ALKALINE-SULFITE/ANTHRAQUINONE (AS/AQ) PULPING OF OLD CORRUGATED CONTAINER AND ELEMENTAL CHLORINE FREE (ECF) BLEACHING OF THE PULP

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Pulping of OCC was carried out applying one of the two levels (16 and 18%) of active alkali, one of the three levels of anthraquinone (0, 0.1 and 0.2% dry weight of the OCC) and one of the two pulping times (120 and 150 minutes). Pulping temperature, Na_2SO_3/NaOH ratio and liquor to OCC ratio were selected as 170 °C, and 30/70 and 8/1 respectively. The highest yield (65.2%) was reached applying 16% active alkali, pulping time of 150 minutes without AQ and the lowest kappa number (8.8) was related to pulps produced applying 18% active alkali, 0.2% AQ and 150 minutes time. The pulp produced applying 18% active alkali, 150 minutes pulping time without AQ exhibited the highest tensile strength index at 24.6 $N.mg^{-1}$. The pulp produced applying 18% active alkali, 150 minutes time and 0.1% AQ was selected for elemental chlorine free (ECF) bleaching ($D_0E_PD_1$ short sequence). The results of ECF bleaching revealed that the application of 1.61% ClO_2 produces brightness, opacity and yellowness of 82.6%, 80.2% and 5.6% ISO, respectively. The bleaching yield was measured as 92.1% and the tensile strength and tear strength indices of bleached pulp were of 17.88 $N{\cdot}mg^{-1}$ and 10.48 $mN{\cdot}m^2g^{-1}$, respectively.

Keywords: alkaline-sulfite/anthraquinone, brightness, old corrugated container, opacity, strength

INTRODUCTION

On the contrary to the general anticipation that the paper products consumption will decline due to the introduction of paperless communication and the expansion of the internet facilities started from the last decade of the 20^{th} century, the production and consumption of paper and paper products has been rising, and the total paper and paperboard production escalated to 394 million tons in 2010.[1] However, the forest resources of the world are diminishing and the pressure from environmentalists is limiting wood harvesting, giving rise to a shortage of wood raw material for the paper industry. Therefore, the concerned communities are searching for different alternatives to fulfill the raw material needs of the expanding paper industry.

The paper industry has pursued different measures to utilize any available fiber supply. However, increasing environmental awareness has been imposing pressures to take further actions. In this context, the paper industry should improve the utilization processes. Since the early days of the paper industry development, waste paper recycling has been the most favorable solution to provide a suitable substitute for virgin fibers.[2] 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 were recovered and mostly reused in paper production favoring lower cost, lower energy requirement, lower environmental impacts and the desire to reach higher recovery rates.[1] Waste paper re-utilization has followed two routes: 1) intense processing including de-inking to produce bleached pulp suitable for the production of writing and printing, as well as tissue paper from printed fine papers, and 2) limited processing of old corrugated container (OCC), by applying cleaning and screening to eliminate the detrimental contaminates without de-inking to produce conventional packaging grades.[3,4] OCC recycling is usually accomplished without any chemical treatment, but recent literature shows reports on the application of chemical or mechanical treatment to further improve the properties of paper produced from OCC.[3,4,5] Upgrading the old corrugated container (OCC) pulp using extended delignification to produce bleachable pulp for the production of white grade papers has also emerged. De Ruvo *et al*. applied alkali-oxygen pulping OCC recycled papers to reduce the lignin content to a level suitable to bleach the pulp using the lignin-eliminating process.[6] Such an attempt was followed by the work of other research groups.[7,8] Nguyen *et al*. also used kraft pulping to reduce the kappa number of old corrugated container pulp.[9] Oxygen delignification[10] and delignification and whitening by hydrogen peroxide[11] have also been applied on OCC.

Successful development of OCC pulping requires a technology capable of exploiting the complete potential of this raw material. Specifically, the selectivity in delignification and bleaching ought to be at a high level, which results in pulp with high yield and strength but at low kappa number. The low kappa number facilitates easier bleaching by environmentally friendly bleaching sequences, such as totally chlorine free or elemental chlorine free bleaching, which leads to elimination or reduction of the chlorine consumption.[12,13,14,15]

Soda and soda-oxygen pulping have been used for pulping OCC. However, 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.[12] The application of alkaline-sulfite (AS) process produces pulp at higher yield and with minor impact on carbohydrates. This pulping process has been examined to produce pulp from different raw materials[12,16] and for delignification of OCC.[17] In particular, the higher brightness of the AS/AQ pulp facilitates bleaching.

The environmental concerns of paper manufacture and the consumer demands related to conventional chlorine-based bleaching have directed the paper industry toward the application of new approaches with reduced adverse ecological impact. Both totally chlorine free (TCF) and elemental chlorine free (ECF) bleaching sequences have been utilized mostly for bleaching of wood chemical pulps with low kappa numbers.[13,14,18,19,20]

The objective of the present paper was to study the application of alkaline-sulfite/anthraquinone pulping on OCC recycled paper to produce pulp containing a lower amount of lignin without serious loss of pulping yield. Also, pulps were bleached applying an elemental chlorine-free bleaching sequence.

EXPERIMENTAL

Material collection and preparation

Old corrugated container (OCC) clippings were collected from a corrugated board container production plant to avoid the need for usual cleaning which is industrially applied on OCC and to be assured that the sample was free from consumer contaminates. However, the presence of starch in OCC is unavoidable. OCC was used as received. The OCC samples were manually cut into 30x30 mm pieces for further processing. The OCC pieces were dried at ambient temperature and after reaching equilibrium moisture content, they were stored in plastic bags until used.

A sample weighing 100 grams (oven dry basis) 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 thoroughly washed with sufficient water on a 200 mesh screen. The fibers that retained on the screen were manually dewatered as much as possible and then used for delignification.

Methods

Pulping

The pulping conditions were set as follows: two levels of active alkali (16 and 18%, based on NaOH), three levels of AQ (0, 0.1 and 0.2% based on the dry weight of the OCC) and two pulping times (120 and 150 minutes after reaching pulping temperature). The pulping temperature was constant at 170 °C and the ratio of sodium sulfite to sodium hydroxide was constant at 30/70. The liquor-to-fiber ratio was adjusted at 8/1. For each combination of variables, two replica pulps were produced.

All cooking processes were performed in a 4 liter rotating digester "Ghomes Wood and Paper Equipment Manufacturing Co." using 100 gram of original OCC (dry basis). At the end of each cooking, the content of cylinder was discharged on a 200 mesh screen. The cooked material was washed using hot water, and the pulping yield was determined.

Elemental chlorine free bleaching

The pulp with the lowest kappa number and acceptable yield and strength was selected for ECF bleaching, applying the D_0EpD_1 short sequence. The kappa factor of 0.25, 0.3 or 0.35 equivalent to the chlorine dioxide (ClO_2) charge of 1.13, 1.38 and 1.61%

(oven dry weight of the unbleached pulp) was used. Two thirds of the ClO_2 were used in the D_0 stage and the rest was used in the final D_1 stage. The hydrogen peroxide reinforced extraction stage (Ep) was applied between D_0 and D_1 using 1% H_2O_2 and 2.5% NaOH (based on oven dry weight of the unbleached sample). The bleaching temperatures in D_0, Ep and D_1 were 60, 70 and 80 °C and the relevant bleaching time was 60, 60 and 120 minutes, respectively.

Bleaching experiments were conducted in polyethylene bags and hot water bath. During the bleaching periods, the sample was hand kneaded. At the end of the reaction time, the content of the bag was discharged on a 200 mesh screen. The pulp on the screen was washed with tap water and manually dewatered. The bleached pulp was dewatered manually, and kept at 3 ºC until pulp evaluation. The bleaching yield was measured.

Pulp evaluation

The TAPPI test methods used for pulp evaluation were: 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 and yellowness, T452 om-08; and opacity, T425 om-06.[21]

Statistical analysis

The collected data were analyzed employing the analysis of variance (ANOVA), and in case a statistically significant difference was observed between the averages, then Duncan Multiple Range Test was used for the ranking of the averages.

RESULTS AND DISCUSSION

The results of OCC fibers pulping as well as pulp properties are summarized in Table 1. OCC fibers have been produced from wood to be suitable for brown paper manufacturing. These fibers still contained a substantial amount of lignin and their kappa number was 63.6. OCC preparation and washing eliminated 13.3% of the received OCC weight, due to the presence of impurities and fines and the fiber yield after washing and cleaning was measured as 86.7%. The highest yield (65.2%) was reached applying 16% active alkali, pulping time of 150 minutes without the addition of AQ and the lowest kappa number (8.8) was related to pulps produced applying 18% active alkali, 0.2% AQ and 150 minutes time. The pulp strength measurements revealed that pulp produced applying 18% active alkali, 150 minutes pulping time without AQ exhibited the highest tensile strength index at 24.6 $N.mg^{-1}$ and the pulp produced applying 18% active alkali, 150 minutes time and 0.2% AQ showed the highest tear strength index at 10.5 $mN.m^2g^{-1}$.

The pulp produced applying 18% active alkali, 150 minutes time and 0.2% AQ were bleached using the ECF bleaching sequence. The results revealed that the application of 1.61% ClO_2 produces brightness, opacity and yellowness of 82.6%, 80.2% and 5.6% ISO, respectively. The bleaching yield was measured as 92.1% (based on the dry weight of unbleached pulp) and the tensile strength and tear strength indices of bleached pulp were of 17.88 $N.mg^{-1}$ and 10.48 $mN.m^2g^{-1}$, respectively (Table 3).

Table 1
AS/AQ pulping conditions and the properties of the pulp produced from OCC*

Pulping trial no.	Active alkali (%)	AQ (%)	Pulping time (min)	Pulping yield (%)	Kappa number	Freeness (mLCSF)	Tear strength index ($mN.m^2g^{-1}$)	Tensile strength index ($Nm.g^{-1}$)
Control	-	-		86.7**	63.6	-	9.8	21.6
P1	16	0.0	120	63.5	21.7^{ab}	530	9.6^{cd}	18.9^{cd}
P2	16	0.1	120	57.9	13.5^{cd}	654	10.5^{ab}	16^{cd}
P3	16	0.2	120	58.5	11.6^{d}	637	10^{cd}	15.5^{cd}
P4	18	0.0	120	61.5	24.3^{a}	590	10.1^{cd}	17.1^{cd}
P5	18	0.1	120	58.2	11.9^{d}	590	9.6^{d}	14.5^{d}
P6	18	0.2	120	61.5	12.3^{cd}	560	9^{e}	18.1^{cd}
P7	16	0.0	150	65.2	20.8^{c}	516	10.3^{bc}	19.3^{c}
P8	16	0.1	150	62.2	15.2^{c}	474	10.5^{ab}	23^{b}
P9	16	0.2	150	62.8	11.7^{cd}	560	10.1^{c}	21.6^{bc}
P10	18	0.0	150	64.6	24.3^{ab}	560	10.3^{bc}	24.6^{a}
P11	18	0.1	150	60.7	12^{cd}	530	10.2^{bc}	19.6^{bc}
P12	18	0.2	150	54.0	8.8^{e}	575	10.5^{a}	16.9^{cd}

*Liquor to fiber ratio: 8/1, and Na_2SO_3/NaOH ratio: 30/70; pulping temperature: 170 °C
**Yield after washing the OCC

Lower case superscript letters indicate the DMRT ranking of the averages

Table 2
Results of the statistical analysis of the data (F value and the significance level)

Properties Variables	Pulping yield	Kappa number	Tear strength index	Tensile strength index
Pulping time	15.264**	0.006^{ns}	12.560**	27.364**
Active alkali	20.400**	0.543^{ns}	2.312^{ns}	0.514^{ns}
Anthraquinone (AQ)	63.893**	386.155**	1.362^{ns}	2.390^{ns}
Pulping time*active alkali	32.902**	0.643^{ns}	3.403^{ns}	0.194^{ns}
Pulping time*AQ	18.557**	10.413**	1.604^{ns}	1.653^{ns}
Active alkali*AQ	3.630*	14.789**	2.687^{ns}	2.459^{ns}
Three variables	31.245**	4.510*	4.065*	7.020**

Significance level: ** 99%; * 95%; ns, not significant

Table 3
Results of ECF bleaching of OCC alkaline sulfite/AQ pulp

Bleaching trial no.	ClO_2 charge (%)	Bleaching stage	Bleaching yield (%)	Kappa number	Tear strength index ($mN.m^2g^{-1}$)	Tensile strength index ($Nm.g^{-1}$)
Unbleached	-	-	100	12	10.23	19.58
BP1	1.13	D_0	97.7	7.02	10.96	21.64
BP2		D_0E_p	93.4	3.1	10.57	19.08
BP3		$D_0E_pD_1$	90	?	11.18	16.88
BP4	1.38	D_0	97	5.41	10.66	17.44
BP5		D_0E_p	93.1	2.29	10.5	18.04
BP6		$D_0E_pD_1$	92	1.02	11.2	20.89
BP7	1.61	D_0	96.8	4.87	10.98	20.81
BP8		D_0E_p	93.1	2.45	11.07	18.04
BP9		$D_0E_pD_1$	92.1	1.35	10.48	17.88

Bleaching conditions: consistency, 10%; D_0: temperature 60 °C, time 60 min; E_p: temperature 70 °C, time 60 min; D_1: temperature 80 °C, time 120 min

Pulping

Old corrugated container (OCC) comprises the major portion of recovered paper, which is commonly converted into brown paper stock without extensive processing. However, surplus OCC is still available, remains unused and usually ends up as fuel for energy generation, which necessitates advanced processing such as bleached pulp production.

The results of alkaline-sulfite/anthraquinone (AS/AQ) pulping of OCC showed that the pulping yield varies between the lowest value of 54 and the highest value of 65.2% (based on OCC as received). The kappa number of the AS/AQ pulps ranged between 8.8 and 24.3, and kappa number of OCC prior to pulping was measured as 63.6.

The disintegrated and washed OCC is in the form of individual fibers, and since these fibers already had passed through at least one pulping process, at first, it was anticipated that the delignification of the OCC fibers would be easy and a mild chemical treatment would be sufficient.[8,22] Contrary to our expectations, the delignification was not as fast and efficient as anticipated, and the kappa number reduction was limited[22] and the pulps were not suitable for bleaching. The OCC fibers are not originated from a single pulp, but rather they are a combination of fibers from different pulping processes, mainly neutral sulfite semi-chemical (NSSC) and kraft pulps. Furthermore, previous pulping advanced the delignification to near the residual delignification stage.[23] It is evident that both conditions make further delignification more difficult. Therefore, intense pulping conditions were applied using longer treatment time, and AQ addition to pulping liquor. The longer time reduced both the yield and kappa number (pulping trials P11 to P12), with kappa number of the pulp ranging between 8.8 and 12. Statistical analysis revealed that the effect of variables on the pulping yield was statistically significant at 99% confidence level, but typically the influence of anthraquinone and the combined effect of pulping time and AQ, active alkali and AQ and all three variables on kappa number were statistically significant (Table 2).

In order to identify the effect of OCC AS/AQ pulping on the fiber damage and strength of the paper from these pulps, the tear and tensile strength indices of the pulps were measured, and are listed in Table 1. The tear strength index of the pulps was almost identical to that of OCC, but pulping reduced the tensile strength index, except in the case of pulp no. P10, which showed a higher tensile strength index. Statistical analysis indicated that the influence of the pulping time and the effect of the combined three variables were statistically significant at either 99% or 95% level (Table 2).

ECF bleaching

Pulp bleaching is a common process that is carried out after the reduction of kappa number to the lowest practical level to save the bleaching chemicals, preserve the pulp strength and reach the highest brightness gain.[14,19,24] However, an excessively low kappa number may entail degradation of the strength properties of the pulp. Therefore, a selection of pulps was made considering the lowest kappa number providing suitable yield and strength for further elemental chlorine free (ECF) bleaching.

The selected pulp with the kappa number of 12 (P11) was bleached, applying the elemental chlorine free sequence, and the results are summarized in Table 3 and Figures 1-3. The $D_0E_pD_1$ bleaching sequence applying 1.61% chlorine dioxide charge increased the brightness of the pulp to 82.6%ISO (Fig. 1) and reduced the yellowness to a low level of 5.6% ISO (Fig. 2). Even though the opacity was limited to 80.2% ISO (Fig. 3), this pulp is suitable for writing and printing paper production. Due to lack of viscosity measurement for the bleached pulps, instead both tensile strength and tear strength indices of the bleached pulps were measured and compared with those of the unbleached pulp (Table 3). No deterioration in the strength values after ECF bleaching was observed, which enabled us to prove the promising potential of such a simple and short bleaching sequence.

The OCC fibers usually contain fibers produced using different pulping processes. Therefore, these fibers contain different types of lignin residuals. So, it is anticipated that the bleaching responses of these fibers will be different. Therefore, one can not expect very easy brightness development to high brightness levels, unless special bleaching methods, such as oxygen delignification, are applied to assist lignin removal (Thomas *et al.*[25]) or stronger bleaching chemistry, such as $D_0E_pD_1D_2P$[19], $D_0E_{op}D_1D_2P$[26] and $D_0E_pD_1E_pD_2$[27], is utilized. Besides, the kappa number of the pulp prior to ECF bleaching must be lower than 10 to be able to develop sufficient brightness.[13,14,19]

Alkaline-sulfite/AQ pulping of OCC fibers showed the possibility of producing bleachable grade pulp at 60.7% yield. The brightness of this pulp was 43.6%. The pulp was ECF bleached to reach 82.6% brightness using $D_0E_pD_1$ bleaching sequence and applying 1.61% chlorine dioxide. The adverse effect of bleaching on pulp strength was not observed. If higher brightness is required, additional processes such as oxygen delignification or additional chlorine dioxide or hydrogen peroxide stage must be foreseen. Bleached alkaline-sulfite/AQ pulp from OCC can be utilized as a reinforcing pulp in the production of newsprint, as well as writing and printing paper, ensuring new sources of fibers for this grade.

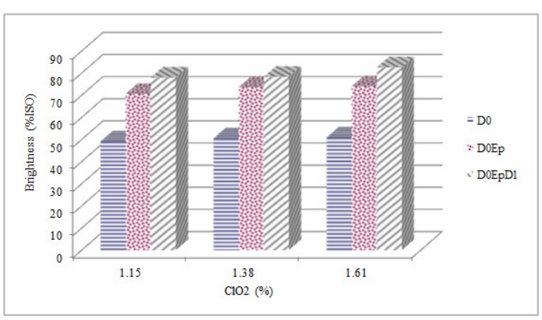

Figure 1: Brightness of the bleached pulp at different stages of ECF bleaching

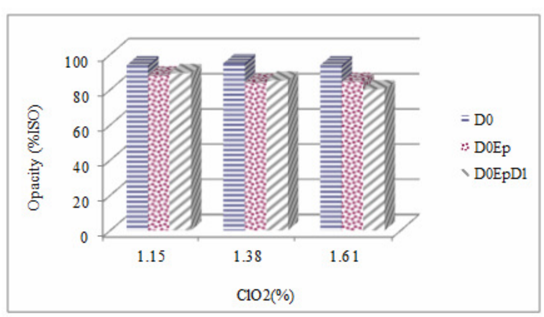

Figure 2: Opacity of the bleached pulp at different stages of ECF bleaching

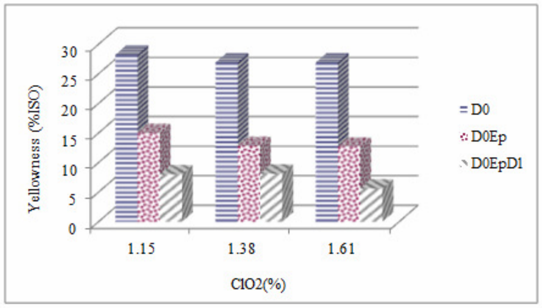

Figure 3: Yellowness of the bleached pulp at different stages of ECF bleaching

CONCLUSION

The application of alkaline-sulfite/AQ pulping on OCC fibers revealed that these fibers can be delignified to a lignin level, which is suitable for ECF bleaching sequence. However, since these fibers contain different types of lignin originating from the fibers, which have been produced from different raw material and different pulping processes, the bleaching response of the pulp is complicated. Therefore, to produce bleached pulp with high brightness, special measures must be taken into consideration in the design of the pulping sequence. The abundant supply of old corrugated container recycled paper justifies additional research, if we need to develop a pulping process for industrial scale application.

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