

Infrared Spectra of Jute Stick and Alkali-Treated Jute Stick

A. K. ROY,* S. K. SEN, S. C. BAG, and S. N. PANDEY

Jute Technological Research Laboratories, Indian Council of Agricultural Research,
12 Regent Park, Calcutta-700 040, India

SYNOPSIS

Defatted jute stick was treated with sodium hydroxide solution (2% w/v) at ambient temperature ($\sim 32^\circ\text{C}$) and boiling water bath temperature ($95\text{--}97^\circ\text{C}$). Infrared (IR) spectra of defatted jute stick and alkali-treated jute stick were studied. The IR spectra of the alkali-treated jute stick were conspicuous by the absence of the 1730 cm^{-1} band, as compared to that of jute stick. Another characteristic feature of the alkali treated jute sticks is the absence of the band at 1240 cm^{-1} , which is replaced by the 1265 and 1225 cm^{-1} bands; other bands in the above samples also recorded significant changes.

INTRODUCTION

The main objective of any pulping process is to facilitate disintegration of wood into its fibrous components. To achieve this, the insoluble crosslinked protolignin must be degraded by breaking bonds within the lignin macromolecules, the fragmented lignin has to be solubilized and removed from the individual fibers. In the soda pulping process, which is most suitable for pulping of hard woods, sodium hydroxide is the major pulping chemical. Chemical treatment of wood chips with NaOH prior to mechanical pulping improves the strength properties of paper produced from mechanical pulps¹⁻⁵ and increases the number of hardwood species including jute stick,⁶⁻⁸ yielding acceptable pulps. Unbleached high yield cold caustic soda pulp, prepared from jute stick, was found suitable for newsprint paper and wrapping paper.^{9,10}

IR spectroscopy using the potassium bromide disk technique has been shown¹¹⁻¹⁴ to be a useful tool for investigating the fine structural characteristics of cellulose and chemically modified cellulose and lignins.¹⁵⁻¹⁸ A slight difference in IR spectra may signal differences in the ratio of constituent units and the order in which they are linked. The study of the differences in spectra of various chemically treated

jute stick and their significance to structure is probably the most valuable area of study in the field of jute stick IR Spectra.

Although no study on the IR spectra of jute stick has been done, fairly detailed work on the infrared spectra of jute fiber has been reported.^{12,18-20} In the present investigation, results on IR spectra of defatted jute stick and alkali-treated jute sticks have been analyzed and discussed.

MATERIALS AND METHODS

Preparation of Jute Stick (JS) Samples

Jute stick (*Corchorus capsularis* JRC 7447) was disintegrated in a Wiley mill, using different sieves. The disintegrated sample was defatted using a mixture of benzene : alcohol (2 : 1 v/v) and passed through 40- and 60-mesh sieves. The 40-60-mesh samples were used to study the major chemical compositions. The ($1 \times 1 \times 3$ mm) defatted jute stick was used for NaOH treatments and 100-mesh samples were used for IR spectral studies.

Sodium Hydroxide Treatment of Jute Stick

Defatted jute stick (15 g) was soaked in a 2% sodium hydroxide (w/v) solution of 1 : 10 liquor ratio at room temperature ($\sim 32^\circ\text{C}$). The alkaline liquor immediately turned yellow and then gradually red in 3 days. This was filtered and the resulting material

* To whom correspondence should be addressed.

Table I Major Chemical Composition of Jute Stick and Alkali Treated Jute Stick Samples^a

	Jute Stick Defatted (%)	Cold Soda Pulp (CSP) (%)	Hot Soda Pulp (HSP) (%)
Yield	—	77.8	72.8
Lignin	23.8	25.21	25.31
Pentosan	22.8	18.11	18.61
α -Cellulose	41.4	53.97	56.61

^a Calculated on 100 g of oven dry jute stick samples; (—) signifies not applicable.

was washed thoroughly with distilled water till it was free from alkali and dried in air. The yield of the sample (Cold Soda Pulp, CSP) was found to be 77.8%.

In another set of experiments, defatted jute stick (16 g) was treated with 2% sodium hydroxide at 1 : 10 liquor ratio at boiling water bath temperature for 2.5 h. The material was washed as in the case of CSP and air dried. The yield of the sample (Hot Soda Pulp, HSP) was 72.8%.

Analysis of Jute Stick and Alkali-Treated Jute Stick

Lignin content was estimated by the TAPPI Standard method²¹ (T13Os54). α -Cellulose was estimated by the modified method of Chattopadhyay and Sarkar²² using 1% sodium chlorite solution. Pentosans were determined using Kröber's tables following the procedure of Schorger.²³

Isolation of Jute Stick Milled Wood Lignin

Brownell's²⁴ procedure was followed for the preparation of milled wood lignin (MWL).¹⁶

Isolation of Jute Stick Hemicellulose and α -Cellulose

Holocellulose was prepared from jute stick by delignification with sodium chlorite by adopting the modified method of Chattopadhyay and Sarkar.²²

The holocellulose was treated with 10% sodium hydroxide at room temperature for 1 h. The alkaline extract was neutralized with acetic acid and hemicellulose was precipitated by adding ethanol (~ 1 vol).²⁵ α -Cellulose was isolated by the modified method of Chattopadhyay and Sarkar.²²

Infrared Spectroscopy

Defatted jute stick and alkali-treated jute stick (100 mesh), and finely mortared lignin (MWL), α -cellulose, and hemicellulose (~ 1–2 mg) as obtained above, were vacuum dried. The samples were mixed thoroughly in a mortar with 200 mg of KBr, which was previously dried at 120–150°C for 16 h. KBr pellets were made in a hydraulic press at a working pressure of 8 tons for 10 min pressing time, under vacuum. The spectra were recorded in Shimadzu double beam spectrophotometer IR-440 under a normal slit program and scanning speed of nearly 19 s/100 cm⁻¹. The α -cellulose and hemicellulose spectra were recorded in a Perkin-Elmer 783 IR spectrophotometer. A blank KBr pellet was used in the reference beam.

RESULTS AND DISCUSSIONS

The major chemical constituents of defatted jute stick (JS), cold soda pulp (CSP), and hot soda pulp (HSP) are given in Table I. The percent loss of lignin, pentosans, and α -cellulose of CSP and HSP are given in Table II.

Table II Percent Loss of the Major Chemical Constituents of Alkali-Treated Jute Sticks^a

	Yield (%)	Percent Loss of Lignin	Percent Loss of Pentosans	Percent Loss of α -Cellulose
Cold soda pulp (CSP)	77.8	17.6	36.8	—
Hot soda pulp (HSP)	72.8	22.6	39.2	0.5

^a (—) signifies nil.

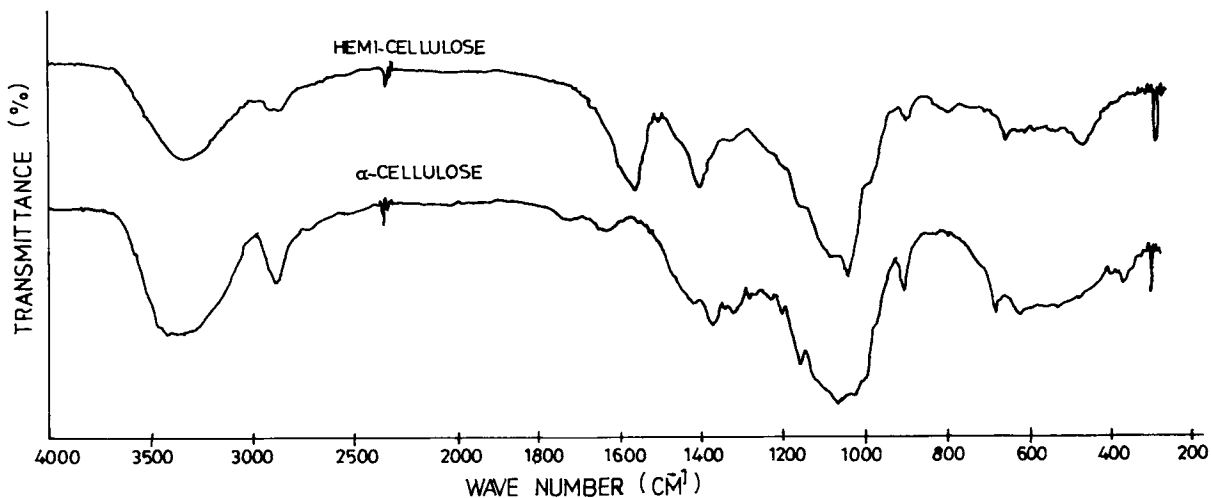


Figure 1A Infrared spectra of α -cellulose and hemi-cellulose of jute stick.

Infrared (IR) spectra of jute stick is influenced by the spectra of its three main biopolymers, namely, lignin, hemicellulose, and α -cellulose. The IR spectra of α -cellulose, hemicellulose, and lignin (MWL) isolated from jute stick are given in Figures 1(A) and 1(B). The band positions and corresponding relative intensities and assignments are given in Tables III, IV, and V.

IR spectra of CSP, HSP, and defatted jute stick are shown in Figure 2. The summary of the results including the significance of bands, the ratios of the absorbance maxima of individual bands, and the 2900 cm^{-1} band have been recorded in Table VI, following the baseline correction method of Sar-kanen et al.²⁶ The 2900 cm^{-1} band has been chosen as an internal standard here, as it is present as a

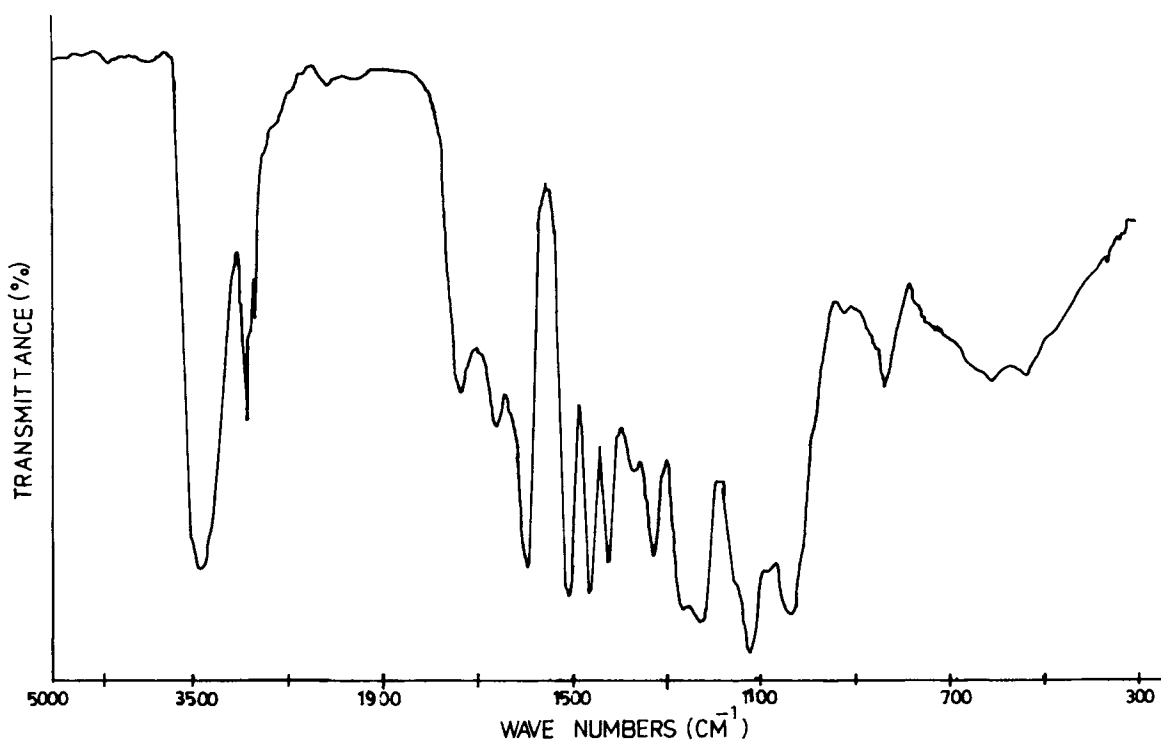


Figure 1B Infra-red spectra of lignin of jute stick (MWL JRC 7447).

Table III Infrared Spectrum of Jute Stick α -Cellulose

Band Position (cm ⁻¹)	Relative Intensity ^a	Assignments
3370	S	H-bonded O—H stretching
2900	S	CH ₂ symmetric stretching
1630	W	Adsorbed water molecules
1425	W	CH ₂ symmetric bending
1365	S	C—H bending
1340	W	O—H in-plane bending
1320	M	CH ₂ wagging
1280	M	C—H bending
1270	W	Same as above
1230	M	O—H in-plane bending
1205	M	O—H in-plane bending
1160	S	Antisymmetric bridge C—O—C stretching
1115	Sh	Antisym in-phase ring stretching
1070	S	Skeletal vibrations involving stretching of C—O and C—C bonds attached to the glucose rings
1040	M	
1000	M	
970	Sh	
905	S	
606	M	O—H out-of-plane bending

^a S = strong, W = weak, Sh = shoulder, M = medium.

Table IV Infrared Spectrum of Jute Stick Hemicellulose

Band Position (cm ⁻¹)	Relative Intensity ^a	Assignments
3360	S	H-bonded O—H stretching
2895	S	CH ₂ sym stretching
1730	Sh	C—O stretching in hemicellulose
1600	Sh	COO ⁻ antisym stretching
1575	S	Aromatic skeleton ring vibration due to lignin impurities
1460	Sh	CH ₂ sym bending in hemicellulose
1410	S	C—H deformation (asym) due to lignin impurity
1345	M	O—H in-plane bending
1230	Sh	Same as above
1160	Sh	Antisym bridge C—O—C stretching
1095	Sh	Skeletal vibration involving stretching of C—O bonds in hemicellulose
1045	S	
995	Sh	
900	S	
800	M	Ring breathing
660	M	O—H out-of-plane bending

^a S = strong, Sh = shoulder, M = medium.

Table V Infrared Spectrum of Jute Stick Lignin (MWL)¹⁶

Band Position (cm ⁻¹)	Relative Intensity ^a	Assignment of Bands
3400	S	H—O stretching (H-bonded)
2900–2950	S	C—H stretching in methyl and methylene
2850–2900	M	Same
1720–1735	M	C—O stretching in carboxyl and unconjugated β ketone
1690	W	C—O in α -position to benzene or double bond
1660	M	Same
1595	S	Aromatic skeletal ring vibration
1500	S	Same
1460	S	C—H deformation (asymmetric)
1420	S	Same
1360–1370	Sh	C—H deformation (symmetric)
1330	S	Syringyl ring breathing with C—O stretching
1270	Sh	Guaiacyl ring breathing with C—O stretching
1220–1230	M	Syringyl ring breathing with C—O stretching
1150–1170	Sh	Aromatic C—H in-plane deformation, guaiacyl type
1120–1130	S	Aromatic C—H in-plane deformation, syringyl type
1090	Sh	C—O deformation of secondary alcohol and aliphatic ether
1030	M	Aromatic C—H in-plane deformation, guaiacyl type and C—O deformation of primary alcohol
920	W	Aromatic C—H out of plane deformation
830	S	Same

^a S = strong, M = medium, W = weak, Sh = shoulder.

strong band in lignin, hemicellulose, and α -cellulose IR spectra. The internal standard, though not fully established, has been adopted for making a comparative study of the spectra. Although the corresponding data of jute stick has been given alongside the two alkali-treated jute stick samples CSP and HSP, the data could not be correlated in all cases because of the complex nature of reactions caused by alkali on the multicomponent system of jute stick.

The band at 3350 cm⁻¹ which is attributed to H-bonded H—O stretching²⁷ has higher absorbance intensity ratios for CSP and HSP as compared to that of jute stick, and the reason can be ascribed to the higher residual lignin and α -cellulose contents in the two alkali-treated samples (see Table I). The 2900 cm⁻¹ band is attributed to C—H stretching in methyl and methylene groups.²⁷

The band near 1730 cm⁻¹ in the IR spectra of wood, attributed to C—O stretching of the carbonyl and acetyl groups in the 4-*O*-methylglucuronoacetyl xylan component of hemicellulose,^{28–30} is absent in both the alkali-treated samples but is present in the jute stick spectrum. The acetyl group is believed to be mostly in association either with xylose or uronic acid residue or with both the hemicellulose com-

ponents of jute stick.³¹ The long hours of alkali treatment eliminates this band as reported in the case of jute fibre by Sao et al.²⁸

The absorption bands at 1635 cm⁻¹ attributed to the vibration of adsorbed water molecules in the noncrystalline regions in cellulose^{27,32} appears as a shoulder in the spectra of CSP and HSP and defatted jute stick.

The aromatic skeleton ring vibration²⁶ at 1595 cm⁻¹ has more or less the same absorbance intensity ratio for the three samples. The absorbance intensity ratio of 1500 cm⁻¹, also due to aromatic skeleton ring vibration, has higher values for CSP and HSP samples compared to that of jute stick and this is in accordance with the higher residual lignin of the two alkali treated jute stick samples (see Table I).

The band at 1460 cm⁻¹ attributed to both lignin and xylan due to CH₃ deformation (asymmetric) in lignin, as well as to CH₂ bending in xylan,³² has higher absorbance ratios for CSP and HSP, as compared to that of jute stick, in concurrence with the higher lignin content of the alkali treated samples (see Table I). The band at 1420 cm⁻¹ also attributed to the above reason has higher absorbance intensity ratio for CSP as compared to that of jute stick and

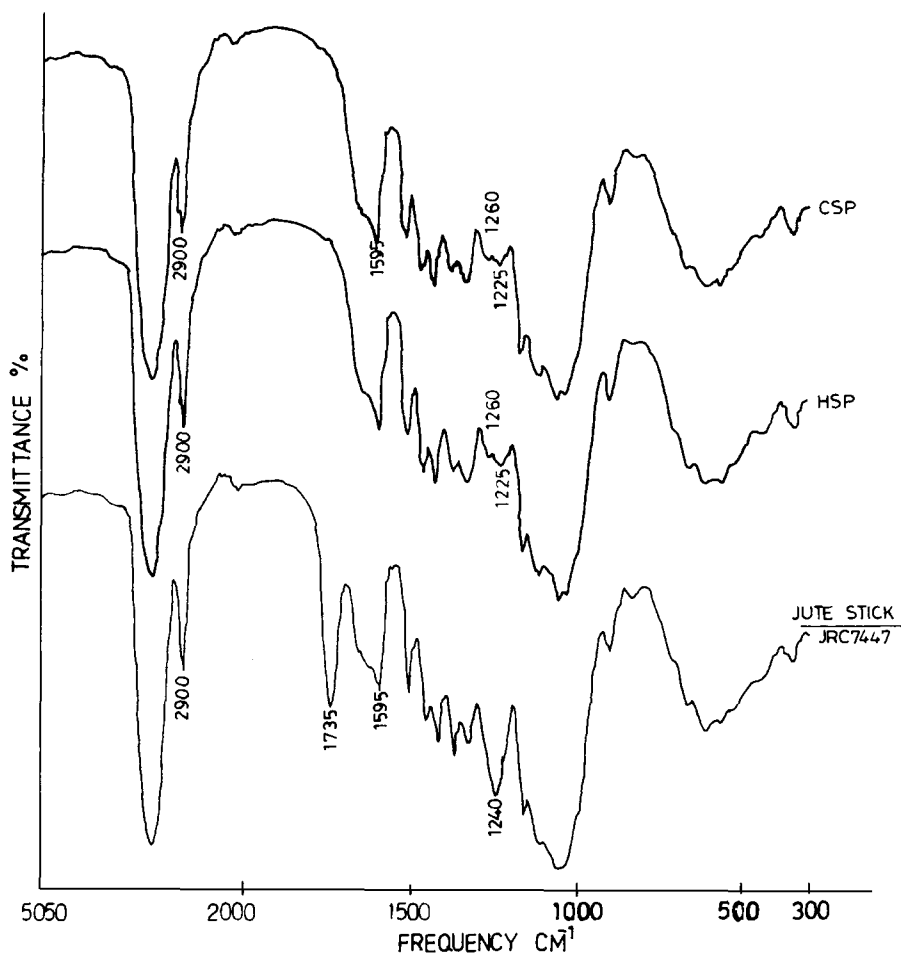


Figure 2 Infrared spectra of cold soda pulp (CSP), hot soda pulp (HSP), and defatted jute stick (JRC7447).

this finding is also in accordance with the higher lignin content of the alkali-treated samples as compared to that of jute stick.

The band at 1370 cm^{-1} , due to C—H deformation (symmetric), which may be caused by lignin and α -cellulose,^{24,33} has higher absorbance intensity ratios for the CSP and HSP samples as compared to that of jute stick sample. This finding is in accordance with the higher lignin and α -cellulose contents of the alkali treated samples (see Table I). The 1320 cm^{-1} band attributed to syringyl ring breathing with C—O stretching in lignin³⁴ and CH_2 wagging in cellulose^{29,30} has higher absorbance intensity ratios for the CSP and HSP samples as compared to that of jute stick sample, and this again is in concurrence with higher lignin and α -cellulose contents of the two alkali-treated samples as compared to that in jute stick.

In the IR spectra of jute stick, a broad and medium band having maxima near 1240 cm^{-1} appears;

this band is similar to that in wood, and is attributed to the C—O linkage in the acetyl group in xylan.^{30,35,36} The acetyl groups in jute are known to be removed completely even in dilute caustic soda at room temperature.³⁷ Alkali treatment splits this medium broad band at $1240\text{--}1265\text{ cm}^{-1}$ and 1225 cm^{-1} bands. The 1265 cm^{-1} band is caused by guaiacyl ring breathing with C—O stretching in isolated lignin, whereas the band 1225 cm^{-1} is attributed to syringyl ring breathing with C—O stretching in isolated jute stick lignin (see Table V). The absorbance intensity ratios for the samples CSP and HSP are almost same, in concurrence with the almost same residual lignin contents of the two samples (see Table I).

The 1160 cm^{-1} band is assigned to antisymmetric bridge C—O—C stretching in cellulose and hemicellulose^{29,32} and to the aromatic C—H in-plane deformation in lignin^{16,17} (see Table V). The absorbance intensity ratios of CSP and HSP at 1160

Table VI Infrared Spectra of Jute Stick and Alkali-Treated Jute Stick^a

Band Position (cm ⁻¹)	Assignments	JS Av/A2900	CSP Av/A2900	HSP Av/A2900
3350	H—O stretching (H-bonded)	0.2435	0.3648	0.3525
2900	C—H stretching in methyl and methylene	1.0 (0.4089)	1.0 (0.3665)	1.0 (0.3625)
1730	C—O stretching in carbonyl and unconjugated β ketone	0.9214	—	—
1635	H ₂ O molecules in noncrystalline cellulose	Shoulder	Shoulder	Shoulder
1595	Aromatic skeleton ring vibration	1.4724	1.4466	1.4543
1500	Aromatic skeleton ring vibration	1.5157	1.8215	1.7503
1460	C—H deformation and CH ₂ (sym)	1.3905	1.6332	1.5597
1420	Same	1.3147	1.5961	0.8844
1370	C—H deformation (symmetric)	1.4514	1.9691	1.8984
1320	Syringyl ring breathing with C—O stretching and CH ₂ wagging in cellulose	1.7094	1.9994	2.0022
1265	Guaiacyl ring breathing with C—O stretching	—	2.9211	2.8849
1240	C—O stretching in acetyl group	1.5157	—	—
1225	Syringyl ring breathing with C—O stretching	—	3.1178	3.0717
1200	Phenolic O—H deformation	—	Shoulder	Shoulder
1160	Antisymmetric bridge C—O—C stretching in cellulose and hemicellulose and aromatic C—H in-plane deformation in lignin	1.4306	1.6193	1.5911
1105	Skeletal vibration involving C—O stretching in hemicellulose and α -cellulose	1.0560	1.2783	1.2924
1050	Same	0.8246	1.0281	1.0110
1030	Aromatic C—H in-plane deformation, guaiacyl type and C—O deformation primary alcohol in lignin and skeletal vibration and C—O stretching in cellulose and hemicellulose	0.7796	1.0139	0.9972
990	Skeletal vibration and C—O stretching in cellulose and hemicellulose	Shoulder	Shoulder	Shoulder
895	Antisym out-of-phase ring stretching due to β linkage in hemicellulose and cellulose	2.3736	2.7285	2.7001
830	Aromatic C—H out-of-plane vibration due to lignin	6.6864	5.4570	5.5172

^a Values in parentheses are the intensities at 2900 cm⁻¹ band; (—) signifies nil.

cm⁻¹ are higher than that in the jute stick sample, in concurrence with the higher cellulose and lignin content of the alkali-treated jute stick samples as compared to that of jute stick (see Table I).

The 1105 cm⁻¹ band is assigned to H-bonding on the skeletal vibrations involving stretching of the C—O bond in hemicellulose and cellulose.^{29,30,38} The absorbance intensity ratios of CSP and HSP at 1105 cm⁻¹ are similarly higher than the intensity ratio of jute stick in accordance with the higher α -cellulose content of the alkali-treated samples.

The 1050 cm⁻¹ band, also assigned to skeletal vibration involving C—O stretching in hemicellulose and cellulose,²⁹ records higher absorbance intensity ratios for CSP and HSP in concurrence with higher

α -cellulose content of the alkali-treated samples (see Table I).

The band at 1030 cm⁻¹ has been assigned to aromatic C—H in-plane deformation, guaiacyl type, and C—O deformation in primary alcohol in lignin^{16,17} (see Table V) and skeletal vibration involving C—O stretching in hemicellulose and α -cellulose.²⁹ The band has higher absorbance intensity ratios for CSP and HSP as compared to that of jute stick, in concurrence with higher residual lignin and cellulose contents of the alkali treated samples (see Table I).

The shoulder of 990 cm⁻¹ is attributed to skeletal vibration involving C—O stretching in cellulose and hemicellulose.²⁹ The 895 cm⁻¹ band assigned to an-

tisymmetric out-of-plane stretching due to β linkage in hemicellulose and α -cellulose²⁹ has higher absorbance intensity ratios for the alkali-treated samples, CSP and HSP, as compared to that in jute stick, in accordance with the higher α -cellulose content of the two alkali-treated samples (see Table I). The band at 830 cm^{-1} attributed to aromatic C—H out-of-plane vibration in lignin^{16,17} (see Table V) is present in all the three jute stick samples.

CONCLUSION

Alkali-treated jute stick obtained by dilute sodium hydroxide (2% w/v) treatment at boiling water bath temperature (HSP) gives pulp of lower yield when compared with that of alkali treated jute stick obtained at room temperature (CSP). This is reflected by the higher percent loss of lignin and pentosans of HSP as compared to that of CSP.

The IR spectra of the two alkali-treated jute stick samples, CSP and HSP, have almost the same structural characteristics. As a result of the dilute alkali treatment, the slight change in the major chemical constituents of the alkali-treated samples are well discernible from the IR spectra of the two samples CSP and HSP, when compared with that of defatted jute stick. This is revealed by the elimination of the band at 1730 cm^{-1} in the two alkali-treated samples in contrast to the control sample, i.e., defatted jute stick. The band at 1240 cm^{-1} in defatted jute stick is similarly obliterated and two new bands appear at 1265 and 1225 cm^{-1} in CSP and HSP, respectively. The new bands are assigned to guaiacyl and syringyl lignin moieties, respectively, in the two alkali-treated samples. Other bands also record significant changes as revealed by the difference in the absorbance intensity ratios as compared to that of defatted jute stick.

REFERENCES

1. T. Kano, T. Iwamida, and Y. Sumi, *Pulp Paper Can.*, **83**(6), 80 (1982).
2. A. Mokvist, M. Jackson, and A. Deravo, *Paper Trade J.*, **196**(11), 42 (1985).
3. M. Webb, *Paper Technol. Ind.*, **26**(6), 281 (1985).
4. M. Jackson, *Paper Technol. Ind.*, **26**(6), 258 (1985).
5. T. H. Wagner, *Tappi*, **65**(8), 103 (1982).
6. S. R. D. Guha, G. M. Mathur, and V. N. Mukherjee, *Indian Pulp Paper*, **27**(2), 153 (1962).
7. S. R. D. Guha, V. N. Mukherjee, and Y. K. Sharma, *Indian Pulp Paper*, **19**, 551 (1965).
8. M. A. Islam and M. A. Khan, *Sci. Ind. (Karachi)*, **5**(1), 102 (1967).
9. S. R. D. Guha and V. N. Mukherjee, *Res. Ind.*, **5**, 275 (1960).
10. S. R. D. Guha and V. N. Mukherjee, *Res. Ind.*, **5**, 314 (1960).
11. R. T. O'Connor, E. F. Du Pré, and E. R. McCall, *Anal. Chem.*, **29**, 998 (1957).
12. R. T. O'Connor, E. F. Du Pré, and D. Mitchum, *Text. Res. J.*, **28**, 382 (1958).
13. F. G. Hurtubise and H. Krassig, *Anal. Chem.*, **32**, 177 (1960).
14. M. L. Nelson and R. T. O'Connor, *J. Appl. Polym. Sci.*, **8**, 1311 (1964).
15. J. Blackwell, P. D. Vasko, and J. L. Koenig, *J. Appl. Phys.*, **41**, 4375 (1970).
16. A. K. Roy, S. C. Bag, and S. K. Sen, *Cell. Chem. Technol.*, **21**, 343 (1987).
17. A. K. Roy, S. K. Sen and S. C. Bag, *Tappi*, **71**(11), 160 (1988).
18. A. C. Mukherjee, A. K. Mukhopadhyay, B. K. Sarkar, A. S. Dutt, and U. Mukopadhyay, *Text. Res. J.*, **51**, 40 (1981).
19. M. Gopal, S. K. Bhaduri, S. K. Bannerjee, and K. P. Sao, *Indian J. Text. Res.*, **10**, 68 (1985).
20. K. P. Sao, M. D. Mathew, A. K. Jain, and P. K. Roy, *Cell. Chem. Technol.*, **21**, 17 (1987).
21. *TAPPI Standard Methods*, Tappi Press, Atlanta, 1971.
22. H. Chattopadhyay and P. B. Sarkar, *Proc. Natl. Inst. Sci. India.*, **12**(1), 23 (1946).
23. C. Doree, *The Methods of Cellulose Chemistry*, 2nd ed., Van Nostrand, New York, 1947, p. 361.
24. H. H. Brownell, *Tappi*, **48**, 513 (1965); H. H. Brownell and K. L. West, *Pulp Paper Mag. Can.*, **62**, 7374 (1961).
25. S. K. Sen, A. K. Mazumder, and P. C. Das Gupta, *Indian J. Technol.*, **4**(8), 248 (1966).
26. K. V. Sarkanen, H. H. Chang, and G. G. Allan, *Tappi*, **50**(12), 583 (1967).
27. M. Tsuboi, *J. Polym. Sci.*, **25**, 159 (1957).
28. K. P. Sao, M. D. Mathew, A. K. Jain, and P. K. Ray, *Cell. Chem. Technol.*, **21**, 17 (1987).
29. R. T. O'Connor, Ed., *Instrumental Analysis of Cotton Cellulose and Modified Cotton Cellulose*, Dekker, New York, 1972.
30. C. Y. Liang, K. H. Bassett, E. A. McGinnes, and R. H. Marchessault, *Tappi*, **43**, 1017 (1960).
31. A. B. Sen Gupta, A. Roy, and M. G. Macmillan, *J. Sci. Ind. Res. (India)*, **19B**, 249 (1960).
32. C. Y. Liang and R. H. Marchessault, *J. Polym. Sci.*, **43**, 71 (1960); **39**, 269 (1959).
33. K. V. Sarkanen and C. H. Ludwig, Ed., *Lignins*, Wiley-Interscience, New York, 1971, p. 273.
34. In Ref. 33, p. 279.
35. R. H. Marchessault and C. Y. Liang, *J. Polym. Sci.*, **59**, 357 (1962).
36. S. Smiljanski and S. Stankovic, *Cell. Chem. Technol.*, **8**, 283 (1974).
37. P. B. Sarkar and A. K. Mazumder, *Text. Res. J.*, **12**, 1016 (1955).
38. H. G. Higgins, C. H. Stewart, and K. J. Harrington, *J. Polym. Sci.*, **51**, 59 (1961).

Received July 25, 1990

Accepted October 5, 1990