

AQ Pulping and ECF Bleaching of Hard Woods with Bark

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ABSTRACT

AQ kraft pulping of hard wood barks, unbarked hard woods and debarked hard woods from juvenile trees has been carried out. Yield, kappa number and viscosity values have been reported. Two bamboo samples have also been studied. The hard woods used are: casuarina equisetifolia, eucalyptus tereticornis, cassia siamea, leucaena leucocephala and bamboos are: dendrocalamus strictus and bambusa arundinacea. The yield, kappa no. viscosity and AA requirements have been determined. DEpD bleaching of AQ treated pulps has been carried out and bleached pulp properties such as yield, viscosity, optical properties, zero span breaking length and FS factor have been reported. The techno-economical feasibility of using bark along with wood in kraft pulping with ECF bleaching has been discussed. The concept of using hardwood with bark in Indian pulp and paper mills, has been highlighted as imperative.

INTRODUCTION

Whole-tree-chipping and utilization of bark are concepts evoked long back (1-3) but it is rarely practised in mills on regular basis because of problems faced during paper manufacturing and for economical reasons (4). Debarking of woods is considered absolutely necessary for quality paper manufacturing. Specifications for pulpwood chips usually limit bark to 0.5% or less (5). However, intake of 1.5 to 2% of bark into the pulp becomes unavoidable as no debarker is 100% efficient and risk of losing some wood part exists if total debarking is attempted (6). Reports of bark acceptance upto 0.5%-2% (7) and upto even 24% are available (3) Acceptance of unbarked wood can be further eased where bamboo-hard wood mix is used with proportion of hard wood being 20-30%. In juvenile trees, the bark contains considerable amount of fibrous portion (4) unlike in matured trees (7, 8-10 years).

Bark is defined to be the outer covering or rind of woody stems and branches. Bark contains 3 types of tissue: Cortex, Periderm and Phloem (6). Bark is formed by cambium. Each year when the cambium generates a layer of wood from its inner surface, it also forms a layer of bark from its outer surface. The outer layers generally crack open because of stresses, caused on increasing girth. Thus younger trees have bark which is smooth and relatively thin while

old trees have bark that has fissured and scaly appearance (4).

In many trees, the inner bark is fibrous having intimate contact with wood and when manually separated, it appears like some sort of bast fibres. However, the outer bark portion lacks in fibre content. Bark of *gmelina arborea* is fragile and cannot be used. Acceptance of bark from trees should be considered from age point of view, namely juvenile and mature. Bark of matured trees may not be acceptable but bark of many juvenile hard woods can be used for paper manufacturing as the present studies will show. It is already being practised in mill scale. It is partly because of shortage of raw materials and debarking cost that mills are forced to use hard woods with bark.

Most of the non-polysaccharide components of bark are dissolved by alkaline pulping liquor. Unlike in sulphite process, kraft cooking can accept bark easily (3). With *eucalyptus deglupta*, it is shown that commercial scale pulping without removing bark should be technically feasible (8). Proximate chemical analysis results of bole bark were found to be variable from tree to tree (9).

The second objective here has been on increasing pulp yield with raw materials containing bark which has rarely been reported in the literature. Anthraquinone pulping process has been employed to increase the pulp yield of debarked woods (10-12) only. Bark

being 10-25% in hard woods (14), its incorporation is bound to increase the yield and AQ pulping will further increase the yield. In place of juvenile tree wood chips here, trees as old as 70-80 years (13) have been employed for AQ pulping previously for which hard wood bark was susceptible to rejection.

EXPERIMENTAL

The following samples, collected from the nearby mill have been studied:

1. Unbarked casuarina equisetifolia (bole portion)
2. Unbarked casuarina equisetifolia (branch portion)
3. Debarked casuarina equisetifolia (bole portion)
4. Debarked casuarina equisetifolia (branch portion)
5. Debarked eucalyptus tereticornis
6. Unbarked cassia siamea (chakunda)
7. Unbarked leucaena leucocephala (subabul)
8. Dendrocalamus strictus (salia)
9. Bambusa arudinacea (daba).

Chipping was carried out in the mill chipper. For proximate chemical analysis, the chips were ground to powder in Wiley grinding mill.

The pulping was conducted in a Rotary digester (15 It capacity) using white liquor from the mill and following to kraft process.

Anthraquinone was added 00.1% in to the white liquor first and the resultant liquor was added to the chips in the digester prior to cooking. AA concentration was varied from 15 to 17%.

RESULTS AND DISCUSSION

The proximate chemical analysis was first carried out, results of which are given in Table 1 for the 4 raw materials studied. The cold and hot water as well as 1% NaOH solubility values vary from sample to sample. In case of leucaena leucocephala and cassia siamea, 1% NaOH solubility values are as high as 24.9%.

However, the A-B extractive values in the unbarked hard woods are not very high; for mixed unbarked casuarina, it is 2.05% and for mixed debarked casuarina it is 1.0%, 3.86% for leucaena leucocephala and 4.6% for cassia siamea. The comparison in unbarked and debarked mangifera indica (25) shows that former has 4.5% and the later, 3.9% i.e. difference of 0.6% which is quite acceptable.

The lignin content in cassia siamea is comparatively very high i.e. 28.9% next being in leucaena leucocephala which is 24.9%. In mixed unbarked casuarina it is 24.8% and in mixed casuarina it is 23.5%; mangifera indica has 21.9% in unbarked and 21% in debarked (25) samples. Unbarked mangifera indica wood thus has lower lignin content and it should be quite acceptable for quality paper manufacturing. The holocellulose content is 69.2% and 70.9% in casuarina, 67.5% in leucaena leucocephala and 69.6% in cassia siamea. The pentosan contents in casuarina, leucaena leucocephala and cassia siamea are 15-19% which are in the acceptable range for hard wood. The ash content of casuarina is 1.94% and 1.83% compared to 2.1% in unbarked mangifera indica (25) and other hard woods. Based on the

Table 1. Proximate chemical analysis

Particular	Casuarina unbarked	Casuarina debarked	Leucaena leucocephala	Cassia siamea
Cold water solubility (%)	3.48	2.52	9.45	12.23
Hot water solubility (%)	3.61	2.51	10.45	10.65
1% NaOH solubility (%)	18.5	17.6	24.9	24.58
A-B extractive (%)	2.05	1.0	3.84	4.6
Kalason Lignin (%)	24.8	23.5	24.9	23.8
Holocellulose (%)	69.2	70.9	67.5	69.0
Pontosan (%)	19.1	18.0	15.2	15.9
Ash content (%)	1.94	1.83	1.71	1.03

Table 2. Pulping characteristics of unbarked casuarina equisetifolia

Particular	Bole portion			Branch portion		
Active alkali as Na ₂ O (%)	15	15	15	15	15	15
AQ dose (%)	0	0.05	0.1	0	0.05	0.1
Screened yield (%)	51.6	52.5	53.2	50.3	51.4	51.25
Reject (%)	0.2	0.4	0.25	0.1	0.48	0.5
Total yield (%)	52.0	52.7	53.8	50.4	51.9	51.8
Kappa No.	19.0	16.3	17.5	21.0	20.1	20.2
Viscosity (cP)	9.2	11.1	9.3	9.9	11.3	10.3
α - cellulose (%)	89.0	-	88.9	85.8	86.0	87.4
β - cellulose (%)	9.78	-	9.8	12.04	11.5	11.84
γ - cellulose (%)	1.22	-	1.3	2.16	2.5	1.16

Table 3. Pulping characteristics of debarked casuarina equisetifolia

Particular	Bole portion		Branch portion		
Active alkali as Na ₂ O (%)	13	13	13	13	13
AQ dose (%)	0	0.1	0	0.05	0.1
Screened yield (%)	53.1	54.1	54.6	54.9	58.9
Reject (%)	0.4	2.4	0.54	0.4	0.4
Total yield (%)	53.5	56.5	55.1	55.3	57.3
Kappa No.	20.2	19.9	20.7	19.9	19.3
Viscosity (cP)	13.4	13.9	13.9	16.1	17.7
α - cellulose (%)	85.05	85.6	79.0	-	83.1
β - cellulose (%)	12.75	12.18	17.7	-	14.8
γ - cellulose (%)	2.2	2.2	3.2	-	2.1

proximate chemical analysis, the unbarked hard woods can very well be used for quality paper manufacturing. These results are comparable with our earlier results for leucaena leucocephala (14) and casuarina (15).

Five different samples of casuarina have been studied, namely of mixed dimensions (25); unbarked and debarked bole and branch portions. The mixed casuarina samples have been cooked at 15, 16 and 17% of active alkali, results of which were presented earlier (25). The AQ doses employed are 0.05 and 0.1%. The AQ pulping process is thus valid in the mixed unbarked casuarina also.

The results of unbarked individual samples are given in Table 2 and for debarked samples in

Table 3. The AA percentage employed in the unbarked samples is 15% while in debarked samples, it is 13%. The earlier mixed sample (25) was from different source and therefore higher AA was employed. In the present unbarked bole samples, the kappa number obtained at 0.05% AQ is reduced to 16.3 from initial value of 19 which is quite significant. However, in the branch unbarked sample the kappa no. remained fixed at 20.1 - 20.2. The yield value without AQ is 51.6% which increased to 53.2% in the bole portion which it increased from 50.3% to 51.2% in the branch sample. These increases of 1.6% in the former and 0.9% in the later are much lower than in the mixed samples studied earlier (25). In case of the debarked samples (Table-3), cooked at 13% of AA, the screened

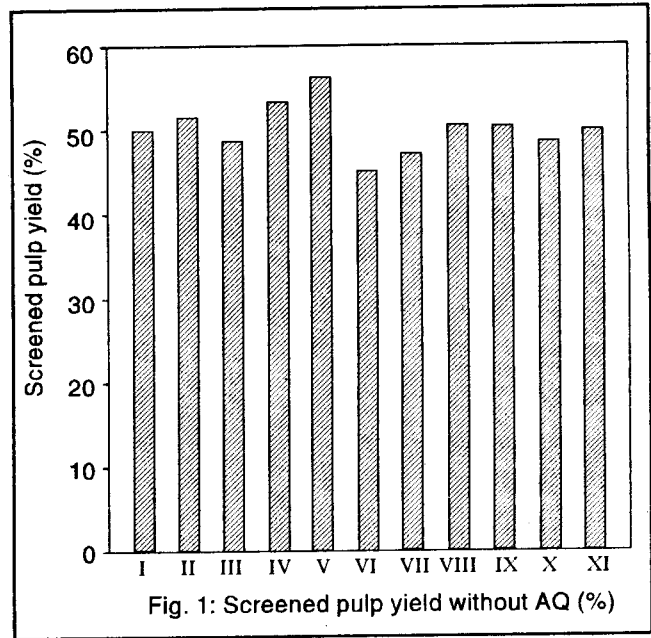
Table 4. Pulping characteristics of debarked eucalyptus tereticornis

Particular	Debarked eucalyptus tereticornis	
Active alkali as Na ₂ O (%)	14	14
AQ dose (%)	0	0.05
Screened yield (%)	46.0	48.9
Reject (%)	0.1	0.15
Total yield (%)	46.1	49.1
Kappa No.	20.1	16.9
Viscosity (cP)	8.1	9.6
α - cellulose (%)	81.1	82.95
β - cellulose (%)	17.18	14.5
γ - cellulose (%)	1.72	2.55

yield value is 53.1% in bole and 54.6% in the branch sample, which increased to 54.1% and 56.9% respectively on AQ addition (0.1%). The rise in yield in the debarked samples compared to the unbarked samples is obvious as the bark has lesser fibrous value than the wood. However, considering the rejection of 12% of bark in the debarked portion, the overall yield in the unbarked samples will be high. The kappa number at 13% AA is 20.2 while it is 19 in unbarked samples with 15% AA.

As in the literature (17), the viscosity values are reported to have increased on AQ application, viscosity has been measured here also. In the unbarked bole sample in particular, the viscosity value increases from 9.2 cP to 11.1 cP on addition of 0.05% of AQ.

The viscosity values of debarked samples are,



however, higher than the unbarked samples. Thus the incorporation of bark causes some decrease in strength property; it is quite high in the branch sample in particular. However, the viscosity values obtained in the unbarked samples, are quite acceptable.

Fig. 1 represents the histograms for screened pulp yield of all the samples studied (I-mixed casuarina (25), II-unbarked casuarina (bole portion), III-unbarked casuarina (branch portion), IV - debarked casuarina (bole portion), V- debarked casuarina (branch portion), VI - debarked eucalyptus, VII - unbarked cassia siamea (25), VIII- unbarked leucaena leucocephala (25), IX - debarked mangifera indica (25), X - dendrocalamus strictus, and XI - Bambusa arundinacea) without AQ and Fig. 2 with AQ. A regular relationship between

Table 5. Pulping characteristics of bamboo

Particular	Dendrocalamus strictus			Bambusa arundinacea		
Active alkali as Na ₂ O (%)	18	18	18	18	18	18
AQ dose (%)	0	0.05	0.1	0	0.05	0.1
Screened yield (%)	50.04	53.8	51.6	50.8	51.5	52.3
Reject (%)	0.1	0.06	0.1	0.05	0.1	0.03
Total yield (%)	50.14	53.7	51.6	50.85	51.6	52.33
Kappa No.	21.1	20.8	20.4	16.7	16.3	15.9
Viscosity (cP)	11.7	12.0	10.4	10.8	11.2	8.4
α - cellulose (%)	86.91	86.74	85.63	88.09	90.86	89.2
β - cellulose (%)	10.99	11.93	12.79	10.7	7.4	7.94
γ - cellulose (%)	2.1	1.33	1.58	1.21	1.74	2.86

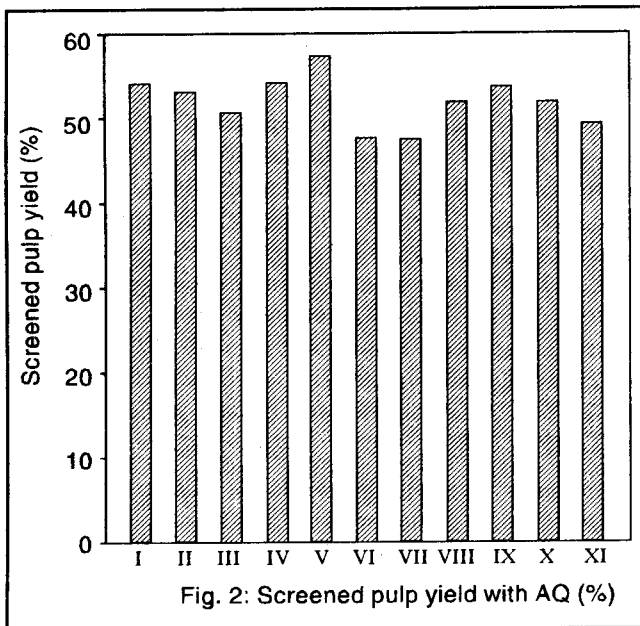


Fig. 2: Screened pulp yield with AQ (%)

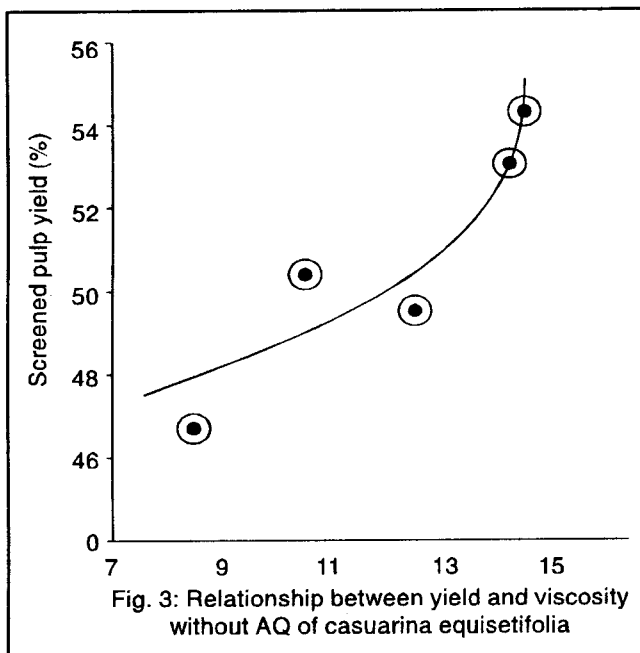


Fig. 3: Relationship between yield and viscosity without AQ of casuarina equisetifolia

screened yield and viscosity has been observed in the casuarina samples without AQ (Fig.3) and with AQ as well (Fig. 4). Higher the screened yield in a sample, higher is the viscosity in general. In order to interpret this relationship, α , β and γ celluloses in all the four casuarina samples have been determined. It is normally accepted that higher strength property is due to more percentage of α -cellulose.

In Table 4, results for debarked eucalyptus on AQ-pulping, cooked with 14% AA are presented. The yield increases by 2.9% with 0.05% AQ. It is

interesting to find decrease of kappa number by 3. The viscosity value of pulp without AQ is 8.1 cP and with AQ, 9.6 cP. These viscosity values are however lower than those of unbarked casuarina samples. The lower cellulose content in eucalyptus compared to that in casuarina corresponds to the low viscosity value in the former.

The results of unbarked cassia siamea were given previously (25) with cooking at 17% AA. The increase in yield due to AQ pulping is only 0.9% which is much lower than in other samples.

Pulping characteristics of unbarked leucaena leucocephala were shown earlier (25). The increase in yield in leucaena leucocephala is 1.7% due to AQ addition. Significant rise in yield (3.4%) was observed on AQ treatment (0.2%) in mangifera indica (25).

Two bamboo samples have also been taken for study, results of which are given in Table 5. Pulping of first sample with 18% AA and the second one with 16% AA, results in kappa no. of 21.1 and 16.7 respectively (without AQ). The corresponding yield values for the two samples are 50.1% and 50.85%, which increased to 53.7% with 0.05% AQ and to 52.3% with 0.1% of AQ. In dendrocalamus strictus, the increase is quite substantial (3.6%). The viscosity values are unexpectedly on the lower sides in bamboo though the cellulose content in bambusa arundinacea in particular is as high as 90.86%.

The increase in yield due to AQ has been summarized in Table-6. The response of AQ pulping

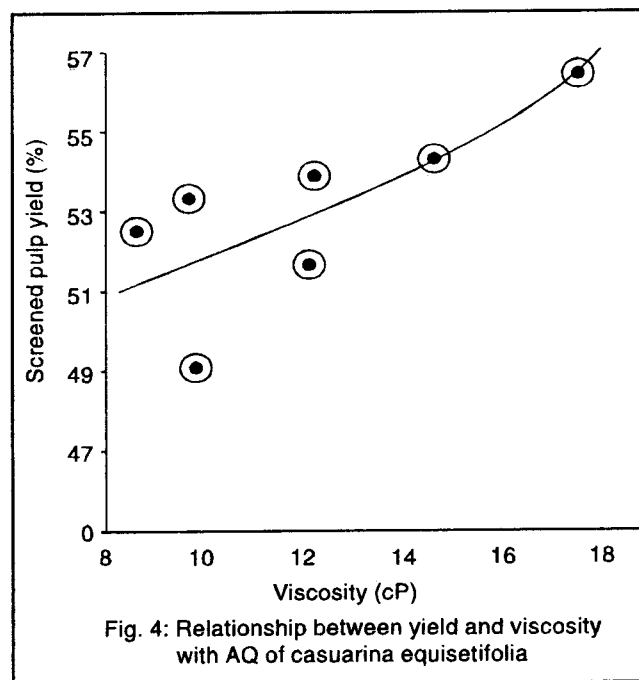


Fig. 4: Relationship between yield and viscosity with AQ of casuarina equisetifolia

Table 6. Maximum increase in yield due to AQ for each raw material

Raw material	AQ dose (%)	Increase in yield (%)
Mixed unbarked casuarina	0.1	3.4
Unbarked casuarina (bole portion)	0.1	1.6
Unbarked casuarina (branch portion)	0.05	1.1
Debarked casuarina (bole portion)	0.1	1.0
Debarked casuarina (branch portion)	0.1	2.3
Debarked eucalyptus	0.05	2.9
unbarked cassia siamea	0.1	0.9
Unbarked leucaena leucocephala	0.1	1.7
Debarked mangifera indica	0.1	2.8
Dendrocalamus strictus	0.05	2.5
Bambusa arundinacea	0.1	1.5

thus varies from raw material to raw material. The increasing trend is as follows:

Casurina equisetifolia > mangifera indica >

dendrocalamus strictus > leucaena leucocephala > bambusa arundinacea > cassia siamea > eucalyptus tereticornis.

Studies have also been conducted on bark alone for casuarina, eucalyptus tereticornis, leucaena leucocephala and cassia siamea, results of which are given in Table 7 and 8. The casuarina represents the mixed samples (25). The screened yield of casuarina bark is 24.6% here which could be elevated to 29.1%, increase of 4.5% on AQ treatment. In eucalyptus, the increase has been from 33.9% to 36.9% i.e. 3.0%; in leucaena leucocephala the increase is from 30.3% to 32.9% (2.6% increase) and in cassia siamea 30.3% to 32.1% (1.8%).

Increase in yield by 4.5% in casuarina due to anthraquinone is noteworthy. Such augmentation in yield due to AQ has been rarely reported earlier. Effect of AQ on casuarina bark has been quite selective compared to other hard woods.

Mechanism through which anthraquinone induces accelerated delignification resulting in lower kappa number and arrests peeling reaction of carbohydrates leading to increased yield, is well documented (18-24). Stabilisation of carbohydrates with AQ takes place by the oxidation of the reducing end groups. The analysis results of γ Band cellulose in Table 2, 3, 4 and 5 can be critically examined along with the increase in yield on AQ addition to focus on the

Table 7. Pulping characteristics of casuarina and eucalyptus bark

Particular	Casuarina bark			Eucalyptus bark		
	15	15	15	17	17	17
AA dose (%)	15	15	15	17	17	17
AQ dose (%)	0	0.05	0.1	0	0.05	0.1
Screened yield (%)	24.6	26.2	29.1	33.9	36.3	36.9
Reject (%)	2	1.7	1.8	-	-	-
Total yield (%)	26.6	27.9	30.9	33.9	36.3	36.9
Kappa No.	24.3	23.9	21.5	22.7	21.4	21.0

Table 8. Pulping characteristics of loucaena leucocephala and cassia siamea bark

Particular	Lecuaena leucocephala bark			Cassia siamea bark		
	17	17	17	17	17	17
AA dose (%)	17	17	17	17	17	17
AQ dose (%)	0	0.05	0.1	0	0.05	0.1
Screened yield (%)	30.3	32.4	32.9	30.3	31.35	32.3
Reject (%)	-	-	-	-	-	-
Total yield (%)	30.3	32.4	32.9	30.3	31.35	32.1
Kappa No.	32.0	26.4	25.8	26.5	24.4	23.1

Table 9. Bleaching characteristics of unbarked casuarina equisetifolia

Particular	Bole portion			Branch portion		
	A	B	C	A	B	C
Sequence	DEpD	DEpD	DEpD	DEpD	DEpD	DEpD
Total ClO ₂ applied (%)	3.18	2.9	2.69	3.39	3.09	3.1
Total ClO ₂ consumed (%)	3.15	2.8	2.67	3.36	3.07	3.07
ClO₂ stage I						
ClO ₂ applied (%)	2.54	2.32	2.15	2.71	2.47	2.48
ClO ₂ consumed (%)	2.53	2.31	2.14	2.7	2.46	2.47
Retention (hr)	4	4	4	4	4	4
End pH	3.1	3.2	3.1	3.6	3.7	3.6
Extraction						
Alkali applied (%)	0.84	0.76	0.71	0.9	0.82	0.82
H ₂ O ₂ applied (%)	0.3	0.3	0.3	0.3	0.3	0.3
End pH	11.2	11.4	11.5	11.7	11.4	11.7
ClO₂ stage II						
ClO ₂ applied (%)	0.63	0.56	0.54	0.67	0.62	0.62
ClO ₂ consumed (%)	0.62	0.55	0.53	0.66	0.61	0.6
Retention (hr)	2	2	2	2	2	2
End pH	3.1	3.2	3.5	3.6	3.2	3.8
Bleached yield (%)	47.5	48.2	49.16	45.9	46.1	46.1
Shrinkage (%)	7.2	6.6	7.5	8.8	10.5	10.0

machanism. In Table 2 in particular, with unbarked casuarina in branch portion, the α cellulose has increased from 85.8% to 87.1% on AQ addition of 0.1% but the β cellulose has decreased from 12.04% to 11.84% and γ cellulose from 2.16% to 1.16%. It is likely that some of β and γ cellulose molecules get converted to cellulose by bonding of the small carbohydrate groups. In case of debarked casuarina for branch portion, this hypothesis is quite valid as the increase of α -cellulose has been from 79% to 83.1% on AQ addition with corresponding decrease of β -cellulose from 17.7% to 14.8% and γ -cellulose from 3.2% to 2.1%. In case of bambusa arundinacea (Table 5) also such trend has been observed. The bark samples in Table 7 and 8 showing increase in yield can have bearing on similar trend.

Bark in casuarina tree is comparatively thin and intimately adhered to the wood so much so that debarking in casuarina becomes quite costly and it may be economical to use unbarked casuarina. Moreover, in casuarina, the bark content amounts to 10-12% unlike in eucalyptus where it may be from

18 to 25%.

Unbarked casuarina is already in use in mill scale for quality paper manufacturing. Extensive works have been carried out to establish that no major problem is confronted during manufacturing. As the trees are juvenile where the bark contains fairly rich fibre value and is devoid of dirt, no problems were encountered. Use of bark has bearing on environmental protection as trees equivalent to bark, i.e. 10-15% need not be felled. The yield and kappa no values indicate clearly that chemical requirements will not be high.

Bleachability

In view of the exigence for ECF bleaching from environmental aspect it has been applied to these raw materials both with and without oxygen delignification (26). Bleaching sequence of DEpD has been employed to the pulps produced with AQ pulping here. The bleaching characteristics of casuarina equisetifolia, unbarked and debarked samples (bole and branch portions) are given in Table 9 and Table 10

Table 10. Bleaching characteristics of debarked casuarina equisetifolia

Particular	Bole portion		Branch portion		
	A	C	A	B	C
Sequence	DEpD	DEpD	DEpD	DEpD	DEpD
Total ClO ₂ applied (%)	2.63	3.06	3.18	3.06	2.96
Total ClO ₂ consumed (%)	2.6	3.02	3.15	3.02	2.94
ClO₂ stage I					
ClO ₂ applied (%)	2.1	2.44	2.54	2.44	2.36
ClO ₂ consumed (%)	2.09	2.43	2.53	2.43	2.35
Retention (hr)	4	4	4	4	4
End pH	3.2	3.6	3.4	3.0	3.9
Extraction					
Alkali applied (%)	0.7	0.8	0.84	0.8	0.78
H ₂ O ₂ added (%)	0.3	0.3	0.3	0.3	0.3
End pH	11.6	11.9	11.3	10.9	11.7
ClO₂ stage II					
ClO ₂ applied (%)	0.52	0.6	0.63	0.6	0.6
ClO ₂ consumed (%)	0.51	0.59	0.62	0.59	0.59
Retention (hr)	2	2	2	2	2
End pH	3.1	3.3	3.1	3.4	4.1
Bleached yield (%)	48.7	50.4	47.3	49.5	52.0
Shrinkage (%)	8.8	7.4	6.0	9.0	8.6

respectively; for eucalyptus in Table 11 and for bamboo (dendrocalamus and bambusa arudinaces) in Table 12. The AQ percentage added, have been represented in the Tables as follows:

A- 0% AQ

B - 0.05% AQ

C - 0.1% AQ.

One common observation made on total ClO₂ consumed is that the consumption decreases with increase in AQ addition level (excepting in debarked bole portion). The increase in cost of AQ can thus partially be compensated by lesser ClO₂ demand. for example in Table 9 for unbarked casuarina, ClO₂ consumption decreases at 1% AQ, to 2.67% from 3.15% without AQ addition. This repercussion is effected in the extraction stage also where comparatively lower alkali is required in AQ treated pulps than that without AQ treatment.

The bleached yield values in all the raw materials have increased on AQ treated pulps compared to pulp without AQ treatment (26). The increases have been

Table 11. Bleaching characteristics of debarked eucalyptus tereticornis

Particular	A	B
Sequence	DEpD	DEpD
Total ClO ₂ applied (%)	3.09	2.6
Total ClO ₂ consumed (%)	3.07	2.58
ClO₂ stage I		
ClO ₂ applied (%)	2.47	2.08
ClO ₂ consumed (%)	2.46	2.08
Retention (hr)	4	4
End pH	4.1	3.6
Extraction		
Alkali applied (%)	0.82	0.69
H ₂ O ₂ applied (%)	0.3	0.3
End pH	11.4	11.6
ClO₂ stage II		
ClO ₂ applied (%)	0.62	0.52
ClO ₂ consumed (%)	0.61	0.5
End pH	3.9	4.9
Bleached yield (%)	43.1	45.9
Shrinkage (%)	5.8	0.6

Table 12. Bleaching characteristics of Bamboo

Particular	Dendrocalamus strictus			Bambusa arundinacea		
	A	B	C	A	B	C
Sequence	DEpD	DEpD	DEpD	DEpD	DEpD	DEpD
Total ClO ₂ applied (%)	3.24	3.2	3.1	2.57	2.5	2.45
Total ClO ₂ consumed (%)	3.14	3.13	3.1	2.54	2.48	2.42
ClO₂ stage I						
ClO ₂ applied (%)	2.54	2.56	2.5	2.04	2.0	1.96
ClO ₂ consumed (%)	2.51	2.5	2.5	2.03	1.98	1.95
Retention (hr)	4	4	4	4	4	4
End pH	3.6	3.2	3.3	3.3	3.3	3.5
Extraction						
Alkali applied (%)	0.84	0.84	0.83	0.68	0.66	0.65
H ₂ O ₂ applied (%)	0.3	0.3	0.3	0.3	0.3	0.3
End pH	11.9	11.4	11.2	11.5	11.4	11.2
ClO₂ stage II						
ClO ₂ applied (%)	0.64	0.64	0.6	0.52	0.5	0.48
ClO ₂ consumed (%)	0.63	0.63	0.59	0.51	0.5	0.47
Retention (hr)	2	2	2	2	2	2
End pH	3.1	3.4	3.2	3.2	3.1	3.1
Bleached yield (%)	45.03	48.9	47.5	46.5	47.4	48.5
Shrinkage (%)	10.0	9.4	8.2	8.6	8.2	7.6

shown in Table 13. The results indicate evidently that anthraquinone helps in increasing the yield in all the raw materials but to different degree in different raw materials. In case of debarked casuarina, it is as high as 4.7% at 0.1% of AQ and in dendrocalamus strictus also it is quite high (3.87% at 0.05% AQ and 2.47% at 0.1% AQ). In the unbarked casuarina, it is upto 1.66% with 0.1% AQ. Thus the increasing trend observed in the unbleached pulp yield also appears in bleached pulp yield due to AQ addition. In debarked casuarina the bleached pulp yield is as high as 50.52% at 0.1% AQ.

The shrinkage in casuarina bole portion remains unchanged on AQ addition unlike in the branch portion in both unbarked and debarked samples. In bamboo, shrinkage decreases while in eucalyptus it remains practically unchanged on AQ-pulping. The optical properties along with viscosity value of the bleached pulp samples are shown in Tables 14 to 17. The brightness values are all above 80% EI, the highest observed being in debarked eucalyptus. In the unbarked casuarina, it is lesser by 1-2 degree from the debarked casuarina. The P.C. no. of all the AA treated pulps

Table 13. Increase in bleached pulp yield at different AQ level

Raw material	0.05% AQ	0.1% AQ
Unbarked casuarina (bole portion)	0.7	1.66
Unbarked casuarina (branch portion)	0.2	0.2
Debarked casuarina (bole portion)	-	1.7
Debarked casuarina (branch portion)	2.2	4.7
Debarked eucalyptus	2.8	-
Dendrocalamus strictus	3.87	2.47
Bambusa arundinacea	0.9	2.0

is worth noting as these are mostly <2. In the unbarked casuarina also it is quite low, 1.6-2 no. Such low P.C. no was not obtained even on oxygen delignified pulp subjected to DEpD bleaching (26).

Table 14. Optical and viscosity properties of unbarked casuarina equisetifolia

Particular	Bole portion			Branch portion		
	A	B	C	A	B	C
Brightness (% EI)	81.0	81.3	79.5	82.0	81.8	82.1
P.C. Number (no.)	1.8	1.7	1.6	1.6	2.1	1.9
Viscosity (cP)	8.4	7.8	7.7	8.8	8.5	9.0

Table 15. Optical and viscosity properties of debarked casuarina equisetifolia

Particular	Bole portion		Branch portion		
	A	C	A	B	C
Brightness (% EI)	82.5	82.2	85.6	83.7	84.0
P.C. Number (no.)	1.8	2.1	1.4	1.8	1.4
Viscosity (cP)	8.1	8.4	8.1	7.8	8.0

Table 16. Optical properties and viscosity of Debarked Eucalyptus tereticornis

Particular	A	B
Brightness (% EI)	85.7	85.8
P.C. Number (no.)	1.7	1.5
Viscosity (cP)	6.5	6.7

The viscosity values of unbarked and debarked bleached casuarina pulps are fairly same (8-9 cP). Thus the strength properties can be considered to be quite good on AQ pulping, following to bleaching with DEPD sequence. Surprisingly, the bleached pulp

viscosity in AQ treated dendrocalamus strictus, is lowered to 6.5 - 6.9 from 8.8 cP.

The zero span breaking length and FS factors for all the bleached pulp samples have been determined in Pulmac trouble shooter, the results being in Tables 18-21. The change in the unbarked casuarina due to AQ addition is not significant however in the debarked sample, the zero span breaking length has increased to some extent namely from 6414 m to 9657 m with 0.1% AQ. In eucalyptus also similar increase was observed but not in the two bamboos studied. The FS factor is also found to have increased from 16.2 to 19.5 in the debarked casuarina with 0.1% AQ. The FS factors in the unbarked casuarina remain practically same on AQ addition. The analysis results of black

Table 17. Optical and viscosity properties of Bamboo

Particular	Dendrocalamus strictus			Bambusa arundinacea		
	A	B	C	A	B	C
Brightness (% EI)	79.9	80.3	80.9	81.1	81.5	81.4
P.C. Number (no.)	2.2	2.0	1.6	1.9	1.7	1.5
Viscosity (cP)	8.8	6.9	6.5	10.0	7.8	8.0

Table 18. Zero span breaking length and F.S. Factor of unbarked Casuarina equisetifolia

Particular	Bole portion			Branch portion		
	A	B	C	A	B	C
Zero span breaking length (m)	6767	6503	6006	7355	6957	7238
F.S. Factor	14.5	14.2	14.5	14.2	13.1	14.2

Table 19. Zero span breaking length and F.S. Factor of debarked *Casuarine equisetifolia*

Particular	Bole portion			Branch portion		
	A	B	C	A	B	C
Zero span breaking length (m)	6767	6503	6006	7355	6957	7238
F.S. Factor	14.5	14.2	14.5	14.2	13.1	14.2

Table 20. Zero span breaking length and F.S. factor of debarked *Eucalyptus tereticornis*

Particular	A	B
Brightness (% EI)	6669	7464
F.S. Factor	13.2	14.8

liquor are planned to be presented in a subsequent paper.

CONCLUSION

AQ pulping process is effective to unbarked hard woods, namely casuarina, leucaena leucocephala and cassia siamea. Unbarked casuarina is shown to attain yield of 54.9%, higher than that in debarked eucalyptus tereticornis (48.9%), bambusa arundinacea (52.3%) and same as in dendrocalamus strictus (53.6%) in AQ pulping. Highest screened yield of 56.9% with kappa no. of 9.3 (13% AA) in debarked casuarina with 0.1% AQ has been obtained. The kappa number for 54.9% yield is 23.5 in mixed casuarina with 15% AA. However, kappa number of 16-17 was obtained in the bole portion with 53-55% yield in 15% AA on AQ application. Increase in yield by 4.5% in casuarina bark due to AQ has been shown. Corresponding increase in bleached pulp yield values (upto 4.7%) due to AQ pulping both in unbarked and debarked casuarina equisetifolia as well as in other raw materials, has been observed. Considering the techno-economical reasons, it has been recommended that juvenile unbarked hard woods can be used safely for quality paper manufacturing.

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REFERENCES

1. Auchter, R.J., *Tappi J.*, 58 (11) : 5 (1975).
2. Mills, C.F., *Tappi J.*, 63 (9) : 39 (1980).
3. Casey, J.P., *Pulp and Paper Chemistry and Chemical Tech.*, 3rd Edn., Vol I, Wiley Intersci, Publ., P. 420 (1980).
4. Parham, R.A., Chapter X, *Pulp and Paper Manufacture*, 3rd Edn., Vol I, Ed. M.J. Kocurek, CPPA, Montreal, P. 73 (1983).
5. Moore, G.A. and Balodis, V., *Appita J.*, 42 (3) : 201 (1989).
6. Smook, G.A., *Hand book for Pulp and Paper Technol.*, Joint text book, Committee of Paper Industry (Tappi CPPA) 16 (1982).
7. Fuller, S.W., Chapter XIII, *Pulp and Paper Manufacture*, 3rd Edn. Vol. I Ed. M.J. Kocurek, CPPA, Montreal, P. 107 (1983).
8. Logan, A.F., Phillips, F.H. and Des-Harries, E., *Appita J.*, 40 (3): 176 (1987).
9. Pereira, H. and Sardinha, R., *Appita J.*, 37 (8) : 660 (1984).
10. Jameel, H., Gratzl, J., Prasad, D.Y. and Chivukula, S., *Tappi J.*, 78 (9) : 151 (1995).
11. Jiang, J. Er., *Tappi J.*, 78 (2) : 126 (1995).

Table 21. Zero span breaking length and F.S. factor of Bamboo

Particulars	Dendrocalamns strictus			Bambusa arundinacea		
	A	B	C	A	B	C
Zero span breaking length (m)	8932	8736	8640	6682	6266	6664
F.S. Factor	16.8	15.7	18.3	16.4	14.4	14.2

12. Parthasarathy, V.R. Smith, G.C., Ruddle, G.F., Detty, A.E. and Steffy J.J., **Tappi J.**, 78 (2) : 113 (1995).
13. Phillips, F.H., Logan, A.F., Balodis, V. and Ward, J.V., **Appita J.**, 44 (3) : 173 (1991).
14. Rath, D.K. and Patel, M., **IPPTA J.**, 7 (4) : 17 (1995).
15. Puhan, PC, Sridhar, P., Gopichand, K. and Patel M., **IPPTA J.**, 5 (5) : 41 (1993).
16. Kumar,A., Gurumurthy, K. and Patel, M., **IPPTA J.**, 8 (4) : 13 (1996).
17. Rawat, R., Sharma, G.D., Bhargava, G.G. and Singh, M.M., **IPPTA J.**, 22 (3) : 39 (1985).
18. Holton, H.H. and Chapman, F.L., **Tappi J.**, 60 (11) : 121 (1977).
19. Fleming, B.I., Kubes, G.J., Macleod, J.M. and Bolker, H.I., **Tappi J.**, 61 (6) : 43 (1978).
20. Revenga, J.A., Rodriquez, F. and Ti Jero, J., **J. Pulp and Paper Sci.**, 21 (3) : J104 (1995).
21. Hart, P.W., Brogdon, B.N. and Hsich, J.S., **Tappi J.**, 76 (4) : 162 (1993).
22. Blain, T.J., **Tappi J.**, 76 (3) : 137 (1993).
23. Bhattacharya, P.K., De. S., Haldar, R. and Thakur, R., **Tappi J.**, 75 (8) : 123 (1992).
24. Blain, T.J. and Holton, H.H., **Pulp & Paper Canada**, 84 (6) : 58 (1983).