

TOTALLY CHLORINE-FREE BLEACHING OF SODA RAPESEED PULP

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ABSTRACT

Soda pulp cooked from rapeseed straw was subjected to the totally chlorine-free bleaching using hydrogen peroxide and peracetic acid as bleaching agents. The five-stage bleaching sequence, Q₁Q₂E_pPaaP, containing two chelation stages, as well as four-stage sequence, AE_pPaaP, with an acidic stage were applied to investigate the properties of bleached soda pulp, namely its brightness and tensile strength. For comparison, once-dried kraft softwood pulp, as well as never-dried oxygen-predelignified kraft softwood pulp and sulphite spruce pulp were bleached under the same process conditions. The results obtained showed that totally chlorine-free bleaching did not bring the sufficient bleaching effect for soda rapeseed pulp. The brightness of 54 % ISO achieved for the AE_pPaaP bleaching sequence was lower comparing to that for kraft and sulphite pulps.

Key words: soda rapeseed pulp; TCF bleaching; brightness; breaking length.

INTRODUCTION

As a result of the concern regarding chlorinated organic compounds formed during chlorine bleaching, conventional bleaching concepts were rapidly replaced by the so-called elemental chlorine-free (ECF) bleaching process, and this became the dominant bleaching technology. However, very few mills are nowadays producing only totally chlorine-free (TCF) bleached kraft pulp (VALCHEV 2013) using mainly oxygen and peroxide stages in combination with chelation or acidic stages along with ozone and peracids as further bleaching agents.

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 anion, presumably through a free-radical mechanism, it is necessary to decrease transition metal ions concentration before peroxide stage using chelation agents (DENCE, OMORI 1986; KEMPF, DENCE 1975; LOUREIRO *et al.* 2011; POTŮČEK, MILICHOVSKÝ 2000, 2001; VAN LIEROP *et al.* 1994; ZERONIAN, INGLESBY 1995). Also, using an acidic stage before the peroxide stage the content of transition metal ions can be

reduced. In addition to that the hexenuronic acids groups consuming bleaching chemicals are undergone a mild acid hydrolysis. Hydrogen peroxide is usually used to brighten pulps during the final bleaching stages to prevent the pulp from losing brightness over time.

As in comparison with hydrogen peroxide peracids have a better leaving groups, their reaction with lignin following mainly an electrophilic pathway is both more rapid and more selective under acidic conditions. Peracetic acid is less sensitive to transition metals than hydrogen peroxide. Hence, peracetic acid is preferred for elemental chlorine-free sequences, with the peracetic acid stage ahead of the final peroxide stage, as well as for totally chlorine-free bleaching with final peracetic acid step under weak acidic conditions (BARROS *et al.* 2010; FLETCHER *et al.* 1997; LIEBERGOTT 1996; LOPEZ *et al.* 2002; POTUČEK, MILICHOVSKÝ 2001). Peracetic acid can be used as an equilibrium solution with a mixture of peracetic acid, acetic acid, and hydrogen peroxide, or as pure distilled acid (VALCHEV 2013). On the other hand, storage and handling of higher concentrations of peracetic acid with high hydrogen peroxide content are restricted due to its potential hazards, mainly in industrial mills.

In this paper, soda pulp cooked from rapeseed straw was subjected to a five-stage and four-stage totally chlorine-free (TCF) bleaching under laboratory conditions. Bleaching sequence consisted of two chelation steps or one acidic stage in combination with subsequent alkaline extraction followed by peracetic acid and hydrogen peroxide stages. Optical and tensile strength properties of soda rapeseed pulp were compared with those obtained for kraft and sulphite pulps cooked from softwoods under industrial conditions.

EXPERIMENTAL PART

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) (POTUČEK, ŘÍHOVÁ 2015) was used for the pulping process. Raw materials consisted mainly of stalks, but approximately one third of total amount were valves of siliques. Chemical composition of both basic components of rapeseed straw, stalks and silique valves, was reported in the previous paper (POTUČEK *et al.* 2014).

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 (o. d.) raw material, and the anthraquinone charge of 0.1 %, based on oven-dried raw material. The cooking temperature was 160 °C. The batch cook was ended as soon as the H-factor reached a desired value of 1,600 h (POTUČEK *et al.* 2014).

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 found to be 18.8, according to the standard Tappi test method T 236 om-99. Using an atomic absorption spectrophotometry method in accordance with SCAN-CM 63:05/P 83:05, the concentrations of transition metals (in mg per kg of o. d. pulp) in the unbleached soda pulp were found to be 22.7, 14.4, and 4.7 for Fe, Mn, and Cu, respectively.

Soda rapeseed pulp was subjected to the five-stage bleaching sequence. The chelation (Q₁, Q₂), alkaline extraction (E_p), peracetic acid (Paa), and hydrogen peroxide (P) stages were carried out in sealed polyethylene bags. The pulp samples were hand kneaded

and treated in a preheated water bath. The consistency of pulp, *i. e.*, mass fraction of moisture-free fibres in suspension expressed in %, in each bleaching stage was maintained at a value of 10 %.

The first and second chelation stages, Q₁ and Q₂, with diethylenetriaminepentaacetic acid (DTPA) dose of 2 kg per 1 tonne of o. d. pulp were performed at a temperature of 60 and 70 °C, pH value of 8.5 and 5.0, and retention time of 120 and 40 min, respectively. The following alkaline extraction stage, E_P, was carried out at a temperature of 80 °C for 90 min. This stage was enhanced by hydrogen peroxide addition in the amount of 15 kg per 1 tonne of o. d. pulp. The NaOH charge was 0.7 % on the basis of o. d. pulp. Then, the pH value was adjusted to 10.8. The peracetic acid charge of 10 kg per 1 tonne of o. d. pulp was applied in the Paa stage operating at 70 °C and pH level of around 4.5 for 150 min. The hydrogen peroxide stage, P, was carried out at a temperature of 90 °C and at the pH value of 10.8 for 120 min. The hydrogen peroxide dose was 25 kg per 1 tonne of o. d. pulp. In order to reduce degradation of cellulose, the charge of 0.5 kg MgSO₄ per 1 tonne of o. d. pulp was always added in the E_P and P stages.

For the AE_PPaaP bleaching sequence, the process conditions in the acidic A stage were as follows: the sulphuric acid dose of 10 kg per 1 tonne of o. d. pulp, pH level of 3.3, temperature of 90 °C, and retention time of 120 min. After each stage a washing at 4 % pulp consistency was performed with distilled water. The pulp was washed thoroughly and then pressed to 25 % consistency.

For comparison, the kraft softwood pulps and sulphite spruce pulp obtained from an industrial source were undergone the Q₁Q₂E_PPaaP bleaching sequence. The kappa number of once-dried kraft softwood pulp, never-dried oxygen predelignified kraft softwood pulp, and never-dried oxygen predelignified sulphite pulp was 18.8, 10.5, and 12.5, respectively. Using the Kajaani FS-100 instrument, the distribution of the fibre length was also measured for soda, kraft, and sulphite pulps tested in this work.

Sample sheets were formed by means of a handsheet former machine. Handsheet grammage in grams per square metre varied from 75 to 85. Using an L&W Elrepho SE 071/070R instrument, the brightness of kraft pulp was measured for twenty samples obtained in each bleaching step. Breaking length and zero-span breaking length, under conditions when the length of a paper strip approaches zero and so the strength properties of fibre bundles are determined, was measured in accordance with Tappi test method T272 for ten samples of paper sheets by means of a breaking strength tester.

RESULTS AND DISCUSSION

Soda rapeseed pulp delignified to the kappa number of 18.8 with starting brightness of 28.7 % ISO was undergone the five-stage Q₁Q₂E_PPaaP bleaching sequence. Simultaneously, once-dried kraft softwood pulp with the kappa number of 18.8, as well as never-dried oxygen predelignified kraft softwood and sulphite spruce pulps with the kappa number of 10.5 and 12.5, respectively, were TCF bleached under the same conditions.

During TCF bleaching, the removal of transition metal ions is important because hydrogen peroxide was applied in the E_P and P stages. In the chelation stages, the pulp was treated with a chelating agent (DTPA) to reduce the transition metal content (especially Mn) in the pulp before peroxide bleaching. By choosing the proper pH in the Q stage, keeping most of the stabilizing Mg in the pulp is possible at the same time as the Mn content is significantly reduced. The best metal profile is obtained if the Q stage is done at pH 5–7. A significant reduction of the Mn content also occurs at pH levels as high as 9–10 (SIXTA *et al.* 2006).

Although the transition metal content was much lower for unbleached soda rapeseed pulp (22.7 mg Fe/kg o. d. pulp, 14.4 mg Mn/kg o. d. pulp, and 4.7 mg Cu/kg o. d. pulp) comparing to kraft pulp after oxygen delignification, in which mainly Mn content of 54.3 mg/kg o. d. pulp for unbleached kraft softwood pulp was found to be too high (POTŮČEK, MILICHOVSKÝ 2000), two chelation stages were inserted prior to alkaline extraction stage.

Figure 1 illustrates the brightness measured for soda, kraft, and sulphite pulps. The bleachability of the soda rapeseed pulp is much lower than that of softwood pulps produced industrially. Bleaching in the $Q_1Q_2E_pPaaP$ sequence produced total brightness increment of 9.9 points only comparing with the total brightness increments of 29.1, 27.6, and 23.5 % ISO achieved for once-dried kraft softwood pulp, never-dried pre-bleached kraft softwood and sulphite spruce pulps, respectively (*cf.* Figs. 1 and 2). For soda rapeseed pulp, an increase in the brightness of around 3 % ISO was achieved in each bleaching stage, whereas, in the case of kraft and sulphite pulps, the brightness increment of 0.02 to 0.46 % ISO attained in the Paa stage was infinitesimal (*cf.* Fig. 2). The results obtained showed that, under given laboratory conditions, the TCF bleaching sequence, was not efficient to achieve the sufficient brightness level of soda rapeseed pulp.

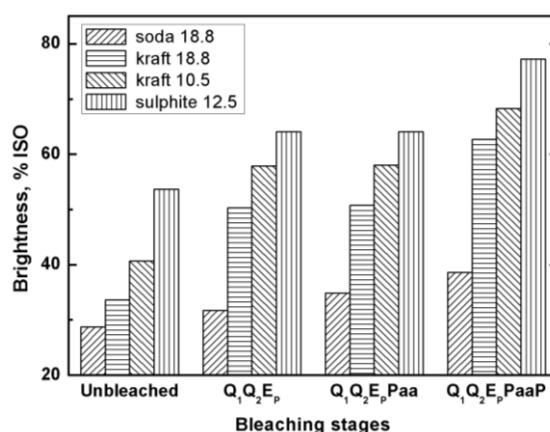


Fig. 1 Pulp brightness after bleaching stages.

Using the $Q_1Q_2E_pPaaP_O$ bleaching sequence with the peroxide stage enhanced by oxygen for kraft softwood pulp after oxygen delignification with the initial brightness of 41.4 % ISO, the total brightness increment of 22 % ISO was reached in the preceding paper (POTŮČEK, MILICHOVSKÝ 2000). For comparison, ENAYATI *et al.* (2009) 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, $D_0E_pD_1$, the final brightness was found to be 78.4 % ISO.

During sequential bleaching operations, pulp fibre properties are gradually changed due to mechanical and chemical treatments. Single fibre strength is very important to paper and paperboard. Also fibres' abilities to form fibre-to-fibre bonds are important for the strength of paper and paperboard.

The evaluation of pulp strength properties by conventional methods only 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. Hence, 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 (LIN *et al.* 2014).

The zero-span breaking length of unbleached pulps and pulps after the TCF bleaching is illustrated in Fig. 3. Since the values of the zero-span breaking length measured for unbleached and bleached pulps lie within the 95 % confidence range, it seems that the TCF bleaching sequence did not have a negative impact on the tensile strength of pulp fibres.

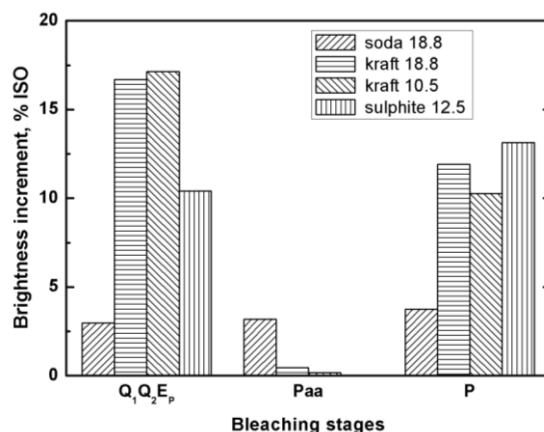


Fig. 2 Brightness increment in bleaching stages of Q₁Q₂E_pPaaP sequence.

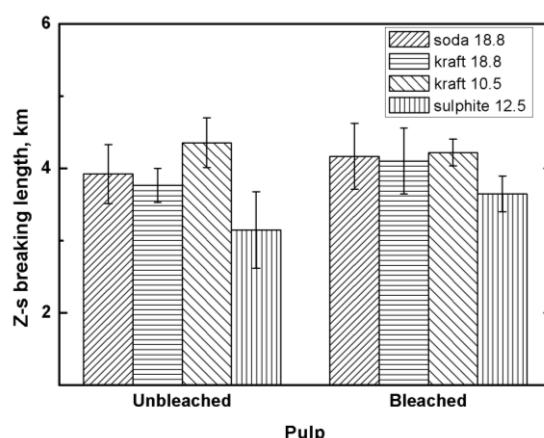


Fig. 3 Zero-span breaking length for unbleached and bleached pulps for Q₁Q₂E_pPaaP sequence (error bars: 95% confidence limits).

As expected, only strength of sulphite pulp fibres is lower comparing with soda and kraft pulp fibres. The values of the zero-span breaking length for soda and kraft pulp are comparable with that of 3.92 km measured for unbleached softwood kraft pulp in the preceding paper (POTŮČEK, MILICHOVSKÝ 2000).

In contrast to fibre strength, the breaking length of pulp sheets influenced by tensile strength of fibres and fibre-to-fibre bond strength was found to be significantly different for soda rapeseed pulp and softwood pulps (*cf.* Fig. 4). As expected, for unbeaten softwood fibres, the breaking length was substantially lower compared to soda rapeseed pulp fibres. This finding can be ascribed to different morphological properties of softwood and rapeseed fibres. The weighted average length of soda rapeseed fibres was only 0.92 mm, while the average length of kraft and sulphite softwood fibres was 2.46 and 2.27 mm, respectively. Furthermore, the TCF bleaching might enhance the binding power of short soda rapeseed fibres so that the breaking length of bleached rapeseed pulp was by 25 % greater than that of unbleached one. It is worth mentioning that both values of the breaking length measured for soda rapeseed pulp lie between values of 3.17 and 6.92 km determined

for soda rapeseed pulp unbleached and beaten to 66 SR, respectively, in the previous paper (POTŮČEK, MILICHOVSKÝ 2011) where soda rapeseed pulp delignified to the kappa number of 37.1 was tested.

Since the brightness of soda rapeseed pulp after the $Q_1Q_2E_P PaaP$ bleaching sequence was not sufficient, the acidic stage was applied instead of two chelation stages and the four-stage $AE_P PaaP$ sequence was tested with soda rapeseed pulp having the kappa number of 21.4 and initial brightness of 27.3 % ISO. Process conditions in the E_P and Paa stages were the same as for the $Q_1Q_2E_P PaaP$ sequence, only the peroxide charge and retention time were changed in the P stage. Besides original conditions given as 20 kg hydrogen peroxide charge per 1 tonne of o. d. pulp and retention time of 120 min, either hydrogen peroxide charge increased to 40 kg or longer retention time of 180 min were applied.

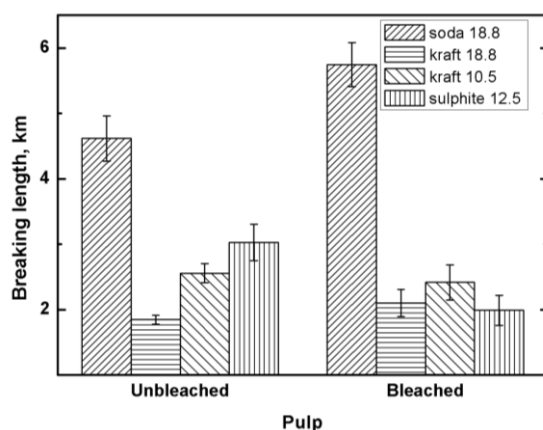


Fig. 4 Breaking length for unbleached and bleached pulps for $Q_1Q_2E_P PaaP$ sequence (error bars: 95% confidence limits).

Figure 5 illustrates that both higher hydrogen peroxide charge and longer retention time in the P stage had a positive impact on the pulp brightness which was increased by 7.4 % ISO and 3.4 % ISO, respectively, in comparison with the original conditions. It is worth pointing out that the alkaline E_P stage after acidic stage gave the brightness of around 35.4 % ISO, *i. e.*, more than twice greater brightness increment was attained as in the $Q_1Q_2E_P$ stages. A higher bleaching effect in the E_P stage may be attributed better removing transition metals in the acidic stage in comparison with chelation stages. Similarly, the P stage revealed greater brightness increment, whereas Paa stage contribution to brightness was low as for the $Q_1Q_2E_P PaaP$ bleaching sequence.

For the unbleached soda rapeseed pulp with the zero-span breaking length of 3.55 km and breaking length of 4.23 km, the influence of higher hydrogen peroxide charge and longer retention time on tensile strength properties was investigated as well. The zero-span breaking length and breaking length were found to be 3.84 and 6.30 km, 3.27 and 5.88 km, and 3.78 and 5.91 km for pulps bleached under original conditions, higher hydrogen peroxide charge, and longer retention time, respectively. As hydrogen peroxide is less selective agent than peracetic acid or chlorine dioxide, a decrease in the zero-span breaking length was evident particularly for the higher hydrogen peroxide charge.

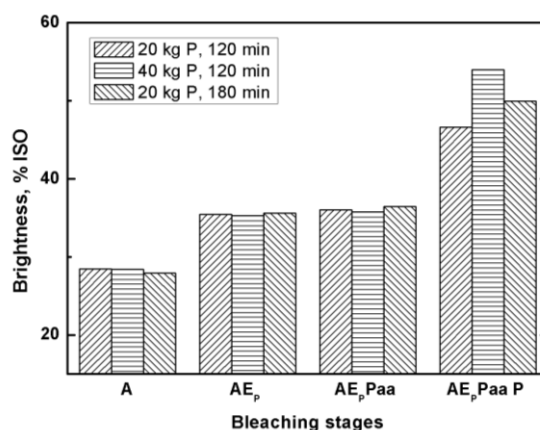


Fig. 5 Influence of hydrogen peroxide charge and retention time on soda pulp brightness for AE_pPaaP sequence.

CONCLUSION

In spite of limited number of experiments, some conclusions valid within the framework of our study can be made. In agreement with ATEŞ *et al.* (2015), the above presented data demonstrates that the totally chlorine-free bleaching sequence did not bring an adequate brightness level to soda pulp cooked from rapeseed straw. The reasons are different anatomic and chemical characteristic of soda pulp fibres from rapeseed straw along with the high ash content in trace elements in comparison with softwood and hardwood pulps. In spite of these facts, the four-stage AE_pPaaP bleaching sequence enables to reach the brightness of 54 % ISO, while the five-stage Q₁Q₂E_pPaaP sequence only 38.6 % ISO. Therefore, the ECF bleaching sequences enabling 84 % ISO brightness seem to be more suitable for soda pulps from rapeseed straw (POTŮČEK, ŘÍHOVÁ 2017).

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ACKNOWLEDGEMENTS

This work was supported by the Ministry of Education, Youth, and Sports of the Czech Republic under the research project SGS_2018_006. The authors would like to thank the Central Laboratory Mondi Štětí a. s. for measuring the transition metals concentrations in the soda pulp.

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