

ELEMENTAL CHLORINE-FREE BLEACHING OF SODA, KRAFT, AND SULPHITE PULPS

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Abstract

Soda pulp cooked from rapeseed straw was subjected to a four-stage elemental chlorine-free bleaching under laboratory conditions using chloride dioxide, hydrogen peroxide, and peracetic acid as bleaching agents. The alkali extraction enhanced with hydrogen peroxide addition followed the first chlorine dioxide delignification. For comparison, an oxygen-predelignified kraft softwood and sulphite spruce pulps, as well as once-dried kraft softwood pulp were undergone to the same bleaching sequence DE_pPPaa. The brightness, zero-span breaking length, and degree of polymerisation were measured for unbleached and bleached pulps. The preliminary results showed that bleachability of soda rapeseed pulp was lower in comparison with kraft softwood pulps and sulphite spruce pulp. The final brightness of 80.0, 84.1, 83.4, and 88.3 % ISO was achieved for soda, once-dried kraft, oxygen-predelignified kraft and sulphite pulps, respectively. However, an increase in brightness was accompanied by a decrease in strength of soda rapeseed pulp fibres. The zero-span breaking length decreased from 4.2 km to 3.4 km for soda pulp, while, for oxygen-predelignified kraft softwood and sulphite pulps, a noticeable decrease in fibre strength was not found.

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

Introduction

The main objective of bleaching is to remove encrusted substances to obtain a pure white product, therefore, the manufacturing process requires further delignification and bleaching of the fibres, as residual lignin is a major contributing factor to colour. During bleaching, the cleanliness of the pulp improves when the fibres of the fibre bundles, or shives, are released as the last of the residual lignin is removed from the pulp and any bark debris dissolves. The chemicals used in bleaching also effectively dissolve extractives contained in the pulp. Multistage bleaching gives the best results regarding both quality and economy, and there are alkaline and acidic bleaching stages. With only alkaline or acidic stages, the target brightness would not be attained, so both are always used in bleaching¹.

Since turning from chlorine to ECF bleaching technologies, chlorine dioxide has become the main agent for kraft pulp bleaching¹. Moreover, 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. 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 peroxide². 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 properties³⁻⁷.

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 a nucleophilic agent². 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. Transition metals like copper, manganese, and iron can induce severe peroxide decomposition². 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 chelation⁸⁻¹⁴.

Hydrogen peroxide is usually used to brighten pulps during the final bleaching stages to prevent the pulp from losing brightness over time.

Comparing 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 stage^{11,12,15-18}.

In this comparative study, the soda pulp cooked from rapeseed straw was subjected to a four-stage elemental chlorine-free bleaching sequence DE_pPPaa under laboratory conditions. The pulp brightness was measured after each bleaching stage in order to examine its changes during the bleaching process. The zero-span breaking length and degree of polymerisation were determined for unbleached and bleached pulp. For comparison, the kraft softwood pulp and sulphite spruce one from an industrial source were bleached under the same laboratory conditions.

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 chopped into 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 earlier¹⁹.

Batch soda-AQ pulping of rapeseed straw was carried out in a laboratory rotary digester comprising six autoclaves of 750 cm³ 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 Na₂O per oven-dried raw material, and the anthraquinone charge of 0.1 %, based on oven-dried (o. d., for short) raw material.

The pulping process including temperature regime was described in detail in our preceding paper²⁰. 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 the standard TAPPI test method T 236 om-99 had a value of 17.9.

Samples of unbleached pulp comprising 22 g of o. d. pulp were subjected to the DE_pPPaa bleaching sequence. The chlorine dioxide solution was prepared by acidification of a sodium chlorite (NaClO₂) solution under laboratory conditions. The first chlorine dioxide stage, D, was performed at a temperature of 60 °C for 60 min. The volume of 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.

Commercial products of hydrogen peroxide having a concentration of 30 mass % and of peracetic acid as a 34 mass % equilibrium solution of peracetic acid, hydrogen peroxide and water were used as further bleaching chemicals. 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 operating at 65 °C and pH level of around 4.4 for 90 min. 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 MgSO₄ 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 kraft softwood pulps and sulphite spruce pulp obtained from an industrial source were undergone the same bleaching sequence. The kappa number of once-dried kraft softwood pulp, never-dried kraft softwood pulp after oxygen delignification, and never-dried sulphite pulp after oxygen delignification was 18.8, 10.5, and 12.5, respectively. The pulp consistency, *i. e.*, mass fraction of moisture-free fibres in suspension expressed in mass %, in each bleaching stage was kept at a value of 10 %.

Pulp handsheets of 80 g/m² 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. The average degree of polymerisation was determined by a viscosity test using a FeTNa solution (iron (III) sodium tartrate complex) as a solvent for pulps according to ISO 5351/2-1981 (ref.²¹).

Results and Discussion

The soda pulp delignified to the kappa number of 17.9 under laboratory conditions was undergone a four-stage bleaching sequence DE_pPPaa. The starting brightness of soda rapeseed pulp had a value of 28.6 % ISO. For comparison, three sorts of pulps produced industrially, namely the once-dried unbleached kraft pulp and never-dried oxygen pre-bleached kraft pulp cooked from a blend of spruce and pine, as well as oxygen-predelignified sulphite pulp with an initial brightness of 33.6, 40.7, and 53.7 % ISO, respectively, were undergone the same bleaching stages simultaneously.

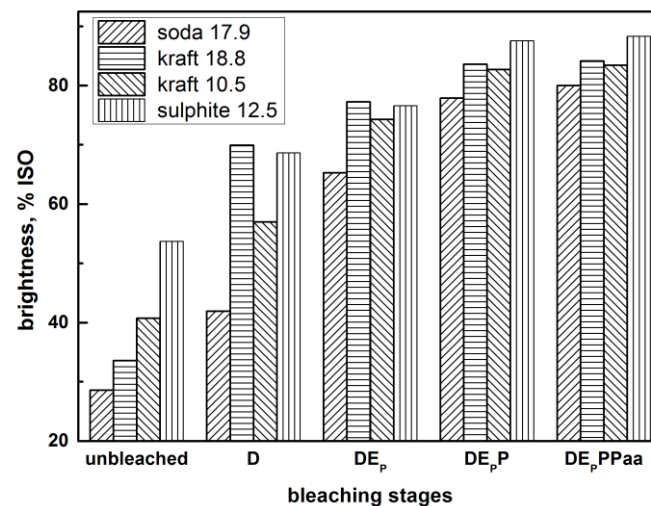


Figure 1. Pulp brightness after bleaching stages for soda, kraft, and sulphite pulps.

The pulp brightness attained after bleaching stages is shown in Fig. 1. After last bleaching stage, the final brightness of soda, once-dried kraft, never-dried pre-bleached kraft and sulphite pulps were found to be 80.0, 84.1, 83.4, and 88.3 % ISO, respectively. The final brightness achieved for the soda rapeseed pulp was lower comparing to kraft and sulphite pulps. The reason can be different anatomic and chemical characteristics, as well as the relatively high ash content in rapeseed straw comparing to coniferous and deciduous wood. However, the total brightness increment of 51.4 % ISO attained for the soda rapeseed pulp was greater comparing to that of 50.4, 42.7, and 34.6 % ISO for once-dried kraft, never dried oxygen-predelignified kraft and sulphite pulps, respectively. Our results can be compared with those by Enayati *et al.*²² who 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, the final brightness was found to be 78.4 % ISO.

For a more synoptical comparison, the brightness increments achieved in each bleaching stage are illustrated in Fig. 2. For soda rapeseed pulp, the brightness increment in the first D 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. It was confirmed that the D chlorine dioxide bleaching stage followed by the alkaline step E_p has predominant influence upon the final brightness of pulps 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 (ClO₂, HClO₂, HClO/Cl₂) present in the solution⁶. 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 dioxide⁵. It was found that a lower pH results in less chlorate formation. Thus, lower pH value of 2.5 in the first D stage may result in a slight loss in delignification efficiency, but, on the other hand, in a substantial removal of non-

process metals. This improved metals removal may reduce peroxide decomposition in the subsequent E_p stage⁴. Nevertheless, the difference in bleachability between various pulps is not easily rationalised particularly when they have approximately the same kappa numbers and brightnesses.

In contrast to chlorine dioxide, peracetic acid used in the last bleaching stage brought a brightness increment of 2.1 % ISO for soda rapeseed pulp, whereas for kraft and sulphite pulps, the contribution of peracetic acid stage was less than 0.7 % ISO (cf. Fig. 2).

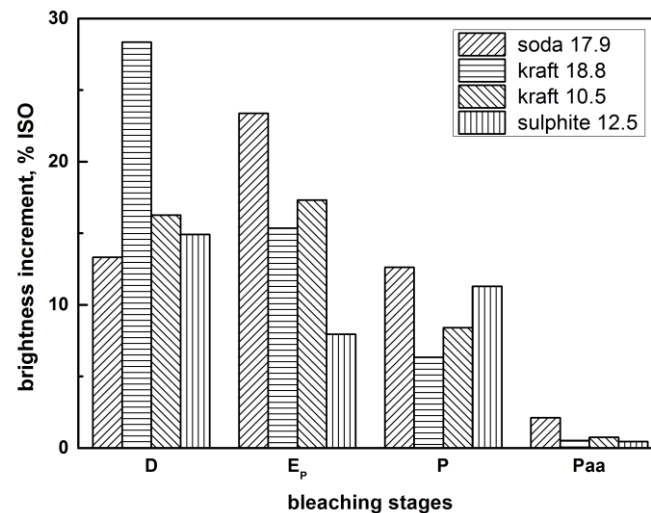


Figure 2. Brightness increments in bleaching stages for soda and kraft pulps.

It is worth mentioning that the final brightness measured for soda, kraft, and sulphite 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^{11, 12}.

During sequential bleaching operations, pulp fibre properties are gradually changed due to mechanical and chemical treatment. Hence, besides brightness, the zero-span breaking length and average degree of polymerisation of unbleached and bleached pulp were 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 jaws²³.

The influence of the ECF bleaching sequence on the zero-span breaking length (ZSBL) of pulps is shown in Fig. 3. The DE_pPPaa bleaching sequence had a negative impact on the fibre strength of soda pulp. The loss in zero-span tensile strength of bleached pulps may be attributed to weakening or deterioration of the fibre matrix by the removal of lignin and the degradation of carbohydrates²³. It is evident that the initial zero-span breaking length of rapeseed pulp fibres was comparable with that for kraft softwood pulps. However, the final zero-span breaking length of 3.4 km seems to be acceptable for using soda rapeseed bleached pulp to paper production. Of course, soda rapeseed fibres are short, predominantly below 1 mm (ref.¹⁹). Their use in paper production will be based on their contribution to surface smoothness and sheet optical properties. Using the $D_0E_pD_1$ bleaching sequence comprising two chlorine dioxide stages, Enayati *et al.*²² 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 conventional tensile strength method.

In the case of kraft softwood and sulphite spruce pulps produced industrially, the ECF bleaching sequence had no substantial effect on the pulp fibre strength so that changes in the zero-span breaking length influenced by bleaching are within the experimental errors. As expected, the lowest strength was found for the oxygen-predelignified sulphite spruce pulp fibres.

Figure 4 illustrates that the ECF bleaching had a substantial effect upon the average degree of polymerisation expect for once-dried kraft softwood pulp. Of course, a reduction in the degree of polymerisation by 33, 46, and 45 % was found for soda rapeseed pulp, oxygen-predelignified kraft softwood and sulphite pulps,

respectively, with an initial average degree of polymerisation of 811, 888, and 760, respectively. It should be noted also that the loss in the degree of polymerisation achieved at an ECF bleaching of soda, kraft, and sulphite pulps was comparable to that ranging of 31 to 50 % after a TCF bleaching sequences using hydrogen peroxide and peracetic acid for oxygen-predelignified kraft softwood pulp with the intrinsic viscosity of 867 mL/g in the preceding papers^{11,12}.

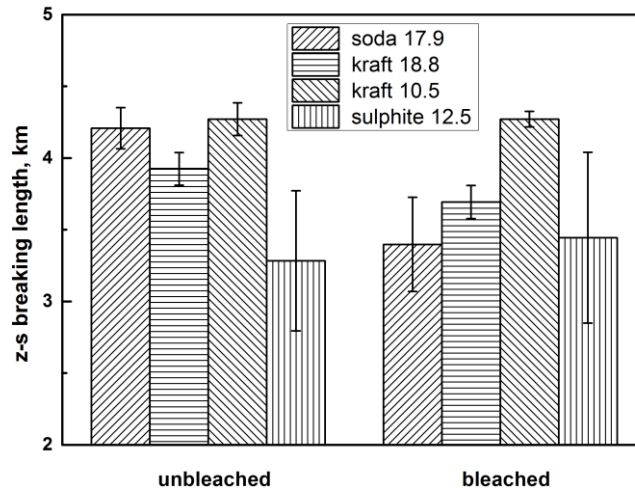


Figure 3. Influence of ECF bleaching on zero-span breaking length for soda, kraft, and sulphite pulps. Error bars – 95% confidence limits.

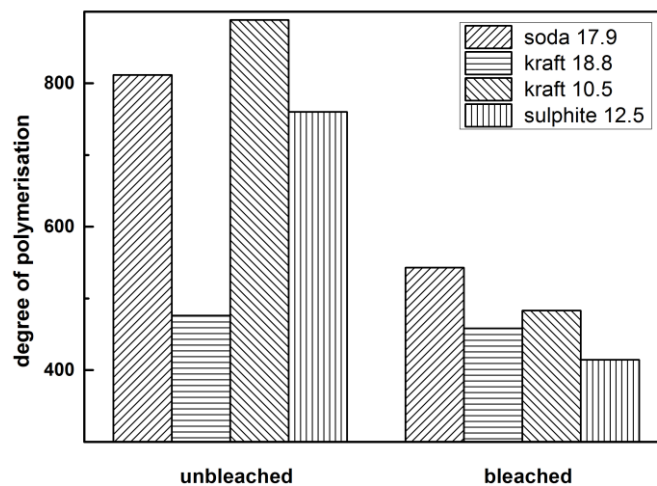


Figure 4. Influence of ECF bleaching on degree of polymerisation for soda, kraft, and sulphite pulps.

Conclusions

The results obtained enabled that some conclusions valid within the framework of our study can be made. The soda pulp cooked from rapeseed straw seems to be difficultly bleachable in comparison with kraft softwood and sulphite spruce pulps.

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 DE_pPPaa sequence was found to be 80.0 % ISO, while for kraft softwood and sulphite spruce pulps the greater values by 4 and 8 % ISO, respectively, were attained. However, the total brightness increment of 51.4 % ISO was greater than that attained for once-dried kraft softwood pulp having

the initial kappa number of 18.8, never-dried oxygen-predelignified kraft softwood pulp with the kappa number of 10.5, and never-dried oxygen-predelignified sulphite spruce pulp with the kappa number of 12.5.

The DE_pPPaa bleaching sequence brought a reduction in the zero-span breaking length from 4.2 to 3.4 km for the soda rapeseed pulp fibres. However, the final zero-span breaking length is comparable with that measured for sulphite spruce pulp. Also, relatively great loss in the degree of polymerisation was found for soda rapeseed pulp, as well as for kraft and sulphite pulps except for once-dried kraft softwood pulp.

With respect to the final brightness and fibre strength, the soda rapeseed pulp subjected to the DE_pPPaa bleaching sequence seems to be acceptable for paper production. Nevertheless, in order to obtain soda rapeseed pulp with brightness above 83 % ISO, the ECF bleaching sequence comprising at least two chlorine dioxide stages will be necessary²⁴.

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