

# Infrared Spectra of Raw and Chemically Modified Pineapple Leaf Fiber (*Annanus comosus*)

S. C. SAHA, B. K. DAS, P. K. RAY, S. N. PANDEY, and K. GOSWAMI<sup>1\*</sup>

Jute Technological Research Laboratories, Indian Council of Agricultural Research, 12, Regent Park, Calcutta 700 040 India and <sup>1</sup>Department of Physics, Jadavpur University, Calcutta 700 032, India

## SYNOPSIS

Infrared spectra of raw and chemically treated pineapple leaf fibers (PALF) have been studied using the KBr disk technique. Bands due to lignin and hemicellulose in the spectra of the fibers and their changes due to chemical (NaOH and NaClO<sub>2</sub>) treatment have been discussed.

## INTRODUCTION

Pineapple leaf fiber (PALF) is multicellular and lignocellulosic like jute fiber.<sup>1</sup> It is obtained from the leaf of the pineapple plant. It contains  $\alpha$ -cellulose, hemicellulose, and lignin as major chemical constituents that are associated with each other in a manner not clearly known. The chemical composition of the fibers are given in Table I. Structural changes after chemical (NaOH and NaClO<sub>2</sub>) treatment were examined by infrared (IR) spectroscopy. Information on IR studies of PALF is lacking in the literature. The present work deals with the study on IR spectroscopy of pineapple leaf fiber, which has good economical promise in near future. The bands due to lignin and hemicellulose in the spectra of pineapple leaf fiber and their changes due to chemical (NaOH and NaClO<sub>2</sub>) treatment have been discussed. It is estimated that at present approximately  $13.22 \times 10^4$  tons of pineapple leaf fiber is available in India. PALF seems to be a very important fiber for building up the agro-based industry. But this potential source of fiber from agrowaste has not yet been properly utilized. Only a small quantity of fiber is needed in cottage industries. In some countries an attempt has been made for the utilization of this agrowaste as a raw material for paper and textile products. A knowledge of the structure and physical properties of this fiber will

be helpful for determining the technological performance of this fiber. It is with this end that the present work has been undertaken.

**Table I Chemical Compositions of PALF (Defatted)<sup>a</sup>**

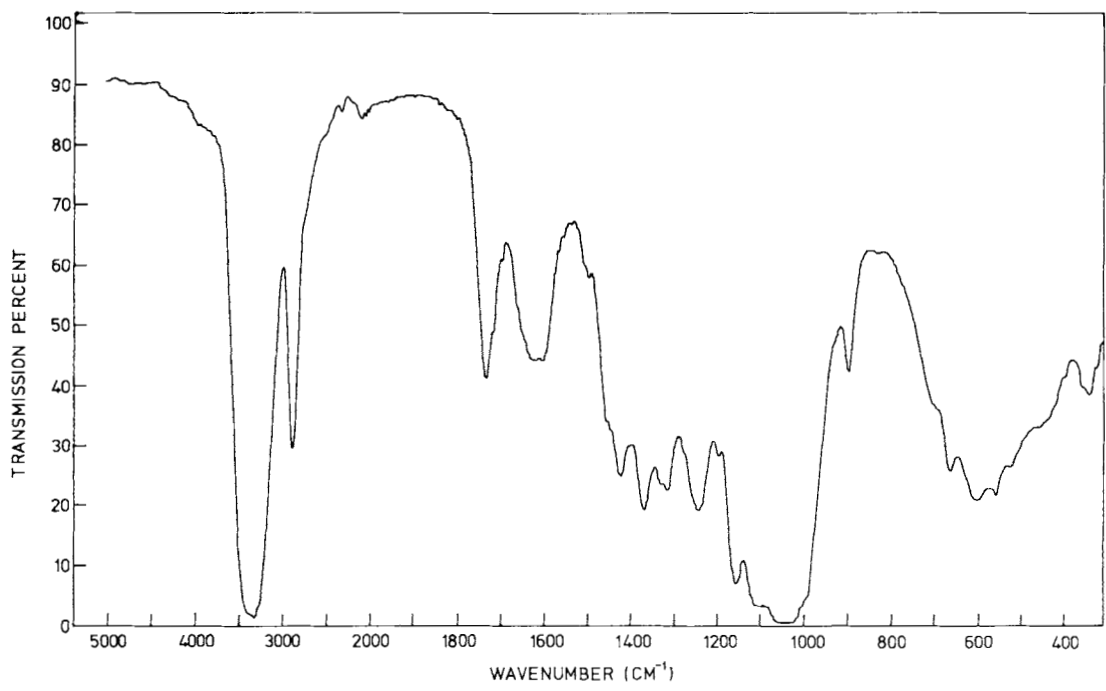
Constituents	Percentage
$\alpha$ -Cellulose	68.50
Hemicellulose	18.80
Lignin	6.04
Pectin	1.10
Fat and wax	3.20
Ash	0.90
Others (protein organic acid, etc.)	1.46

<sup>a</sup> The calculations are based on oven dry basis.

**Table II Percentage of Hemicellulose and Lignin Content in the Raw and Chemically Treated PALF**

Specimen	Hemicellulose Percentage (%)	Lignin Percentage (%)
Raw	18.80	6.04
5% NaOH tr.	11.16	5.44
10% NaOH tr.	7.28	5.06
18% NaOH tr.	7.10	4.98
0.5% NaClO <sub>2</sub> tr. (45°C)	15.60	2.84
0.5% NaClO <sub>2</sub> tr. (80°C)	14.80	2.09
0.7% NaClO <sub>2</sub> tr. (80°C)	13.20	1.80

\* To whom correspondence should be addressed.



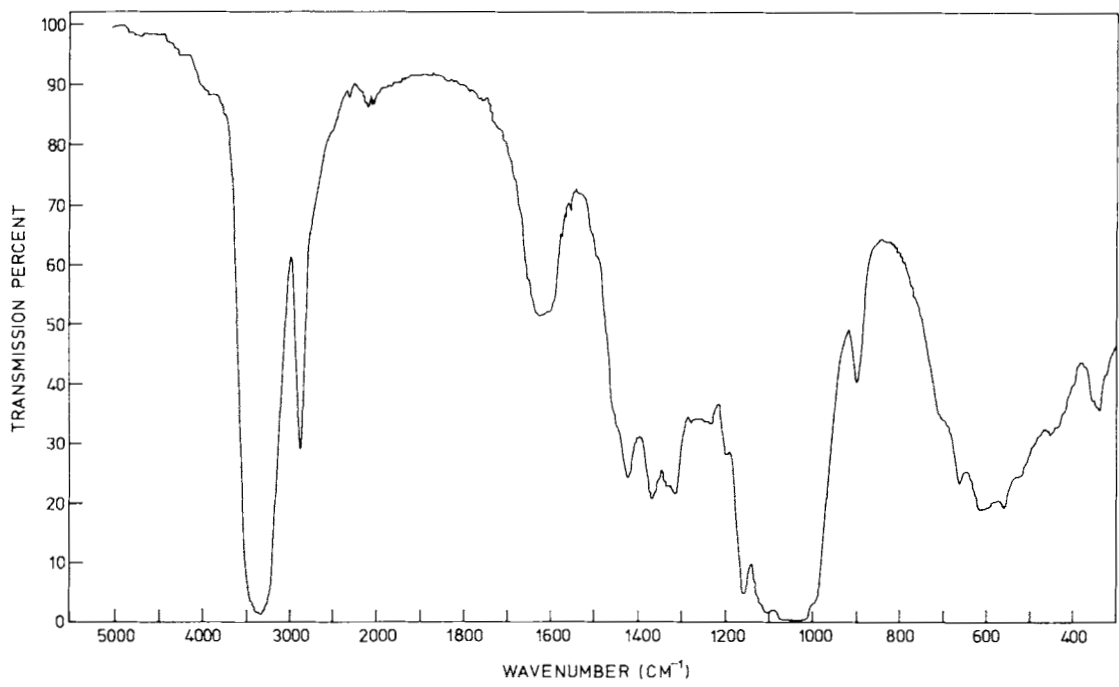
**Figure 1** IR spectra of raw PALF.

**EXPERIMENTAL**

**Materials**

PALF samples (representatives of the whole lot) were taken from middle portions of the reeds and

treated with alkali (sodium hydroxide, w/v) solution of different concentrations (i.e., 5, 10, and 18%) for one hour at room temperature (30°C) with occasional shaking.<sup>2</sup> After treatment the samples were washed with distilled water, dilute hydrochloric acid, and finally with distilled water and air-dried.



**Figure 2** IR spectra of NaOH-treated PALF for (a) 5%, (b) 10%, and (c) 18%.

Delignification was carried out by the chlorite method,<sup>3</sup> which is reported to have minimum action on the other constituents of the fiber. The fiber specimens were treated with 0.5 and 0.7% sodium chlorite solution (liquor ratio 1 : 25) at pH 4 (buffered with acetic acid and sodium acetate) for 2 h.

The reaction temperature was varied between 45 and 80°C with a view to obtaining various degrees of delignification. The chemical constituents of the fibers were determined by standard methods.<sup>3-6</sup> The hemicellulose and lignin contents of the samples are shown in Table II.

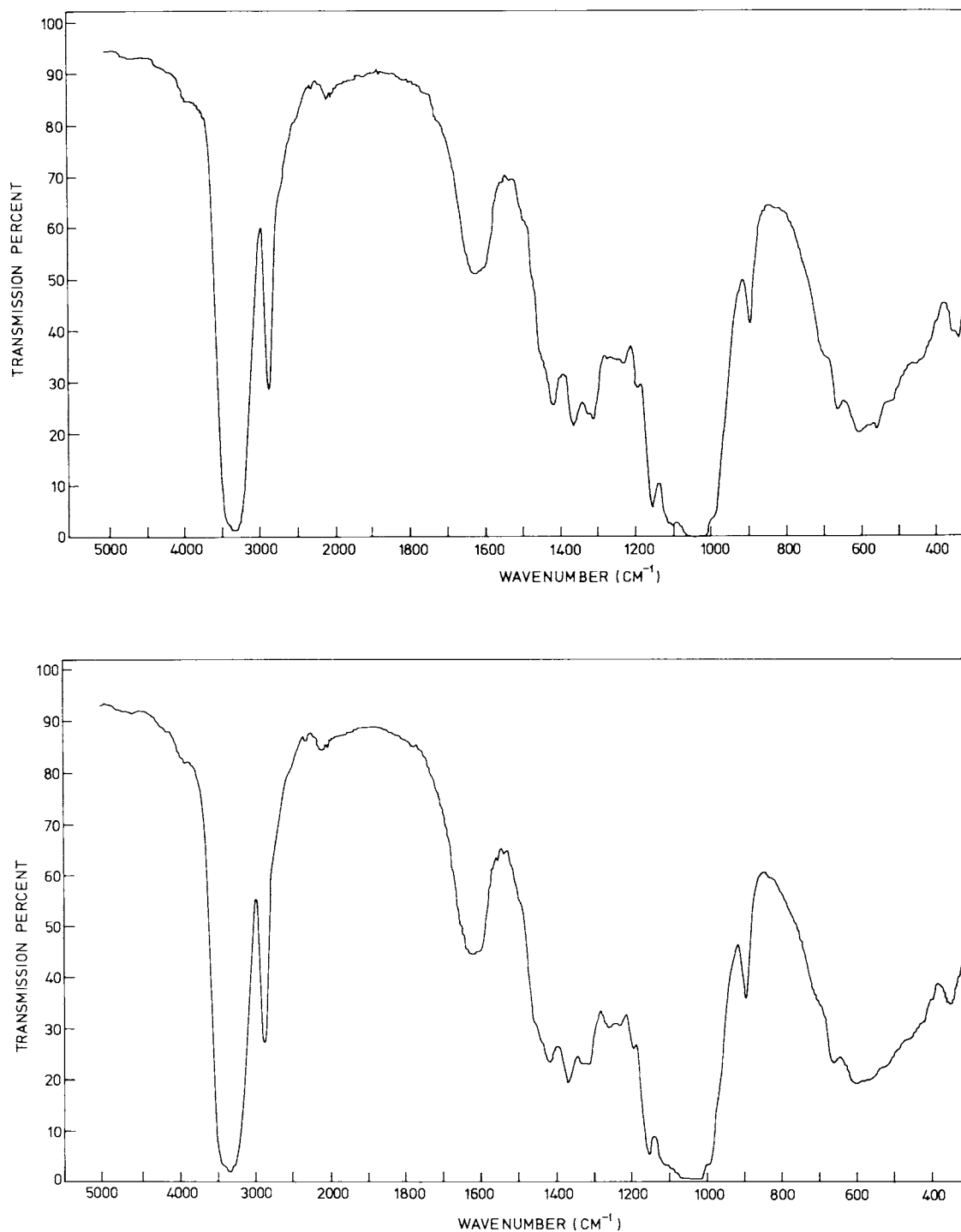
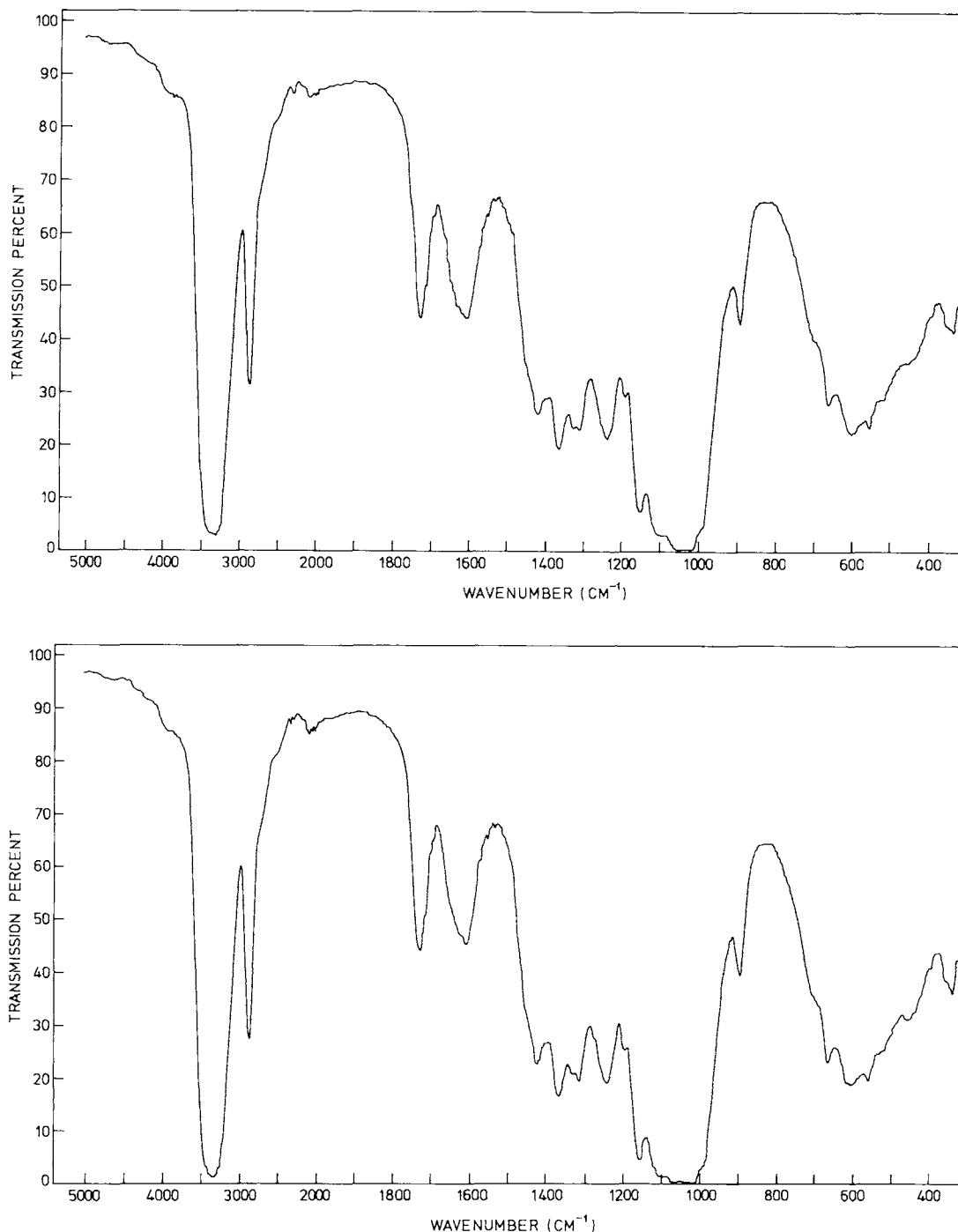


Figure 2 (continued from the previous page)



**Figure 3** IR spectra of  $\text{NaClO}_2$ -treated PALF for (a) 0.5% at  $45^\circ\text{C}$ , (b) 0.5% at  $80^\circ\text{C}$ , and (c) 0.7% at  $80^\circ\text{C}$ .

### Procedures

The fiber samples were cut into small pieces by scissors. Then 2 mg powder of fiber samples and 200 mg of KBr were taken and mixed uniformly in a mortar. The mixed powder was pressed under  $8^+$  tons of pressure to convert it to a pellet.

The IR spectra were recorded with the help of a Shimadzu double-beam IR spectrophotometer

(model IR-440). A KBr pellet without sample was used in the reference beam.

### RESULTS AND DISCUSSION

The characteristic features of the IR spectra of PALF are due to its lignin and hemicellulose com-

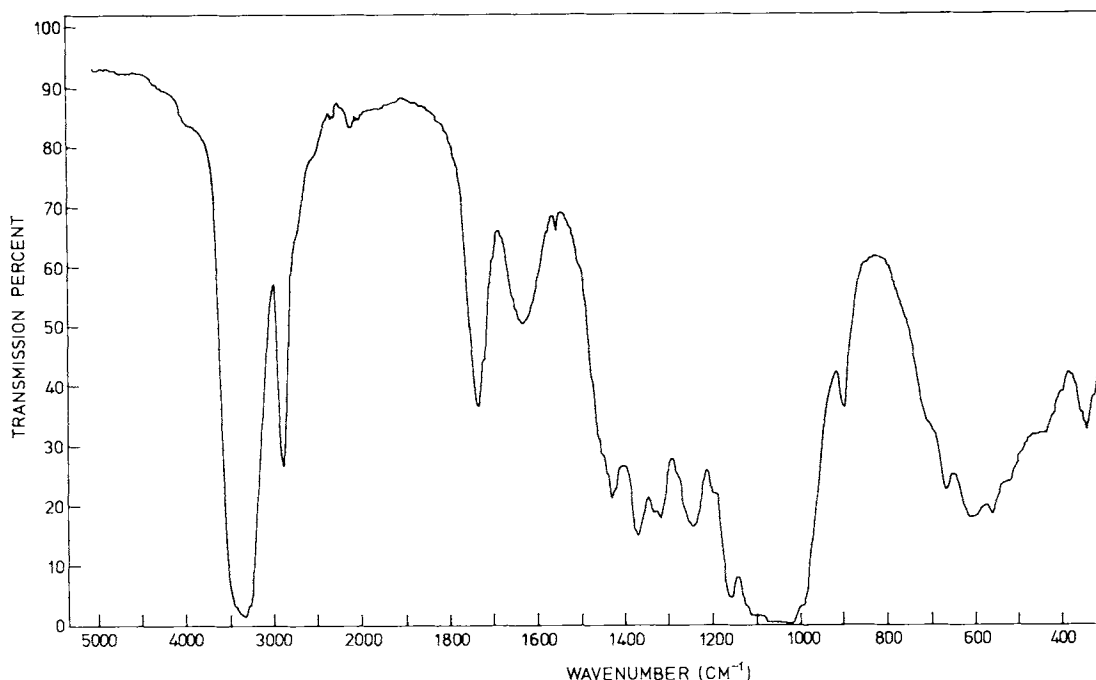


Figure 3 (continued from the previous page)

ponents, which exist in the middle lamella of the ultimate fibers. The IR spectra of raw, alkali (NaOH) treated (5, 10, and 18%) and delignified PALF are shown in Figures 1-3. From these figures the following peaks have been observed:

3300-3400  $\text{cm}^{-1}$  and 2900  $\text{cm}^{-1}$ : The strong broad peak at 3300-3400  $\text{cm}^{-1}$  in the spectra of PALF is the characteristic hydrogen-bonded OH stretching vibrations.<sup>7-9</sup> The strong peak at 2900  $\text{cm}^{-1}$  is due to CH stretching vibrations.<sup>7,10</sup>

2500-2000  $\text{cm}^{-1}$ : In this region there are a number of shoulders and weak peaks that are also found in the IR spectra of jute<sup>11</sup> and bhindi fibers.<sup>12</sup> Tsuboi,<sup>7</sup> who worked with natural fibers, has listed a few parallel polarized, very weak peaks in this region.

1730  $\text{cm}^{-1}$ : The peak at 1730  $\text{cm}^{-1}$  is the characteristic band for carbonyl (C=O) stretching. With the alkali treatment this band disappears (Fig. 2) as in the case of jute<sup>11</sup> and bhindi fibers.<sup>12</sup> It appears that in alkali treatment a substantial portion of uronic acid, a constituent of hemicellulose xylan, is removed resulting in the disappearance of this peak. On delignification it is observed that the intensity of this band increases with the gradual decrease in lignin content of the fiber (Fig. 3). The bleaching treatment may initiate breakage of glucourono xylan and formation of OH groups in the amorphous region resulting in the increase of peak height of the band at 1730  $\text{cm}^{-1}$ .

1630  $\text{cm}^{-1}$ : This broad band is observed with the lignin band near 1600  $\text{cm}^{-1}$  and appears to be sharply

defined on delignification [Fig. 3(a) to 3(c)]. This band in cellulose has been attributed to the vibration of adsorbed water molecules in the noncrystalline region.<sup>7,13,14</sup>

1420  $\text{cm}^{-1}$ : The band near 1420  $\text{cm}^{-1}$  is assigned to the CH<sub>2</sub> symmetrical deformation<sup>13,14</sup> and shows a reduction in intensity and a slight shift toward the low-frequency side in the spectra of 18% alkali-treated fibers. The effect has been related to change in the environment of the C<sub>6</sub> carbon atom due to formation or breaking of the hydrogen bond involving the atom O<sub>6</sub>. This indicates the change in lattice from cellulose I to cellulose II when alkali concentration is 18%.

1370, 1330, and 1310  $\text{cm}^{-1}$ : These bands are due to CH deformation, OH in plane bending, and CH<sub>2</sub> wagging, respectively.<sup>7,9,15</sup> Both cellulose and xylan might contribute to these bands. The bands near 1330 and 1310  $\text{cm}^{-1}$  are merged into a broad band in 18% alkali-treated fibers. The broadening may be due to the effect of lignin. In the spectra of delignified fiber these bands are well resolved (Fig. 3).

1245 and 1220  $\text{cm}^{-1}$ : The band near 1245  $\text{cm}^{-1}$  is possibly due to -C-O-C- bond in the cellulose chain.<sup>16</sup> Lignin and cellulose might also contribute to this broad band in spectra of raw fiber. This band persists on delignification, but on alkali treatment this band is reduced and another band at 1220  $\text{cm}^{-1}$  is observed.

1200  $\text{cm}^{-1}$ : The band near 1200  $\text{cm}^{-1}$ , assigned to OH in plane bending, shows as a weak band (1195

$\text{cm}^{-1}$ ) in the spectra of samples treated with 18% alkali concentration [Fig. 2(c)]. This might be due to the weakening of the hydrogen bonding system upon transition to cellulose II from cellulose I.

1160  $\text{cm}^{-1}$ : The band near 1160  $\text{cm}^{-1}$  is assigned by Liang and Marchessault<sup>13,14</sup> to antisymmetrical bridge  $-\text{C}-\text{O}-\text{C}-$  stretching. O'Connor<sup>15</sup> assigned it to C—O stretching or O—H bending of the C—OH group. Its slight shift toward the low-frequency side is evident in the spectra of 18% alkali-treated fibers. A similar peak is observed in the case of jute fiber.<sup>11</sup> Liang et al.<sup>17</sup> attributed the bands near 1160  $\text{cm}^{-1}$  in the spectra of wood sections, due to cellulose and hemicellulose.

900  $\text{cm}^{-1}$ : The important peak near 900  $\text{cm}^{-1}$  is characteristic of  $\beta$ -linkage, and its intensity increases in 18% alkali-treated fibers. But it remains unchanged on delignification. This band was assigned to the  $\text{C}_1-\text{H}$  bending mode in  $\beta$ -linkage.<sup>18</sup> The increase in intensity of this band relates to the rotation of glucose residue around the glucosidic bonds<sup>19</sup> and indicates the transition from cellulose I to cellulose II. Both celluloses in xylan<sup>20</sup> may contribute to this band.

660, 610, 560, and 340  $\text{cm}^{-1}$ : We observed weak bands in this region. These bands are also present in the spectra of delignified fibers. The bands near 660 and 610  $\text{cm}^{-1}$  are reduced in the spectra of 18% alkali-treated fibers. According to Pray,<sup>21</sup> in the cellulose I spectrum, the torsional vibrations of Pyranose rings are associated with these bands. The diminishing intensity of these bands in 18% alkali-treated PALF corroborate clearly with the findings of Blackwell et al.<sup>22</sup>

## CONCLUSIONS

The characteristic features of the IR spectra of pineapple leaf fiber are due to its lignin and hemicellulose components. From the IR spectra of 18% alkali-treated fibers, we observed the partial transition from cellulose I to cellulose II. This transition is accompanied by crimp development in the fibers.

The low-frequency region below 700  $\text{cm}^{-1}$  shows marked changes in the 18% alkali treatment.

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