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Bleaching of Soda Pulp from Rapeseed Straw

Theses of the Doctoral Dissertation

Pardubice 2018

Study program: Chemistry and Technology of Materials

Study field: Surface Engineering

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Year of the defence: 2018

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ŘÍHOVÁ, Martina. Bleaching of Soda Pulp from Rapeseed Straw. Pardubice, 2018. 177 pages. Dissertation thesis (PhD.). University of Pardubice, Faculty of Chemical Technology, Institute of Chemistry and Technology of Macromolecular Materials. Supervisor Prof. Ing. František Potůček, CSc.

Abstract

The dissertation thesis deals with the bleaching of soda pulp cooked from the rapeseed straw. The first part of this thesis is focused on the batch cooking of soda pulp with a relatively low degree of delignification. In the second part, the TCF (totally chlorine-free) and the ECF (elemental chlorine-free) bleaching of soda rapeseed pulp is carried out using chlorine dioxide, hydrogen peroxide, and peracetic acid as bleaching agents.The results obtained for the soda rapeseed pulp were compared with those for the kraft and sulphite pulps produced industrially. It is demonstrated that the ECF four-stage bleaching sequence comprising at least two chlorine dioxide stagesis suitable to yield the bleached soda pulp with sufficient brightness, strength properties, and degree of polymerization compared to the soda pulp after TCF bleaching.

Abstrakt

Cílem této disertační práce bylo vybělit natronovou buničinu ze slámy řepky olejky. První část této disertační práce je zaměřena na uvaření natronové buničiny ze slámy řepky olejky na požadovaný stupeň delignifikace. V druhé části disertační práce je natronová buničina bělena dvěma způsoby, a to bělením bez použití chloru a jeho sloučenin (TCF) a bělením bez elementárního chloru (ECF) s použitím bělicích chemikálií, jako je peroxid vodíku, kyselina peroctová a oxid chloričitý. Získané výsledky byly porovnány s průmyslově vyráběnou sulfátovou a sulfitovou buničinou. Dosažené výsledky ukázaly, že natronová buničina vybělená ECF způsobem s alespoň dvěma chlordioxidovými stupni se jevila jako vhodná vláknina s dostatečně vysokou bělostí, pevností vláken a stupněm polymerace.

Keywords

Soda pulp, totally chlorine-free bleaching, elemenal chlorine-free bleaching, hydrogen peroxide, peracetic acid, chlorine dioxide, brightness, strength of fibres, degree of polymerization

Klíčová slova

Natronová buničina, bělení zcela bez chloru a jeho sloučenin, bělení bez elementárního chloru, peroxid vodíku, kyselina peroctová, oxid chloričitý, chlordioxidový stupeň, bělost, pevnost vláken, stupeň polymerace

Table of Contents

Introduction

Bleaching is defined as a chemical process aimed on the removal of colour in pulps derived from residual lignin and other coloured impurities (for example certain extracts and dirt making contrast colour on the sheet) (Valvech, 2013; Sixta, 2006). Totally chlorine-free (TCF) and elemental chlorine-free (ECF) bleaching sequences have been utilized mostly for the bleaching of wood chemical pulps with low kappa numbers (Chemical pulping, 2010; Latibari *et al.* 2014).

Annual plants have different morphological and chemical properties from woody raw materials. Therefore, they required another cooking and different bleaching conditions (Abrantes et al., 2006). For the production of pulp from annual plants, a natron method is usually used employing anthraquinone as a catalyst that protects the reducing aldehyde groups of saccharides against alkaline degradation and improves the solubility of lignin (Hedjazi *et al*., 2009). Elementary chlorine-free bleaching sequences seem to be more suitable for pulps from agricultural residues (Potůček and Říhová, 2017).

Rapeseed is mainly used for the vegetable oil and the biodiesel production and it is widely cultivated in the world (Potůček *et al*., 2014). Rapeseed (*Brassica napus* L. *convar. napus*), ranking among short fibered annual plants, is a dominant agricultural crop in many countries all over the world (Housseinpour *et al.*, 2010). The major rapeseed producer countries are China, Canada, India, France, Germany, and Australia. The average amount of production is in the range from 5 to 10 t ha^{-1}. About 20 % of plant material remains on the field. However it has a potential to be used for the production of pulp for the paper industry. Therefore, its thorough investigation for this purpose is required (Kasmani *et al*., 2011). This need is essentially motivation for this work. Until now, however, rapeseed fibres have been investigated only to a limited extent for its use in paper industry.

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 in this work.

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 carried out at the liquor-to-raw material ratio from 5:1 to 9:1, alkali charge of 15 – 19 % expressed as Na_2O per oven-dried raw material, and the anthraquinone charge of 0.1 %, based on oven-dried raw material.

Two TCF, $Q_1Q_2E_PPaaP$ and AE_PPaaP, and three ECF, DE_PPPaa, $D_0E_PD_1P$, and $D_0E_PD_1D_2$, were carried out under laboratory conditions.

The first and second chelation stages, Q_1 and Q_2, with diethylenetriaminepentaacetic acid (DTPA) dose of 2 kg per 1 tonne of oven dried 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 oven dried pulp.

The peracetic acid charge of 10 kg per 1 tonne of oven dried pulp was applied in the Paa stage operating at 70 °C and the 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 the degradation of cellulose, the charge of 0.5 kg $MgSO_4$ 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 oven dried pulp, pH level of 3.3, temperature of 90 °C, and retention time of 120 min.

The first chlorine dioxide stage, D_0, 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 D_1 and D_2 stages were performed at 80 °C with the active chlorine dose of 26 kg and of 8 kg per 1 tonne of o. d. pulp and at the pH value of 4.0 and 4.5, respectively, for 180 min.

For a comparison, the oxygen-prebleached kraft softwood (kappa no. of 10.5) and sulphite spruce (kappa no. of 12.5) pulps, as well as the kraft once-dried softwood (kappa no. of 18.8) pulp produced at industrial scale underwent the same complete TCF and ECF bleaching sequences

Result and discussion

Cooking parameters

In the first set of the preliminary soda pulping runs, an influence of the active alkali charge and liquor-to-straw ratio on the degree of delignification and amount of rejects was investigated.

The influence of the active alkali (*AA*) charge (ranging within the limits of 0.17 to 0.21 g of Na_2O per g of oven dry straw) on the kappa number and amount of rejects, expressed as a mass fraction in the cooked pulp, is illustrated in Fig. 1. With increasing

AA charge, both the kappa number and the amount of rejects decrease.

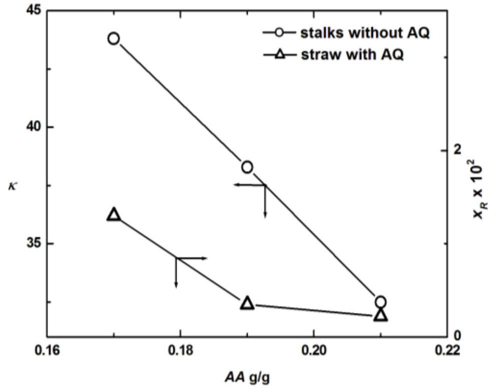

Fig. 1. Kappa number, κ, and amount of rejects, x_R, as a function of *AA* charge, x_{AA}, at *L*/*S* = 7 for pulp cooked from rapeseed straw and stalks

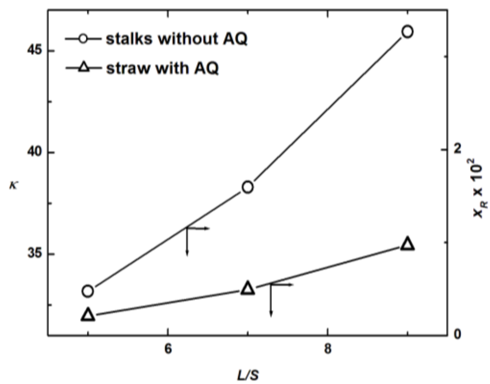

Fig. 2. Kappa number, κ, and amount of rejects, x_R, as a function of liquor-to-straw ratio, *L*/*S*, at *AA* charge of 0.19 g Na_2O/g ODP for pulp cooked from rapeseed straw and stalks

Figure 2 shows how the kappa number and the amount of rejects increased with increasing liquor-to-straw ratio (*L/S*).

The soda pulp cooked at the liquor-to-raw material ratio of 5:1, active alkali charge of 19 %, and the anthraquinone charge of 0.1 %, based on oven-dried raw material, was used for the bleaching experiments.

TCF bleaching

Soda rapeseed pulp delignified to the kappa number of 18.8 with starting brightness of 28.7 % ISO was undergone the five-stage $Q_1Q_2E_P$PaaP 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 for comparison.

Figure 3 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. 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.

TCF bleaching sequence did not have a negative impact on the tensile strength of pulp fibres. The zero-span breaking length of the soda pulp, once dry kraft pulp and never dry sulphite pulp were found increasing after bleaching about 6, 9 and 16 %, respectively, while the zero-span breaking length for bleached, never dry kraft pulp was found without change. The values of the zero-span breaking length for the soda pulp and the kraft pulp are comparable with that of 3.92 km measured for unbleached softwood kraft pulp in the preceeding paper (Potůček and Milichovský, 2000).

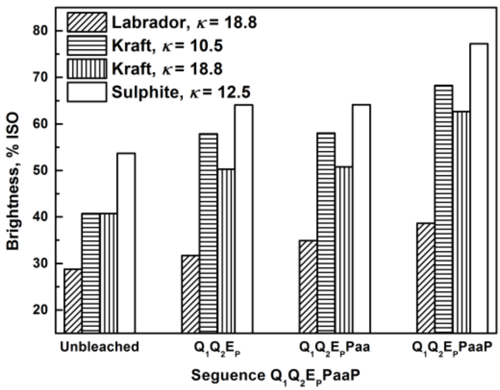

Fig. 3. Pulp brightness after $Q_1Q_2E_P$PaaP bleaching stages

By TCF bleaching, the degree of polymerization of the soda pulp, never dry kraft pulp, once dry kraft pulp and sulphite pulp were achieved as 586, 615, 370 and 562, respectively, *i. e.*, lower values were achieved compared to unbleached pulps.

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. The four-stage AE_PPaaP 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 dose and the retention time were changed in the P stage. Besides original conditions given as 20 kg H_2O_2/t ODP and retention time of 120 min, either hydrogen peroxide dose increased to 40 kg or longer retention time of 180 min were applied. 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 $Q_1Q_2E_P$PaaP 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 dose 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.

ECF bleaching

The soda pulp delignified to the kappa number of 17.9 under laboratory conditions was subjected to the ECF four-stage bleaching sequences. Values of brightness, zero-span breaking length and degree of polymerization were compared with the laboratory bleached kraft and sulphite pulps.

The pulp brightness attained after the bleaching sequence DE_PPPaa is shown in Fig. 4. The final brightness of 80.0, 84.1, 83.4, and 88.3 % ISO were attained for the soda, once-dried kraft, never-dried pre-bleached kraft and pre-bleached sulphite pulps, respectively. Thus, the final brightness achieved for the soda rapeseed pulp was lower compared to kraft and sulphite pulps.

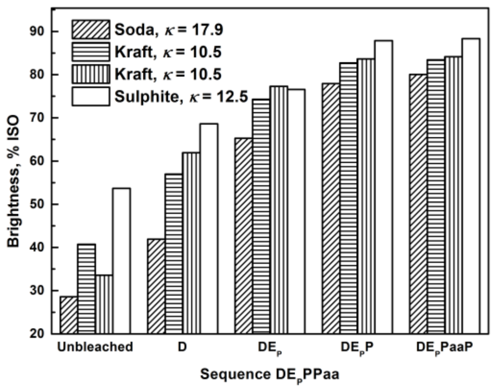

Fig. 4. Pulp brightness after DE_PPPaa bleaching stages

The DE_PPPaa bleaching sequence had a negative impact on the fibre strength of soda pulp. The zero-span breaking length of the bleached soda pulp was decreased about 13.22 %, whereas never dry kraft pulp was decreased only about 3.22 %. Bleached, once dry kraft pulp and bleached sulphite pulps had zero-span breaking length of about 1% and 9 % higher, respectively.

The degree of polymerization for the bleached soda pulp was achieved as 543, while kraft and sulphite pulps found lower degrees of polymerization of 414 to 483 after bleaching.

The pulp brightness attained after the bleaching sequence of $D_0E_PD_1P$ is shown in Fig. 5. The final brightness of soda pulp (82.96 %), once dry kraft pulp (88.05 %) and predelignified kraft pulp (88.05 % ISO) and sulphite pulp (90.17 % ISO) were achieved greater in comparison with the final brightness for the DE_PPPaa sequence.

The results of strength for the bleached soda pulp and the never dry kraft pulp were found decreased of about 16.46 % and 5.11 %, respectively. The strength properties of the bleached, once dry kraft and never dry kraft pulp were found increasing of about 2 and 0.3 %, respectively.

Degree of polymerization of bleached soda pulp, once-dried kraft pulp, never-dried kraft pulp and sulphite pulp were found to be 533, 451, 302, and 401, respectively after bleaching. Lower values of the degree of polymerization were achieved in comparison with bleached pulps after the bleaching sequence of DE_PPPaa.

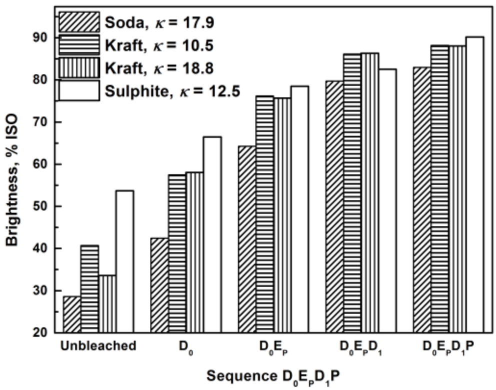

Fig. 5. Pulp brightness after $D_0E_PD_1P$ bleaching stages

The pulp brightness attained after $D_0E_PD_1D_2$ is shown in Fig. 6. The final brightness of 83.51 % ISO for the soda pulp was greater than that obtained in the $D_0E_PD_1P$ sequence (82.96 %). On the other hand, the bleachability of the once dry kraft pulp (87.56 % ISO), never dry pre-delignied kraft pulp (87.82 % ISO) and sulphite pulp (89.82 % ISO) were found lower in comparison with bleached kraft and sulphite pulps after the $D_0E_PD_1P$ sequence.

The zero-span breaking length of bleached soda pulp, never dry kraft pulp and sulphite pulp were decreased of about 8.98, 7.13 and 9.21 %, respectively. However, the zero-span breaking length for once dry kraft pulp was increased of about 2.89 % after $D_0E_PD_1D_2$ sequence.

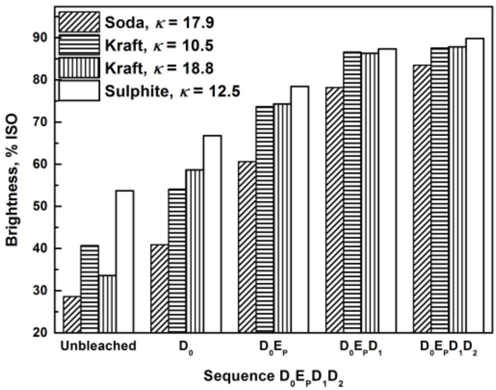

Fig. 6. Pulp brightness after $D_0E_PD_1D_2$ bleaching stages

Results of the degree of polymerization of bleached soda pulp (551), never dry kraft pulp (512) and sulphite pulp (419) were almost the same as the bleached pulps had after the DE_PPPaa sequence. But once dry kraft pulp had the degree of polymerization only of 312, almost similar to the bleached kraft pulp after the sequence containing two chlorine dioxide stages.

Conclusion

Considering the number of experiments and obtained results in this work, following conclusions valid in the framework of this work can be made:

(i) The preliminary runs focused on the investigation the suitability of soda pulp cooking parameters, with and without anthraquinone addition, showed that the active alkali charge of 19 % based on oven dry straw and the liquor-to-straw ratio of 5:1 were sufficient to prepare soda and soda-AQ pulp with low amount of rejects.

(ii) The brightness data achieved for bleached pulp demonstrated that the totally chlorine-free bleaching sequence did not bring an adequate brightness level to soda pulp cooked from the rapeseed straw in comparison to the soda pulp, bleached by the ECF bleaching sequences. 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. Hence, the ECF bleaching sequence, consisting of at least two chlorine dioxide stages, was necessary to obtain the soda pulp with a brightness value above 83 % ISO.

(iii) The fibre strength seems to be acceptable for utilization of the soda pulp bleached for the paper production.

(iv) All bleaching sequences resulted in relatively large loss in the degree of polymerisation for both soda, kraft and sulphite pulps tested in this work.

Nevertheless, the results for bleached soda pulp after ECF bleaching sequence were satisfactory. Thus, it can be concluded that the rapeseed straw represents a suitable source of the pulp raw material for the paper industry mainly in regions with the lack of hardwood.

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