

FUNCTIONAL COMPOSITION AND IR SPECTRA OF COTTONSEED HUSK HYDROLYSIS LIGNIN AND ITS DERIVATIVES

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The functional compositions of cottonseed husk hydrolysis lignin and its derivatives have been determined and their IR spectra have been studied. A possible formation of stronger hydrogen bonds in derivatives of hydrolysis lignin has been shown.

Technical lignins, especially hydrolysis lignin (HL), which is a local waste raw material, possess a developed surface. In the chemical respect, HL is a polymer of aromatic nature consisting of phenylpropane structural units. The presence of reactive hydroxy, carbonyl, and carboxy groups permits HL to be considered a possible sorbent for many classes of compounds. In view of this, we have investigated the physicochemical properties of cottonseed husk hydrolysis lignin (CSHHL) and its derivatives. In the present paper we give the characteristics (compositions and formulas) of CSHHL and its derivatives and the results of their IR-spectral study.

The CSHHL was purified as described in the literature: when technical lignins are treated with water residual traces of sulfuric acid and of reducing substances are washed out [1]. Organic solvents (ethanol) eliminate lignocarbohydrate and resinous substances [2, 3].

As a result of such purification a product with a high specific surface freed from ballast substances, sterile, and not changing the pH of a medium, is obtained.

Modified derivatives were obtained from the purified CSHHL: sulfolignin (SL), nitrolignin (NL), chlorolignin (CL), demethylated lignin (DML), piperidinomethylated hydrolysis lignin (PMHL), phosphorylated piperidinomethylated hydrolysis lignin (PPMHL), oxidized hydrolysis lignin (OHL), and phosphorylated hydrolysis lignin (PHL). From their elementary and functional analyses (Table 1), we calculated the semiempirical formulas of the initial CSHHL and its derivatives (Table 2).

TABLE 1. Elementary and Functional Compositions of CSHHL

Lignin sample	C	H	Heteroatoms: S, N, P, Cl	OCH ₃	OH _{tot}	OH _{phen}	COOH	CO
1. CSHHL	54.5	5.3	-	5.4	7.1	4.7	1.8	7.1
2. SL	54.1	4.5	1.2	0.8	8.0	6.8	4.5	6.0
3. NL	52.5	5.2	4.5	2.9	6.0	3.3	9.8	7.6
4. CL	53.5	5.0	10.0	4.9	9.5	4.8	2.0	7.3
5. DML	66.4	6.6	-	1.2	13.2	8.3	2.6	6.5
6. PMHL	47.8	7.0	3.1	0.8	7.1	5.5	0.4	7.0
7. PPMHL	49.3	6.3	3.2 (N) 6.8 (P)	4.2	4.9	2.3	2.8	5.6
8. OHL	54.5	5.7	-	3.2	6.2	2.8	2.1	6.5

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TABLE 2. Semiempirical Formulas of the CSHHL and its Derivatives

Lignin sample	Semiempirical formula
1. CSHHL	$C_9H_{11.38}O_{3.88}(OCH_3)_{0.37}(OH_{tot})_{0.59}(OCO)_{0.55}(OOHCOOH)_{0.12}$
2. SL	$C_9H_{7.7}O_{3.24}(OCH_3)_{0.05}(OH_{phen})_{0.8}(OH_{al})_{0.14}(OCO)_{0.57}(OOHCOOH)_{0.20}S_{0.10}$
3. NL	$C_9H_{8.52}O_{3.11}(OCH_3)_{0.19}(OH_{phen})_{0.4}(OH_{al})_{0.33}(OCO)_{0.56}(OOHCOOH)_{0.45}N_{0.66}$
4. CL	$C_9H_{8.52}O_{2.47}(OCH_3)_{0.30}(OH_{tot})_{0.67}(OCO)_{0.57}(OOHCOOH)_{0.08}Cl_{0.57}$
5. DML	$C_9H_{7.60}O_{1.90}(OCH_3)_{0.06}(OH_{phen})_{0.90}(OH_{al})_{0.47}(OCO)_{0.48}(OOHCOOH)_{0.03}$
6. PMHL	$C_9H_{9.80}(OCH_3)_{0.10}(OH_{phen})_{0.98}(OH_{al})_{0.32}(OCO)_{0.85}(OOHCOOH)_{0.03}N_{0.51}$
7. PPMHL	$C_9H_{11.5}O_{5.9}(OCH_3)_{0.42}(OH_{phen})_{0.45}(OH_{al})_{0.05}(OCO)_{0.62}(OOHCOOH)_{0.19}N_{0.41}P_{0.50}$
8. OHL	$C_9H_{9.60}O_{3.25}(OCH_3)_{0.27}(OH_{phen})_{1.35}(OH_{al})_{0.49}(OCO)_{0.63}(OOHCOOH)_{0.12}$

TABLE 3. Frequencies of the Stretching Vibrations of OH and C=O Groups in CSHHL and its Derivatives

Lignin sample	OH, cm^{-1}	C=O, cm^{-1}	Content per C_9 , %	
			COOH group	CO groups
1. CSHHL	3421	1752	0.12	0.55
2. SL	3397	1750*, 1702	0.20	0.57
3. NL	3406	1751, 1700	0.45	0.56
4. CL	3357	1751*, 1700	0.08	0.57
5. DML	3404	1751*, 1703	0.03	0.48
6. PMHL	3353	1750*, 1700 1663	0.03	0.85
7. PPMHL	3400	1752, 1701	0.19	0.62
8. OHL	3351	1751, 1701	0.12	0.63
9. FGL	3406	1751, 1701		

*This absorption band appears in the form of a shoulder on a wing of the 1750 cm^{-1} absorption band.

The semiempirical formulas more clearly reflect the structure of the phenylpropane unit of lignin. As can be seen from Table 2, differences are observed mainly in the contents of methoxy, hydroxy, carbonyl, and carboxy groups. The values of OCH_3/C_9 in the lignins investigated ranged from 0.05 to 0.49%. These are considerably less than those of the dioxane lignins from the cotton plant (0.82—1.23) and from kenaf (1.16—1.50) [4]. The comparatively low value of OCH_3/C_9 in the lignins investigated is evidence of a greater degree of condensation as compared with the dioxane lignin preparations.

The different amounts of oxygen not involved in OCH_3 , OH, CO groups (1.90—6.51/ C_9) shows that this oxygen probably belongs to all the other ether groups in the lignins. These may be, in the first place, the alkyl—alkyl ether bonds of pinosresinol and syringaresinol and other types of alkyl—alkyl and diaryl ether bonds.

The different contents of aliphatic and phenolic hydroxy groups and carbonyl and carboxy groups must explain the different natures of the intramolecular interactions (electronic, spatial) to which the frequencies of the stretching vibrations of the functional groups of the substances investigated are sensitive. To confirm this hypothesis, we undertook an IR spectral investigation of CSHHL and its derivatives.

An analysis of literature information [5—12] showed the absence of systematization of the IR spectral characteristics describing the structural and physicochemical features of technical lignins and their derivatives. During the study of the IR spectra of CSHHL and its derivatives we found the frequencies of the stretching vibrations that are most sensitive to the structural features of lignins: those of OH and C=O groups (Table 3).

As can be seen from Table 3, the highest frequency of the stretching vibrations of hydroxy groups (3421 cm^{-1}) was observed for the CSHHL. A particularly appreciable decrease in the stretching vibrations of OH groups was observed in the

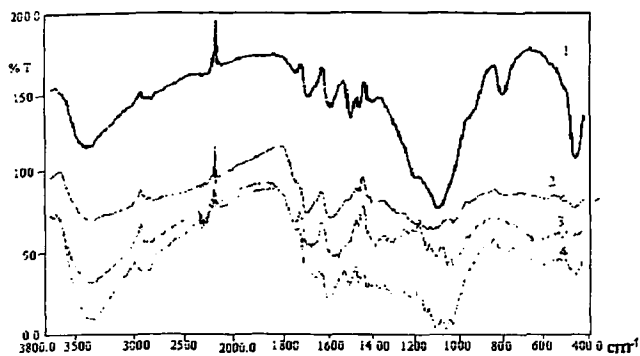


Fig. 1

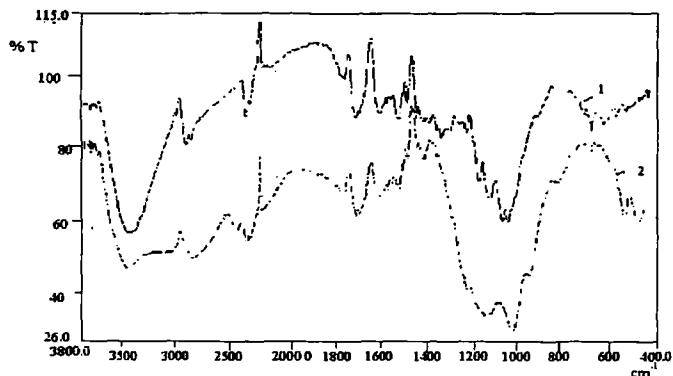


Fig. 2

Fig. 1. IR spectra of CSHHL (1), SL (2), NL (3), and PMHL (4).

Fig. 2. IR spectra of PPMHL (1) and PHL (2).

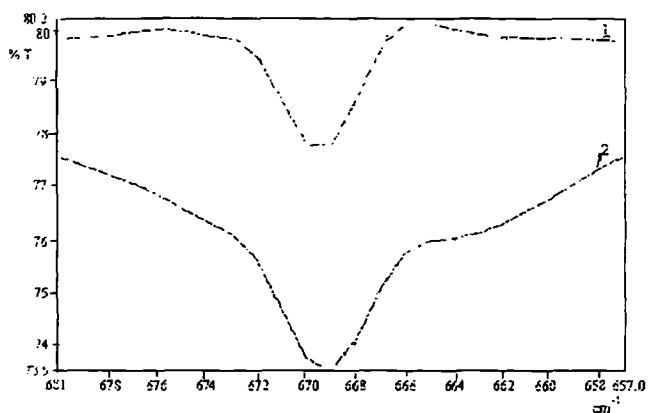


Fig. 3

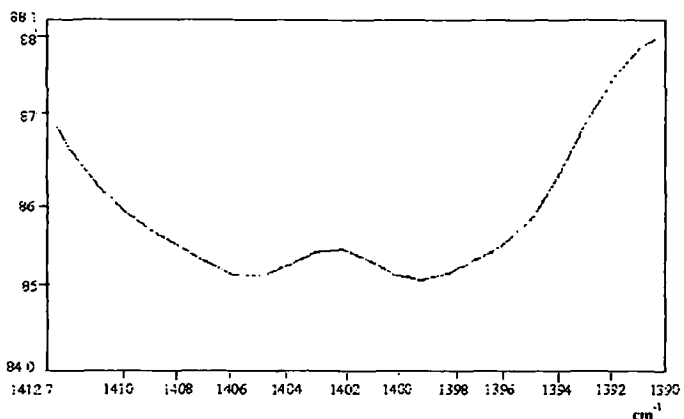


Fig. 4

Fig. 3. IR spectra in the frequency range of 680—658 cm^{-1} : 1) PPMHL; 2) PHL.

Fig. 4. IR spectrum of NL in the frequency range of 1412—1290 cm^{-1} .

spectra of sulfolignin, chlorolignin, and oxidized lignin — i.e., samples with a low number of carboxy groups per C_9 unit. Moreover, in the spectra of lignin samples 2—6 and 8 (see Table 3) a fall in the intensity of the band with a maximum at 1104 cm^{-1} that is the result of the mixed vibrations of the C—O bonds of alcoholic (alkyl) and phenolic C—OH groups and ether groups was observed relative to the intensities of the corresponding bands in the spectrum of CSHHL (Fig. 1).

In the case of the phosphorylated piperidinomethylated lignin (sample 7) and the phosphorylated lignin (sample 9), an increase in the intensity of the band at 1100 cm^{-1} is probably connected with the fact that the stretching vibrations of the P=O bonds are also revealed by an absorption band in the frequency region of $1100\text{—}1200 \text{ cm}^{-1}$.

On the basis of what has been said above, it may be assumed that the introduction into lignin of proton-accepting groups (NO_2 , SO_2 , Cl, OCH_3) leads to the formation of stronger hydrogen bonds with alcoholic and phenolic hydroxy groups, while a fall in the content of carboxy groups probably favors a stereochemical structure of the lignin macromolecules that is energetically suitable for the formation of strong proton donor-acceptor associations, particularly in SL, CL, and OHL.

The anomalously low frequency of the stretching vibrations of C=O groups found in the IR spectrum of PMHL (1663 cm^{-1}) is probably due to not only their participation in the formation of hydrogen bonds but also to the effect of the conjugation of the acceptor carbonyl groups with the donor substituents (NH , OH_{phen}) of the aromatic ring.

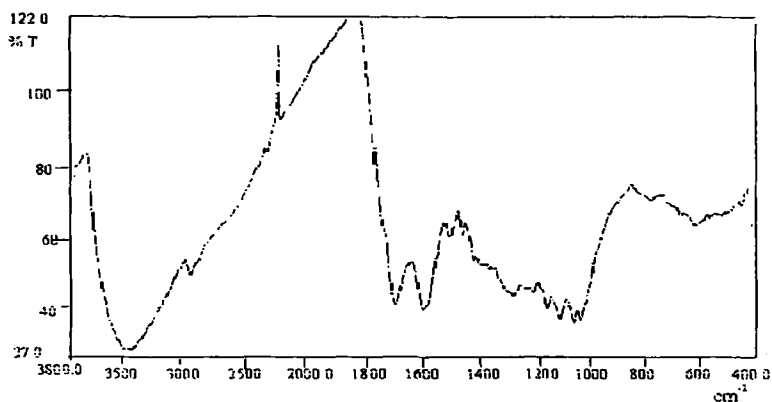


Fig. 5. IR spectrum of CL.

Although the accurate assignment of the frequencies characterizing the stretching vibrations of the P=O group in PHL is difficult because of the overlapping of the absorption bands of the C—OR and C—OC stretching vibrations, nevertheless the appearance of a new maximum at 1019 cm^{-1} shifted in the low-frequency direction by 200 cm^{-1} in comparison with that in the spectrum of phosphorous acid [6] presupposes participation of the P=O group in the formation of hydrogen bonds with the phenolic and the alkyl hydroxy groups of the lignin (Fig. 2).

An additional characteristic feature in the spectra of PHL and PPMHL may be the appearance of an absorption band at 670 cm^{-1} due to the vibrations of the C—O—P bond (Fig. 3).

In the IR spectrum of nitrolignin, the presence of bands at 1559 and 1398 cm^{-1} characterizes the asymmetric and symmetric stretching vibrations of the nitro group, while the presence of a band at 1398 cm^{-1} facilitates the identification of a nitro group in the IR spectrum of a lignin sample (Fig. 4).

The presence of weak bands with different contours in the $600\text{—}700\text{ cm}^{-1}$ region complicates the assignment of the frequencies of the stretching vibrations of the C—Cl bond (Fig. 5).

Thus, the IR spectral analysis of CSHHL and its derivatives has permitted an assignment of their characteristic frequencies and a revelation of the functional groups determining their reactivity. The main reactive groups of the lignins studied are alcoholic (alkyl) and phenolic hydroxy groups and carbonyl and carboxy groups. This conclusion is in harmony with the results of functional analysis and the calculation of the semiempirical formulas of the lignins investigated.

EXPERIMENTAL

The IR spectra of the samples were taken on a Perkin-Elmer Fourier IR spectrometer (Sweden), system 2000, resolution 4 cm^{-1} , rate of scanning 0.2 cm/s , number of scans 500. The samples were prepared in the form of tablets by molding with KBr.

The cottonseed husk hydrolysis lignin was purified by washing out sulfuric acid residues with distilled water until the wash waters had a neutral reaction and then extracting it with ethyl alcohol to eliminate carbohydrates and resinous substances.

The amounts of OH, CO, COOH, and OCH_3 groups were determined by the procedures given in [13]. The amounts of nitrogen, sulfur, chlorine, and phosphorus in the modified CSHHLs were determined as described in [14—17], respectively.

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