Reduction in Effluent Pollution Load Under CEpHD Bleaching Sequence by Lowering Kappa No. of Pulp

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Abstract

Combined cooking is carried out for raw material mix consisting of 65% bamboo and 35% hard woods (Eucalyptus, Subabool, Casurina, Sal and other tropical hard woods). Bamboo requires relatively milder cooking conditions compared to hard wood and therefore unbleached pulp of higher 25-27 Kappa is maintained to develop desired pulp properties. Lowering of kappa during chemical cooking beyond a certain stage effects severely bamboo pulp with generation of fines, which effects runnability of paper machine at higher machine speeds. Bleachable grade pulp of higher (25:3) and lower (20.4) kappa were prepared by Kraft cooking of bamboo + mixed hard wood (65:35). The pulps were bleached under C-E_p-H-D sequence for pulp brightness 87±1% P.V. and analyzed for fibre classification and physical strength properties. Characteristics of effluent at each stage of bleaching were analyzed for different parameters to examine the benefit of lowering kappa. As expected redution in chlorine consumption due to lowering of kappa reduced shrinkage, colour reversion (P.C. No.) and ash content of pulp viscosity and strength properties improved. Considerable reduction of COD, suspended solids, dissolved solids and chloride content was observed in the effluent generated at the bleach plant.

INTRODUCTION

Bleaching in pulp making is a multistage process involving use of various bleaching chemicals such as Chlorine, Calcium hypochlorite, Chlorine dioxide, Oxygen, Hydrogen peroxide, Ozone etc amongst various bleaching agents normally employed in pulp making Chlorine and chlorine compounds have been used predominantly as they are highly effective besides being economical. In alkaline stage sodium hydroxide is employed after Chlorine treatment for removal of chlorolignins formed. The fragments of lignin macromolecules are modified during bleaching process is chlorinated lignin or oxidized lignin depending on the agent employed. It is the presence of chlorinated lignin compounds in bleach effluent which have detrimental effect on environment (1,2).

The increased environmental awareness, and imposition of stringent discharge norms have forced the paper mills to adopt cleaner product options to reduce kappa of unbleached pulp so as to minimize or eliminate the chlorine based bleaching chemicals[3]. Many countries have enacted legislation to limit the levels of specific compounds in bleach plant effluents. They govern the levels of absorbable organic halides (AOX), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS) and colour (3-5).

Lower kappa of pulp in the range 11-13 can be achieved by employing modern technologies like RDH, Super batch and Oxygen delignification (6). Oxygen deliginfication technology combined with extended delignification makes it possible to produce pulps entering the bleach plant with kappa less than 8 for hard woods and 10-12 for soft woods (7). These pulps can be bleached to high brightness with comparable strength properties without use of chlorine compounds. However in order to achieve the reduction in kappa huge investment is required for installation of totally different type of cooking street as against the conventional cooking system.

Table 1. Kraft Cooking of Silo discharge belt chips

Particulars	Cook No. 1	Cook No. 2	Cook No. 3
Alkali used as Na_2O, %	17.5	18.0	18.5
Sulphidity, %	17.8	17.8	17.8
Bath ratio	1:3	1:3	1:3
Cooking cycle:			
i) Ambient to 100°C, mnts	60.0	60.0	60.0
ii) 100 to 135°C, mnts	60.0	60.0	60.0
iii) 135 to 165°C mnts	60.0	60.0	60.0
iv) 165°C, mnts	60.0	60.0	120.0
Unbleached pulp yield, %	41.50	41.15	40.72
(On O.D. chips)			
K. No.	16.5	15.5	14.4
Kappa No.	25.2	23.8	20.4
Rajects, % (On O.D. chips)	1.60	1.20	0.70
Black Liquor Analysis:			
i) °TW at 60°C	25.0	25.0	26.0
ii) R.A.A., g/l	18.6	21.7	21.7

Experimental

Bamboo and mixed hard woods in the ratio 65:35 are cooked together in a stationary digester for 25-27 Kappa. If the Kappa of the pulp is brought down to 18-20, higher quantum of fines is generated which ultimately affect the paper machine runnability. Hydrogen peroxide reinforced oxidative extraction minimizes the generation of pollution load (8). The advantage of alkaline conditions as well as higher temperature at the extraction stage was exploited and hydrogen peroxide was introduced at the alkali extraction stage (9,10) to utilize the dead load retention time to increase the final brightness higher by one or two degrees. The alkaline conditions in alkali extraction stage helps in the formation of perhydroxyl ions (OOH^-), which oxidize the colour and renders the pulp with increase in brightness. The reaction of hydrogen peroxide and lignin rich pulp leading to brightening effect are considered to nucleophilic addition of perhydroxyl anion to unsaturated aldehydes, conjugated double bonds and the side chain carbonyls attached to the substituted benzene ring.

Hydrogen peroxide being a mild oxidizing agent and the lignin skeleton largely remains unchanged with which some individual chromophores and auxochrome groups are attacked (11, 12). Thus the strong alkaline conditions with peroxide favours brightening of pulp rather than delignification (13).

Both the unbleached pulps of higher (25-27) and lower kappa (18-20) were bleached on a lab scale under C-E_P-H-D sequence for pulp brightness 87±1% P.V. and the effluent characteristics analyzed at every stage of bleaching for higher and lower Kappa pulps.

RESULTS AND DISCUSSION

In order to bleach higher and lower kappa pulp under C-E_P-H-D sequence to observe the effect on bleached pulp quality and effluent characteristics, following studies were carried out.

Kraft cooking of chips

Accepted chips (-28mm, +3mm) were cooked with 17.5%, 18.0% and 18.5% alkali as Na_2O

Table 2. Bleaching of Higher and Lower Kappa pulps under C-E_p-H-D sequence.

Particulars	Higher Kappa pulp bleached under C-E_p-H-D sequence	Lower Kappa pulp bleached under C-E_p-H-D sequence
Chlorination Stage :		
i) Cl_2 applied/consumed, %	5.1/4/97	4.1/3.71
ii) End pH	2.1	2.5
iii) Consistency, %	3.0	3.0
iv) Temp, °C	Room	Room
v) Time, mnts	60	60
Alkali Extraction stage:		
i) NaOH applied, %	1.53	1.22
ii) H_2O_2 applied, %	0.4	0.4
iii) End pH	10.8	10.9
iv) Consistency, %	10.0	10.0
iv) Temp, °C	70±1	70±1
v) Time, mnts	60	60
Calcium Hypo chlorite Stage:		
i) Hypo chlorite applied/Consumed, %	4.0/3.96	2.7/2.69
ii) Sulphamic Acid, %	0.1	0.1
iii) Alkali added as buffer, %	0.8	0.7
iv) End pH	7.8	8.0
v) Consistency, %	10.0	10.0
vi) Temp, °C	40±1	40±1
v) Time, mnts	120	120
Chlorine dioxide Stage:		
i) ClO_2 applied/Consumed, %	0.7/0.68	0.7/0.65
ii) End pH	5.4	6.0
iii) Consistency, %	10.0	10.0
iv) Temp, °C	70±1	70±1
v) Time, mnts	120	120
Final Results:		
i) Total Cl_2 applied/consumed, %	9.1/8.93	6.82/6.4
ii) ClO_2 applied/consumed, %	0.7/0.69	0.7/0.65
iii) Pulp Brightness, % P.V.	87.0	87.0
iv) Pulp Viscosity, (0.5% C.E.D.Cps)	6.0	6.5
v) Pulp Shrinkage, % on O.D. bleached pulp	12.8	12.0
vi) P.C. No.	2.8	2.37
vii) Ash in bleached pulp, %	0.71	0.53

(sulphidity, 17.8%) under identical cooking conditions with 90 and 120 mts. hold time at 165°C in cook No 2 & 3. The unbleached pulp yield with 17.5% and 18.5% alkali was 41.5% and 40.72% and the corresponding kappa No. in cook No. 1 and 3 was 25.3 and 20.4 respectively.

Cooking conditions and results are tabulated Table 1.

Bleaching of higher & lower kappa under C-E_P-H-D sequence

C-E_P-H-D sequence alone cannot increase the pulp brightness beyond 85% I.S.O. without sacrificing pulp strength properties. Hence there should be sufficient brightness at calcium hypochlorite stage to increase it further. This is achieved by using Hydrogen peroxide at the alkali extraction stage in C-E_P-H-D bleaching sequence (14-16).

Both the unbleached pulps of higher (25.2) and lower (20.4) kappa were bleached under C-E_P-H-D sequence (Table 2) to achieve the pulp brightness 87±1% P.V. Higher kappa (25.3) and lower kappa (20.4) pulps require 9.1% and 6.8% total chlorine and 0.7% chlorine dioxide to achieve the target brightness. The bleached pulp yield was 36.2% and 35.8% respectively. As expected the viscosity was on higher side in lower kappa bleached pulp but reverse trend was observed with P.C. No. and ash content as compared to higher kappa bleached pulp.

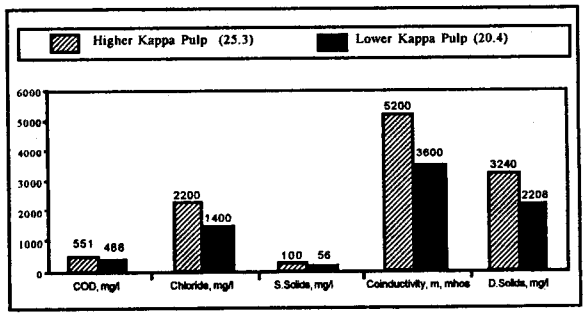
Theoretically AOX generation with higher and lower kappa pulps bleached under C-E_P-H sequence would be as follows.

Particulars	C-E_P-H-D Bleaching sequence	
	Higher Kappa	Lower Kappa
Total Chlorine Consumption, %	8.93	6.4
ClO_2 Consumption,%	0.69	0.65
AOX, Kg/Ton of pulp	7.7	5.66

Fibre classification of higher and lower kappa bleached pulps

Fibre classification of higher and lower kappa bleached pulps was carried out in a Bauer Mcnett classifier. Higher kappa (25.3) pulp bleached under C-E_P-H-D sequence resulted in lowering of fibre percentage retained on 40 mesh and increase in fines percentage passing through 140 mesh as compared to lower kappa pulp bleached under C-E_P-H-D sequence and are carried away within mat formation at the washers.

Fig. 1. Characteristics of Chlorination stage effluent of higher & lower kappa pulps bleached under C-E_P-H-D sequence.



Comparison of pollution load generated by bleaching higher & lower kappa pulps under C-E_P-H-D sequence

Effiuent characteristics at each stage of bleaching of higher and lower kappa pulps are determined (Table 4) and discussed as follows.

Chlorination stage effluent

Chlorine was applied as required for higher and lower kappa pulps. Reduction in chlorine application has helped in reduction of COD (11.43%), Chloride (36.36), Dissolved solids (31.97%), Suspended solids (44.0%) and Conductivity (30.77%) as compared to effluent 'characteristics of higher kappa pulp. Comparison of chlorination stage effluent parameters for

Table 3. Fibre classification of higher and lower kappa pulps bleached under C-E_P-H-D sequence.

Mesh size	Higher kappa C-E_P-H-D sequence bleached pulp	Lower kappa C-E_P-H-D sequence bleached pulp
	Fibre Retention, %	
+ 40	40.61	43.61
- 40, +70	20.63	21.74
-70, +100	13.76	13.19
-100, +140	3.21	2.93
-140	22.19	18.53

Table 4. Comparison of effluent characteristics of higher and lower kappa pulps bleached under C-E_p-H-D sequence

Particulars	Higher Kappa C-E_p-H-D sequence bleached effluent	Lower Kappa C-E_p-H-D sequence effluent
Chlorination Stage :		
i) pH	2.1	2.5
ii) COD, mg/l	551	488
iii) Chloride, mg/l	2200	1400
iv) S. Solids, mg/l	100	56
v) D. Solids, mg/l	3246	2208
vi) Total Solids, mg/l	3346	2264
vii) Conductivity, m, mhos	5200	3600
viii) Colour, Pt-Co unit	173	60
Caustic Extraction stage:		
i) pH	10.9	10.8
ii) COD, mg/l	2412	1980
iii) Chloride, mg/l	770	530
iv) S. Solids, mg/l	212	310
v) D. Solids, mg/l	4456	3936
vi) Total Solids, mg/l	4668	4246
vii) Conductivity, m, mhos	7000	5800
viii) Colour, Pt-Co unit	5700	4300
Hypochlorite Stage:		
i) pH	8.0	7.8
ii) COD, mg/l	1812	1412
iii) Chloride, mg/l	7000	4800
iv) S. Solids, mg/l	378	362
v) D. Solids, mg/l	13884	9742
vi) Total Solids, mg/l	14262	10104
vii) Conductivity, m, mhos	20400	14700
viii) Colour, Pt-Co unit	60	90
ix) Calcium, mg/l	4680	3920
Chlorine dioxide Stage:		
i) pH	5.4	5.5
ii) COD, mg/l	648	480
iii) Chloride, mg/l	900	800
iv) S. Solids, mg/l	178	182
v) D. Solids, mg/l	3342	2588
vi) Total Solids, mg/l	3520	2770
vii) Conductivity, m, mhos	4800	3500
viii) Colour, Pt-Co unit	33	33

Fig. 2. Characteristics of caustic extraction stage effluent of higher & lower kappa pulps bleached under C-E_p-H-D sequence.

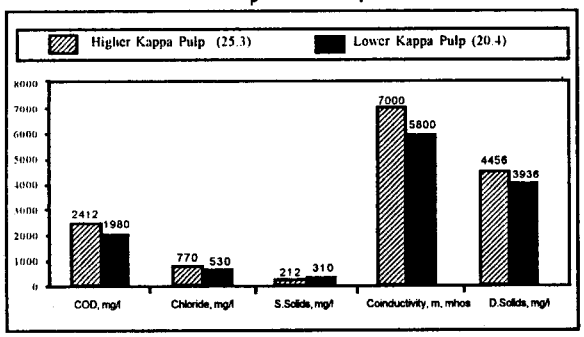
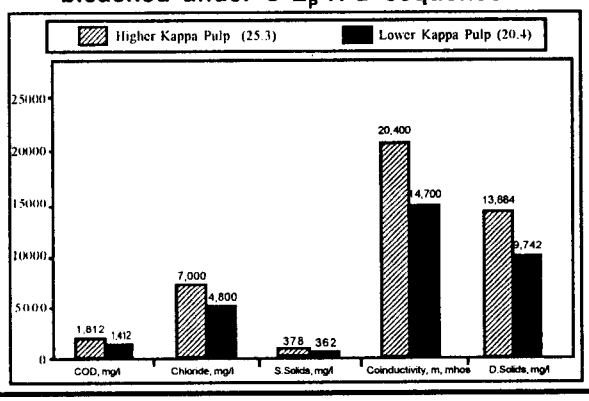


Fig. 3. Characteristics of Hypochlorite stage effluent of higher & lower kappa pulps bleached under C-E_p-H-D sequence.



higher & lower Kappa pulps is shown in Fig. 1.

Caustic extraction stage effluent

Caustic was applied in the extraction stage according to chlorine requirement in 1st stage of bleaching to remove chloro lignins. Reduction in COD (17.9%), chloride (31.17%), dissolved solids (11.67%), conductivity (17.14%) and colour (50.57%) was observed as compared to effluent parameters of higher Kappa pulp. Comparison of caustic extraction stage effluent parameters is shown in Fig.2.

Calcium hypochlorite stage effluent

Calcium hypochlorite was applied according to the requirement for higher and lower kappa pulps. Reduction in COD (22.1%), chloride (31.42%), suspended solids (4.23%), dissolved solids (29.83%) and conductivity (27.94%) was observed compared to effluent parameters of higher kappa bleached pulp. A graphical presentation of hypochlorite stage effluent parameters is shown in Fig. 3.

Chlorine dioxide stage effluent

Both the hypochlorite bleached pulps of higher and lower Kappa pulps were treated with 0.7% chlorine dioxide to get optimum pulp brightness. Reduction in effluent parameters COD (25.9%), chloride (11.11%), dissolved solids (22.56%) and conductivity (27.08) was observed. A graphical presentation of parameters of higher and lower kappa pulp effluent is depicted in Fig. 4.

Comparison of strength properties of higher and lower kappa pulps under C-E_p-H-D sequence

Higher and lower Kappa bleached pulps were beaten to 30°SR and physical strength properties

Fig. 4. Characteristics of chlorine dioxide stage effluent of higher & lower kappa pulps bleached under C-E_p-H-D sequence.

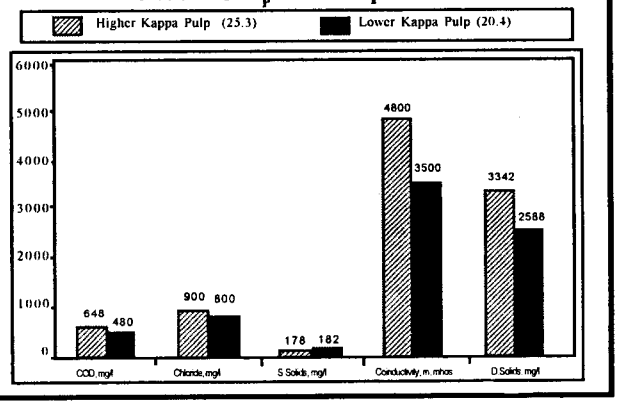


Fig. 5. Strength properties of higher & lower kappa bleached pulps

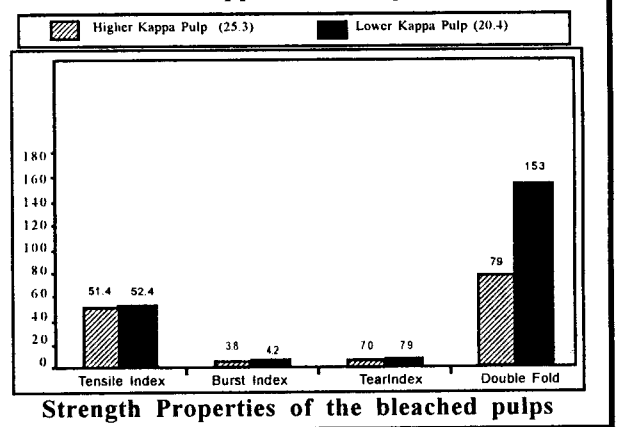


Table 5. Physical strength properties of higher and lower kappa pulps bleached under C-E_p-H-D bleaching sequence.

Particulars	Higher Kappa C-E_p-H-D sequence bleached pulp	Lower kappa C-E_p-H-D sequence bleached pulp
Number of beating revolutions in a P.F.I. mill	4000	4400
Final freeness, °SR of pulp	30	29
Bulk, c.c/gram	1.43	1.42
Tensile index, N. m/g	51.39	52.39
Tear Index, Nm^2/g	7.03	7.91
Burst Index, K. $Pa.m^2/g$	3.8	4.23
Double fold	79	153

of standard sheets were determined (Table 5). Tensile index, Burst index, Tear index and Double fold were found to be higher in lower kappa bleached pulp than higher kappa bleached pulp as shown in Fig. 5 which is in in accordance with higher pulp viscosity and less damage to the fibres by using lower percentage of calcium hypochlorite.

CONCLUSION

By lowering kappa no. of pulp from 25.3 to 20.4, the bleach consumption could be reduced by 28.33% under C-E_p-H-D bleaching sequence. Effluent parameters mainly dissolved solids, chloride, COD and conductivity are considerably reduced in every bleaching stage.

REFERENCES

1. Corner, O.B.I., T.G. Koracs, R.H. Voss and P.H. Mertel, J. of Pulp & Paper Scie. 19 (1), 33-9 (1993).
2. Chinnaraj S., Malathi, R, Reddy K.P., and Veakoba Rao. G IPPTA, J.-12, (4), -99 (2000).
3. Mc.donugh, T.J., Courchene, C.E., Shaket A, Ragauskas, A.J., Khandelwal, B. and Magnotte, V.L., CPPA Conf., Montreal, Q.C.J., 307 (1999)
4. M.E., Sakhawy, IPPTA J.-14, (2), 69 (2002).
5. Patricia Walsh B, Tappi J.-74, (1), 81 (1991).
6. Gupta, R.K., IPPTA J.-2, (4), 9 (1999).
7. Singh R.P., "The Bleaching of Pulp" 3rd Edn, Tappi Press, (1979).
8. Makkar, M.K., and Jauhari, M.B. IPPTA J.-13, (1), 9 (2001).
9. Tendulkar S.R. and Shinde, J.K. IPPTA J., -13, (1), 51 (2001).
10. Andrews, D.H., Singh R.P., "The Bleaching of Pulp" Tappi Press, P-216-218, (1991).
11. Sridhar P., Reddy, J.V.R., Venugopal, C.S. and Karmakar, G.R., IPPTA Conv. Issue, 55, (1998).
12. Yasudian K, Reddy J.V., Raghavulu. V.V., Thomas T.D., Alias C.M., Fernandes J.D. and Bhargava S.C., IPPTA J.-5, (1) (1993).
13. Bugajer, Danials, Pulp & Paper Can. J., (12), T.216-218, (1988).
14. Lachapelle, R.C., Strunk, W.G. and Klein, R.J., **Tappi J.**, 181, (1992).
15. Teresa Vidal & Jore F. Colom, Tappi, J.Vol.75 (7) 213, (1992).
16. Sarkar, P.K., Murthy, N.V.S.R., Sagar C.H.V.V. and Rao P.V.V.S., IPPTA J-6, (3) 109 (1994).