Journal of Thermal Analysis and Calorimetry, Vol. 68 (2002) 265–273

THERMAL DEGRADATION OF HYDROLYZED AND OXIDIZED LIGNINS

A. M. A. Nada[1], *H. Abou Yousef*[1] *and S. El-Gohary*[2]

[1]Cellulose and Paper Department, National Research Center, Dokki, Cairo, Egypt
[2]National Institute of Oceanography and Fisheries, Kayet Bay, Alexandria, Egypt

(Received January 16, 2001; in revised form July 12, 2001)

Abstract

The infrared spectra of lignin treated with hydrochloric acid and peroxyacetic acid is investigated. The hydrolysed lignin spectra show a high intensity phenolic OH band at 1375 cm^{-1} and a decrease in the intensities of CH vibration of methoxyl group at 2920–2810 cm^{-1} and of the linkage (β–O–4 linkage) at 1120 cm^{-1}.

In contrast, the intensity of methoxy group band increases in the case of lignin treated with peroxyacetic acid. This treatment increases also the intensity of the C=O band at 1710 cm^{-1}. The intensity of C=C of aromatic ring band at 1605 and 1505 cm^{-1} is highly affected by the treatment of lignin with peroxyacetic acid, it decreases with large value than in case of lignin treated with HCl.

The thermal behavior of these types of lignin has also been studied. The initial and char temperatures of lignin were determined to be 280 and 700°C respectively for unreacted lignin while were 265 and 550; 220 and 580°C for lignins treated with hydrochloric and peroxyacetic acid respectively. The rate constants of the mass loss of untreated, hydrolysed and oxidized lignins were found to be 0.05, 0.045 and 0.044 min^{-1} respectively.

Keywords: hydrolysed lignin, lignin, oxidized lignin, peroxyacetic acid, thermal analysis

Introduction

Huge quantities of technical lignin are produced annually as by-product of pulping processes. Technical lignin is burned in order to gain energy and recover the inorganic pulping chemicals. The large-scale utilization requires the understanding of its structural features. Lignin is cross-linked and practically insoluble in the native state. Molecular structure of lignin has mainly based on the wet chemicals [1] and spectroscopic analysis [2–5].

Acid catalysts lower the pyrolysis temperature, accelerate the rate of decomposition and change the product distribution of model component [6]. Many papers have been published on the carbonization of cellulose [7, 8], hemicellulose, and lignin [9, 10].

Pyrolytic methods are commonly used in the analysis of biomass and its component [11]. Thermogravimetry (TG) is a simple technique for studying the pyrolytic

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

behavior of materials. The mass loss occurring during slow heating under an inert atmosphere can be measured.

Activation energy and volatilization rates for cellulose materials were determined Madorsky [12]. Many workers [13] noted first-order kinetics for pyrolysis [14].

One goal in this investigation is to find a correlation between the yield of thermal degradation and functional groups in lignin. Using infrared spectroscopy followed the functional groups in the treated lignin.

Experimental

Lignin was precipitated by 10% sulfuric acid at pH 3–4 from produced waste black liquor resulted from pulping of cotton stalks in autoclaves at 170°C for 2 h at 5:1 liquor ratio.

– Lignin was hydrolysed with concentrated HCl in autoclave at 140°C for different time intervals, liquor ratio was 5:1 (lignin:HCl).

– Another batch of lignin was oxidized by using peroxyacetic acid in autoclave at 85°C for 1.5 h at liquor ratio 5:1 (lignin:peroxyacetic acid of 1.5 content).

– Infrared spectra were recorded by Jasco FT/IR FouriSpectrophotometer. Transform infrared, using KBr disc technique.

– TG was recorded by Perkin Elmer Thermal Analysis Controller AC7/DX TGA7, using heating rate of 10°C $\min^{-1}$ in nitrogen atmosphere.

Results and discussion

Infrared spectroscopy

Infrared spectra of untreated, hydrolysed and oxidized lignins predicted different functional groups. The intensities of these group vary according to the treatment. The relative intensities of these groups in three types lignins are listed in Table 1, while Fig. 1 shows the infrared spectra of lignin and treated lignin with concentrated hydrochloric acid and peroxyacetic acid. Apparently, the intensities of the band in the oxidized lignin with peroxyacetic acid, due to the polar carboxyl group bands are strong. This is a distinct advantage when investigating the oxidized lignin. On the other hand, the intensity of the broad OH band (maximum at 3411 cm^{-1}) is seen to decrease relatively to the intensity of the bands at 2937 and 2850 cm^{-1} which are characterized of CH vibration of CH_3 of methoxy groups. This indicates that lignin undergoes oxidation and/or formylation of hydroxyl groups or the ring cleavage [15] leading to the formation of lactones.

Moreover, peroxyacetic acid oxidative treatment induces an increase in the intensity of the band at 1715–1720 cm^{-1}, which is due to C=O groups of carboxylic acid [15]. Quinones and α-carbonyl and olefin usually show bands at 1660–1620 cm^{-1} due to the oxidation, which occurred, on the hydroxyl groups and the lignin aromatic ring, as a result of treatment of lignin with peroxyacetice acid. On addition, the relative absorbance of the guaicyl unit of peroxyacetic acid lignin at 1260 cm^{-1} is lower than that in case of untreated one [16, 17].

Table 1 Relative absorbance (band intensity of different group/band intensity of CH vibration of aromatic ring at 1500 cm^{-1}) of different groups of lignin, hydrolyzed and oxidized lignin

Group	Wavenumber/ cm^{-1}	Relative absorbance of lignins		
		Untreated	Hydrolyzed	Oxidized
OH group	3411	2.22	1.87	1.76
2nd	1325	0.90	0.72	0.94
2nd	1220	1.52	1.13	1.50
1ry	1035	0.96	0.61	0.52
Phenolic OH group	1375	0.63	0.72	1.21
β-aryl ether bond	1120	2.02	1.19	1.44
$-OCH_3$	2920	1.47	1.07	1.59
	2820	0.92	0.56	1.12
	1475	1.04	0.98	1.15
	1425	0.84	0.78	1.56
C–H vibration	1600	1.26	1.15	0.92
of aromatic ring	1605	1.00	1.00	1.00
C=O	1700	1.16	0.54	1.50
Guaicyl unit	1668	1.16	0.981	1.02

The relative absorbance of CH vibration of the aromatic ring at 1600 is lower than that at 1505 cm^{-1}. This indicates that the guaicyl type lignin has been dissolved in preference to the syringyl type of peroxyacetice acid lignin [18]. The relative absorbance of OH group bands at 3421, 1325, 1220 and 1035 cm^{-1} of hydrolyzed lignins with acid are lower than that in case of untreated lignin due to the cleavage of aliphatice hydroxyl group i.e. decrease in secondary and primary OH group [19]. On the other hand, the relative absorbance of phenolic OH group band at 1370–1375 cm^{-1} of hydrolyzed lignin is higher than that of untreated lignin due to the possibility of cleavage of β-aryl ether [20]. This can be confirmed by the decrease of the relative absorbance of β-aryl ether link band at 1120 cm^{-1} of hydrolyzed lignins. Due to the acidolysis of lignin, the relative absorbance of OH vibration of methoxyl group bands at 2930, 2825, 1475 and 1425 cm^{-1} decrease due to the hydrolysis of this group to phenolic groups. This can be seen from the increase in the relative absorbance compared with the unreacted one. In contrast, the relative absorbance of CH vibration band of aromatic ring at 1600 cm^{-1} of the hydrolyzed lignin is higher than that in case of oxidized lignin.

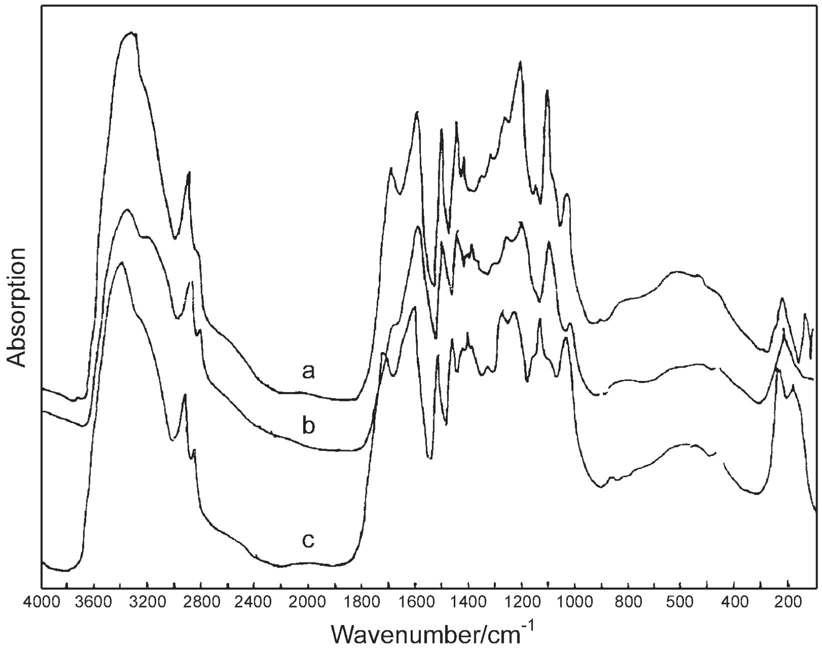

Fig. 1 Infrared spectra of a – untreated lignin, b – treated lignin with HCl and c – treated lignin with peroxyacetic acid

Thermal properties of lignin

The thermal decomposition of lignin takes place along a broad temperature range, resulting in 30–50% char and a significant amount of low molecular mass volatiles, in addition to the monomeric and oligomeric products. Table 2 shows the chemical constituents of the used lignin.

Table 2 The chemical constituents of the different lignins

Lignin type	Lignin/%	Hemicellulose/%	Ash/%
Untreated	93.50	5.30	1.20
Hydrolyzed	98.00	1.20	0.50
Oxidized	97.80	1.40	0.60

It is evident from Table 2 that the treatment of lignin with hydrochloric acid or peroxyacetic acid decreases not only the carbohydrate fraction, but also the ash content. Treatment with HCl or peroxyacetic acid affects also the function groups of the products as previously mentioned. The thermal behavior is expected to change with lignin treatment.

Thermal analysis

Thermogravimetric analysis

TG curves reveal some analogies and differences in the thermal behavior of different lignins. It is clear that the decomposition takes place in a wide temperature range. The major devolatilization steps occurring between 200 and 700°C. The char residues at nearly about 800°C vary between 3 to 5% for treated and untreated lignins respec-

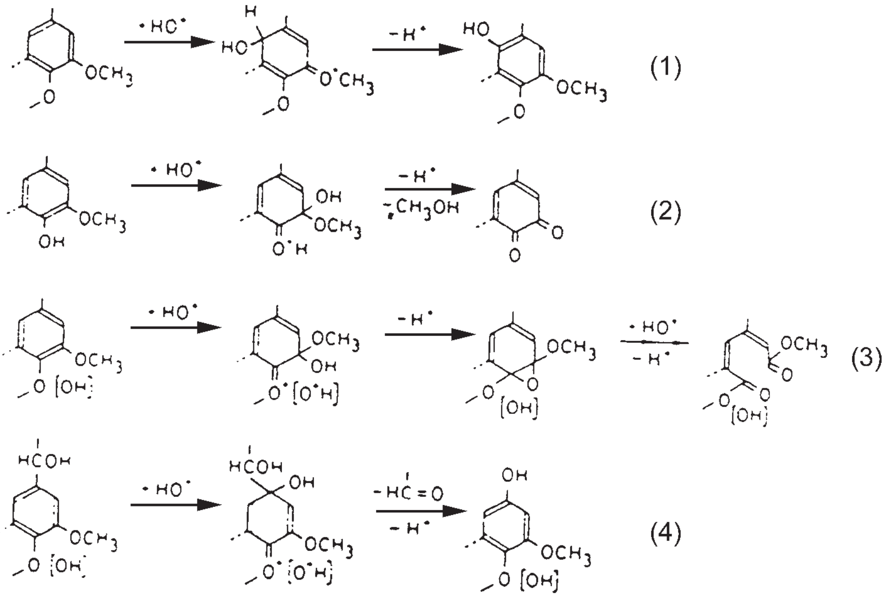

Fig. 2 Reactions of phenolic and non-phenolic structures with hydroxonium ions

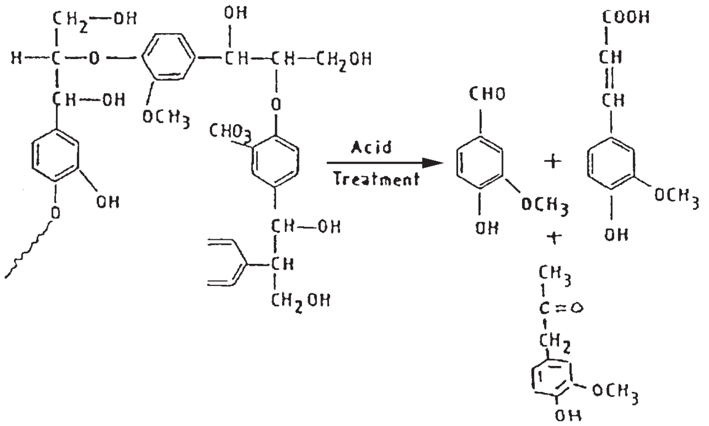

Fig. 3 Acidic hydrolysis of lignin

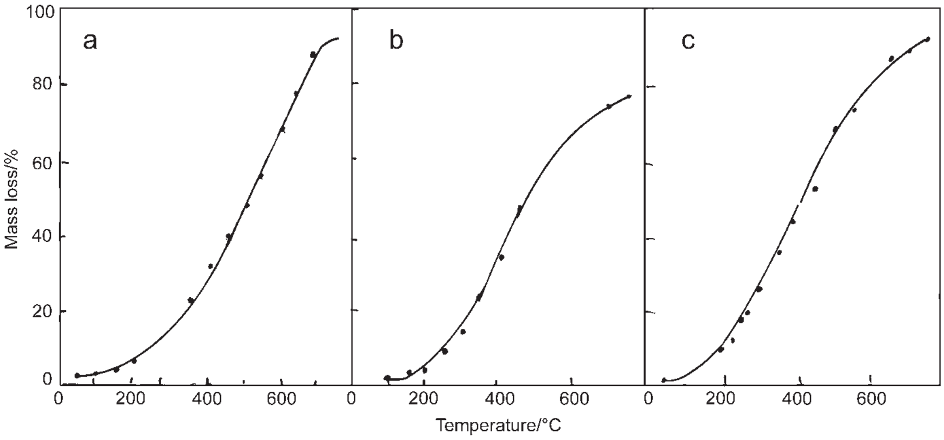

Fig. 4 The curves of a – unreacted lignin, b – treated lignin with HCl and c – treated lignin with peroxyacetic acid

tively, depending on the type of lignins [21]. On the other hand, the fundamental groups composition affect not only the volatile product chars but also the mass ratio [22]. The water formation explains 4–9% of the mass loss for the heated lignin. The release of the adsorbed water accounts for the peak around 100°C (Fig. 4). The water evolution occurs over an abroad temperature range, indicating of the multiple origin of the water. After initial loss of moisture at 100–120°C other thermal decomposition processes take place with successive loss. A loss is attributed to the actual pyrolysis by minor decomposition reaction at 270, 260, 240°C for unreacted lignin, hydrolyzed and oxidized lignin (Fig. 4). The minor decomposition of the treated lignin lower than the untreated lignin, due to the degradation and depolymerization which occurred in lignin during hydrolysis of oxidation process. On the other hand the higher ash content of the untreated lignin than the treated lignin, Table 3, enhances the minor decomposition temperature of the untreated lignin. Moreover, the untreated lignin has a higher major decomposition than the hydrolyzed and oxidized lignins. This is due to the higher molecular mass and the ash content of the untreated lignins. So, the loss of mass at the major temperature was about 85, 68 and 75% for untreated, hydrolyzed and oxidized lignin respectively.

Table 3 Initial and charring temperature of lignin, hydrolyzed and oxidized lignin

Lignin type	Initial decomposition/°C	Charring temperature/°C
Untreated	280	700
Hydrolyzed	265	550
Oxidized	220	580

Differential thermal analysis

DTA curves of different lignins are shown in Fig. 5. It is clear that the first endothermic peak occurs at about 100–120°C for all lignins due to the loss of moisture and desorption of gases. Other endothermic peaks occurred at 363.6, 363.67 and 269°C for untreated, hydrolyzed and oxidized lignin with peroxyacetic acid respectively. It is found that the endothermic peak of the oxidized lignin with peroxyacetic acid has a lower value than other two lignins due to the depolymerization, degradation and aromatic degradation of lignin [23] (as seen from infrared spectra).

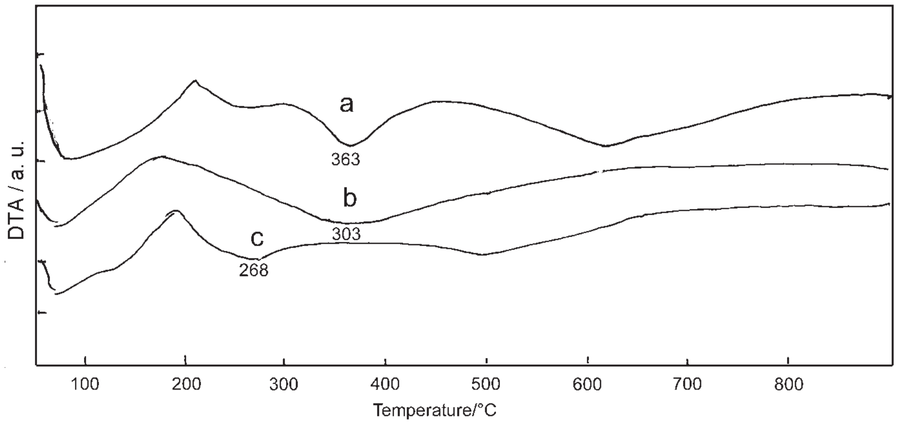

Fig. 5 DTA curves of a – unreacted lignin, b – treated lignin with HCl and c – treated lignin with peroxyacetic acid

Activation energy

The data obtained from TG curves were analyzed by the differential method of Tang [24] in which ln$(W_0-W_\infty)/(W_t-W_\infty)$ is plotted *vs*. time (t), where W_0 is the initial mass, W_t is the mass at time (t) and is the mass of the ash remaining after the final heating. The slop of the obtained line is the rate constant for the thermal decomposition [24]. As shown in Fig. 6, plotting of ln$(W_0-W_\infty)/(W_t-W_\infty)$ *vs*. time under isothermal conditions gave two parts. The first part, which occurs over the initial 25–30 min, is due to the first loss of water. The second part of the straight line is due to the thermal decomposition of the different lignins. This indicates that the loss in mass due to the thermal decomposition is nearly first order. The calculated reaction rate constant of mass loss due to the thermal decomposition are 0.05, 0.045 and 0.044 min^{-1} for untreated, hydrolyzed and oxidized lignins, respectively.

Activation energy in the main decomposition temperature region 300–700°C was calculated using Arrhenius plot for first order reaction [25, 26]. The activation energies are 34.82, 27.81 and 30.40 kcal mol^{-1} for untreated hydrolyzed and oxidized lignins. It is seen that oxidized lignin has the lowest activation energies due to the ox-

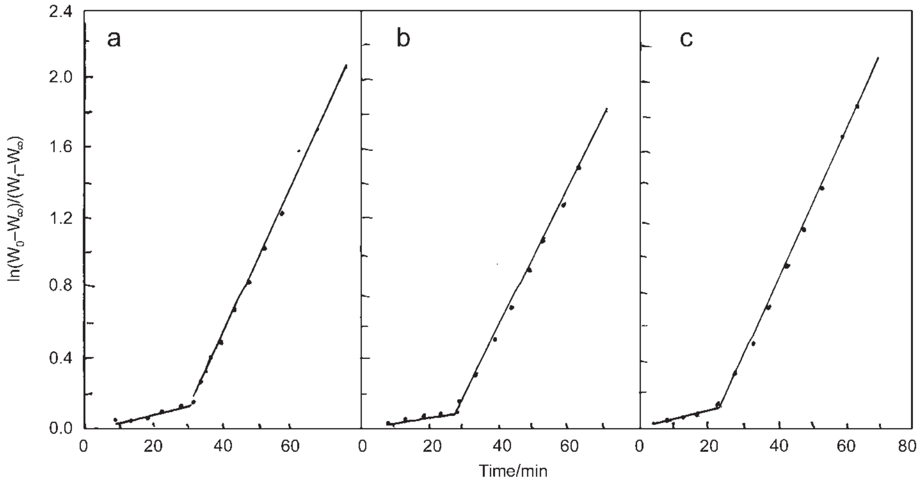

Fig. 6 Relation between ln(W_0–W_∞)/W_t–W_∞) *vs*. time for a – unreacted lignin, b – treated lignin with HCl and c – treated lignin with peroxyacetic acid

idation and depolymerization which occur during the treatment of lignin with peroxyacetice acid.

Conclusions

- The hydrolysis of lignin with HCl increases the phenolic groups, the methoxyl groups and the ether linkage of the hydrolyzed lignin.
- Treatment of lignin with peracetic acid increases the carbonyl group of the oxidized lignin.
- The minor decomposition of treated lignin is lower than that of the untreated lignin. The ash content of the untreated lignin is higher than the treated lignin.
- The untreated lignin has a higher major decomposition than the hydrolyzed and oxidized lignin.
- The reaction rate constant of the thermal decomposition of untreated lignin is higher than the hydrolyzed and oxidized lignin.
- The activation energy of untreated lignin is higher than the oxidized and hydrolyzed lignin.

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