Effect of anthraquinone in low sulphidity kraft pulping of muli bamboo (Melocanna Baccifera)

KSHUDIRAM BHOWMICK*
A. JABBAR MIAN**
A.F.M. AKHTARUZZMAN***

ABSTRACT

Low sulphidity kraft pulping of mill-cut muli bamboo *(Melocanna baccifera)* with anthraquinone (AQ) addition was studied in the laboratory scale. AQ acted as a pulping catalyst and increased the rate of delignification or decreased the alkali demand. Addition of a small amount of AQ (0.05%) increased the pulp yield by 2 percent on OD bamboo compared to kraft cook at 15 % sulphidity and 0 8 percent on OD bamboo compared to normal kraft pulping. The viscosity of AQ catalysed low sulphidity kraft pulps was almost equal to the kraft control and better than the pulp of 15% sulphidity.

It was also observed that the burst, tear and tensile strength properties of the pulp increased on addition of AQ. The strength properties were almost same or better than the pulp obtained in normal kraft pulping. Thus, the use of AQ is beneficial at a low sulphidity level in presserving the pulp yield and improving the quality of the pulp. This will reduce the air pollution problems because of a lower sulphidity input in the cooking.

INTRODUCTION

It is well recognised that sodium sulphide in the alkaline cooking liquor increases the rate of delignfication and improves pulp quality (1, 2). Under ordinary mill conditions, a change in sulphidity from 20 to 30% does not affect pulp quality (3,4). At very high sulphidities between 45 to 50%, the pulp tends to be very dark and very difficult to bleach and beat. Jauhari and Bhargava (5)showed a significant change in strength properties of pulp were produced at a sulphidity between 21-24% with *Bambusa arundinacea.* At a higher sulphidity over 31%, the strength properties have the tendency to decline. However, less than 12% sulphidity results in pulps more closely related to soda pulps than to kraft pulps (6). Low sulphidity results in retarded rate of delignification, enhanced degradation of cellulose as well as poorer pulp properties. In Bangladesh, a kraft mill is in operation using muli bamboo as the main fibrous raw material. In the meantime, the mill maintains the sulphidity within the range 8-17% (7) due to want of salt-cake.

These problems can be overcome by an addition of Anthraquinone (AQ) in white liquor. The use of AQ in soda and kraft pulping of softwoods has been established (8-16). Small amount of AQ in kraft and soda pulping markedly promotes the rate of delignification,

*Chemist, Research & Development, Karnaphuli Paper Mills Ltd.,
Chandraghona, Rangamati Hill District, Bangladesh.

**Professor, Department of Chemistry, University of Dhaka, Dhaka, Bangladesh.

***Head, Pulp & Paper Division, Bangladesh Forest Research Institute, Soloshar, Chittagong, Bangladesh.

increases pulp yield (17, 18) and minimises air pollution (12). These benefits are particularly more pronounced for soda pulping than kraft pulping (12, 19 20). The performance of AQ has also been examined on full mill scale trials (12, 21-24).

AQ is less benificial at normal sulphidity in kraft pulping (25) and benefits incsrease as the sulphidity decreases (I5, 26, 27). Even the AQ and sulphidity are interchangeable (28, 29). Blain (30) stated that in case of black spruce, the use of AQ in the sulphidity range 5-15% maintained the pulping rate and effective alkali requirement to level of kraft pulping at 25% sulphidity for liner board pulp. Low sulphidity AQ pulping of hardwood mixture results in improving pulp strength properties (31). Thus, the use of AQ enables to reduce alkali requirement without a loss in pulping rate as well as it improves pulp yield and viscosity at any sulphidity level within the range 0-25% sulphidity (28).

MacLeod (32) reported that kraft +AQ pulps from Western hemlock, D. fir, and Eastern Canadian mixed hardwoods were quite similar to their kraft counterparts in strength properties. On the other hand kraft +AQ black spruce pulp was worse than kraft. And soda+AQ softwood pulps were all weaker than kraft at low 30's kappas. The variation of the pulp quality were also reported in the literature (33) These observations warrant an investigation on the effect of AQ on a particular species.

It was reported that the effect of AQ on pulping is species dependent (20, 32, 34). Previously, most of the studies were done on wood species. A very few studies deal with the bamboo species in India (35-37), Taiwan (38,39) and Japan (40). *Melocanna baccifera* the main species for pulping in Bangladesh has been utilized in Karnaphuli Paper Mills by the kraft process. There is no information on the effect of AQ at low sulphidity of muli bamboo. Thus, there is a good scope of improving the pulp yield in the mill. Hence, the study has been undertaken.

EXPERIMENTAL

Handling of chips

Mill cut muli bamboo chips were collected from Karnaphuli paper mills, washed with water to remove adhering impurities, air-dried for 15 days and then hand sorted to remove the undersized and cversized chips as well as decayed bamboo. The chips passing 32 mm. round hole screens but retained on 6 mm. were the accepts. After moisture determination the chips were stored in a cold storage at a temperature of 4°C for use in the experiments. The dry content of the chips was about 87%.

Cooking

The pulping experiments were carried out in 2 litre stainless steel autoclaves with 6 bombs at a time in an air bath, the air being electrically heated. 300 g, OD chips were added to each bomb. The cooking liquor was prepared from technical grade sodium hydroxide and sodium sulphide and then analysed.

Pulping was done by kraft process at a sulphidity of 15% (kraft $_{15}$) with and without AQ along with the kraft control at 25% sulphidity. AQ was added at the rate of 0.05% and 0.10% on OD chips. Other cooking conditions were

Active alkali as NaOH, 18%
Liquor to bamboo ratio, 4:1
Cooking temperature, 170°C
Rise of temperature to 70°C in 15 minutes and 70°C to 170°C in 90 minutes and
Total cooking time (excluding 15 minutes for the rise in temperature), varying.

Post cooking treatment

After cooking the bombs were cooled as rapidly as possible by immersing them in cold water and cooked chips were discharged. Black liquor samples were collected. The cooked chips were then washed with running water and disintegrated in a high speed laboratory disintegrator. The pulp was screened on a flat vibratory screen with 0 508 mm. slot. The screened pulp was pressed to remove excess water, shredded and weighed. The screening rejects and a portion of the screened pulp were dried at 105±2°C for pulp yield as per SCAN-C 3.78. The screened pulp in sealed polythene bag was stored in a refrigerator for subsequent analysis.

Analytical work

After cooling to room temperature, the black liquor samples were analysed for residual alkali as per Swedish method (41) with the help of a digital pH meter model 640 WAPA.

The screened pulp was tested for kappa number according to SCAN-C 1:59 and viscosity with CED solution according to SCAN-C 15:62. The pulp was beaten in a Jakro mill to verying SR freeness levels. Standard handsheets were made in a Karl-Frank laboratory sheet forming machine, conditioned at a temprature of 23±1°C and relative humidity of 50±1% before evaluating strength properties as per SCAN-C 28:69. The strength properties were evaluated at 30 and 40 SR° by interpolation.

RESULTS AND DISCUSSION

From the results on the effect of AQ in kraft $_{15}$ pulping of *Melocanna baccifera* given in Table 1, Fig.1, it is seen that the addition of AQ markedly reduced the cooking time to reach a particular level of delignification. The desired kappa number of 22 could be attained in normal kraft with a cooking time of 180 minutes and in kraft $_{15}$ pulping in 210 minutes. The same kappa number reached in kraft$_{15}$ +0.05% AQ cook in 150 minutes. It is observed from Fig. 1 that an addition of 0.05% AQ in the white liquor of 15% sulphi dity reduced the cooking time even when compared to the kraft control by 16.7% and at temperature reduction is 33.3%. Further Fig. 1 shows that when compared to karft$_{15}$ cook, the reduction of cooking time is 28.6% and at temperature is 50%. On increasing the AQ to 0.10%, the cooking time also decreases from the kraft control. In this case, the diminution of cooking time at temperature is about 66.7%. Thus, use of AQ in low sulphidity kraft pulping can lower down the cooking time even when compared to normal kraft cooking.

Compared with normal kraft pulping, kraft$_{15}$+AQ pulping shows a marked increase in unbleached pulp yield (Fig.2). The addition of 0.05% AQ increased the yield at a kappa number of 22 by about 0.8 percent on OD bamboo when compared to conventional kraft cook and 2.0 percent on OD bamboo when compared to karft$_{15}$ cook. With an use of 0.10% AQ, the yield gain was about 2.5 percent on OD bamboo when compared to kraft$_{15}$ and 1.3 percent on OD bamboo when compared to normal kraft cook. Thus the yield protection in low sulphidity pulping of muli bomboo can be achieved by a small addition of AQ say, 0.05%. The tendency of yield gain is in agreement with literature (8, 26, 35) and is due to stabilization of carbohydrates and acceleration of lignin removal by AQ(42,43).

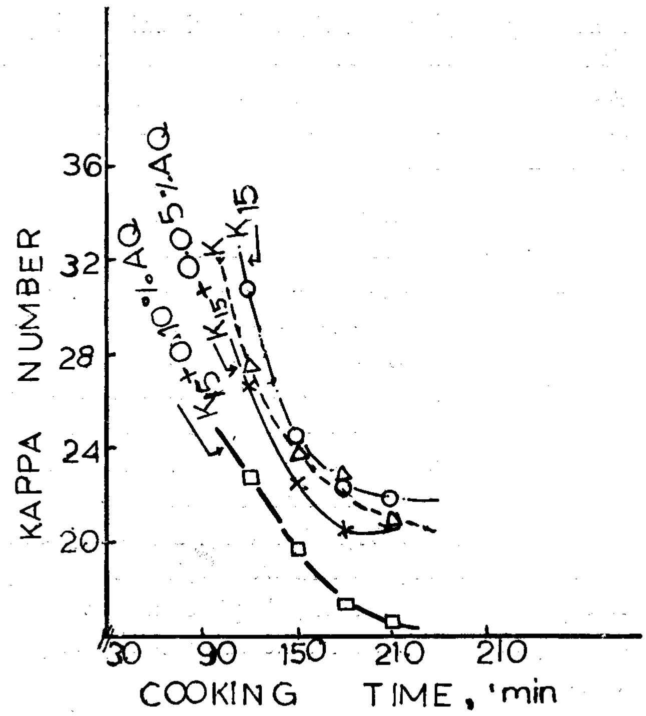

Fig. 1. Deliginification during low-sulphidity kraft and kraft+AQ pulping of muli bamboo including normal kraft as a control (K stands for kraft)

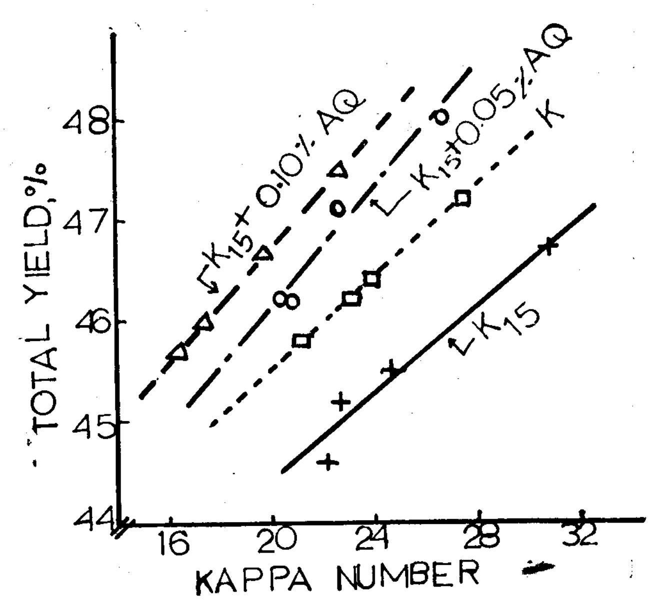

Fig. 2. Total yield as a function of kappa number during low-sulphidity kraft, kraft+AQ and normal kraft pulping of muli bamboo.

Table—1 : Effect of anthraquinone in low sulphidity kraft pulping of muli bamboo.

Active alkali as NaOH	Sulphidity	AQ dose	Total cooking time*	Active alkali consumed	Total yield	Reject	Kappa number	Viscosity	Physical strength properties of pulps: Tensile Index, SR° 30	Tensile Index, 40	Burst Index, 30	Burst Index, 40	Tear Index, 30	Tear Index, 40	Density, 30	Density, 40
%	%	%	min	%	%	%		dm^3/g	Nm/g		$kPa.m^2/g$		$mN.m^2/g$		Kg/m^3	
18	15	0	120	16 5	46.7	0.5	30.8	1064	55.0	59 0	4.6	4.8	20.5	18 0	579	587
18	15	0	150	16.7	45 5	0.4	24.6	1030	55.0	59 5	4.7	4.9	22.5	18.1	584	588
18	15	0	180	17.0	45.2	0.4	22.4	1004	56.0	59.0	4.4	5.3	22.0	17.5	596	628
18	15	0	210	17.0	44.6	0.3	21.9	987	55.5	58.8	4.8	5.2	20.0	17.4	582	609
18	15	0.05	120	16.7	49.0	0.5	26.7	1083	57.5	58.9	4.5	4.9	20.4	18.2	603	617
18	15	0.05	150	16.8	47.1	0.3	22.5	1050	60.0	62.0	4.8	5.4	22.5	19.5	614	630
18	15	0.05	180	17.0	46.2	0.2	20.4	1025	61.0	62.2	4.8	5.3	21.0	18.5	607	622
18	15	0.05	210	17.0	45.9	0.1	20.7	1015	58.0	62.0	4.7	5.3	18.0	17.1	618	635
18	15	0.10	120	16.7	47.5	0.5	22.8	1060	58.0	60.2	4.5	5.1	19.3	19.0	613	626
18	15	0.10	150	16.9	46.7	0.3	19.8	1041	58.0	61.2	4.8	5.6	20.7	19.0	602	622
18	15	0.10	180	17.1	46.0	0.2	17.4	1005	57.5	61.6	5.2	5.7	19.2	18.4	618	637
18	15	0.10	210	17.2	45.7	0.1	16.4	998	56.0	60.5	5.1	5.5	20.0	18.0	611	623
18	25	0.0	120	16.7	47.2	0.6	27.5	1108	57.0	60.0	5.0	5.5	17.9	17.0	584	608
18	25	0	150	16.9	46.4	0.5	23.8	1080	59.0	60.0	5.0	5.5	19.5	18.4	606	618
18	25	0	180	17.0	46.2	0.4	23.0	1072	58.0	59.8	4.6	5.5	18.5	18.3	612	626
18	25	0	210	17.1	45.8	0.2	21.0	1044	58.5	59.9	4.5	5.1	19.0	18.0	618	633

* excluding 15 min. time of rise of temp. from room temp. to 70°C.

Figure 3 shows the variation of screening rejects visavis the kappa number. It is seen that screening rejects at the same kappa number of the pulp are independent of the AQ dose which is in agreement with earlier studies (18,33, 35). Thus, the gain in screened pulp remains the same as in the total yield. The screening rejects is dependent on the degree of delignification.

$Kraft_{15}$+AQ pulping consumes less alkali when compared to normal kraft cook (Fig. 4). With an AQ charge of 0.05%, the alkali consumption is lower by 0.2 percent on OD bamboo at a kappa number of 22. With 0.10% AQ charge, the alkali reduction is about 0.3 percent on OD bamboo for the same kappa number when compared to kraft control. The figure further shows that the consumption of alkali in both $kraft_{15}$+ 0.05% AQ and $kraft_{15}$+0.10% AQ is also lower than that of the $kraft_{15}$ pulping. The lower consumption of alkali in AQ-catalysed pulping shows that AQ has oxidised the end groups of cellulose preventing end wise degradation. Because of lower degree of degradation, lesser quantities of carbohydrates are available for dissolution, thereby reducing the alkali consumption. This evident from the gain in the viscosity of pulp (Fig. 5). The figure shows that the viscosity of $kraft_{15}$+AQ pulp is almost equal to kraft control. The viscosity of $kraft_{15}$ pulp is lower than $kraft_{15}$+AQ and kraft control The viscosity value of $kraft_{15}$+0.05% AQ pulp is 1045 dm^3/g and $kraft_{15}$+0.10% AQ is 1050 dm^3/g. The corresponding viscosity of kraft control pulp is 1060 dm^3/g and that of $kraft_{15}$ is 990 dm^3/g. Figure 5 indicates that even an addition of 0.05% AQ is sufficient to protect the cellulose degradation

In regard to the physical strength properties, $kraft_{15}$ pulping produced an inferior pulp (Table 1). The quality of the pulp at the same °SR freeness level improved with an addition of AQ in the low sulphidity kraft pulping. It is seen from Fig. 6 that the tear index of $kraft_{15}$+AQ is better than that of $kraft_{15}$ pulping and kraft control.

0.05% AQ in $kraft_{15}$ cooking results in slightly higher tear index by about 6% when compared to kraft control and 10% higher than that of the $kraft_{15}$ pulp. The increase in tearing strength of pulp in $kraft_{15}$+0.05%

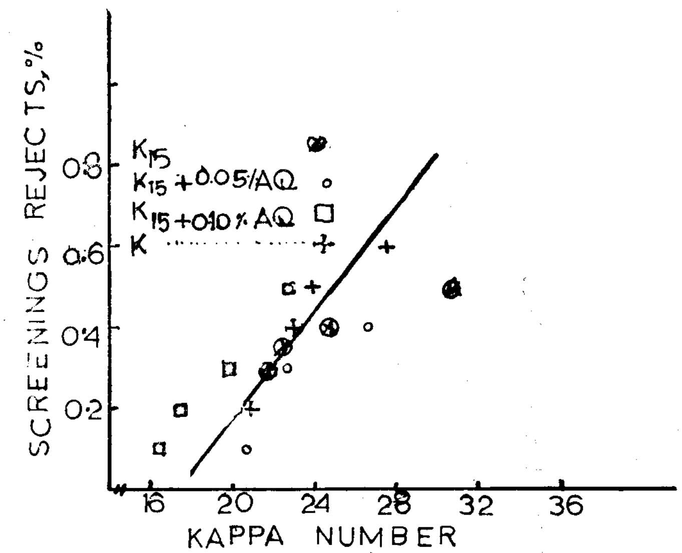

Fig. 3. Screening rejects as a function of kappa number in low-sulphidity kraft, kraft+AQ and normal kraft pulping of muli bamboo.

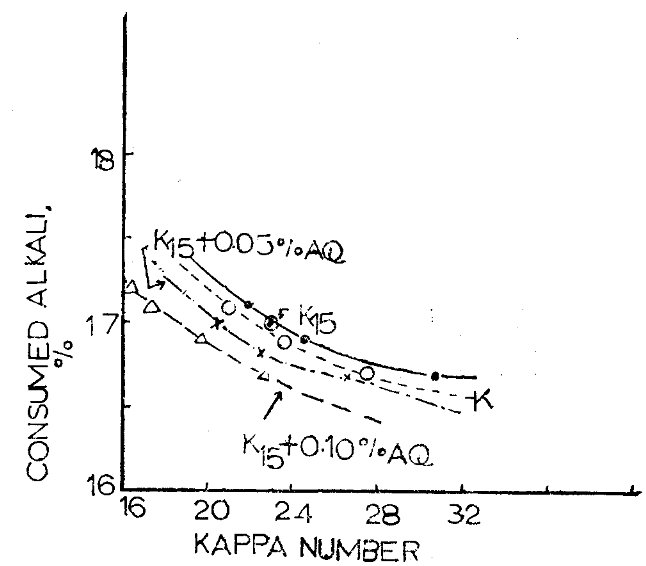

Fig. 4 Influence of AQ on consumption of activie alkali during low-sulphidity kraft pulping of muli bamboo including kraft as a con'rol.

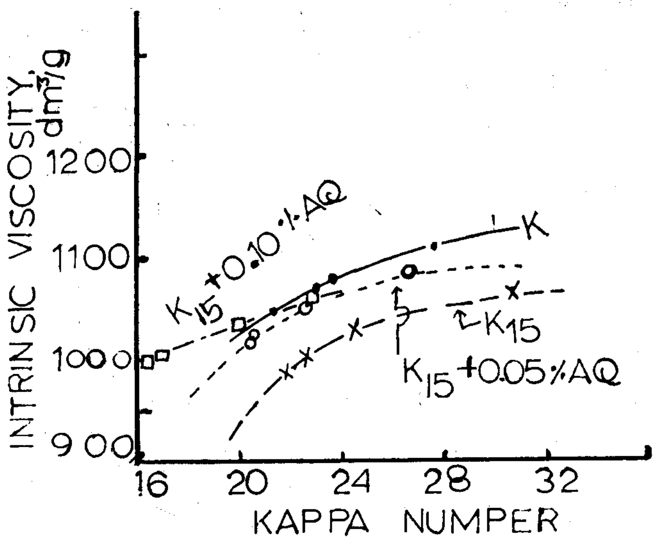

Fig. 5. Intrinsic viscosity as a function of kappa number in low-sulphidity kraft, kraft+AQ and normal kraft pulping of muli bamboo.

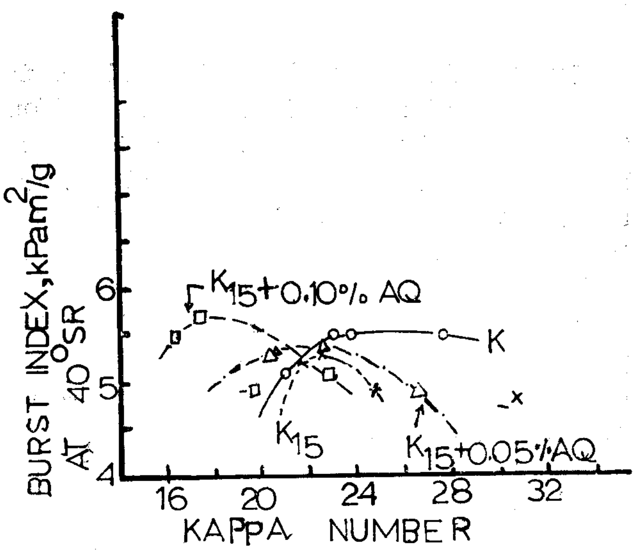

Fig. 7. Burst-kappa plots for unbleached low-sulphidity kraft, kraft+AQ and normal kraft pulping of muli bamboo.

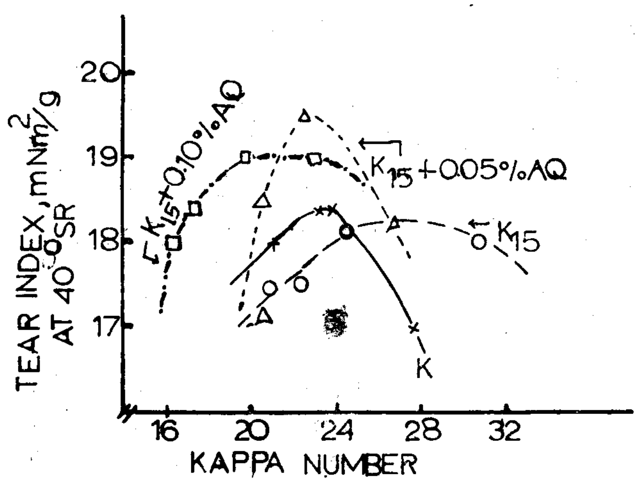

Fig 6. Tear index as a function of kappa number during low-sulphidity kraft pulping of muli bamboo with addition of AQ inclnding normal kraft as a control.

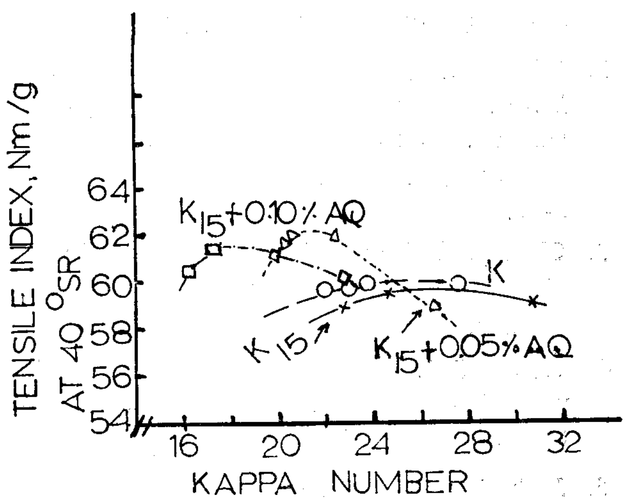

Fig. 8. Tensile -erength as a function of kappa number during low-sulphidily kraft, kraft+AQ and normal kraft pulping of muli bamboo.

AQ cook is almost the same as that of $karft_{15}+0.10\%$ AQ. Figure 7 shows that burst index of $kraft_{15}+AQ$ pulp is almost similar to kraft control. The tensile index of $kraft_{15}+AQ$ pulp is superior to that of the kraft control pulp. From Fig. 8, it is seen that the tensile strength of the pulp obtained in $kraft_{15}+0\ 05\%$ AQ pulping is slightly better (about 4 4%) than that of the kraft control. Thus, AQ addition in low sulphidity kraft pulping of muli bamboo improves the tear, burst and tensile indices of the pulp.

CONCLUSION

Based on the study carried out, it can be concluded that in respect of muli bamboo, with the addition of 0 05% AQ at 15% sulphidity, the total cooking time can be reduced by, 16.7% and at temperature by 33.3% when compared to kraft control. The unbleached pulp yield increases by 2.0 percent on od bamboo when compard to the $kraft_{15}$ cook and 0.8 percent on od bomboo when compared to normal kraft cook. Low sulphidily+AQ pulping produces pulp with better tear, burst and tensile indices. The viscosity of the pulp is almost equal to kraft control.

ACKNOWLEDGEMENT

I am grateful to the Karnaphuli Paper Mills Ltd. and the Bangladesh Chemical Industries Corporation for permission to conduct this study.

REFERENCES

1. Rydhom, S.A., 1965: Pulping processes, Interscience publications N.Y. et, pp. 588-596.
2. Mishra, B.P., Joshi, R.C., Banthia, U.J., Singh, M.M , 1982 : Effect of sulphidity pulping of bamboo, mixed hardwoods and a mixture of bamboo and mixed hardwoods, IPP. vol. 39 (3) : 3-16.
3. Cheslay, K.G. and Gilmont, P.L., 1955 : Sulphidity in southern pine kraft pulping Tappi 38 (5): 279-282.
4. Treiber, S.S. and Boyle, J.J , 1980: Experimental validation of a kraft mill simulation. Tappi 63 (6): 81-85.
5. Jauhari, M.B., and Bargava, R.L., 1967: Influence of sulphidity on alkaline pulping of bamboo chips. IPPTA 4 (2) : 43-46.
6. Libby, C E., 1962 : Pulp and paper science and technology vol. 1, Magrow-Hill book comp. bup. pp. 170-171.
7. Rudhra, S.N and Barua, I.B , 1990: Process control report ref. Q C.-63/90 (108 & 113).
8. Holton, H H. 1977: A major new process, The soda additive pulping of softwoods, 63rd annual meeting of tech. selection, C.P.P.A. Feb. 1-2, Montreal pulp and paper. Canada, : 107-112.
9. Hanson, J.P. and Michaels, W.T., 1978: Anthra quinone pulping-is it magic ? Pulp and Paper (May) : 86-90.
10. Ghosh, J.S., and Hannah, M.A. 1978:Soda-AQ pulping of hardwoods process models, Tappi 61 (8) : 57-59.
11. Ghosh, G., Venkatoesh, V., Chain, W.J. and Gratzl, J.S., 1977: Quinoline additive in soda pulping of hardwood, Tappi 60 (11) : 127-131.
12. Tenn. T.I., 1979: AQ pulping of wood. Chemi-Eng. vol. 86 (26) : 46-55, ABIPC 50 : 9404
13. Goel, K. Ayround, A.M , Branch, B. 1979: AQ in kraft pulping, Tappi pulping conf. proc. (Seattle): 210:220. Sept. 24-26.
14. Fossum, G., Hogglund, S and Lindqvist, B, 1980: Part 1, Kraft pulping pine and birch with anthraquinone as additive. Svensk Papperstidning 83 (3): 430-434.
15. Waller, M.H , and Eyike, Y.N., 1982 : Soda-anthraquinone pulping of lobolly pine. CPPA. Ann Mtg. (Montreal) reprints 68 B: 77-80. ABIPC 53 (9) : 9544 (M).
16. Upadhyaya, T.S. and Singh, S.P., 1986: Studies on kraft+AQ pulping of mixed hardwoods, Aolzfschung und. Holzverwertung 38 (3): 62-66.
17. Fossum, G , Hogglund, S., & Lindqvist, B., 1980 : Part 2, soda pulping of pine and birch with anthraquinone as additive, Svensk Papperstidning, 83 (16) : 455-460.
18. Akhtaruzzaman, A.F.M., Das, P. and Bose, S.K., 1987 : Effect anthraquinone in alkaline pulping of *Acacia auriculifomis*. Babo Biggyan Patrika, vol. 16 (1 & 2) : 3-7.
19. Ghosh, K.L., 1979 : Evaluation of addition in soda pulping of hardwoods, Ph. D, thesis, North Ca. State Univ. 164 p.
20. Akhtaruzaman, A.F.M., 1984 : Alternative to kraft pulping. Bano Biggyan Patrika, Vol. 13 (1 & 2) : 76-82.
21. Holton, H.H. and Chapman, F.L , 1977 : Kraft pulping with anthraquinone, Tappi 60(11):121-125.
22. Farringtons, A., Nelson, F.P. Vanderhock, N. 1979 : A mill trial of soda-anthraquinone pulping. Appita 33 (3) : 207-209.

23. Kleppe, J.P., 1980 : A mill trial with addition of a small amount of AQ to kraft and polysulfide pulping, EUCEPA symposium Helsinki, Paper No. 13. voll-11, 14 p.

24. Masura, V., Velik, J. Bucek, J., Prokop, V., 1982 : Mill trials with AQ addition during sulfate delignification. Papir Cellulose 37 (5) : 80-86.

25. Bhowmick, K., Mian, A.J., & Akhtaruzzaman, A.F.M., 1991 : Anthraquinone as an additive in kraft pulping of muli bamoo, to be pub.

26. Van Allen, N.J., Holton, J.V., Gee, W.Y., 1981 : Effect of sulphidity in alkaline pulping of white sprouce white sprouce with anthraquinone, Tappi 64 (6) ; 64-66.

27. Rao, V.G., 1983 : Quinoline additive in pulping-a new strategy for better economy and ecology. IPP. 37 (4) : 13-24.

28. Blain T.J., 1979 : Anthraquinone as a pulping additive-its effectiveness in alkaline pulping of hardwoods. CPPA. Trans. Tech. Sect 5 no 1:3-12.

29. Bhandari, K S., Srivastawa, A., Sharma, Y.Z., 1980 : Low-sulphidity kraft anthraquinone pulping of Eucalyptus grondis. Journal of the Eucalyptus of the Timber Dev. Asso. of India, 32 (1) : 19-28.

30. Blain, T.J., 1979 : Low-sulphidity pulping with anthraquinone, Tappi 26 (6) : 53-56.

31. Parthasarathy, V.R., Singh, B., Chandra, S.S., Saksana, U.L., Chowdhury, L N., 1983 : Low-sulphidity AQ additive pulping of hardwoods and softwoods mixtures, Appita 37 (1) : 70-72.

32. MacLeod, M. 1979: Yellow magic-AQ pulping appears poised for success. Pulp and paper canada 50(12):54-56.

33. Akhtaruzzaman,A F.M,and ahowdhury,A,R.,1991: Alkaline pulping of *Albizia falcatria* with anthraquinone as in additive. Manuscript sent for presentation in 10th World Forestry congress, to be held in Paris.

34. Clayton. D.W., 1980: New chemical accelerators for alkaline pulping, Innovation paper Ind. corporate Exc. conf. venice). Proc: 13-23. ABIPC 54 (4):3822.

35. Nayak, R.G., Handigol, S.g., Meshramakar, P.M. and Dev., U.K. 1979. : Anthraquinone as an additive in kraft pulping of bamboo (D. strictus), IPP vol.33 (5): 17-27.

36. Jauhari, M.B., Ghosh, P.C., 1985: High yield alkaline sulfite AQ pulping of bamboo. IPTTA. vol. 21(1): 45-50.

37. Goyal, P., Misra, N.D., 1982: Economics of bamboo and hardwood pulping by AQ-catalysed kraft process, IPPTA 19(1) : 1—5.

38. Wang, K.T., 1982 : Alkaline sulphite pulping of bambussa arundinacea with addition of AQ. Bull. Taiwan Forestry Res. Ins. 378 (Sept.): 12pp.

39. Wang.H. and Teng, T.Y., 1982 : Study on high yield pulping of bamboo waste, Tech. Bull. Expt Forest, Natl. Taiwan University, 135 : 16p.

40. Oye, R, 1987: bamboo pulping, Tokyo University of Agri. & Techno Bamboo Journal no 4 : 62-68.

41. Anon, 1974: Lab-25, Koknings-Laborationer. Lab-Anvisn. Y-104, Sveriges. Skogindustri-forbund, Markanynd.

42. Gratzl, S.J., 1980: The reaction mechanisms of anthraquinone in alkaline pulping. EUCEPA symposium, vol-2 no 12,pp. 1-27.

47. Lowendahl, L. and samuelson, O., 1977: Carbohydrate stabilization during kraft cooking with addition of anthraquinone. Svensk papperstindning, vol. 80 (17): 549-551.