

# Effect of anthraquinone in soda pulping of muli bamboo (*Melocanna Baccifera*)

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## ABSTRACT

Conventional soda pulping results in lower pulp yield and strength properties. Anthraquinone (AQ) is used as an additive in soda pulping to overcome the problems. Laboratory studies on soda+AQ pulping of mill-cut muli bamboo (*Melocanna baccifera*) show that AQ accelerated delignification, improved pulp yield at a particular kappa number and reduced the active alkali dose or cooking time compared to normal soda cook. An addition of AQ as low as 0.05% on OD raw material lowered the alkali demand by 4% on OD bamboo. Such a low dose of the catalysis increased the pulp yield by 3% on OD bamboo. Such a low dose of the catalysis increased the pulp yield by 3% on OD bamboo. The yield was almost similar to the kraft control. Use of 0.10% AQ further increased the pulp yield to surpass the kraft control. But the gain in yield with 0.10% AQ was not as remarkable as with 0.05% AQ.

The beating characteristics and strength properties of pulp improved by the addition of AQ during soda pulping. The soda+AQ pulp is almost equal to the kraft control. This investigation has shown that AQ is a promising additive in soda pulping of muli bamboo.

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## Introduction :

The dominating chemical pulping to-day is the kraft process. This is because the process has many advantages, such as versatility in using any type of raw material, production of the strongest quality pulp, higher pulp yield compared to soda process, etc. It has, however, some serious problems. The stringent environmental regulations have recently made the kraft process more challenging. This is because of emission of organic sulphur containing compounds generated by the action of sodium sulphide during the operation (1). Such compounds are hydrogen sulphide, methyl mercaptan, dimethyl sulphide, etc., (2, 3). These compounds are highly odourous and thus objectional to the environment. On the otherhand, soda pulping has no

such pollution problems. But it requires a longer cooking time and a higher alkali charge to make a pulp at a certain kappa number resulting in lower pulp yield and inferior quality of pulp compared to the kraft. These difficulties in soda pulping can be overcome by addition of additives which could either partially or entirely replace the sodium sulphide in kraft and thus reducing the air pollution problems in the mill. Soda pulping with several additives, such as, anthraquinone (AQ) or its derivatives, ethylenediamine (EDA), etc., has received considerable attention in replacing kraft pulping (1).

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Of all these, (AQ) is a suitable additive in soda pulping without the need for sulphur containing compounds. The net effect of AQ addition in soda cooking is almost similar pulp yield and strength properties compared to the existing kraft process (4-8). It is recognised that AQ has a marked catalytic effect on delignification in both kraft and soda pulping of softwoods and hardwoods. The catalytic effect of AQ is more pronounced in hardwoods than in softwoods (8-10).

During alkaline pulping, AQ stabilizes the carbohydrates towards endwise degradation (11). This results in an increased yield of pulps (4, 12). A very small amount of AQ at the rate of 0.05 to 0.10% on OD wood is sufficient in enhancing the rate of delignification and in improving the yield in soda pulping without any adverse effect on pulp properties (12-14). It is also reported that the influence of the AQ addition is more pronounced in soda than in kraft pulping (4, 15). AQ does not contribute any toxic property to the effluent (2, 16). Thus, soda+AQ pulping is a viable alternative to kraft pulping to face the increasing environmental problems (10, 12).

Several studies have been carried out on the effect of AQ in alkaline pulping process. The studies were mostly done with wood species. A very few studies deal with the bamboo species in India (13, 17, 18); Taiwan (19, 20); Japan (21), etc.

Although the role of AQ on alkaline pulping is quite clear as to delignification and yield protection, the question remains on the quality of the pulp. The quality of soda+AQ pulp appears to be species dependent (8, 22). Soda+AQ pulps from black spruce have 15-20% lower tearing strength than kraft (1, 22). Douglas-fir showed a tear reduction of about 10% (22). *Albizia falcataria* indicated a 6% lower value in tearing strength (23). On the otherhand, the tearing strength did not impair in a mixture of spruce, balsam and pine (22), *Pinus radiata* (24) and *Acacia auriculiformis* (25). Other strength properties were equal to the kraft counterpart (22, 25). In the case of a mixture of hardwoods and bagasse, soda+AQ and kraft are quite similar in all strength properties (22). Thus, it is essential to study the effect of AQ in the pulping of a particular species

There is no study on the effect of AQ in soda pulping of muli bamboo. Karnapuli Paper Mills are now using about 45,700 AD tonnes of bamboo as the fibrous material. So there is an opportunity to study this aspect with the particular species, i.e., muli bamboo.

## EXPERIMENTAL

### Handling of chips

Mill-cut muli bamboo chips were collected from the Pallman Chipper of Karnaphuli Paper Mills, washed with water to remove adhering impurities, air-dried for 15 days and then hand-sorted to remove the under-sized and oversized chips as well as decayed bamboo. The chips passing through 32 mm round hole screens but retained on 6 mm were accepted and then bagged in air-tight containers. 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 with 300 g of chips (oven-dry basis) in 2 litre stainless steel autoclaves with 6 autoclaves at a time in an assembly rotating in an air bath, the air being electrically heated. Cooking liquor was prepared from technical grade sodium hydroxide and sodium sulphide. Analyses were done according to SCAN N 2:63.

Pulping was done by soda and soda + AQ processes alongwith the kraft control. AQ was added at the rate of 0.05% and 0.10% based on OD bamboo. As an active alkali charge of 18% (as NaOH) was not sufficient to reach the target kappa number, normal soda cook was done with 22% alkali (as NaOH). Other cooking conditions were maintained at

- 18% active alkali as NaOH (for soda+AQ and kraft),
- 25% sulphidity for kraft,
- 4:1 liquor to bamboo chips ratio,

- 15 minutes to raise the temperature to 70°C, and 90 minutes to raise the temperature from 70°C to 170°C,
- Cooking time at 170°C, varying,

### Post-cooking treatment

After cooking, the autoclaves were cooled as rapidly as possible in the water bath. The cooked chips were discharged and black liquor samples were collected. The cooked chips were then washed in running water overnight. After washing, the cooked chips were disintegrated in high speed laboratory disintegrator and screened on a flat vibratory screen with 0.508 mm slots. The screened pulp was collected in a cloth bag, then pressed to remove excess water, shredded and weighed. The screening rejects and a portion of the screened pulp were dried at  $105 \pm 2^\circ\text{C}$  for the pulp yield determination as per SCAN-C 3:78. The screened pulp was stored in a refrigerator in sealed polythene bags for subsequent analyses.

### Analyses

After cooling to room temperature, the black liquor samples were analysed for residual alkali according to the Swedish method (26). The kappa number was determined with screened pulp according to SCAN-C 1:59 and viscosity with CED solution as per SCAN-C 15:62. The viscosity of the soda pulps obtained with 18% alkali charge was not determined as the pulps were difficult to dissolve in CED solution. The pulp was beaten in a Jokro mill at different SR°. Standard handsheets of 60 g/m<sup>2</sup> were made in a Karl-Frank laboratory sheet forming machine, conditioned at a temperature of  $23 \pm 1^\circ\text{C}$  and a relative humidity of  $50 \pm 1\%$  and then tested for physical strength properties according to SCAN-C 28:69 Test Methods. The strength properties were evaluated at 30 and 40 SR° by interpolation.

### Results And Discussion

Pulping data and results for soda+AQ, soda and kraft control of muli bamboo are shown in Table-1 Fig.

1-presents the relationship of kappa number with cooking time. It is observed that addition of AQ markedly increased the rate of delignification in soda pulping. Under the applied condition, it was not possible to attain at the target kappa number of 22 in soda cooking without AQ addition. In such a case, the minimum kappa number was 36.1 at a total cooking time of 210 minutes. This is a high kappa number for a bleachable grade of pulp. Thus, the pulping was done with an alkali charge of 22% as NaOH to achieve at the desired delignification in normal soda pulping. In this case, the delignification could be continued to a kappa number of 22.3 at a total cooking time of 210 minutes. Table 1 shows that an addition of 0.05% AQ in Soda cooking containing 18%alkali as NaOH could delignify to the target kappa number at a total cooking time of 210 minutes. Thus, a small addition of 0.05% AQ can reduce the alkali charge by 4% on od bamboo. A lower alkali demand was also required in wood pulping (12,24). Fig. 1 further shows that the total cooking time in soda pulping with 0.05% AQ and kraft pulping were almost the same. This reveals that an addition of 0.05% AQ in soda pulping can reduce the alkali demand and at the same time can delignify at the almost the same cooking time as in kraft cooking. Fig. 1 also shows that an addition of 0.10% AQ in the soda cook, the delignification was slightly better. Thus, the effect of AQ in soda pulping is almost similar to kraft cook.

Fig 2 shows the effect of AQ on the total yield. Soda+AQ pulping provides a clear increase in unbleached pulp yield. An addition of 0.05% AQ in soda pulping resulted in an yield gain of about 3% on od bamboo when compared to normal soda cook at a kappa number of 22. The total yield was 45.9% in soda+0.05% AQ pulping. The corresponding yield in normal soda pulping was 42.9%. The yield in soda+0.05% AQ cook was lower by only 0.1 percent on od bamboo when compared to kraft control. It is, therefore, logical to conclude that soda+0.05% AQ pulping is almost equal to that of the kraft counterpart as far as the pulp production is concerned. The total yield in normal kraft pulping was 46.0% at a kappa number of 22. Soda + 0.10 % AQ cook recorded an yield of 46.4 %. Thus, soda pulping with 0.10% AQ gave an yield gain by 0.4 percent on od bamboo, compared to the kraft counterpart. The

Table I :—Effect of anthraquinone in soda pulping of muli bamboo

Active alkali as NaOH	Sulphidity %	AQ dose %	Total cooking time min	Active alkali %	Total yield %	Re-jects %	Kappa number	Viscosity dm <sup>3</sup> /g	Physical strength properties of pulps							
									Tensile index		Burst index		Tear index		Density	
									SR <sup>0</sup>							
									30	40	30	40	30	40	30	40
									Nm/g	KPam <sup>2</sup> /g	mN.m <sup>2</sup> /g		Kg/m <sup>3</sup>			
18	0	0	120	17.1	48.7	0.8	48.4	—	48.0	54.0	3.6	4.4	20.5	18.0	540	562
18	0	0	150	17.2	47.3	0.6	41.4		48.5	55.0	4.2	4.7	20.5	19.0	548	568
18	0	0	180	17.3	46.5	0.5	38.6	—	50.5	55.5	4.4	4.9	20.0	19.0	552	570
18	0	0	210	17.4	45.9	0.4	36.1	—	49.0	53.0	4.0	4.3	20.1	18.5	547	580
18	0	0.05	120	16.8	47.6	0.6	30.7	1010	54.5	59.0	4.6	5.1	19.5	17.6	579	598
18	0	0.05	150	16.9	46.7	0.5	25.6	965	56.3	59.9	4.6	5.1	19.5	19.5	584	602
18	0	0.05	180	17.0	46.1	0.3	23.0	953	58.0	61.8	4.7	5.2	21.5	19.0	597	617
18	0	0.05	210	17.1	45.7	0.1	21.7	930	58.0	61.8	4.3	4.8	19.5	18.5	590	601
18	0	0.10	120	16.8	47.6	0.5	29.2	1057	56.5	59.5	4.7	5.1	20.5	19.0	582	596
18	0	0.10	150	16.9	46.6	0.4	22.9	1001	56.8	61.0	4.9	5.3	20.5	19.3	601	624
18	0	0.10	180	17.0	46.3	0.3	21.9	982	57.5	61.0	4.6	4.9	23.5	20.0	598	607
18	0	0.10	210	17.0	46.0	0.2	20.8	950	56.5	60.5	4.1	4.5	21.0	19.0	598	620
18	25	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	1030	59.0	60.0	5.0	5.5	19.5	18.8	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	58.0	59.9	4.5	5.1	19.0	18.0	618	633
22	0	0	150	18.9	44.5	0.5	30.7	775	51.8	55.5	3.2	4.5	18.5	17.4	575	600
22	0	0	180	19.3	43.6	0.2	25.5	729	51.7	56.2	4.3	4.9	18.8	17.7	570	585
22	0	0	210	19.9	42.8	0.1	22.3	684	51.0	56.0	4.1	4.7	18.7	17.6	550	570

\*excluding rise of temperature from room temperature to 70°C

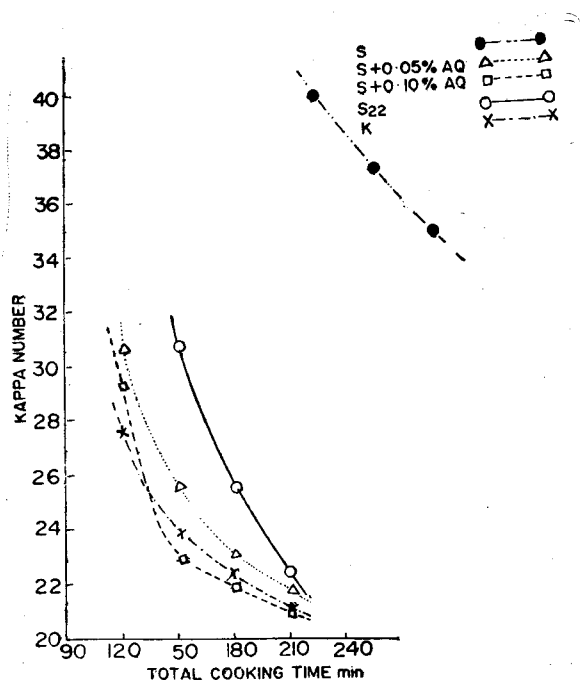


Fig. 1. Delignification during soda, soda+AQ and kraft pulping of muli bamboo (S stands for soda and K for Kraft).

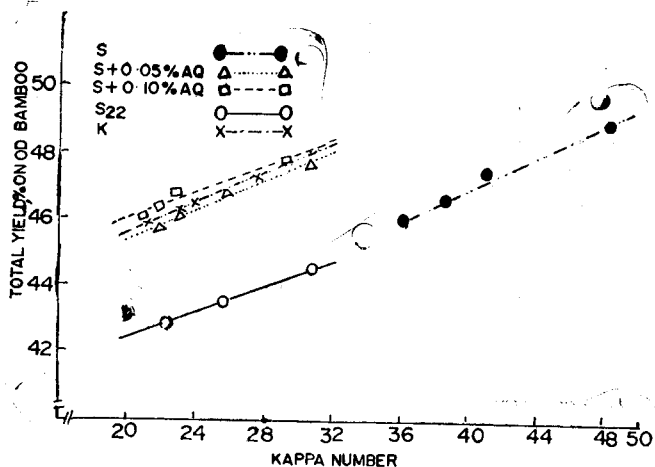


Fig. 2. Total yield as a function of kappa number in soda, soda+AQ and kraft pulping of muli bamboo.

maximum benefit in yield protection was, therefore, achieved by a small addition of AQ say 0.05%. Similar findings were also reported earlier in wood pulping

(4, 8, 24). The improvement in the yield at a particular kappa number is evidently due to effect of catalyzed delignification and oxidative stabilization of the end groups in cellulose and hemicellulose (27-29).

The screening rejects at the same kappa number of the pulp were found to be independent of the AQ dose (Fig. 3). They were also of the same magnitude as in the kraft. This is in agreement with the findings of previous investigations (13, 23). Consequently, the gain in screened pulp yield remains the same as in the total yield. The reject is primarily dependent on the degree of delignification.

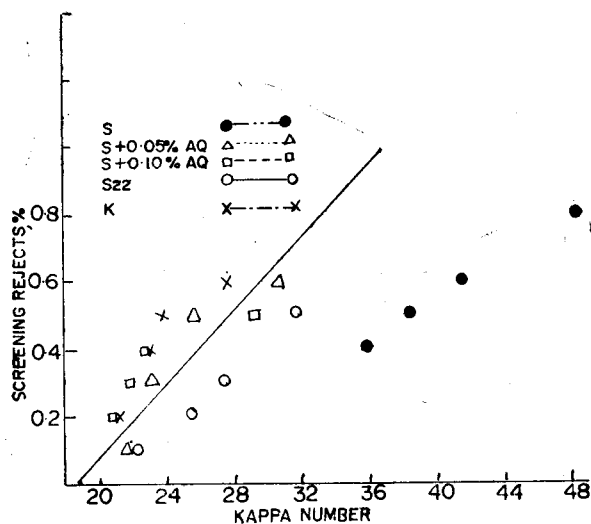


Fig. 3. Screening rejects as a function of kappa number in soda+AQ and kraft pulping of muli bamboo.

Soda+AQ pulping consumed less alkali compared to normal soda cook (Fig. 4). In presence of 0.05% AQ the active alkali consumption decreased by 2.8% on od bamboo and with 0.10% AQ by 2.9% on od bamboo when compared to that in normal soda cook at a kappa number of 22. Soda+AQ and kraft pulping were almost identical in respect of alkali consumption.

The effect of AQ on pulp viscosity is shown in Fig. 5. The viscosity of pulp obtained with 18% active alkali charge in soda pulping was not determined due to difficulty in dissolving such pulp. All the soda

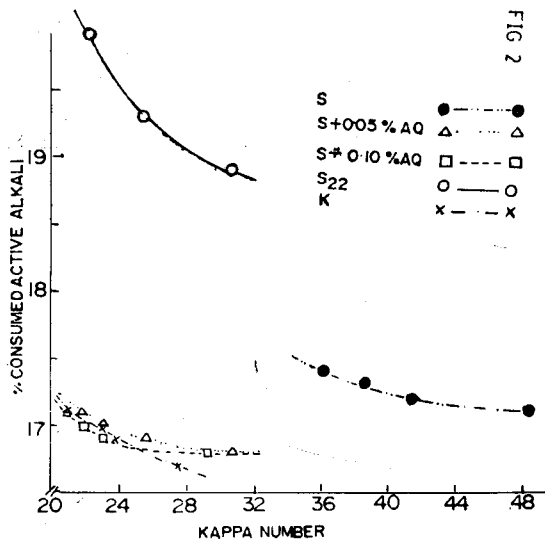


Fig. 4. Influence of AQ on consumption of active alkali during soda pulping of muli bamboo including kraft as a reference.

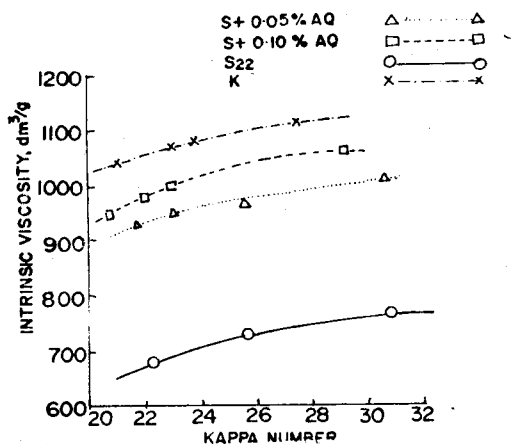
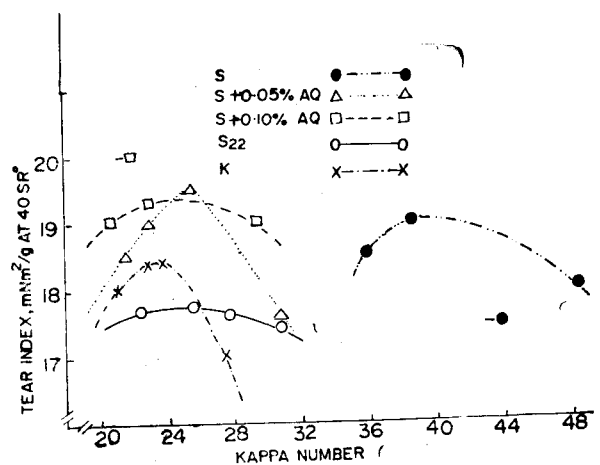


Fig. 5. Intrinsic viscosity as a function of kappa number in soda, soda+AQ and kraft pulping of muli bamboo.

pulps had lower viscosity than the kraft control. Similar results were also obtained in wood pulping (23). The pulp degraded severely in normal soda pulping as is evident from the viscosity measurement (Fig. 5). On addition of AQ, cellulose degradation retarded. The viscosity values of soda+AQ approached to a kraft like quality, although the kraft pulp show-

ed the highest viscosity. Fig. 5 indicates that a small amount of 0.05% AQ is sufficient to minimise the cellulose degradation. The viscosity of unbleached pulp in soda+0.05% AQ cook was 940  $\text{dm}^3/\text{g}$  at a kappa number of 22. The corresponding viscosity of soda pulp was 670  $\text{dm}^3/\text{g}$  and that of the kraft control was 1,060  $\text{dm}^3/\text{g}$ . The viscosity of soda+0.05% AQ pulp was higher by about 40% and with 0.10% AQ by 46% when compared to soda cook. Thus, the catalytic action with these two different doses of AQ is almost equal at kappa number of 22.

The tear, burst and tensile strength properties at a particular  $\text{SR}^\circ$  are presented in Fig. 6-8. The pulp produced in the soda process are the most inferior in respect of the physical strength properties. The quality of the pulp at the same  $\text{SR}^\circ$  improved with the addition of AQ during soda pulping. It is seen from Fig. 6 that the tearing strength of the pulp obtained in soda+0.05% AQ cook was slightly better than the kraft counterpart. It is about 2% higher than that of the corresponding kraft control. The soda+0.05% AQ pulp was even more superior at a slightly higher kappa number. With the use of 0.10% AQ, the tearing strength increased by about 6% at a kappa number of 22. Soda+0.05% AQ and soda+0.10% AQ pulp were almost similar in tearing strength. The bursting strength of soda+0.5% AQ and soda+0.10% AQ pulps were almost similar. The tensile strength was, however, slightly superior (3-5%) to kraft control.



6. Tear index as a function of kappa number during soda pulping of muli bamboo with addition of AQ including kraft as a control.

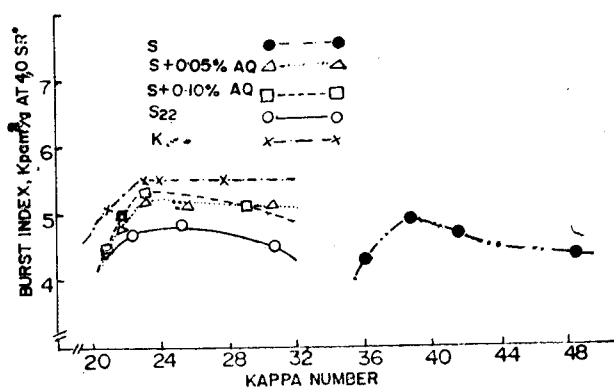


Fig. 7. Burst—kappa plots for unbleached soda, soda +AQ and kraft pulps of muli bamboo.

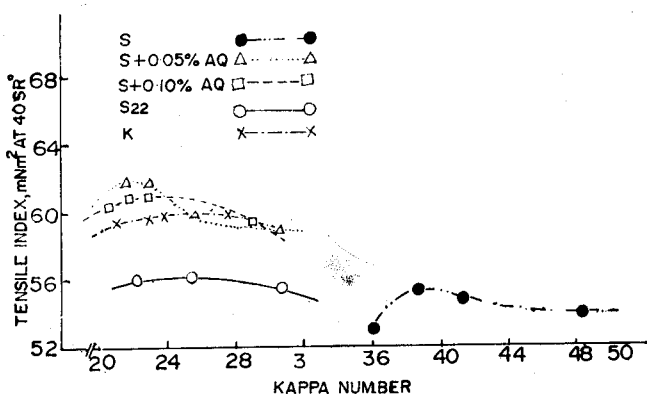


Fig. 8. Tensile strength as a function of kappa number during soda, soda+AQ and kraft pulping of muli bamboo.

It is well established that properties of the pulp are interdependent. Hence, it is a more common practice to look into the tear-tensile relationship of the pulp. They are considered to be the most important strength properties and at the same time they are inversely related in the majority of cases. Such a relationship for the pulps at almost similar degree of cooking for soda+AQ and kraft control is shown in Fig. 9. The figure clearly shows that the normal soda pulps are the most inferior. The pulp properties rapidly increased with an addition of AQ in soda pulping. The tearing strength of soda+AQ pulp at a given

tensile strength was superior to the kraft counterpart. Fig. 9 further shows that AQ addition by 0.05% in soda pulping is sufficient to improve the quality of pulp. Thus AQ addition in soda pulping of muli bamboo produces a superior pulp compared to normal kraft pulping.

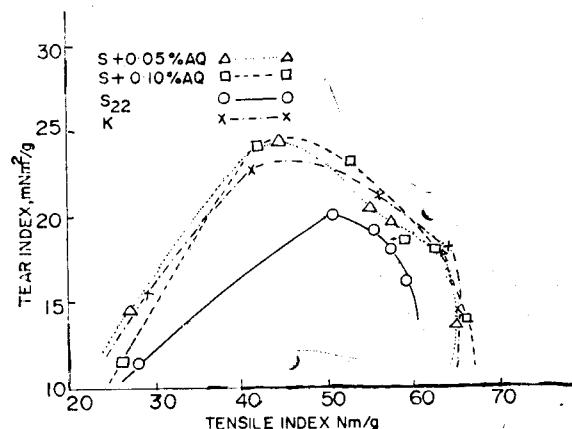


Fig. 9. Tear - tensile relationship for pulps at a kappa number of  $20 \pm 2$  in soda Pulping of muli bamboo with addition of AQ including kraft as a reference.

## Conclusions

The findings of this study lead to the following conclusions in soda pulping of muli bamboo :

- AQ is found to be an effective pulping additive.
- Addition of anthraquinone results in increasing pulp yield and delignification rate, reducing the cooking time and/or alkali requirement, improving the viscosity and the quality of pulp in soda process.
- An addition of AQ by 0.05% is sufficient to bring the benefits.

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