

EXTENDED DELIGNIFICATION OF OLD CORRUGATED CONTAINER AND TOTALLY CHLORINE FREE BLEACHING OF THE PULP

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The paper industry has taken various steps to address environmental concerns and raw material limitations. Among them, paper recycling has been shown to be a viable option. In this study, the alkaline sulfite pulping of old corrugated containers (OCC) to produce bleachable pulp was investigated. A combination of one of the three active alkali levels (14, 16, and 18%; Na₂O, and oven-dry weight of OCC); one of two pulping temperatures (145 and 175°C), and one of two pulping times (60 and 120 minutes) and sodium sulfite to sodium hydroxide ratio of 30/70 (mol/mol) were examined. After preliminary pulping and evaluation, pulp with a kappa number of 18.3 and brightness of 50.2%, which was produced applying 18% active alkali, sodium sulfite to sodium hydroxide ratio of 30:70, and pulping time and temperature of 120 minutes and 175°C, respectively, having the yield of 64.0% (based on oven dry weight of washed OCC) and 72.7% (based on original weight of the OCC as received), respectively, was selected for totally chlorine free (TCF) bleaching trials. Brightness, opacity, tensile, and tear strength indices of this pulp were measured as 50.2%, 81.4%, 27.7 N.m/g, and 12.35 mN.m²/g, respectively. Bleaching of this pulp applying 3% H₂O₂ and 2.25% NaOH at 90 minutes generated bleached pulp with brightness and opacity as 57.1% and 78.2%, respectively. The bleaching yield was measured as 92%. Tensile and tear strength indices of this pulp were measured as 25.1 Nm/g and 12.4 mN.m²/g, respectively.

Keywords: Old corrugated container pulp; Delignification; Alkaline sulfite; Active alkali; Totally chlorine free

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INTRODUCTION

Global production and consumption of paper and paper products has been increasing at very rapid rate, and the total paper and paperboard production rose to 394 million tons in 2010 (FAO 2011). On the other hand, the forest resources of the world are diminishing, giving rise to a shortage of wood raw material for the paper industry. Therefore, concerned communities are searching among different alternatives to fulfill the raw material needs of the expanding paper industry. Annual plant residues and the utilization of low quality wood sources have been shown to be viable sources of raw material, especially in developing countries (Hedjazi et al 2008).

Even though the paper industry has taken different measures to reduce its environmental impacts, increasing awareness has been imposing pressure to take further action to

help preserve our environment. In this context the paper industry is obligated to improve utilization processes to increase the production yield and the life cycle of the product. Different high-yield pulping processes have attracted the interest of the paper industry (Pan and Leary 2000; Mustajoki et al. 2010).

Since the early days of the paper production, waste paper recycling has been the most favorable solution to provide a suitable substitute for virgin fibers (Mckinney 1995). Consequently, various countries, especially those that are faced with the lack of suitable fibers, have expanded waste paper recycling. In 2010, almost 185.7 million tons of paper was recovered, thanks to lower cost, lower energy requirement, and lower environmental impacts (FAO 2011).

Waste paper re-utilization has followed two paths; 1) intensive processing including de-inking to produce bleached pulp suitable for the production of writing and printing as well as tissue paper, and 2) limited processing, by applying cleaning and screening to eliminate the detrimental contaminants without de-inking to produce packaging grades.

Recently, the upgrading the OCC pulp using extended delignification to produce bleachable pulp for the production of white grade papers has emerged. The original work of de Ruvo et al. (1986) applied alkali-oxygen delignification to reduce the lignin content of the OCC to a level suitable for lignin-eliminating bleaching. Such attempts were followed by the work of Markham and Courchene (1988) and Bisner et al. (1993). Nguyen et al. (1993) applied kraft pulping on old corrugated container fibers to reach lower kappa number. Oxygen delignification (Nguyen 1994) and delignification and whitening by hydrogen peroxide (Simrad and Nguyen 1996) have also been applied on OCC.

Successful development of OCC delignification requires a technology that is able to exploit the complete potential of this raw material. Specifically, the selectivity in delignification and bleaching ought to be at a high level, resulting in pulp with high yield and strength but at low kappa number to facilitate easier bleaching by environmentally friendly bleaching sequences, such as a totally chlorine free sequence, aimed at elimination of chlorine consumption (Misra et al. 2001; Bajpai et al. 2006; Potucek and Milichovsky 2002; Zeinaly et al. 2009).

Even though soda and soda-oxygen pulping have been used for delignification of OCC, these processes impart disadvantages. Alkaline cooking liquor decomposes carbohydrates by peeling reactions and alkaline hydrolysis. Under such conditions, lignin undergoes condensation reactions, which reduce the reactivity of residual lignin, thus also having an impact on bleaching (Hedjazi et al 2008). This particularly holds true for most chlorine-free bleaching. The alkaline-sulfite (AS) process has potential for delignification of OCC (Rodriguez et al. 2007; Gullichsen and Fogelholm 1999). In particular, the higher brightness of the pulp facilitates chlorine-free bleaching.

To develop a suitable delignification process for OCC to produce pulp containing low content of lignin without serious loss of pulping yield, alkaline-sulfite pulping of OCC was investigated. Pulp was bleached applying a totally chlorine-free bleaching sequence.

EXPERIMENTAL

Material Collection and Preparation

Old corrugated container clippings was collected from a corrugated board container production plant to be assured that the sample was free from consumer contaminants. However, the presence of starch in the OCC is unavoidable, and we used the OCC as received. The OCC samples were manually cut into 30 x 30 mm wafers for further processing. The OCC wafers were dried at ambient temperature and, after reaching equilibrium moisture content, they were stored in plastic bags until used.

100 grams (oven dry basis) of sample was selected and slushed in water at 5% consistency using a laboratory pulp disintegrator. However, after disintegration, the pulp consistency was reduced to about 1%, and the suspension was dewatered and then thoroughly washed with sufficient water on 200 mesh screen. The fibers that remained on the screen were manually dewatered as much as possible and then used for delignification.

Delignification

The delignification conditions were set as follows: three levels of active alkali (14, 16, and 18%, on o.d. OCC), two pulping temperatures (145 and 175°C), two pulping times (60 and 120 minutes), and the constant ratio of sodium sulfite to sodium hydroxide ratio of 30/70 (mol/mol). The liquor-to-fiber ratio was adjusted to 9/1. For each combination of variables, two replica pulps were produced.

All cooks were performed in a 4 liter rotating digester “Ghomes Wood and Paper Equipment Manufacturing Co.” using 100 g of unwashed OCC (dry basis). At the end of each cook, the content of cylinder was discharged on a 200 mesh screen. The cooked material was washed using hot water, and the remaining liquor was separated by hand pressing the cooked material. Then the pulping yield was measured.

The spent liquor was used for the determination of the residual active alkali. The residual sodium hydroxide and sodium sulfite were measured and the residual active alkali (based on Na₂O) was calculated (Ingruber 1993)

Totally Chlorine Free Bleaching

Pulp with the lowest kappa number was selected for TCF bleaching, applying QP sequences. First the pulp sample (10 grams dry basis) was chelated with 0.5% DTPA at 70°C for 30 minutes in polyethylene bags and water bath. The pulp consistency and pH were adjusted to 3% and 5, respectively. The initial concentration of H₂O₂ was 37%. At the end of the chelating time, the pulp was washed with de-ionized water and manually dewatered for bleaching.

Bleaching was performed by applying one of the four charges of 2, 3, 4, and 5% (based on oven dry weight of pulp) and one of the two bleaching times (60 and 90 minutes) at 10% consistency and 70°C in a polyethylene bags in a constant temperature water bath. The H₂O₂/NaOH ratio was held constant at 4/3 for all bleaching trials. The contents of the bag were hand-kneaded at 10 minutes intervals during the reaction time. The sodium silicate and MgSO₄ dosage was constant at 3% and 0.5%, respectively, for all bleaching experiments.

At the end of the reaction time, the contents of the bag were discharged on a 200 mesh screen, and the spent liquor passing through the screen was collected for the determination of residual chemical. The pulp on the screen was washed with tap water and manually dewatered. The pH of the bleached pulp was adjusted to 7 using dilute H₂SO₄ (1% solution), dewatered, and kept at 3°C until pulp evaluation. The bleaching yield was measured.

Pulp Evaluation

The following TAPPI test methods were used for pulp analysis: kappa number, T236 om-99; freeness, T227 om-99; handsheet preparation, T205 om-95; tear strength, T414 om-04; tensile strength, T494 om-92; brightness, T452om-08; and opacity, T425om-06.

Statistical Analysis

The collected data were analyzed applying factorial experimental design, and in case a statistically significant difference at 99% confidence level was observed between the averages, the Duncan Multiple Range Test was used for the grouping of the averages.

RESULTS AND DISCUSSION

Delignification

Environmental and economic concerns necessitate the re-utilization and recycling of the waste paper to provide alternative raw material for pulp and paper manufacture. During 2010, almost 185.7 million tons of paper were recovered, and 76.2 million tons of recovered fiber pulp was used for paper production, applying suitable processes (FAO 2011).

The results of alkaline-sulfite pulping of OCC are summarized in Table 1.

Table 1. Pulping Conditions and the Properties of Alkaline-Sulfite Pulp from OCC*

Pulping Trial No.	Active alkali (%)	Pulping temp. (°C)	Pulping time (min.)	Pulping yield (%)		Residual active alkali (%)	Kappa No.	Freeness (mL CSF)
				OCC**	Washed OCC			
Control	-	-	-	100	88.0	-	66.7	-
P1	14	145	120	73.2	83.2	5.6	48.4	675
P2	16	145	120	69.8	79.3	6.7	44.1	690
P3	18	145	120	68.8	78.2	8.3	41.7	690
P4	14	175	60	68.5	77.8	4.5	30.3	630
P5	16	175	60	68.2	77.5	5.2	34.7	600
P6	18	175	60	68.4	77.7	2.9	27.0	630
P7	14	175	120	67.8	76.9	3.7	27.3	630
P8	16	175	120	66.9	76.0	3.1	24.3	630
P9	18	175	120	64.0	72.8	4.0	18.3	600

*Liquor to Fiber ratio; 9/1 and Na₂SO₃/NaOH ratio;30/70; ** Based on OCC as received

The pulping yield varied between the lowest value of 64.0 and the highest value of 73.2% (based on OCC as received) and 72.7% and 83.2% (based on washed OCC). OCC preparation and washing eliminated 12.0% of the OCC as received. The kappa number of the pulps ranged between 18.3 and 48.6. The kappa number of OCC prior to pulping was 66.7.

The OCC after disintegration and washing is in the form of individual fibers, and since these fibers already had passed through at least one pulping process, we anticipated that the delignification of the OCC fibers would be easy (Bizner et al. 1993). Therefore, initially milder pulping condition (pulping trials P1-P3) were applied. Contrary to our expectations, the delignification efficiency was not as good as anticipated, and the kappa reduction was only 37.5% (based on the original kappa number of washed OCC). These pulps were not suitable for bleaching. The OCC fibers had not originated from a single pulping process, but rather they were a combination of fibers from different pulping process, mainly neutral sulfite semi-chemical and kraft. Furthermore, previous pulping reached the delignification to near residual delignification stage. Both conditions make further delignification harder. Consequently, we decided to apply more intensive pulping conditions using higher temperature. The higher temperature reduced both the yield and kappa number (pulping trials P7 to P9), and the kappa number of the pulp ranged between 18.3 and 27.3.

It is common to bleach pulps after the kappa number has been reduced as low as practical to save the bleaching chemicals and to reach the highest brightness gain (Sarwar Jahan et al. 2010; Yadav et al. 2010; Potucek and Milichovsky 2002). However, an excessively low kappa number may entail degradation of the strength properties of the pulp. Therefore we selected three pulps with the lowest kappa number to examine the impact of pulping and kappa reduction on the strength of the pulps and to reach a compromise for the selection of the pulp with suitable strength and kappa number for further TCF bleaching.

The results of strength and optical properties evaluation are listed in Table 2. The results revealed that applying higher active alkali deteriorated the tensile strength index and breaking length of the pulps, but tear strength index and brightness were improved due to the removal of more lignin from the fibers. The opacity of the pulp was reduced. The influence of the higher active alkali charge on tensile strength and tear strength indices was statistically significant, but the impact of active alkali on either brightness or opacity was not statistically significant. The Duncan Multiple Range Grouping of the averages is shown in Table 2 using lower-case letters.

Table 2. Strength and Optical Properties of Selected Alkaline-sulfite Pulps from OCC

Pulping Trial No.	Active Alkali (%)	Tensile strength index (Nm/g)	Breaking length (km)	Tear strength index (mN.m ² /g)	Brightness (%)	Opacity (%)
OCC	-	32.6 ^b	3.33	11.1 ^a	47.30 ^a	84.5 ^a
P7	14	36.8 ^c	3.75	11.5 ^{ab}	50.43 ^b	81.1 ^b
P8	16	26.8 ^a	2.73	11.1 ^a	50.29 ^b	81.0 ^b
P9	18	27.7 ^a	2.83	12.3 ^b	50.17 ^b	81.4 ^b

*Liquor to fiber ratio; 9/1:Na₂SO₃/NaOH ratio; 30/70: time:120 minutes, and temperature:175°C

Based on the results of strength and optical properties measurements, pulp with lowest kappa number (pulping trial P9) was selected for TCF bleaching. The selected pulp, having the kappa number of 18.3, was bleached, applying a TCF sequence, and the results are summarized in Table 3.

Table 3. Results of TCF Bleaching of Alkaline Sulfite Pulp Produced from OCC

Bleaching Trial No.	Chemical charge (%)		Bleaching time (min)	Bleaching Yield (%)	Kappa No.	Brightness (%)	Opacity (%)	Tensile strength index (Nm/g)	Tear strength index (mN.m ² /g)
	H ₂ O ₂	NaOH							
Unbleached	-	-	-	100	18.3	50.2	81.4	27.7	12.3
BP1	2	1.5	60	92	14.5	54.3	79.1	20.9	10.6
BP2	3	2.25	60	91.7	13.2	54.9	79.2	24.9	11.6
BP3	4	3	60	90	13.3	54.9	79.2	23.5	10.5
BP4	5	3.75	60	91	12.7	57.2	76.5	20.7	10.3
BP5	2	1.5	90	92	13.2	55.1	78.1	21.4	9.8
BP6	3	2.25	90	93	11.4	57.1	78.2	25.1	12.4
BP7	4	3	90	92	12.1	57.2	78.1	21.8	11.6
BP8	5	3.75	90	91	11.3	52.2	79.3	31.2	12.3

*Temperature: 70°C; Sodium silicate: 3%; MgSO₄: 0.5%; Consistency: 10%

Recent literature reveals an interest in the utilization of magnesium hydroxide or sodium carbonate as the alkali in hydrogen peroxide bleaching (Mustajoki et al. 2010; Ghasemi et al. 2010; Zeinaly et al. 2009; Attioghe et al. 2010). It has been acknowledged that substituting the new alkali will increase the bleaching yield and lower chemical cost at the expense of lower brightness and strength. However, due to unknown behavior of this newly developed pulp, we decided to use sodium hydroxide. The brightness development of the bleached pulps showed a fast response of these pulps toward bleaching, and after 60 minutes (bleaching trial BP4), the brightness increased to 57.2% ISO. A longer bleaching time did not improve the brightness anymore (bleaching trials PB6-BP8).

The OCC fibers usually contain different lignin residuals that have different chromophores, and varying bleaching responses are exhibited. Therefore, one cannot expect the potential for brightness development to high degree, unless special measures such as oxygen delignification are applied to assist lignin removal (Thomas et al 2007) or stronger bleaching chemistry such as elemental chlorine-free (ECF) systems are utilized. The kappa number of pulp prior to TCF bleaching must be lower than 10 to be able to develop sufficient brightness (Sarwar Jahan et al. 2010; Bajpai et al. 2006; Potucek and Milichovsky 2002). Even though the brightness of this pulp could reach 57.2% ISO with 3% hydrogen peroxide dosage in only one stage, TCF bleaching of wheat straw pulp after application of 6% hydrogen peroxide reached about 60%.

Both tensile strength and tear strength indices of the bleached pulps were measured and compared with the unbleached pulp (Table 3). No significant deterioration of the strength values was observed after TCF bleaching; these results demonstrate the potential of such a simple bleaching sequence for this application.

CONCLUSIONS

1. The paper industry around the world produces about 206 million tons of unbleached wrapping and packaging papers. A very high percentage of these papers are recovered and re-used in the production similar paper grades. However, since in total 185.7 million tons of waste paper is recovered and only 76.2 million tons of recovered pulp is produced and used in paper production, some surplus waste paper exists, and part of this surplus paper is likely to consist of wrapping and packaging grades. The availability of surplus packaging papers as a low-cost source of paper-making fibers can help the paper industry, especially in fiber-deficient countries, to develop local papermaking potential.
2. Alkaline-sulfite delignification of OCC fibers showed the possibility of producing bleachable grade pulp at 64.0% yield based on the weight of the collected OCC. Unbleached pulp kappa number was 18.3, and the tensile and tear strength indices were measured as 27.7 Nm/g and 12.4 mN.m²/g, respectively. The brightness of this pulp was 50.2%.
3. The alkaline-sulfite pulp from OCC was TCF bleached to reach 57.2% brightness using 3% hydrogen peroxide. The adverse effect of bleaching on pulp strength was not observed. If higher brightness degree is required, then additional measures such as oxygen delignification must be foreseen. Our preliminary elemental chlorine free (ECF) bleaching experiment on this pulp showed the possibility of reaching higher brightness.
4. Bleached alkaline-sulfite pulp from OCC can be utilized as reinforcing pulp in the production of newsprint as well as writing and printing paper.

REFERENCES CITED

- Attighe, F. K., Bose, S. K., Wang, W., McNeillie, A., and Francis, R. C. (2010). "The peroximonocarbonate anions as pulp bleaching agent. Part 1; Results with lignin model compounds and chemical pulp," *BioResources* 5(4), 2208-2220.
- Bajpai, P., Anand, A., Sharma, N., Misra, S. P., Bajpai, P. K., and Lachenal, D. (2006). "Enzymes improve ECF bleaching of pulp," *BioResources* 1(1), 34-44.
- Bisner, H. M., Champbell, R., and Mckean, W. T. (1993). "Bleached kraft pulp from OCC," *Prog. Paper Recycling* 3(1), 10- 27.
- deRuvo, A., Farnstrand, P. A., Hagen, N., and Haglund, N. (1986). "Upgrading pulp from corrugated containers by oxygen delignification," *Tappi J.* 6(7), 100-105.
- Food and Agriculture Organization statistics, (2011). Rome, Italy, WWW.FAOSTAT.COM.
- Ghasemi, S., Behrooz Eshkiki, R., Fatehi, P., and Ni, Y. (2010). "Impact of acid washing and chelation on Mg(OH)₂- based hydrogen peroxide bleaching of mixed hardwood CMP at a high consistency," *BioResources* 5(4), 2258-2267.
- Gullichsen, J., and Fogelholm, C. J. (eds). (1999). *Paper Making Science and Technology, Book 6A-Chemical Pulping*, FAPET OY, Helsinki, Finland.

- Hedjazi, S., Kordsachia, O., Patt, R., Jahan Latibari, A., and Tschirner, U. (2008). "Alkaline sulfite-anthraquinone (AS/AQ) pulping of wheat straw and totally chlorine free (TCF) bleaching of pulps," *Ind. Crops Prod.* 29, 27-29.
- Ingruber, O.V. (1993). "Process measurement and conditions," *Sulfite Science and Technology, Pulp and Paper Manufacture*, Vol. 4, O. V. Ingruber, M. J. Kocurek, and A. Wong (eds.), TAPPI Press, Atlanta, GA. USA, Chapter 3.
- Markham, I. D., and Courchene, C. E. (1988). "Oxygen bleaching of secondary fiber grades," *Tappi J.* 71(12), 168-175.
- Mckinney, R. W. J. (1995). *Technology of Paper Recycling*, Blackie Academic and Professional, An Imprint of Chapman and Hall, London, UK, 401 pp.
- Misra, D. K., Joshi, H. C., Bhatia, H. S., Chandarana, D. P., and Lakhota, R. L. (2001). "Enzyme pre-bleaching towards ECF pulp: A successful attempt at Century Pulp and Paper," *IPPTA Convention Issue* 5-14.
- Mustajoki, S., Leponiemi, A., and Dahl, O. (2010). "Alkaline peroxide bleaching of hot water treated wheat straw," *BioResources* 5(2), 808-826.
- Nguyen, X. T., Shariff, A., Earl, R. F., and Eamer, R. J. (1993). "Bleached pulp for printing and writing papers from old corrugated containers," *Prog. Paper Recycling* 2(3), 25-32.
- Nguyen, X. T. (1994). "Oxygen delignification of waste cellulosic paper products," *United States Patent* 5,302,244.
- Pan, G. X., and Leary, G. J. (2000). "Comparison of sodium carbonate and sodium hydroxide as alkali source in the alkaline peroxide mechanical pulping of wheat straw," *Tappi J.* 83(5), 14 pp.
- Potucek, F., and Milichovsky, M. (2002). "Kraft pulp bleaching with hydrogen peroxide and peracetic acid," *Chem. Papers* 54(6a), 406-411.
- Rodriguez, A., Jimenez, J., and Ferre, J. L. (2007). "Use of oxygen in delignification and bleaching of pulps," *APPITA Journal* 7(3), 57-63.
- Sarwar Jahan, M., Ni, Y., and He, Z. (2010). "Chlorine dioxide bleaching of soda-anthraquinone jute pulp to a very high brightness," *BioResources* 5(2), 870-880.
- Simard, L., and Nguyen, X. T. (1996). "On the delignification of OCC with hydrogen peroxide," *Proceeding International Pulp Bleaching Conference* 10-13, Feb. 1996. TAPPI Standard Test Methods (2010), TAPPI Press, Atlanta, GA, USA.
- Thomas, R., Singh, S. P., and Subramanyam, V. (2007). "A study on oxygen delignification of *Melocannabaccifera* (Muli bamboo) kraft pulp," *BioResources* 2(3), 430-441.
- Zeinaly, F., Shakhes, J., Dehghani Firozabadi, M., and Shakeri, A. (2009). "Hydrogen peroxide bleaching of CMP pulp using magnesium hydroxide," *BioResources* 4(4), 1409-1416.
- Yadav, R. O., Chaudhry, S., and Dhiman, S. S. (2010). "Biopulping and its potential to reduce effluent loads from bleaching of hardwood kraft pulp," *BioResources* 5(1), 159-171.

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