JOURNAL OF MATERIALS SCIENCE **25** (1990) 2925–2928

# Infrared spectroscopic study of thermally treated lignin

A. A. SHABAKA, A. M. A. NADA*
*Spectroscopic Department and *Cellulose and Paper Department, National Research Centre, Dokki, Cairo, Egypt*
M. FADLY
*Physics Department, Faculty of Science, Helwan University, Helwan, Cairo, Egypt*

Precipitated lignin from black liquor produced from rice straw pulping was thermally treated at different temperatures (25 to 260° C) for 1 h. Lignin was also thermally treated at 230° C for various time intervals (0.5 to 2 h). The infrared spectra from 200 to 4000 $\mathrm{cm^{-1}}$ were studied. It was found that the absorbance of OH as well as $OCH_3$ bands decreased with increasing temperature and heating time. On the contrary, C=O increased with increasing temperature and time. The OH and $OCH_3$ vibrational bands began to disappear when the temperature rose above 230° C. A correlation between the absorbance of OH, $OCH_3$ and C=O is made to give more information concerning the effect of thermal treatment on the molecular structure changes of lignin.

## 1. Introduction

The chemistry of lignin has been studied by many authors. A factor common to all lignins is that they are built up of phenylpropane units which are said to be randomly formed by ether bonds and C–C bonds. The main reactive groups of lignin are the groups which are present in the side chain and p-substituted phenolic hydroxyl groups, either free or etherified. The electronic spectra of lignin measured in aqueous solution were investigated. The position and width of bands of different groups of lignin are virtually unaffected, but the band heights are affected by pH [1]. Bolker [2, 3] suggested that a band near 1710 $\mathrm{cm^{-1}}$ in the infrared (IR) spectrum of isolated lignins arose as a result of the cleavage of a bond between lignin and carbohydrates. During pulping, lignin is demethoxylated and degraded which consequently causes an increase in phenolic hydroxyl content [4, 5]. Oxidation of lignin in an alkaline medium produces vanilline (aromatic aldehyde) [6]. The effect of increasing the pH and temperature of the pulping process on the relative absorbance of the precipitated lignins from their liquors increases the hydroxyl groups [7] due to the hydrolysis of $OCH_3$.

In this work, the IR spectroscopic technique was used to study the molecular structural changes of thermally treated lignin at different temperatures (25 to 260° C) and different times (0.5 to 2 h).

## 2. Experimental details

Lignin was separated from desilicated soda black liquor, a by-product from industrial pressure soda cooking of rice straw at Rakta Pulp and Paper Mill, Alexandria, Egypt, by acidifying with sulphuric acid [8]. It had the following analysis: lignin 89.1%, ash 1.5% and carbohydrate 10.4%.

Lignin samples were placed in a previously heated oven at 180, 220, 230, 240 and 260° C for 1 h. Other samples were heated at 230° C for different times (0.5 to 2 h). The heated lignin samples were cooled to room temperature. IR spectra of these heated samples were carried out using a Beckman 4250 spectrophotometer. The KBr disc technique was used at room temperature. The frequencies of the bands are reproducible to within $\pm 1\ \mathrm{cm^{-1}}$.

## 3. Results and discussion

The precipitated lignin from black liquor of rice straw pulping was thermally treated at 180, 220, 230, 240 and 260° C for 1 h and the IR absorption spectra of unheated and thermally treated lignin were recorded in the region from 200 to 4000 $\mathrm{cm^{-1}}$ as shown in Fig. 1. From this figure, it is clear that some bands show a detectable relative intensity change, especially the OH stretching and bending vibrations at about 3400 and 1200 to 1000 $\mathrm{cm^{-1}}$ respectively. The stretching $OCH_3$ at about 2900, 2840 and bending at about 1420 to 1260 $\mathrm{cm^{-1}}$ were also changed. The weak shoulder at about 1715 $\mathrm{cm^{-1}}$, representing C=O stretching vibration, showed a detectable increase with increasing temperature.

From the above, it is interesting to study quantitatively the effect of temperature on the intensity of the $OCH_3$, OH and C=O bands to obtain information about the molecular structural changes due to the thermal treatment of lignin. The absorbance of the mentioned characteristic IR spectral bands was calculated at different temperatures and the values are listed in Table I.

Fig. 2 represents the effect of temperature on the absorbance of OH at 3400 $\mathrm{cm^{-1}}$, $OCH_3$ at 2900 $\mathrm{cm^{-1}}$ and C=O at 1715 $\mathrm{cm^{-1}}$. From this figure it is noticed

0022-2461/90 $03.00 + .12

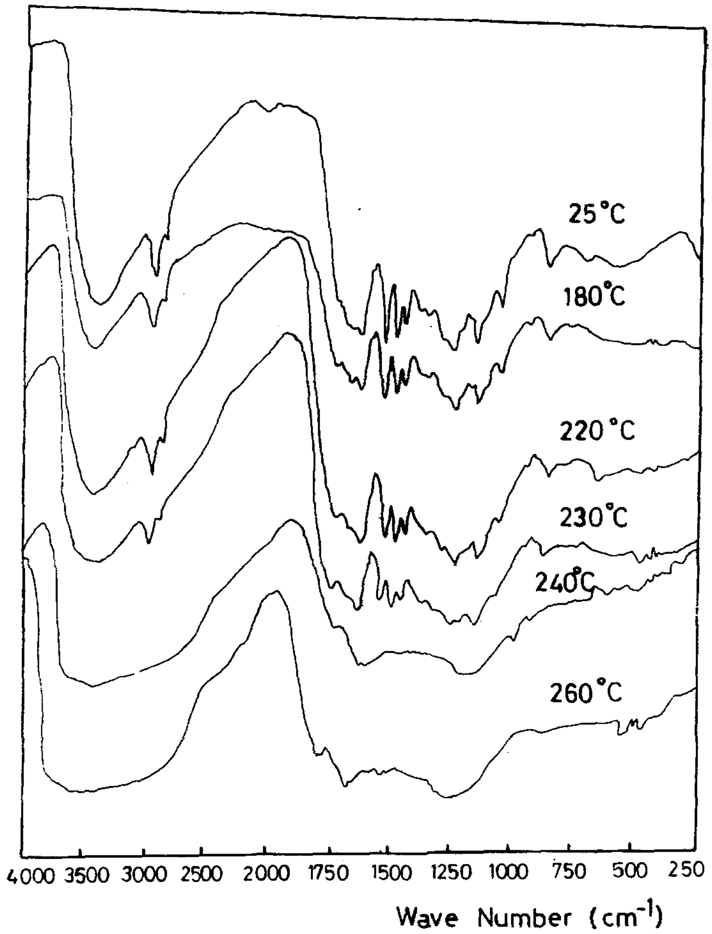

*Figure 1* The IR absorption spectra of untreated and thermally treated lignin.

that the absorbance of bonded OH and $OCH_3$ stretching vibrations showed a slight linear decrease with increasing temperature up to 230° C. On increasing temperature above 230° C, a sharp linear decrease in the OH and $OCH_3$ band intensities was observed. The rate of decrease in the OH band intensity with increasing temperature is lower than that of the $OCH_3$ vibrational band. This may be attributed to the hydrolysis of $OCH_3$ group to OH groups as an intermediate step before the formation of C=O groups. On the other hand, the absorbance of the C=O stretching vibration showed a smooth linear increase with increasing temperature to about 220° C. A sharp increase in the absorbance of this band occurred on increasing the temperature above 220° C. This indicates that OH and $OCH_3$ groups are thermally oxidized to C=O. However, at 260° C, the $OCH_3$ groups are completely decomposed and have disappeared.

From the above discussion, it is interesting to observe that both the OH and $OCH_3$ groups are oxidized to C=O at 1710 cm$^{-1}$. As a confirmation of this mechanism, summation of the absorbance of these bands was made and the results are listed in Table I. From the table, it is clear that the mean values of the

TABLE I Effect of temperature on the absorbance of different groups of thermally treated lignins for 1 h

| $\nu$(cm$^{-1}$) | Absorbance at (° C) | | | | | | Assignment |
|---|---|---|---|---|---|---|---|
| | 25 | 180 | 220 | 230 | 240 | 260 | |
| 1043 | 3.8 | 3.0 | 2.5 | 2.0 | – | – | OH |
| 1115 | 4.5 | 3.5 | 3.0 | 2.7 | – | – | |
| 1200 | 3.5 | 3.0 | 2.5 | 2.2 | – | – | |
| 3400 | 38 | 35 | 34 | 33.5 | 23 | 13 | |
| Mean value of OH absorbance | 12.4 | 11.2 | 10.5 | 10.1 | – | – | |
| 1260 | 2.0 | 1.5 | 1.0 | 1.2 | – | – | $OCH_3$ |
| 1420 | 4.0 | 3.5 | 3.0 | 2.6 | – | – | |
| 2840 | 5.0 | 4.5 | 5.0 | 4.0 | – | – | |
| 2900 | 9.0 | 7.9 | 7.5 | 6.5 | – | – | |
| Mean value of $OCH_3$ absorbance | 5.0 | 4.4 | 4.2 | 3.6 | – | – | |
| 1715 | 0.5 | 1.5 | 2.0 | 2.8 | 3.0 | 4.0 | C=O |
| Mean value of total absorbance of OH, $OCH_3$ and C=O | 5.9 | 5.7 | 5.6 | 5.5 | – | – | |

summation of the band intensity of OH, $OCH_3$ and C=O groups are nearly the same at different temperatures (5.7 ± 0.2). These results confirm that the OH and $OCH_3$ groups are thermally transformed to C=O group. On increasing the temperature to more than 230° C, the summation of the absorbance of these bands is not the same. Thus at temperatures above 230° C these bands are partially decomposed to $CO_2$. This observation can be proved by a detectable loss in the weight of the thermally treated sample at this temperature.

The effect of thermal treatment of lignin at 230° C for time intervals between 0.5 and 2 h on the IR spectra is recorded as shown in Fig. 3. The absor-

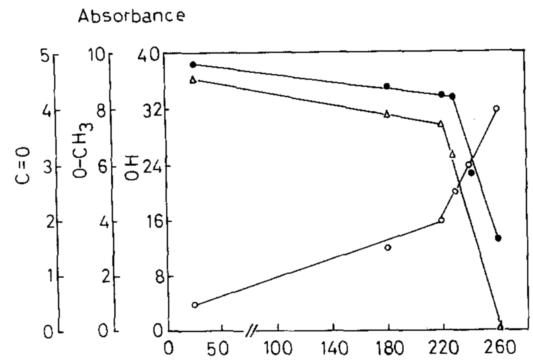

*Figure 2* Effect of temperature on the absorbance of (●) OH, (△) $OCH_3$ and (○) C=O bands of lignin.

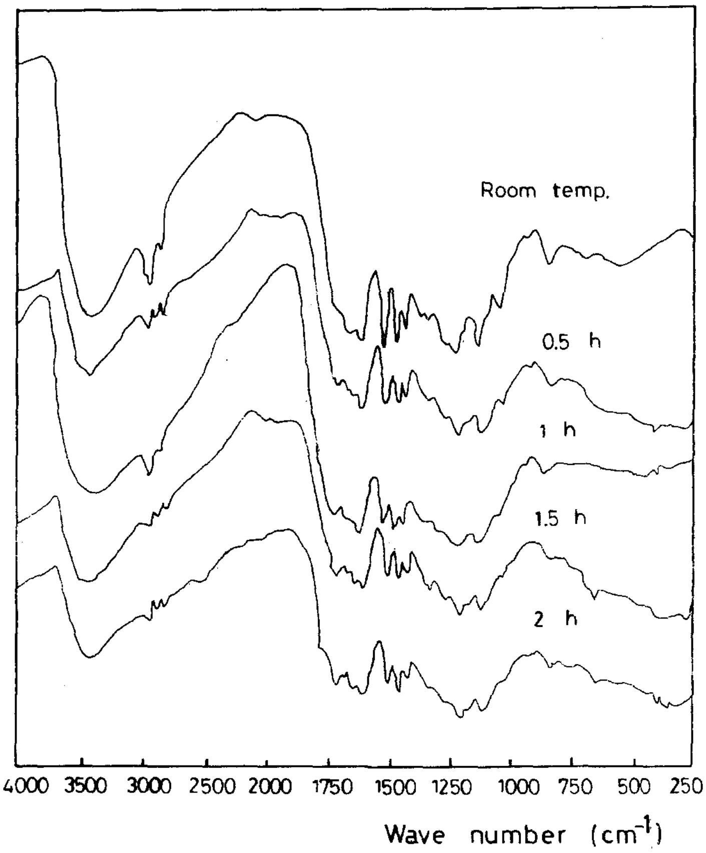

*Figure 3* The IR absorption spectra of lignin heated at 230° C for different times.

TABLE II Effect of heating time of thermally treated lignin at 230° C on the absorbance of different groups

| $\nu$(cm$^{-1}$) | Absorbance at (h) | | | | | Assignment |
|---|---|---|---|---|---|---|
| | 0.0 | 0.5 | 1 | 1.5 | 2 | |
| 1043 | 3.5 | 2.0 | 2.0 | 1.0 | 0.8 | OH |
| 1115 | 4.5 | 3.5 | 2.7 | 2.5 | 2.5 | |
| 1200 | 3.5 | 3.0 | 2.2 | 2.5 | 2.5 | |
| 3400 | 38 | 25 | 33.5 | 29.8 | 28.8 | |
| Mean value of OH absorbance | 12.4 | 10.9 | 10.1 | 8.95 | 8.65 | |
| 1260 | 2.0 | 1.5 | 1.2 | 1.1 | 1.0 | $OCH_3$ |
| 1420 | 4.0 | 3.0 | 2.6 | 2.0 | 2.0 | |
| 2840 | 5.0 | 4.0 | 4.0 | 1.5 | 1.5 | |
| 2900 | 9.0 | 7.5 | 6.5 | 4.3 | 4.3 | |
| Mean value of $OCH_3$ absorbance | 5.0 | 4.0 | 3.6 | 2.3 | 2.2 | |
| 1715 | 0.5 | 2.0 | 2.8 | 3.5 | 4.0 | C=O |
| Mean value of total absorbance of OH, $OCH_3$ and C=O | 5.9 | 5.7 | 5.5 | 4.92 | 4.96 | |

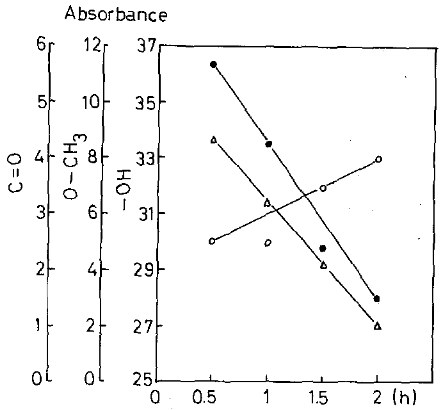

*Figure 4* Effect of heating time at 230° C on the absorbance of (●) OH, (△) OCH$_3$ and (○) C=O bands of lignin.

bances of thermally sensitive characteristic bands of lignin are listed in Table II. The effect of heating time at 230° C on the absorbance of OH, OCH$_3$ and C=O vibrational bands of thermally treated lignin is clearly seen in Fig. 4. From this figure it is seen that the absorbances of OH at about 3400 cm$^{-1}$ and of the OCH$_3$ band at about 2900 cm$^{-1}$, decrease linearly with increasing heating time at 230° C. This decrease is accompanied by a linear increase in the absorbance of C=O groups. However, the summation of the absorbance of the different modes of OH groups, decreases on increasing the heating time to 1.5 h. After 1.5 h, the summation is nearly the same as at 2 h. Also, the same trend was observed for the different modes of OCH$_3$ vibrational bands. On the other hand, the absorbance of C=O groups increases with heating time and reaches 4 after 2 h heating time. Thus, in addition to the oxidation of the OH and OCH$_3$ to C=O, an internal transformation between different types and modes of the OH and OCH$_3$ bands within the lignin structure is found.

## References

1. K. NILSSON, H. NORRSTRÖM and A. TEDER, *Svensk Papperstidning* **18** (1972) 733.
2. H. BOLKER, *Nature* **1197** (1963) 489.
3. H. BOLKER and N. G. SOMEVILLE, *Pulp Paper Mag. Can.* **64T** (1963) 187.
4. T. N. KLEINERT and S. T. COTTON, *Tappi* **40** (1970) 813.
5. H. IBRAHEM, A. E. EL-ASHMAWY and Y. FAHMY, *Egypt J. Chem.* **21** (1978) 443.
6. O. Y. MANSOUR and M. SEIF EL-DIN, *Paper J. Puu* **4a** (1972) 198.
7. K. FREUDENBERG, W. BELZ and C. NUMANN, *Chem. Ber.* **62** (1929) 56.
8. H. EL-SAIED, *J. Appl. Chem. Biotechnol.* **27** (1977) 443.

*Received 27 February*
*and accepted 30 August 1989*