

Studies on the Organic Acid Lignin from Rice Straw

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Isolated lignins from the spent liquor of rice straw formic acid pulping, residual formic acid pulp have been investigated by UV, FT-IR and ¹HNMR spectroscopy and compared with soda-AQ liquor and dioxane rice straw lignins. The UV spectra showed two absorption maxima at 280 and 310nm in all lignins, which are common in grass lignin. Strong band was observed at 1720 cm⁻¹ in FT-IR spectra in formic acid liquor and pulp lignins as compared to soda-AQ liquor and dioxane rice straw lignins. NMR spectra showed that lignins were to undergo demethylation, condensation, ring opening, formylation of hydroxyl groups during formic acid pulping.

Keywords : Rice Straw, Formic acid lignin, Hydroxyl group, Demethylation and Ring opening.

INTRODUCTION

Lignin is a natural polymer of plants that is conventionally obtained from the black liquor of pulping processes, such as kraft and sulfite processes. But the lignin from the conventional pulping processes is not used as high value added products due to alteration of structure. Organic acid pulping has proved to be a promising process to achieve complete utilization of lignocellulosics without impact to environment. By this process (1 - 3) wood and nonwood can be simply fractionated to pulp, lignin and monosaccharides (mainly from hemicellulose), which make it easy to utilize them for more valuable products. The lignin can be converted to valuable products, such as carbon fiber (4), activated carbon fibers (5) and additives (6). From the monosaccharides, chemicals, sweetening materials, food additives, fuel and polymers can be produced (7). Other derivatives from lignin such as adhesives, ion exchange resins, metal ion chelating resins etc may be produced.

For proper use of lignin, information of chemical structure of lignin is needed. Acetic

acid lignin from rice straw (RL), birch (BL) and fir (FL) were characterized by Pan and Sano (8). They showed that RL had higher contents of residual polysaccharide and protein and remarkably fewer acetyl group than BL and FL. Rice straw had more conjugated and fewer unconjugated carbonyl groups than that the wood lignin (9). Polysaccharides in acetic acid lignin were much higher than the alkaline lignin (10). They showed that polysaccharides in acetic acid lignin consisted mainly of arabinose and xylose and they accounted of nearly 84% of the total sugars. On the contrary, glucose was the major sugar (nearly half of the total sugar in alkaline lignin followed by xylose and arabinose. Lignin from the spent liquor of peroxyformic acid pulping was also investigated by Hortling *et. al* (11). They showed that hydro hydrolysis of *o*-aryl ether was occurred during formic acid treatment. In the case of softwood this reaction was restricted by condensation reactions, during which inter- and intramolecular α -5 bond might be formed. In this investigation, lignins isolated from the spent liquor of formic acid pulping and formic acid pulp were characterized by UV, FT-IR and ¹HNMR

analysis and compared these data with native rice straw and soda-AQ liquor lignins.

EXPERIMENTAL

Pulping

Rice Straw pulping was done in a polyethylene bag, which was immersed in thermostatic water bath. The temperature was set at 80°C for 2h in the liquor ratio of 10. The formic acid concentration was 80% (V/V).

Soda-anthraquinone pulping of rice straw was done in a 1-liter capacity autoclave, which was heated to 150°C for 1h in a thermostat control oil bath. NaOH concentration was 14% on oven dry RS in the liquor ratio of 6.

Separation of lignin from spent liquor and rice straw

After desired period of pulping spent liquor was separated by filtration in a buckner funnel. The collected liquor was concentrated under reduce pressure and poured into five volumes of water. Precipitated formic acid lignin were filtered out, washed with water and lyophilized. Lignin from the soda-AQ spent liquor was precipitated by adjusting pH to 2 with 1N HCl. Lignins were isolated from rice straw meal and formic acid pulp by refluxing the pulp with dioxane-water-HCl media in the ration of 90:8:1.6 for 1h. After completing reflux time, meal dioxane mixture was filtered in Buckner funnel using filter no.2 The residue was washed with dioxane solution (9:1). The filtrate was concentrated in vacuum evaporator at 40°C. Then conc. dioxane soln. was added drop wise to ion exchange water to precipitate lignin. Precipitate was centrifuged and washed till neutrality and dried in vacuum over P₂O₅.

Purification of lignin

Lignins were dissolved in dioxane-water (8:2, v/v) and the precipitate was removed by centrifugation. The supernatent was added drop by drop to ten volumes of diethyl ether-petroleum ether (1:1, v/v) and finally dried under vacuum.

Acetylation of lignin

Lignin 100 mg was added in 1.5 ml of dry pyridine-acetic anhydride (1:1) and kept for 72 h. The solution was added to a 10-fold volume of ice-cold water whereupon the acetylated sample was recovered as a precipitate, which was purified by successive washing with water and dried under vacuum over P₂O₅.

Spectroscopy

Ultraviolet Spectra

Purified lignins were dissolved in dioxin-water in the ratio of 9:1. The spectra were recorded in UV-VIS spectrophotometer Model 756MC.

Fourier Transform Intra Red

IR spectra were recorded by using a Shimadzu FTIR spectrometer model 8201PC. The dried samples were embedded in KBr pellets in the concentration of about 1mg/100mg KBr. The spectra were recorded in the absorption band mode in the range 4000-400 cm⁻¹.

¹HNMR

100 mg of acetylated lignin was dissolved in 0.5 ml CDCl₃ for ¹HNMR Spectra.

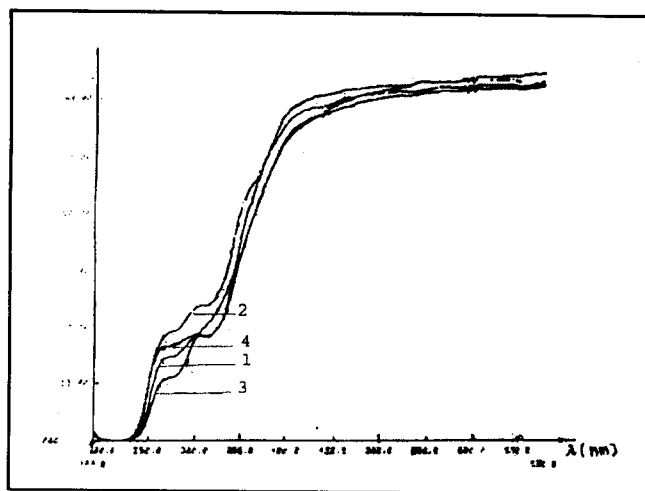
RESULTS AND DISCUSSION

Ultraviolet Spectrum of the lignins of formic acid liquor, formic acid pulp, soda-AQ and

Table 1 . FT-IR absorption bands of different rice straw type of lignin.

Band cm^{-1}	Assignment	Type of lignin			
		Formic acid liquor	Formic acid pulp	Soda AQ liquor	Diox. rice straw
1738-1709	C=O stretch in unconjugated ketone, carbonyl and ester groups	1722	1709	-	1709
1675-1655	C=O stretching in conjugated, p-subst., aryl ketones.	1653	-	1647	1655
1593-1605	Aromatic skeletal vibrations plus C=O stretching; $S>G; G_{\text{condensed}} > G_{\text{esterified}}$	1601	1601	1601	1601
1505-1515	Aromatic skeletal vibrations ($G>S$)	1512	1512	1512	1510
1450-1470	C-H deformations (in $-\text{CH}_3$ and $-\text{CH}_2-$)	1460	1460	1460	1460
1422-1430	Aromatic skeletal vibrations combined with C-H in plan deformation	1423	1425	1425	1425
1365-1370	Aliphatic C-H stretching in CH_3 (not in OMe) and phen	1363	1360	1363	1362
1325-1330	Condensed S and G rings (G ring bound via position 5)	1330	1333	1333	1333
1266-1270	G ring plus C=O plus stretching	1257	1263	1257	1257
1221-1230	C-C plus C-O plus C=O stretching ($G_{\text{condensed}} > G_{\text{esterified}}$)	-	-	1221	-
1166	Typical for HGS lignins; C=O in ester groups (Conj.)	1171	-	1166	1167
1125-1128	Typical for S units; also secondary alcoh. and C=O stretching	1122	1128	1120	1122
1030-1040	Aromatic C-H in plane deformation ($G>S$) plus C-O deform, in primary alco. plus C=O stretching (unconj.)	1043	1036	1038	1038
830-840	C-H out of plane in C- 2 and C- 6 of syringyl units and all the positions of the p-hydroxyphenyl units	837	837	835	837

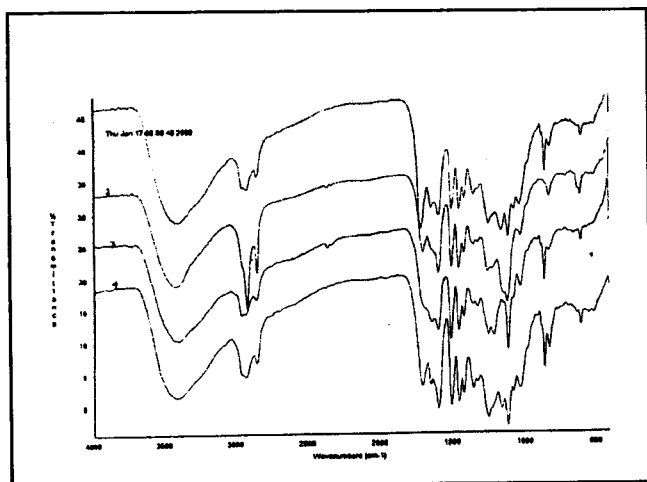
Fig. 1. UV Spectra of different lignins from rice straw (1-FA liquor lignin, 2-FA pulp lignin, 3-Soda-AQ liquor and 4- dioxane rice straw lignin



milled rice straw are given in Figure 1. Lignin from wood had only one absorption maximum, near 280 nm. But it is seen from Figure 1. that different type of rice straw

lignins had two absorptions maxima at about 270 and 310 nm. The peak at 315 for milled wood grass lignins was also obtained by Huguchi et. at. (12). Authors explained this peak, due to the ferulic acid and *p*-coumaric acid in the lignin. The specific location of maxima around 280 nm depends on the position and nature of the substituents in the benzene ring. It is known that the guaiacyl compounds exhibits maxima in the region of 280 nm. However, the substituent of an extra methoxyl group in the 5 position shift the maxima to a lower wavelength (13). Absorption at 310 nm was stronger in formic acid liquor and formic acid pulp lignin than soda-AQ liquor and dioxane rice straw lignin. Formic acid pulping influenced the absorptivity of rice straw lignins.

Fig. 2. FT-IR spectra of different rice straw lignins (1-FA liquor lignin, 2-FA pulp lignin, 3-Soda-AQ liquor lignin and dioxane RS lignin



FT-IR spectroscopy

Figure 2 show the FT-IR spectra of the lignins and the Table 1. lists the locations of the observed bands assigned by Faix (14). The two bands at 1600 and 1500 cm^{-1} were observed considerably in all lignins. These two bands are characteristics of aromatic compounds and due to vibrations of the aromatic skeletal. The intensities of these two bands were approximately equal in all lignins (Figure 2.). The band at 1720 cm^{-1} and 1655 cm^{-1} were due to carbonyl groups. The band at 1720 cm^{-1} was considerable in formic acid liquor and formic acid pulp lignins as compared to soda-AQ liquor lignin. The intensity of the band at 1720 cm^{-1} was

increased due to the formylation of the lignin. This was also observed in milox liquor lignin of Reed canary grass (15). But soda-AQ liquor lignin of rice straw and dioxane rice straw lignin had strong bands at 1655 cm^{-1} as compared to formic acid liquor and formic acid pulp lignins. Evidence for the more carbonyl moieties in formic acid liquor, pulp and milled rice straw lignins at 1160 cm^{-1} due to $-\text{C}=\text{O}$ ester groups (conj.), which is typical for annual plant lignin (HGS). The *p*-hydroxyphenyl units can be identified by the band at 834 cm^{-1} in dioxane straw lignin.

$^1\text{H-NMR}$ spectroscopy

$^1\text{H-NMR}$ spectroscopy has frequently been used in lignin structural studies, at qualitative and quantitative level (16). The different protons present in the acetylated lignins can be used to quantify various structural elements of the polymer such as arylglycerol *b-O-4* units, methoxyl groups, aromatic units, aromatic and aliphatic acetate, and also some minor condensed structures. The $^1\text{H-NMR}$ spectra of formic acid liquor, formic acid pulp, soda-AQ liquor and dioxane straw lignins are presented in Figure 3; the labelled peaks, their assignments and quantitative estimates are shown in Table 2. A clear signal is observed near 8.1 ppm in formic acid liquor lignin. This is attributed to formyl protons of both *a*- and *g*- aliphatic

Table 2. Number of protons in the different functional groups obtained by integration of the proton NMR spectra of acetylated lignin. (The values of the integral for the different functional groups are compared with those of methoxyl protons)

Type of lignin	Integration areas in chemical shift (ppm)							
	8.3-7.9 (C=O)H	7.6-6.7 G	6.7-6.3 S	6.3-5.8 H_α	5.8-4.0 $\text{H}_{\alpha,\gamma}$	4.0-3.5 OCH_3	2.5-2.2 phenol	2.2-1.8 alcoh.
Formic acid liquor	0.266	0.91	0.38	0.57	1.82	2.46	1.2	2.5
Formic acid pulp	-	0.92	0.44	0.43	2.49	1.73	1.74	3.3
Soda-AQ liquor	-	0.97	0.56	0.33	2.2	2.27	1.32	1.97
Dioxane RSL	-	1.11	0.43	0.49	2.79	2.50	1.2	2.8

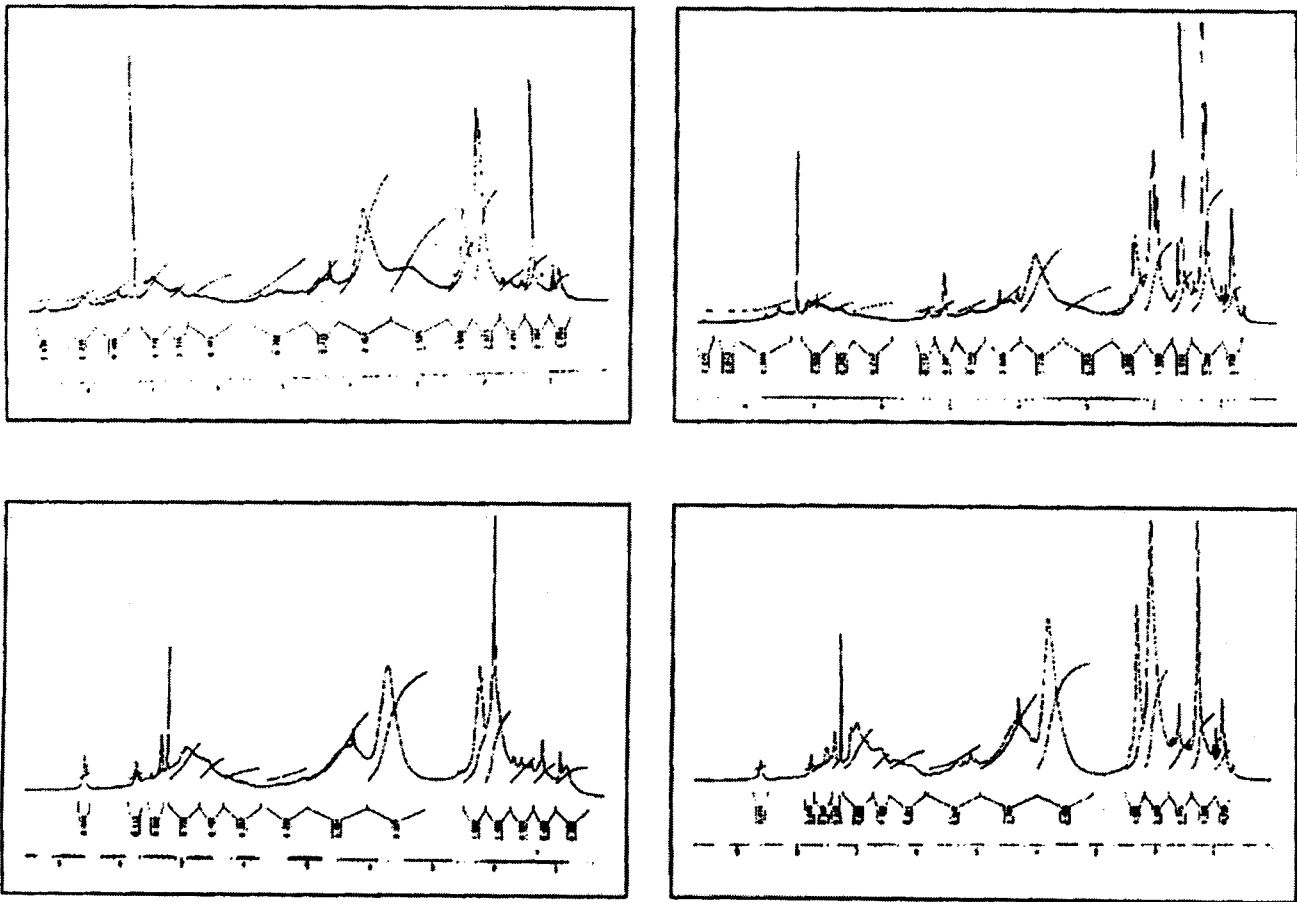


Fig. 3. ¹H-NMR spectra of different rice straw lignins (1-Formic acid liquor, 2-formic acid pulp lignin, 3-soda-AQ lignin and 4-Dioxane rice straw lignin)

formate groups formed during formic acid pulping (17,18). This signal was absent in formic acid pulp lignin. In the aromatic proton region the presence of guaiacyl and syringyl units were observed in all lignins. In addition a clear signal between 7.8 to 7.4 ppm was observed in all lignins, which can be assigned to the olefinic and aromatic protons of *p*-coumaric and ferulic acids (19), usually found in grass lignins (20). But this signal was weakened in formic acid pulp lignin.

It is seen from Table 2. that aromatic proton was lower in formic acid liquor lignin than the dioxane straw lignin. This suggests that the lignin is more substituted or condensed and/ or that ring opening reactions occurred during formic acid pulping. This was also

evident in formic acid/ peroxyformic acid pulping of wood (11).

Dioxane straw lignin showed the highest and the formic acid pulp lignin lowest proton at 5.8-4 ppm indicating, that during acid hydrolysis the aliphatic C-O bonds were broken down. But formic acid pulp lignin remained relatively unchanged during acid hydrolysis. The number of methoxyl protons (4.0-3.5ppm) was lowest in formic acid pulp lignin followed by soda-AQ liquor lignin. The results suggested demethylation and probably ring opening reactions. The intensity in the region on 2.5-2.2 ppm in Figure 3. indicates the acetyl protons from acetylated free phenolics. The number or protons in this region was higher in soda-AQ liquor and formic acid pulp lignins than

the dioxane straw lignin. This is in accordance with the assumption that demethylation reactions and formation of new phenolic hydroxyl groups occur through the reaction of HO⁺ ions with the benzene nucleus together with hydrolysis of the aryl ether bonds. The content of alcoholic groups in the region 2.2-1.8 ppm was higher in formic acid pulp lignin, which may be due to the higher concentration of α -, β - and γ - (OH groups in the lignins. This is in accordance with the greater number of α -, β - and γ -) protons bonded to aliphatic carbons bonded to oxygen, which is indicated in the region of 5.8-4.0ppm.

CONCLUSIONS

Lignin isolated from formic acid liquor, pulp were analyzed in UV, FT-IR, and ¹H-NMR spectroscopy and compared with soda-AQ and dioxane straw lignins. Different rice straw lignins had two absorptions maxima at about 270 and 310 nm, which may be explained by the ferulic acid and *p*-coumaric acid in the lignin. Formic acid treatment increased absorption band at 1720 cm⁻¹ may be due to the formylation of lignins. This was further observed in ¹H-NMR at 8.1ppm for formic acid liquor lignin.

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