Utilisation of Hardwood Bark in Paper Manufacturing and Extraction of Chemicals

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ABSTRACT:- Casuarina and acacia with and without bark as well as the bark portion alone have been evaluated for production of quality paper. The level of deterioration in strength and optical properties of paper due to bark has been established. Results of proximate chemical analysis pulping and bleaching characteristics, physical strength properties, fiber morphology and optical properties of casuarina and acacia with and without bark are given. Strength and brightness properties of wood with 10, 20, 30 and 40% bark have been reported. The FS and bond factors have been determined using Pulmac Trouble Shooter. Processes for extraction of vanilin and fatty acid from bark have been presented.

INTRODUCTION

The recent crisis faced by paper manufacturers on the increasing market demand for quality paper with high brightness on the one hand and raw material scarcity on the other hand, were the reason for reinvestigating the properties of bark with a view to optimise its addition for manufacturing of quality paper.

Bark differs from woods in both anatomy and composition. In general, the same compounds that are present in the wood of a species are also found in bark, although the proportion may vary. The variety and extractive materials are usually much higher in bark than in wood. Hydroxy acid complexes do not occur in wood, but are the significant component in many barks. Bark lignins are accompanied by considerable amounts of alkali soluble substances that are phenolic in nature, that contains carbonyl group, and that has a lower methoxyl content than lignin (1).

For the most part, bark is formed by the cambium. The part of the bark that is produced directly by the dividing cells of the cambium is called phloem. This is composed mainly of thin-walled

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conductive cells called sieve tubes and parenchyma cells which are short, non-fibrous cells with contents of tannin and related organic materials that are sources of the dark colour of bark.

The goal of debarking (2) is to remove the maximum amount of the bark. leaving the wood intact and undamaged. The ease of removing bark from wood varies with a number of factors associated with the wood itself. The amount of bark that can be tolerated depends on the pulp-mill operations and equipments as well as on the intended use of the pulp.

Before the woods are chipped for pulping, they are debarked as per common practice. The debarking of hardwoods in forests produces large quantities of wastes, which need commercial exploitation, taking into account of environmental case. Pulping of woods with the barks of acceptable quality is one of the ways of solving the problem of pollution caused by these bark waste. Besides that the cost of debarking and bark disposal etc.. would also be eliminated.

Pulp and Paper Research Institute, JAYKAYPUR - 765 017 (Orissa) Pulping of hard woods with and without bark such as Anogeissus latifolia, Adina cardifolia, Burraserra serrata, Garuga pinnata, lannea grandis and xylia xylocarpa etc. have been carried out previously (3). Eucalyptus with bark has extensively studied in past (4-6). Effect of Douglous fir bark for pulping quality has also been studied (7-9). Chemical composition of Eucalyptus globulus laboratory bark has been reported by Sardinha and co-workers (10). However, in all these works, acacia bark was not examined and secondly optimisation study with varying percentage of bark to wood was not carried out.

EXPERIMENTAL

The unbarked wood samples of Acacia Catechu and Casuarina equisitifolia were collected from PAPRI Plantation area. Both the species were of 7 years age. Each wood log was manually debarked and the percentage of bark was determined on O.D. basis. In both cases, after removing the barks, the logs were chipped in the mill chipper. The chips were classified in the laboratory chip classifier.

PROXIMATE CHEMICAL ANALYSIS

The samples of wood and bark portions were taken separately and ground in Wiley mill. The powder was made to pass through 40 mesh and then analysed for different constituents following to TAPPI Standard. Holocellulose was determined by chlorite method (11).

PULPING

Pulping and bleaching experiments have been

carried out according to standard procedures (12-14).

RESULTS AND DISCUSSION

Characteristics of bark from casuarina and acacia are given in Table-1. Proximate chemical analysis of casuarina and acacia wood, wood with bark and bark samples are given in Table-2. The wood samples show normal properties. However, comparison of these properties with the other two, notably with that of bark, is found to be of interest which may be quite important in manufacturing of quality paper using either casuarina or acacia with bark.

The cold water solubility of casuarina bark is 11.7% and 14.9% in acacia bark compared to 2-3% in both the wood as well as wood with bark samples. This indicates that the bark contains lot of inorganic salts and monosaccharides. As acacia bark is thicker than that of casuarina, the amounts are more in the former.

The hot water solubility is correspondingly quite high in the bark samples, compared to 2-4% in the

Table-1

Characteristics of Bark

Particulars	1	2
Species	Casuarina equistifolia	Acacia Catechu
Bark content on O.D. basis (% w/w)	9.9	12.32
Bark thickness (mm)	5.1	6.3
Green volume density of wood. (g-cc)	0.55	0.52
Green volume density of bark. (g/cc)	0.38	0.41

			Table-2				
		Proximate	Chemical A	Analysis			
Property		Wood	Casuarina Wood with bark	Bark	Wood	Acacia Wood with bark	Bark
Cold water solubility	(%)	2.52	3.46	11.67	1.71	2.77	14.9
Hot water solubility	(%)	2.51	3.61	26.49	2.3	3.78	15.7
1% NaOH solubility	(%)	17.6	18.5	44.15	13.67	17.6	37.8
Alcohol-Benzene solubility	(%)	1.0	2.05	3.85	1.24	2.8	4.4
Klason Lignin.	(%)	23.5	24.8	32.5	27.56	29.3	34.9
Holocellulose.	(%)	70.9	69.2	58.4	69.9	64.9	53.0
Pentosan.	(%)	18.6	19.1	13.4	16.61	17.4	13.3
Ash,	(%)	1.83	1.94	5.5	2.17	2.54	3.8

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wood or wood with bark samples. The abnormally high value of 26.5% in casuarina bark (15.7% in acacia bark) is indicative of the fact that the inorganic material as well as carbohydrates and tannins are bonded with the fibre portion which requires hot water treatment for removal. Dark red colour is emitted from casuarina bark when put in water.

1% NaOH solubility is 44.15% in casuarina bark while it is 37.8% in acacia bark compared to 18% in both casuarina and acacia wood with bark.

Alcohol-benzene extractive in the bark is 3.85and 4.4% in the bark samples of casuarina and acacia respectively. When bark is there along with the wood, the corresponding values are 2.05 and 2.8%.

Lignin content of both casuarina and acacia wood with bark is higher by 1.3% than the wood sample (kappa no. increased (15) by (8.5%). In the bark samples of casuarina and acacia, the Klason lignin percentage is 32.5 and 34.9% respectively. The wood when used with bark for paper manufacturing will thus have a higher chemical demand than when wood alone is used (16-18).

The bark samples of both casuarina and acacia have quite low holocellulose content (58.4% for casuarina and 53% for acacia) compared to the wood part (70.9% and 69.9% respectively). In case of casuarina, the wood with bark, the holocellulose part decreases by only 1% while in acacia, it is 5% compared to the wood samples. Thus, in paper manufacturing, as far as strength properties are concerned, casuarina will make little difference when accompanied by bark but not acacia. The pentosan content in the samples of wood with and without bark remains more or less same. The ash content in casuarina bark is as high as 5.5% which is 3.8% in acacia bark. Therefore, high ash content of the barks, especially in casuarina is likely to cause scaling problems in the system.

The pulping characteristics of both casuarina and acacia wood, wood with bark and bark are given in Table-3. The active alkali (17%). bath ratio (1:2.7) steaming time (120 minutes) and cooking time (90 minutes) applied here are as per standard practice for kraft pulping process. The screened pulp yield of wood with bark is lower than in wood alone. In casuarina without bark the yield is 47.4% while in wood with bark, it is 46.5%. Acacia wood without bark has 47.3% of yield compared to 46.6% in the wood with bark. Thus there is increase in yield by 1.5% when bark is not contained in the raw material. Acacia has higher pulp vield than casuarina. The bark portion alone presents low yield: 19.6% in casuarina and 24.6% in acacia bark. As the lignin and A-B extractives are higher in bark, the debarked wood naturally presents higher yield than wood with bark. The rejects are also comparatively higher in the wood with bark. The total pulp yield of both casuarina and acacia wood are quite good (49.1% and 49.3%) but the wood with bark gives also fairly good yield 47.3% for casuarina wood with bark and 47.5% acacia wood with bark. In view of high lignin

			Table-3				
	Pulp	ing charac	teristics of	wood san	ıple		
Particulars		Wood	Casuarina Wood with bark	Bark	Wood	Acacia Wood with bark	Bark
Active alkali	(%)	17	17	21	17	17	21
Bath ratio		1:2.7	1:2.7	1:3	1:2.7	1:2.7	1:3
Steaming time (min)		120	120	120	120	120	120
$50^{\circ}C = 165^{\circ}C$ (min)		90	90	90	90	90	90
Cooking time at 165°C Screened pulp yield	(%)	47.4	46.5	19.6	47.6	47.0	24.6
· Rejects	(%)	0.5	2.2	2.8	0.8	2.3	2.6
Total pulp vield	(⁹ %)	47.9	48.7	22.4	48.4	49.3	27.2
Kappa number		18.7	21.3	37.0	16.8	18.5	35.7

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and A-B extractive in bark, the kappa no. is quite high in wood with bark, specially in casuarina. The black liquor analysis results are given in Table-4. The pH is 10.4 which is mariginally alkaline. The residual active alkali (as Na₂O) of bark is minimum compared to the wood and wood with bark. The total solids in the black liquor are 23-24% for all the three samples of casuarina and 24-25% in acacia.

The pulping conditions corresponding to casuarina with various proportions of bark are same as in Table-3. The pulp yield values are given in Table-5. As the proportion of bark increases, the yield value decreases and reject percentage increases. With 20% addition of bark to the wood, the yield value decreases to 42% while on 30% addition, the yield is 40%. Considering the yield and other properties, discussed below, bark can be added upto 20% to the wood.

The bleaching characteristics of casuarina and acacia pulp of three different categories i.e. wood, bark and wood with bark are furnished in Table-3. The results clearly show the difference in chemical consumption between wood and bark. Bark has a darker shade, higher kappa no. and lower pulp yield than wood and wood with bark in both casuarina and acacia. It can be found from the table that the wood with bark has a kappa number 2-3 no. more than in wood alone, while the kappa no. of bark (37) is double than that of wood (18.7).

Consequently, the chemical consumption is in following order:

Bark > Bark with wood > Wood.

Similar to the kappa no.. the chlorine consumption in bark is about double than in wood, the increase being intermittent for wood with bark.

The results of strength properties (Table-4) of hand sheets from bleached pulp for casuarina and acacia indicate lower strength for wood with bark than wood alone while strength of bark sample is very poor. These results correspond to the proximate chemical analysis, namely cellulosic fibre and lignin. The % reduction in strength properties of wood with bark compared to wood are as follows:

	Casuarina	Acacia
Burst factor	6.3	9
Tear factor	4.13	10.3
Breaking length	6.3	8.18
Double fold	18	5.71

	Table-4				
Black	liquor anal	ysis			
	Casuarina			Acacia	-
Wood	Wood with bark	Bark	Wood	Wood with bark	Bark 10.4 8.7 25.1
10.4	10.5	10.1	10.3	10.5	10.4
11.8	10.5	9.3	12.0	10.5	8.7
22.9	23.5	24.5	23.6	24.5	25.1
	Wood 10.4 11.8	Black liquor anal Casuarina Wood Wood with bark 10.4 10.5 11.8 10.5	Table-4Black liquor analysisCasuarinaWoodWood with barkBark bark10.410.510.111.810.59.3	Table-4Black liquor analysisCasuarinaWoodWood with barkBark Wood10.410.510.110.311.810.59.312.0	Table-4Black liquor analysisCasuarinaAcaciaWoodWood with barkBark WoodWood with bark10.410.510.110.310.511.810.59.312.010.5

Table-	5
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Pulping yield of casuarina with varying properties of bark

Property		Casuarina	Wood and bar	k ratio		
	100:0	90:10	80:20	70:30	60:40	0:100
Screened yield	47.4	46.5	39.6	37.1	32.3	19.6
Rejects	0.5	2.2	2.4	2.5	2.8	2.8
Total yield	47.9	48.7	42.0	39.6	35.1	22.4

This information may be quite useful for mills using wood with bark for production of superior grade paper. On the other hand, for production of inferior quality of paper, it is obvious that wood with bark can be used. The paper produced from bark alone has poor strength properties.

The optical and viscosity properties are shown in Table-5. It can be seen that the brightness in wood with bark decreases by 2.53% El compared to wood, while the corresponding increase in P.C. No. is 1. Bark of acacia has higher brightness than casuarina. The viscosity of wood is also marginally higher than wood with bark because of corresponding cellulose content.

As the above results show, bark alone cannot be used and therefore, it was added with wood in 10, 20, 30 and 40% and the resultant pulp was examined for strength properties (Table-6) in case of casuarina only. It can be seen that even at 40% addition level, the breaking length is 3826 m with tear factor of 50.2 and burst factor of 20.4, which may be suitable for even same grade of quality paper.

The brightness value goes on decreasing with increase in percentage of bark (Histogram-Fig.-1) in wood similar to the strength properties. However, with 40% addition of bark, brightness of 70.9% El is obtained which is 75.6% El at 30% and 78.4% El at

20% addition of bark. Thus; 30% addition of bark can safely be made for production of same quality paper, i.e., 10% additional to the wood without debarking.

The fibre classification result (Table-7). determined from the Bauer McNett classifier. shows high fraction of fines in the bark (45.4% in casuarina and 40.6% in bark in-100 mm fraction).

The fibre morphology of bark (Table-8) again is found to be quite inferior compared to wood. The poor strength properties of bark correspond to the low fibre length of bark.

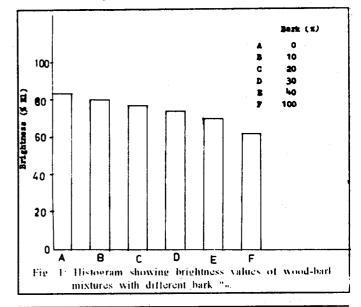


Table-6

Bleaching Characteristics of hard wood

Particulars		Wood	Casuarina Wood with bark	Bark	Wood	Acacia Wood with bark	Bark
Kappa No.		18.7	21.3	37	16.8	18.5	35.7
Chlorination:							
Chlorine added,	0.0	5.61	6.4	11.0	5.1	5.55	10.7
Chlorine consumed.	9-u	5.54	6.1	10.8	4.8	5.1	9.8
Final pH.		1.8	1.8	1.5	1.8	1.8	1.5
Extraction:							
Alkali added.	0/0	1.75	1.75	2.7	2.1	2.4	3.5
as NaOH							
Final pH		10.7	10.5	10.3	11.0	11.1	10.5
Нуро:							
Hypo added,	9/e	1.9	2.15	3.7	1.7	1.85	3.6
Buffer added.	0/0	1	0.5	0.5	0.5	0.5	0.5
Final pH.		8.3	.8.5	8.1	8.3	8.3	8.0
Chlorine consumed,		1.85	2.15	3.4	1.7	1.75	3.1

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	P	nysical stren	gth properti	es at 40°	SR		
Property		Wood	Casuarina Wood with bark	Bark	Wood	Acacia Wood with bark	Bark
Bulk. Burst factor, Tear factor, Breaking length, Double fold Zero span breaking	(cc/g) (m) (no) (m)	1.68 34.29 57.1 5679 22 11,852	1.64 32.13 54.74 5322 18 11,297	0.48 11.45 28.57 2354 1	1.36 37.6 37.24 5755 35 12,063	34.26 33.4 5284 33 11,598	13.24 20.84 2773 1 7,126

Optical	and Viscosity Pr	operties of	Table-8 Casuarina a	nd Acaci	a with and	without bar	rk
Property		Wood	Casuarina Wood with bark	Bark	Wood	Acacia Wood with bark	Bark
Brightness	(% El)	82.8	80.3	62.0	83.5	80.4	68.0
P.C. Number Viscosity	(Cp)	10.8 6.8	11.6 6.3	15.0 3.1	10.7 7.2	11.5 6.7	14.5 3.8

Tahle-9

1.1.

			Table->				
Physical Strength Properties of Casuarina with varying proportion of bark							
Properties		Wood without bark 100 : 0	Wood with bark* 90 : 10	Wood : Bark 80 : 20	Wood : Bark 70 : 30	Wood : Bark 60 : 40	Bark 0 : 100
Bulk Burst factor	(cc/gm)	1.68 34.29	1.64 28.13	1.48 25.98 56.82	1.45 23.42 51.05	1.38 20.36 50.24	0.48 11.45 28.57
Tear factor Breaking Length Double fold Brightness	(m) (m) (% El)	5679 22 82.8	4348 15 80.3	56.82 4140 13 78.4	4020 11 75.6	3826 8 70.9	2354 1 72

* Wood containing bark; in others, bark added separately.

Table-10									
	Bauer McNe	tt Clas	sification of	pulp (B	leached)				
Particulars (Mesh size in mm)		Ca: Wood	suarina (% Retain Wood with bark	ied) Bark	A Wood	Acacia (% Retained Wood with bark) Bark		
+16		0.5	0.7	0.2	1.2		0.3		
-16 +30		38.3	35.3	17.5	9.0		24.2		
-30 +50		21.0	22.4	14.8	43.8		11.5		
-50 + 100		13.8	12.6	22.1	28.0		23.4		
-100		26.4	29.0	45.4	18.0		40.6		

The strength properties of unbleached pulp of wood, wood with bark and bark of casuarina and acacia are shown in Table-9 respectively. In both the cases, wood with bark has lower strength properties than wood. The hand sheets prepared from bark possess very poor strength properties in both casuarina and acacia. bark portion have been studied here extensively, as such studies had not been made earlier (4). Casuarina bark has been added to the mixed pulp of bamboo-casuarina with bark (80:20) in 2, 5, 7, 10, 15, 20 and 30% from which hand sheets were made and both FS factor and bond factor were determined (Table-10). It is interesting to observe that the FS factor systematically decreases with increase

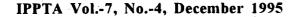
The changes in FS and bond factors due to the

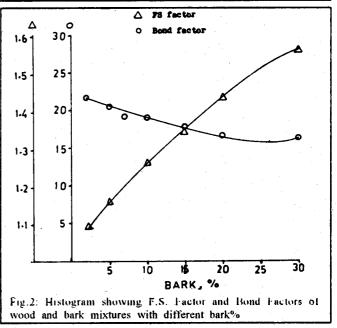
				Fable-11				
		Fib	er Morpho	ology (Blea	ached Pulp)		
Particulars			Wood	Casuarina Wood with bark	Bark	Wood	Acacia Wood with bark	Bark
Average Fiber Le Fiber Diameter	· • ·	nm) nm)	0.89 15	0.96 16	0.73 9	0.94 18	0.97 17	0.89
			,	Table-12				
• <u>•</u> ••••••••••••••••••••••••••••••••••	Physical	Strength	Properties	of unblea	ched hand	sheets at	40°SR	
Property			Wood	Casuarina Wood with bark	Bark	Wood	Acacia Wood with bark	Bark
Bulk Burst factor Tear factor Breaking Length	(1	sc/g) n)	1.66 30.86 60.73 4538	1.65 27.92 54.26 4336	0.55 10.24 29.7 1756	1.69 30:72 61.24 4886	1.66 28.64 55.31 4520	0.82 11.29 30.5 2051 2
Double fold	1)	No.)	16	15 Table-13	2	21	16	
F.S. and Bo	ond Factor	of mixed H			th varying	proportion	n of Casual	rina Bark
Properties M	ixed Bamboo suarina BCWB	BCWB : CB 98 : 2	BCWB : CB 95 : 5	BCWB : CB 93 : 7	BCWB : CB 90 : 10	BCWB : CB 85 : 15	BCWB : CB 80 : 20	BCWB : CF 70 : 30
F.S. Factor Bond factor	23.12 1.097	22.89 1.112	21.65 1.124	19.47 1.138	19.24 1.462	18.93 1.481	18.85 1.506	18.76 1.529
BCWB = Bamboo	– Casuarina w	ood with bark	CB = Casuarin	a bark.				
				Table-14				
Silvi Chemical						· · · · · · · · · · · · · · · · · · ·		
Vanilin Fatty acid	, ,	%) %)		1.8 1.67			1.85 1.78	
in the bark co	ontent (23.1		. On the oth	ner	Δ O	△ 78 fac		

hand, surprisingly the bond factor increases with increases in the bark portion. The high amount of fines present in the bark portion, helps in improving the bonding properties due to ease in packing of the voids (19), as shown in Fig.-2.

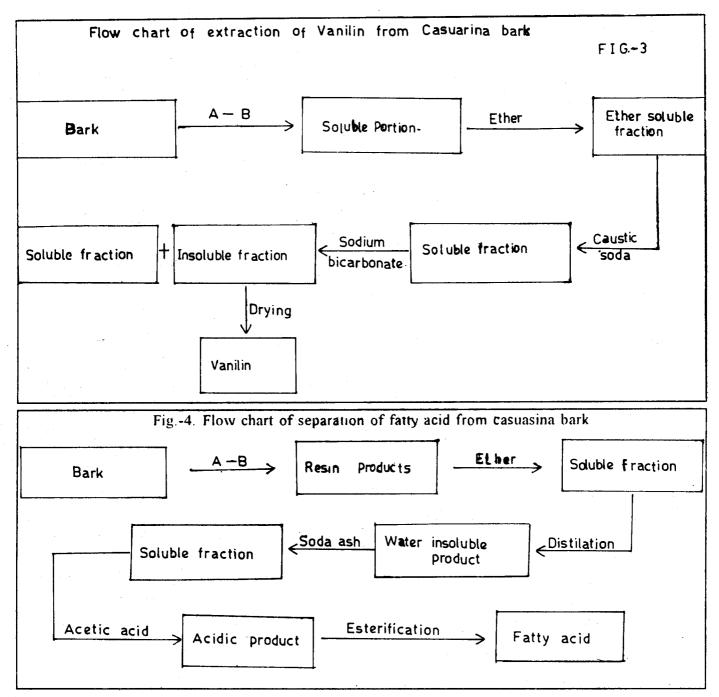
According to the proximate chemical analysis results (Table-2), the bark contains comparatively higher proportion of A-B, extractive and 1% NaOH soluble fractions. Therefore, attempt has been made to extract products such as vanilin and fatty acids which have immediate industrial use. The extraction processes are shown through flow diagrams in Fig.-3 and 4 for vanilin and fatty acid.

The amounts of vanilin and fatty acid extracted from the Casuarina and Acacia brak are (1.8%, 1.7%) and (1.85%, 1.8%) respectively. Presence of





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the chemicals have been confirmed from thin layer chromatography (20). However, it requires to be further studied for establishing the economical viability of extracting these chemicals from the bark.

CONCLUSIONS

Wood containing bark in both Casuarina and Acacia shows deterioration in strength properties and more so for the brightness property (2.5% El in Casuarina and 3% El in Acacia) compared to the wood which is very important for manufacturing of high quality paper. The bark portion alone is not suitable for production of paper. However, bark upto 30% can safely be added with wood for low grade paper.

The bark portion contains higher amount of A-B extractive and NaOH solubility according to the proximate analysis. Two new chemicals, vanilin and fatty acids from the bark ($\approx 1.8\%$) have been extracted.

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