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Modified Kraft Pulping of Bagasse: Infrared Spectroscopy of Lignin

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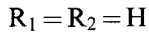
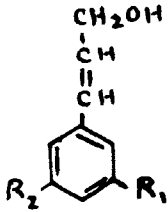
The infrared spectroscopy of precipitated lignin from waste black liquors of bagasse pulping with kraft sulfite pulping process was investigated. Also the effect of anthraquinone and methanol addition in the soda, kraft and kraft-sulfite pulping liquor on the infrared spectra of the precipitated lignin was studied. The presence of methanol in the pulping liquor causes an increase in the degradation as well as increase in the carboxylic group in the precipitated lignin. Also, the phenolic hydroxyl group in case of kraft lignin is higher than soda lignin. Presence of sulfite in the kraft-sulfite pulping liquor produces lignin hydroxyl groups.

Keywords: Kraft pulping; bagasse; lignin; structure; infrared spectroscopy

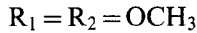
INTRODUCTION

Lignins are polymeric materials occurring in the plant kingdom. They are formed through polymerization of three basic precursors coniferyl, sinapyl and coumaryl alcohols. The polymerization process results in the formation of randomly branched and crosslinked structure.

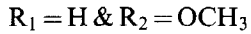
*Corresponding author.



P-cumaryl alcohol

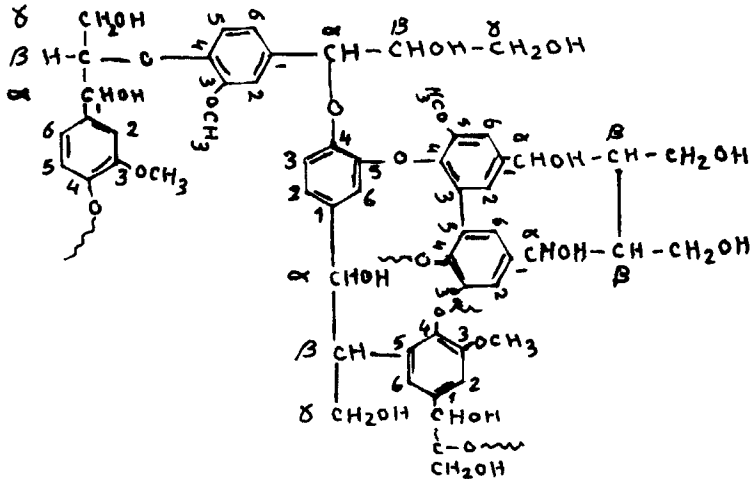


sinapyl alcohol



coniferyl alcohol

Lignin structural units are linked to each other with various types of linkages, namely β -O-4, α -O-4, 4-O-5 (diaryl), β -5, β - β , 5-5 (biphenyl) and β -1. The first three types are ether bonds and the rest are carbon-carbon bonds.



Adler found that the β -O-4 linkages is the major one and β -5 is the secondary important linkage [1].

EXPERIMENTAL

Sugar cane bagasse was cooked by the following methods:

- (1) pulping: bagasse was cooked by 18% NaOH in presence and absence of 0.1% AQ and methanol (22% from the total pulping liquor).

- (2) Kraft pulping: bagasse was cooked by kraft process using 13.5% NaOH and 4.5% Na_2S in presence and absence of 22% methanol.
- (3) Kraft-sulfite pulping liquor for bagasse was prepared by using 13.5% NaOH and different percentage of sodium sulfite (5–40%) from the 4.5% sodium sulfide.

All pulping process was carried out at 170°C for 2 hours using 4.5: 1 liquor ratio in stainless steel cups of 2 L capacity using ethylene glycol bath and electrically heated. After pulping process the black liquors were collected, and lignin was precipitated using 10% H_2SO_4 . The different lignins were filtered and washed till neutrality then dried in air.

IR spectra of lignin was carried out using KBr disc technique using JASCO FT/IR-300 E: apparatus. Relative absorbance of any band = intensity of the band/intensity of CH vibration band of aromatic ring at 1505 cm^{-1} .

RESULTS AND DISCUSSION

Soda and Kraft Lignin

From Table I, it is clear that the mean value of relative absorbances of the different hydroxyl groups bands in case of kraft lignin is higher than in soda lignin. On the other hand, the relative absorbance of the phenolic hydroxyl group at 1375 cm^{-1} in kraft is higher than that in soda lignin. This can be due to that, the cleavage of aryl ether bonds is lower in case of soda lignin than kraft lignin [2]. This can be confirmed by the lower relative absorbance of the ether linkage at 1120 cm^{-1} for the kraft lignin than soda lignin. On the other hand, the hydrosulfide ions in the kraft pulping process attack some of methoxyl groups in the phenolic groups. This causing an increase in the phenolic hydroxyl group intensity and decrease in the relative absorbance of the methoxyl group. This could be seen from the table in which the mean value of methoxyl groups in kraft lignin is lower than the soda lignin.

The relative absorbance of C—O stretching vibration in syringyl at $1230\text{--}1220\text{ cm}^{-1}$ is lower in case of kraft lignin than soda lignin. In case of C—O stretching vibration in guaiacyl at $1270\text{--}1260\text{ cm}^{-1}$ is higher for kraft lignin than soda lignin [3,4]. This is due to the

TABLE I Absorbance intensity of different lignin bands relative to intensity of CH vibration of aromatic ring at 1505 cm^{-1}

Bands cm^{-1}	Kinds of lignin						
	Soda	Kraft	Soda + AQ	Kraft + AQ	Soda + Methanol	Kraft + Methanol	Soda + AQ + Methanol
OH gp.							
3421	1.66	1.95	1.70	2.48	1.50	1.70	1.72
1375	0.09	0.11	0.10	0.12	0.14	0.16	0.16
1325	0.17	0.17	0.18	0.20	0.21	0.15	0.14
1260	0.05	0.15	0.06	0.04	0.05	0.06	0.06
1220	0.57	0.53	0.58	0.72	0.62	0.59	0.44
1155	0.10	0.03	—	—	0.01	0.06	0.06
1035	0.50	0.60	0.79	0.84	0.72	0.56	0.69
Mean	0.45	0.51	0.49	0.63	0.46	0.47	0.46
1120	1.55	1.38	1.45	1.35	1.30	1.06	0.86
OCH ₃ gp.							
2910	0.43	0.40	0.48	0.48	0.46	0.44	0.61
2830	0.26	0.23	0.27	0.24	0.23	0.24	0.36
1475	0.74	0.78	0.82	0.76	0.72	0.74	0.86
1425	0.45	0.30	0.45	0.44	0.41	0.41	0.53
Mean	0.47	0.43	0.51	0.45	0.46	0.46	0.59
CH of aromatic							
1605	0.91	0.98	0.94	1.36	1.26	1.08	0.97
1509	1.00	1.00	1.00	1.00	1.00	1.00	1.00
835	0.19	0.20	0.15	0.24	0.28	0.26	0.19
Mean	0.70	0.73	0.70	0.87	0.85	0.78	0.72
880	0.07	—	0.06	—	—	—	—
C=O gp.							
1700	0.24	0.18	0.21	0.03	—	—	0.20
1640	—	—	—	—	0.08	0.03	—

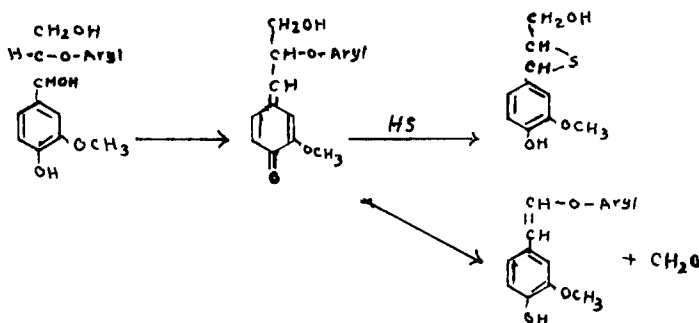
attacking of the hydrosulfide ion, in the kraft pulping process, to the methoxyl groups of lignin [5, 6].

Greater intensity of CH vibration of aromatic ring band at 1600 cm^{-1} as compared to that at 1500 cm^{-1} supports the presence of *P*-hydroxyphenyl propane units. So the ratio of relative absorbance of 1600 cm^{-1} band is higher in case of kraft than soda lignin. *I.e.*, kraft lignin has more *P*-hydroxyphenyl propane units indicating less degradation of kraft lignin than soda lignin [7].

From Table I, the relative absorbance of the carboxyl group band at 1700 cm^{-1} is higher in soda lignin than kraft lignin. This means that

the kraft lignin is less degraded during pulping. Also, kraft pulping of bagasse prevents the formation of stable vinyl ether structure by adding the quinone methide intermediate. The α -mercaptane group formed in kraft lignin assists the hydrolysis of aryl ether bonds.

So, comparison of kraft and soda lignin indicates that, kraft pulping process causes an increase in phenolic hydroxyl content through cleavage and loss of methoxyl group



and, possibly, some loss of aliphatic hydroxyl groups either through dehydration or sulfide formation [8]. In case of kraft lignin a weak band at 630 cm^{-1} is found which is assigned to C—S stretching [9].

Soda-AQ and Kraft-AQ Lignin

Presence of anthraquinone in the pulping liquor (soda or kraft) reduces lignin during the delignification process, thus avoiding significant change in chemical structure. So, the percentage of OCH₃ and OH groups are nearly similar for both soda and soda-AQ [10]. However it is clear, from Table I, that the mean value of relative absorbance of hydroxyl groups bands at 3421, 1375, 1325, 1260, 1220, 1155 and 1035 cm^{-1} of soda is lower than soda-AQ lignin.

On the other hand, presence of AQ in the pulping liquor causes an promotion of breaking lignin cross link as well as stabilization of both polysaccharides and lignin, the latter toward condensation [11]. For this reason, the relative absorbance of the β -O-4 ether linkage at 1120 cm^{-1} for soda-AQ lignin is slightly lower than in case of soda lignin due to the reduction effect of hydroquinone (AHQ). This also

causes a slight increase in the relative absorbance of phenolic group band at 1375 cm^{-1} of soda-AQ lignin above that of soda lignin. During pulping process, a partial demethoxylation of lignin occurred [12]. Demethoxylation of the soda-AQ lignin is lower than in case of soda lignin. So, this is clear from the mean value of the relative absorbance of the methoxyl groups bands at 2910, 2830, 1475 and 1425 cm^{-1} which is higher in case of soda-AQ than with soda lignin.

The relative absorbance of the carboxyl group at 1700 cm^{-1} in case of soda-AQ lignin is lower than in case of soda lignin. This is due to the reducing character of hydroanthraquinone [13, 14].

In case of kraft-AQ, the trend is similar to that of soda-AQ. So, the mean value of the relative absorbance of hydroxyl group bands is higher than in case of kraft-AQ than kraft. Also, the relative absorbance of phenolic hydroxyl group is higher than in case of kraft lignin. This due to, not only the increase of the reduction effect of hydroanthraquinone and the hydrosulfide ion, but also the increase of the degradation of the β -O-4 ether linkage at 1120 cm^{-1} . On the other hand, the kraft-AQ lignin has a very small amount of carbonyl group at 1700 cm^{-1} . Also the mean value of the relative absorbance of CH vibration of methoxyl groups of kraft-AQ lignin is higher than in case of kraft lignin. This also was seen in case of CH vibration of aromatic ring. This mean that, presence of AQ in the pulping liquor causes an stabilization of the cellulosic material and also decreases from degradation of lignin.

Comparing between kraft, soda, kraft-AQ and soda-AQ it is found that the demethoxylation of lignin during the different pulping process has the following sequence kraft < kraft-AQ < soda < soda-AQ.

The degradation in β -O-4 ether linkages has the following sequence kraft-AQ < kraft < soda-AQ < soda. The same sequence is observed in case of carboxyl group, *i.e.*, kraft-AQ < kraft < soda-AQ < soda.

Methanol in the Pulping Liquor

Presence of methanol in the pulping liquor increases from the delignification rate and causes an increase in the degradation of lignin (Tab. I).

So, from the Table I, it is clear that, soda-methanol and kraft-methanol lignin have a higher phenolic hydroxyl group than soda and

kraft lignins. This can be due to that lignin is more easily degraded especially the β -O-4 etheric linkage. This can be confirmed by the lower relative absorbance of β -O-4 bands at 1120 cm^{-1} of soda and kraft methanol lignin than soda, kraft, soda-AQ and kraft-AQ. On the other hand, the relative absorbance of the carbonyl group at $1710\text{--}1660\text{ cm}^{-1}$ band is weaker in case of kraft and soda-methanol, than in case of soda, kraft, soda-AQ and kraft-AQ [15, 16]. Relative absorbance of hydroxyl groups band at 3421 cm^{-1} appears to be slightly stronger for soda or kraft lignins than soda- or kraft-methanol lignins respectively. This may be due to the ability of soda and kraft pulping system to form more OH group than soda- or kraft-methanol system [17].

Comparing the relative absorbance of the different group bands of soda, soda-AQ, soda-methanol and soda-methanol-AQ lignins, it is found that the relative absorbance of phenolic hydroxyl group bands of soda-AQ-methanol lignin at 1375 cm^{-1} is higher than soda, soda-AQ, and soda-methanol lignin. This can be due to the increase of the degradation of β -O-4 linkage at 1120 cm^{-1} . This can be seen from the table in which, the relative absorbance of β -O-4 at 1120 cm^{-1} band has the lowest value in case of soda-AQ-methanol lignin. On the other hand presence of AQ beside methanol in the pulping liquor causes a stabilization in the methoxyl group, *i.e.*, decreases from the demethoxylation of the lignin. So the mean value of relative absorbance of methoxyl groups at different bands has a higher value in case of soda-AQ-methanol lignin than other different lignin, *i.e.*, increase in the phenolic hydroxyl groups is obtained by the degradation of β -O-4 etheric linkage and not by the hydrolysis of methoxyl groups. In general the produced lignin from soda pulping in presence of methanol has a higher mean value of relative absorbance of C—H vibration of aromatic ring than soda and soda-AQ. This mean that presence of methanol lower from the degradation of lignin with stabilization of cellulosic chains.

Sulfide–Sulfite Lignin

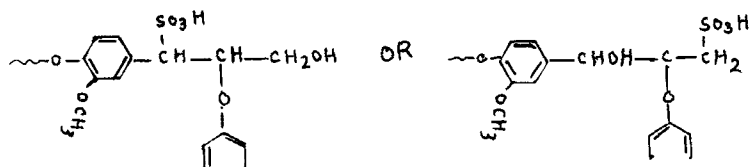
Table II shows the relative absorbance of the different groups bands of sulfide–sulfite (kraft-sulfite) lignin.

From this table, it is clear that the relative absorbance of hydroxyl group bands at 3421 cm^{-1} of sulfide–sulfite lignin decreases by

TABLE II Absorbance intensity of different lignin bands relative to intensity of CH vibration of aromatic ring at 1505 cm^{-1}

Bands cm^{-1}	Kinds of lignin						
	Na_2S	$\text{Na}_2\text{S} + 5\% \text{Na}_2\text{SO}_3$	+ 10%	+ 20%	+ 40%	20% $\text{Na}_2\text{SO}_3 + 0.1\% \text{AQ}$	+ 22% methanol
3421	1.95	1.72	1.58	1.55	1.53	1.59	2.90
1375	0.11	0.09	0.09	0.08	0.07	0.10	0.07
1325	0.17	0.15	0.14	0.18	0.13	0.18	0.17
1260	0.15	0.05	0.04	0.04	0.04	0.01	0.03
1220	0.53	0.55	0.53	0.50	0.34	0.55	0.63
1155	0.03	—	0.05	0.05	0.06	0.04	0.03
1035	0.60	0.51	0.50	0.48	0.46	0.73	0.70
Mean	0.51	0.43	0.42	0.41	0.41	0.46	0.65
1120	1.38	1.19	1.16	1.06	1.00	1.08	1.08
2910	0.40	0.40	0.42	0.47	0.44	0.53	0.43
2830	0.23	0.23	0.26	0.24	0.19	0.31	0.20
1475	0.78	0.75	0.77	0.76	0.81	0.80	0.73
1425	0.30	0.43	0.47	0.41	0.38	0.47	0.40
Mean	0.43	0.45	0.48	0.47	0.45	0.53	0.44
1600	0.98	0.96	1.00	0.94	0.94	1.08	1.40
1505	1.00	1.00	1.00	1.00	1.00	1.00	1.00
835	0.20	0.19	0.21	0.21	0.13	0.22	0.30
Mean	0.73	0.72	0.72	0.71	0.69	0.77	0.90
880	—	—	—	0.09	0.06	0.04	0.08
1700	0.18	0.17	0.14	0.14	0.13	0.04	—
1640	—	—	—	—	—	—	0.07
655	—	0.01	0.03	0.05	0.07	—	—

increasing the percent of sulfite in the pulping liquor. This can be attributed to that, the sulfonic group enter mainly in the — position in the side chains and also some — position receive this groups [18].



This can be confirmed by the lower relative absorbance of the bands of primary and secondary OH group at 1035 and 1325 cm^{-1} respectively for sulfide – sulfite lignin than kraft lignin. On the other hand

the relative absorbance of band at $1700-1720\text{ cm}^{-1}$ of sulfide-sulfite lignin is somewhat lower than in case of kraft lignin [18].

The relative absorbance band of β -O-4 etheric linkage, band at 1120 cm^{-1} , is higher in case of kraft lignin than sulfide-sulfite lignin, and this relative absorbance decrease by increasing the concentration of sulfite in pulping liquor.

The mean value of the relative absorbance of the methoxyl group bands at 2910, 280, 1475 and 1425 cm^{-1} in case of sulfide-sulfite lignin is higher than in case of kraft lignin. This mean that, these methoxyl group is undergone to the hydrolysis and demethoxylation in kraft pulping of bagasse more than sulfide-sulfite pulping. This prove the higher relative absorbance of the phenolic hydroxyl group band at 1375 cm^{-1} in kraft more than sulfide-sulfate lignin.

Presence of AQ in kraft-sulfite liquor of bagasse causes an increase in the mean value of OH and methoxyl groups. On the other hand the presence of the AQ in the kraft-sulfite liquor decreases from the degradation of the lignin. This can be confirmed by the high relative absorbance of β -O-4 linkage band at 1120 cm^{-1} and higher relative absorbance of the mean value of the methoxyl group in case of kraft-sulfite-AQ lignin than kraft-sulfite lignin (columns 5 and 7). Also presence of AQ in the kraft-sulfite liquor decreases from the formation of carbonyl group of precipitated lignin.

Addition of methanol in the kraft-sulfite pulping liquor increases the mean value of the relative absorbance of OH group and decreases that of methoxyl groups. In case of the relative absorbance of carbonyl group it slightly decreases by presence of methanol in pulping liquor (columns 5 and 8).

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