occur in lignin-retaining bleaching. These reactions generally take place in alkaline media and involve anions and, to a much lesser extent, radicals[1].

Chlorine dioxide is a typical delignifying chemical and reacts primarily with free phenolic hydroxyl groups under acidic conditions. Chlorine dioxide is reduced through a series of steps involving several intermediated. Hypochlorous acid and chlorine are among these intermediates, and they are capable of forming organochlorine compounds just as molecular chlorine. Another unwanted intermediate is the chlorate ion, which is not reactive. Hence, it is important, when using chlorine dioxide for delignification, to manipulate reaction conditions to minimize the formation of chlorate and free chlorine or hypochlorous acid so as to improve delignification efficiency and minimize the formation of chlorinated organic matter. This implies that pH should be low when chlorine dioxide is used in the first stage of bleaching[1].

Since elemental chlorine is no longer used in modern pulp mills because of environmental reasons, chlorine dioxide has become the most important bleaching chemical. Chlorine dioxide is a multi-purpose bleaching agent. It is efficient in delignification, but it is still more important in brightening pulp by reducing or eliminating residual lignin content without significant carbohydrate losses and by reducing chromophores in pulp. 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[2–6].

Usually, the alkaline extraction stage follows chlorine oxide delignification. The purpose of an alkaline extraction stage is to dissolve and then remove compounds made alkali-soluble in the preceding acidic delignification treatment. Extraction can be enhanced by adding oxidants such as oxygen and/or hydrogen peroxide[1].

In this paper, soda pulp cooked from rapeseed straw was subjected to a four-stage elemental chlorine-free bleaching sequence $D_0E_PD_1D_2$ under laboratory conditions. Bleaching sequence comprised three chlorine

dioxide stages in combination with an alkaline extraction which followed the first delignification stage. Optical and strength properties of pulp measured after each bleaching step were compared with those obtained for kraft softwood pulp produced in industrial scale.

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[7].

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[7], 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 determined according to standard method ISO 302 had a value of 17.9.

Unbleached pulps were subjected to a $D_0E_PD_1D_2$ bleaching sequence. Chlorine dioxide (ClO_2) solution was applied as bleaching agent. The chlorine dioxide solution was prepared by acidification of a sodium chlorite ($NaClO_2$) solution under laboratory conditions. Commercial product of hydrogen peroxide (H_2O_2) having a concentration of 30 mass % was used for enhancing the alkali extraction. 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 alkaline extraction stage.

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 $D_0E_PD_1$ D_2 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. For comparison, the once-dried kraft softwood pulp having the kappa number of 18.8 was undergone elemental chlorine-free bleaching under the same conditions.

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 stage. 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 as bleaching chemical. A simplified flowsheet of the $D_0E_PD_1D_2$ 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 17.9. For comparison, the once-dried 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 28.6 % ISO and 33.6 % ISO, respectively.

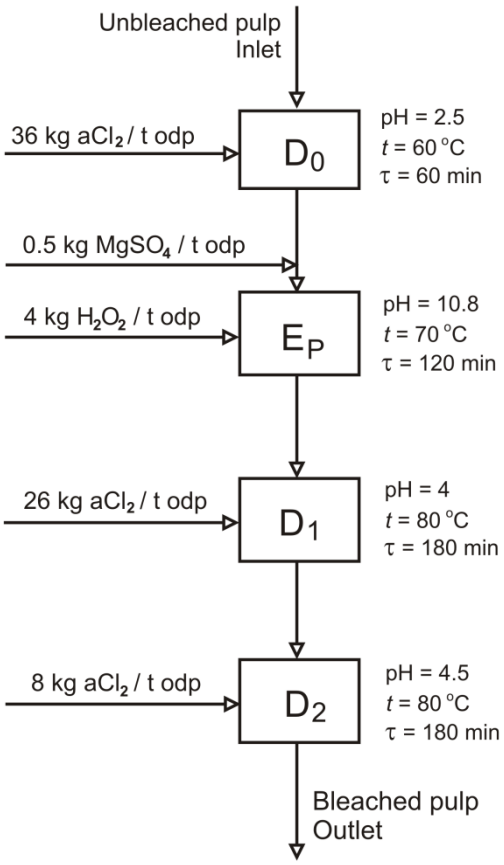

Figure 1. Simplified flowsheet of $D_0E_PD_1D_2$ bleaching sequence.

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 83.5 % ISO and 87.8 % ISO, respectively. The difference in brightness of 5.0 % ISO for unbleached pulps slightly decreases to 4.3 % ISO for bleached pulps. Thus, the total brightness increments of 54.9 % ISO and 54.2 % ISO were achieved for soda and kraft pulps, respectively. The results obtained showed that chlorine dioxide provides pulp of high brightness. It should be noted also that no chlorine dioxide residuals were found after completion of chlorine dioxide bleaching stages for both pulps.

Figure 3 illustrates the brightness increments attained in each bleaching step for soda and kraft pulps. The brightness increment in the D_0 stage, where delignification is the primary goal, was too low for soda pulp comparing with kraft pulp. While the brightness increment of 12.3 % ISO was reached for soda pulp, an increase in brightness was 25.1 % ISO for kraft pulp. It was confirmed that the D_0 chlorine dioxide bleaching step has predominant influence upon the final brightness of kraft pulp treated by the ECF bleaching. However, for soda rapeseed pulp, the alkaline extraction stage is clearly beneficial from a brightness point of view.

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.[4]). Moreover, the pH governs the proportion of each reactive component (ClO_2, $HClO_2$, $HClO/Cl_2$) present in the solution[6]. 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[5]. 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[4]. 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 both chlorine dioxide D_1 and D_2, the brightness increment of soda pulp was greater than that of kraft pulp so that the difference in brightness decreased. 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 acid[8].

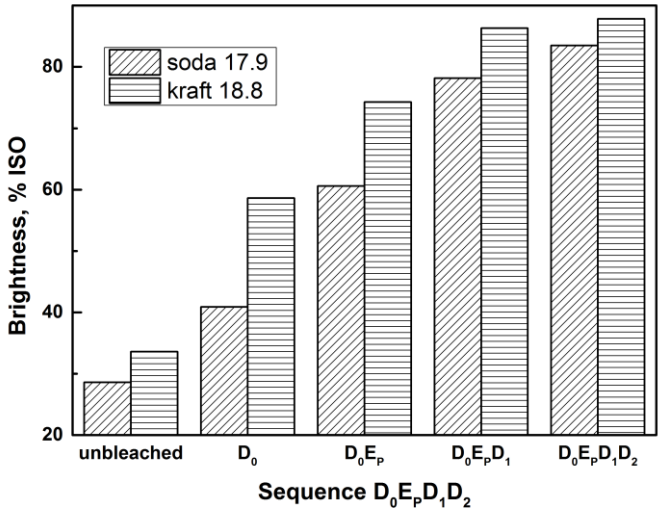

Figure 2. Pulp brightness after bleaching stages for soda and kraft pulps.

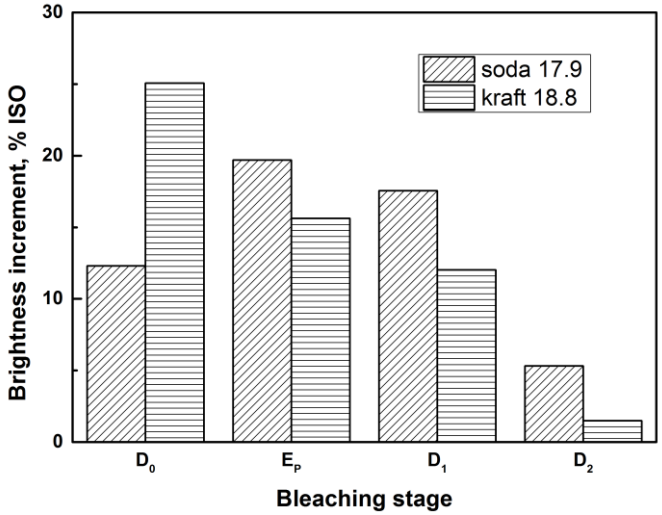

Figure 3. Brightness increments in bleaching stages for soda and kraft pulps.

For comparison, Enayati *et al*.[9] 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. For this three-stage bleaching sequence, the final brightness reported for wheat straw pulp by Jimenéz *et al*.[10] and Tschirner *et al*.[11] was about 80 % ISO and 87.5 % ISO, respectively, while for corn stalks the brightness of 88.9 and 85.4 % ISO was achieved by Tschirner et al.[11] and Jahan and Rahman[12], respectively.

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[13].

The influence of the bleaching steps on the zero-span breaking length (ZSBL) of soda and kraft pulps is shown in Fig. 4. The $D_0E_PD_1D_2$ bleaching sequence had a negative impact on the fibre strength of soda pulp. It is evident that the all bleaching stages contributed to a strength decrease. However, the final zero-span breaking length of 3.3 km seems to be acceptable for using soda rapeseed bleached pulp to paper production. For comparison, Enayati *et al.*[9] 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.

In contrast to soda pulp, the bleaching stages, excepting the D_0 stage, had no substantial effect on the zero-span breaking length of the kraft pulp fibres. Thus, the final zero-span breaking length of once-dried kraft softwood pulp was around 4 km. The results obtained for kraft pulp showed that chlorine dioxide reactions with carbohydrates are minimal so there is very little pulp strength deterioration in chlorine dioxide bleaching.

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[8].

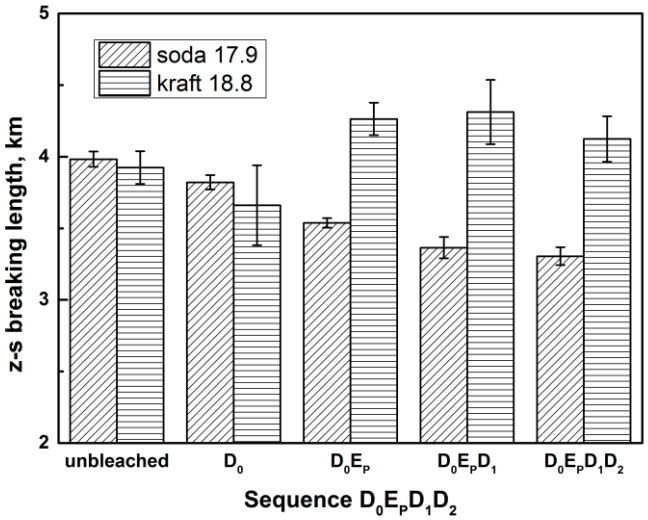

Figure 4. Influence of bleaching steps on zero-span breaking length for soda and kraft pulps. Error bars – 95% confidence limits. Legend: Type of pulp, kappa number

Conclusions

In conclusion, the final brightness of soda pulp with the initial kappa number of 17.9 and the initial brightness of 28.6 % ISO subjected to the four-stage $D_0E_PD_1D_2$ sequence was found to be 83.5 % ISO. The total brightness increment of 54.9 % ISO was slightly greater than that of 54.2 % ISO attained for once-dried kraft softwood pulp having the initial kappa number of 18.8. For kraft softwood pulp, the $D_0E_PD_1D_2$ bleaching sequence did not have a negative impact on fibre strength. However, for never-dried soda rapeseed pulp, the initial zero-span breaking length of 4.0 km decreased to 3.3 km after completion of bleaching. The final the zero-span breaking length seems to be acceptable for paper production from bleached soda rapeseed pulp.

In comparison with the $D_0E_PD_1P$ bleaching sequence mentioned in our preceding paper[14], the $D_0E_PD_1D_2$ sequence comprising three chlorine dioxide stages brought an increase in the final brightness of soda rapeseed pulp by 11.5 % ISO. This fact confirms the important role of chlorine dioxide in bleaching process and its impact on the pulp brightness in elemental chlorine-free bleaching. It can be concluded that chlorine dioxide is certainly the most important bleaching chemical with high oxidation power mainly in combination with a subsequent alkaline extraction.

Acknowledgements

This work was supported by the Internal Grant Agency of University of Pardubice under the research project SGSFCHT_2017_006.

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