CHEMICAL MODIFICATION AND CHARACTERIZATION OF STRAW LIGNIN

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This work aims at describing the modification and characterization of lignin separated from annual plants (wheat straw) by their delignification through the alkaline method. The lignin has been subjected to the hydroxymethylation reaction, for introducing hydroxyl groups into its structure, thus assuring a more complete exploitation of this natural aromatic polymer. Chemical and spectral analyses (FTIR, UV-VIS, fluorescence, HPLC), and thermal stability characterization (TG, DTG) have been carried out to evidence the transformations occurring in the lignin macromolecule. The experimental data show that the hydroxymethylation reaction induces the modification of lignin functionality and polymolecularity. Further, the properties of modified lignin were demonstrated in experiments on wood bioprotection.

Keywords: wheat straw lignin, hydroxymethylation, FTIR, UV-VIS, fluorescence, HPLC, thermogravimetry

INTRODUCTION

Lignin, representing the second major component of biomass – a photosynthesis renewable resource –, has a high service potential and its complex practical applications turn it into a research material of great interest, if considering the need for diversifying the existing resources of raw materials and energy.

So far, the attempts made at creating an industry that would capitalize lignin have had only partial success. This is due, on the one hand, to the difficulties encountered in using and processing lignin – because of its chemical complexity, diversity of its structural units and relationships with the other wood components –, and, on the other, to the influence of the economic aspects concerning profitability, as part of the complex capitalization of this natural aromatic polymer.

However, introducing lignin among the adhesive systems used in wood processing and its testing as a possible bioprotection agent for wooden supports are estimated as a possible direction in lignin usage. This situation is determined by the fact that lignin also acts as an adhesive in the wooden tissue, both by its compatibility with the environment and by the fact that it can substitute products of petrochemical origin.[1-4]

For obtaining composite structures with improved properties, lignin is usually incorporated into various polymeric materials. In such systems, the introduced quantity of lignin can reach a level at which a minimum decrease of the mechanical properties is recorded.

Lignin, a much more chemically active macromolecular compound than either cellulose or any other natural polymer, due to the functional groups contained in its macromolecule, evidences high stability in the presence of acids, but a reduced

resistance when subjected to the action of oxidants.[5-8] The presence of phenolic and aliphatic hydroxyl groups in the lignin macromolecule determines its utilization as a partial or total substitute of phenol in the synthesis of certain adhesive systems (lignin-phenol-formaldehyde or lignin-urea-formaldehyde) with multiple applications. Unlike phenols, due to its high polymerization degree, lignin contains a reduced number of OH-phenol groups, so that few active centers from the aromatic ring can bind the formaldehyde.

The condensation reaction of non-modified lignin with formaldehyde will result in a three-dimensional structure (resin) with a limited number of branching points, therefore it will be a more brittle resin than the phenol-formaldehyde one.[1,8,9]

The chemical modification of lignin – a polymer resulted from wood delignification[8] – through hydroxymethylation (Fig. 1) allows its more effective practical application.

This work aims at describing the modification and characterization of the lignin found in annual plants. The experimental data show that the hydroxymethylation reaction allows the modification of lignin functionality and polymolecularity. Further, the properties of modified lignin are demonstrated in experiments on wood bioprotection.

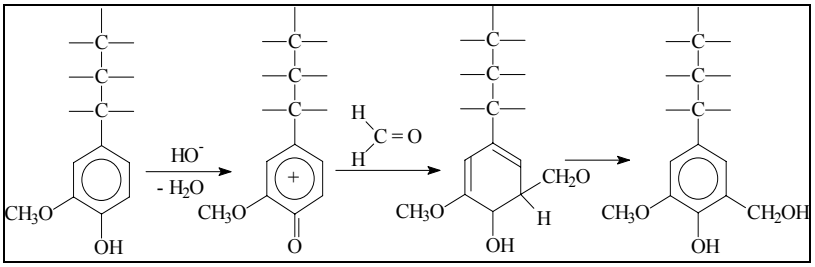

Figure 1: General scheme of the chemical modification of lignin through hydroxymethylation

EXPERIMENTAL

Wheat straw lignin (L_1), offered by Granit Recherche Développement S.A. Lausanne, having the characteristics described in Table 1, and straw lignin modified through hydroxymethylation, have been used in the study.[8] 37 g of lignin samples (wheat straw powder – L_1) were dissolved in 100 mL of NaOH solution of 3% concentration, at different ratios of NaOH/L (w/w), at room temperature. The pH of the reaction medium was of about 10-10.5. Then, a formaldehyde solution (37%) was added at different ratios of CH_2O/L and the temperature was raised up to 55 and 90 °C, respectively. The total reaction time was of 3 h.

Table 1
Characteristics of non-modified straw lignin L_1

Characteristics	L_1
Relative humidity, %	5.00
Ash, %	2.30
pH in suspension	2.70
p-OH	1.70
Manganese, %	0.7
Nitrogen, %	1
Uronic acid, %	0
Solubility in acids, %	1

The consistence of the reaction medium was of nearly 30%. Formaldehyde consumption was monitored by the iodine method, in an alkaline medium, and was reported in percentage or moles per 100 g lignin. Finally, the hydroxymethylated lignin was separated by precipitation with a

solution of HCl 1 N, at a pH of 1.5-2. The precipitated lignin, isolated by centrifugation, was then washed with distilled water and dried in a vacuum oven, at 40 °C.

After being dried out, the hydroxymethylated product L_1H_4 was ground in a jar and subjected to spectral analyses. To carry out the structural analysis of the non-modified straw lignin L_1 and of the modified L_1H_4, the Fourier transform spectroscopy (FTIR) was used.[10-13]

The FTIR spectra of lignin and its derivative were registered, in a KBr pellet, with a DIGILAB–EXCALIBUR FTS 2000 spectrometer, in the 4000-400 cm^{-1} range, with a resolution of 4 cm^{-1}.

UV-VIS absorption spectra were registered on a JASCO 550 spectrophotometer, using quartz cells for liquids with a volume of 1 mL: absorption region – 200-800 nm, scan speed – 200 nm/min, resolution – 1 nm. The processing of the spectra obtained from the tests was done with a specialized program from the Spectra Manager series.

The fluorescence emissions of both unmodified and modified lignins were registered on a Perkin Elmer LS 50 B luminescence spectrometer, using cells with a liquid volume of 1 mL at a 350 nm excitation length, in the 400-600 nm absorption region. The obtained spectra were processed with a specialized program from the FLWinLab series.

The two types of lignin have been also characterized by thermogravimetric analysis. The TG and DTG curves were registered on a PAULIK-PAULIK ERDEY MOM BUDAPEST derivatograph, at a heating rate of 12 °C/min, in air, at a flow rate of 30 mL/min, within a temperature range of 0-1000 °C, the sample mass being of 50 mg.

In the case of HPLC, the study of lignins L_1 and L_1H_4 has been carried out on a system equipped with a Varian 9010 pump, autosampler waters 717 plus, UV-VIS waters 486 detectors, the ORIGIN LAB 7.5 program being used to process the obtained data. The measurements were performed at room temperature, with a Nova-Pack C18 column (3.9 x 150 mm). The flow rate of the mobile phase was of 0.4 mL/min and the wavelength used was λ = 280 nm. The mobile phase was represented by a system made up of the following solvents: methanol, water, acetic acid (50:48:2).

RESULTS AND DISCUSSION

Figure 2 plots the FTIR spectra evidencing the characteristic absorptions for the various functional groups, as well as the main absorption bands recorded for both non-modified (L_1) and modified straw lignin (L_1H_4).

The content of carbonyl and hydroxyl groups, as well as the ratio of the aromatic (Ar) and aliphatic (Al) groups from the chemically modified lignin macromolecule, have been also determined by FTIR (Table 2). The experimental data obtained indicate that the hydroxymethylation reaction allows the modification of lignin functionality.

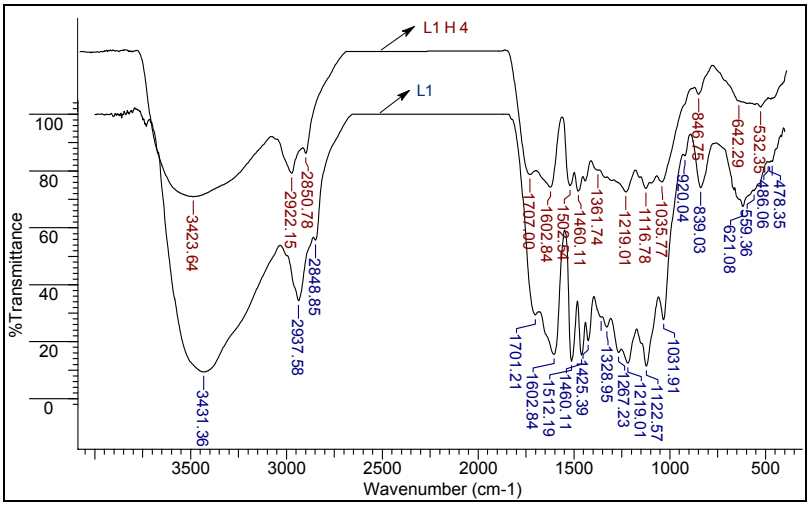

Figure 2: FTIR spectra for L_1 and L_1H_4

Table 2
Characteristics of non-modified (L_1) and modified lignin (L_1H_4) for different relative absorption values, determined by FTIR spectral analysis

Sample	Characteristics				
Non-modified straw lignin (L_1)	Al/Ar A2930/A1510 ratio	Total OH (moles/C_9)	Phenol OH A1365/A1510	Carbonyl groups C = O A1710/A1510	Alcohol OH (moles/C_9)
	0.81	0.89	0.73	0.65	0.16
	Al/Ar A2930/A1600 ratio	Total OH (moles/C_9)	Phenol OH A1365/A1600	Carbonyl groups C = O A1710/A1600	Alcohol OH (moles/C_9)
	0.78	0.99	0.82	0.72	0.17
Modified straw lignin (L_1H_4)	Al/Ar A2930/A1510 ratio	Total OH (moles/C_9)	Phenol OH A1365/A1510	Carbonyl groups C = O A1710/A1510	Alcohol OH (moles/C_9)
	0.84	0.99	0.69	0.73	0.3
	Al/Ar A2930/A1600 ratio	Total OH (moles/C_9)	Phenol OH A1365/A1600	Carbonyl groups C = O A1710/A1600	Alcohol OH (moles/C_9)
	0.90	0.99	0.74	0.79	0.24

Al/Ar ratio; Al – aliphatic; Ar – aromatic

Thus, an increase in the content of the OH-alcohol groups from 0.16 (Al/Ar A2930/A1510 ratio) and respectively 0.17 (Al/Ar A2930/A1600 ratio) for non-modified lignin L_1 (Table 2), to 0.30 (Al/Ar A2930/A1510 ratio) and respectively 0.24 (Al/Ar A2930/A1600 ratio) (Table 2), for modified lignin L_1H_4, can be noticed. The same situation is valid for the carbonyl groups.

The carbonyl groups content for non-modified lignin L_1 fluctuates between 0.65 (Al/Ar A2930/A1510 ratio) and 0.72 (Al/Ar A2930/A1600 ratio), whereas the content of the carbonyl groups for modified lignin L_1H_4 can reach 0.73 (Al/Ar A2930/A1510 ratio) and 0.79, respectively (Al/Ar A2930/A1600 ratio) – Table 2.

However, lignin hydroxymethylation contributes to decreasing the content of the OH-phenol groups, which varies – for non-modified lignin – between 0.73 (Al/Ar A2930/A1510 ratio) and 0.82, respectively (Al/Ar A2930/A1600 ratio) while, for modified L_1H_4 lignin, the values recorded are 0.69 (Al/Ar A2930/A1510 ratio) and 0.74, respectively (Al/Ar A2930/A1600 ratio) – Table 2.

By analyzing the FTIR spectroscopy data, the optimum conditions to achieve lignin hydroxymethylation can be settled (Table 3).

To have a more detailed characterization of both non-modified and modified lignin, thermogravimetry (TG) and differential thermogravimetry (DTG) – Figure 3 – have been used, along with high performance liquid chromatography (HPLC) – Figure 4.

Table 4 shows that the values of the activation energy for the thermal degradation of modified lignin increases compared to those registered for the non-modified lignin, so that the thermal stability of the hydroxymethylated lignin is improved. The treatments applied could lead to the defragmentation of the polymers, due to the large amount of substitutions.

Table 3
Optimum conditions for lignin modification through hydroxymethylation

Sample	Characteristics					
	NaOH/L ratio (w/w)	CH_2O/L ratio (w/w)	CH_2O (moles/100 g L_1)	pH	t (h)	c (%)
Modified straw lignin (L_1H_4)	0.0830	0.2583	0.8300	10.50	3	29.6
	0.0806	0.2583	0.8300	10.50	3	29.6

pH – pH of the aqueous suspension; t – duration; c – concentration

Table 4
Thermogravimetric data for non-modified (L_1) and modified lignin (L_1H_4)

Sample	t_i (°C)	t_m (°C)	t_f (°C)	Ea (kJ/mol K)
		Peak 1		
L_1	197.9	258.9	269.9	29.33
L_1H_4	-	-	-	-
		Peak 2		
L_1	278.2	355.3	446.2	67.07
L_1H_4	267.0	364.3	444.9	64.57

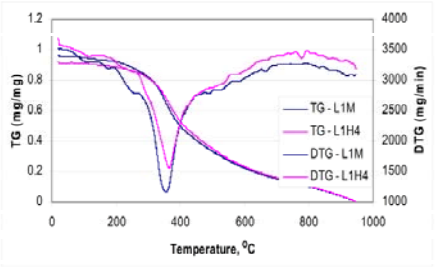

Figure 3: Thermograms recorded for non-modified lignin L_1 and for hydroxymethylated derivative L_1H_4

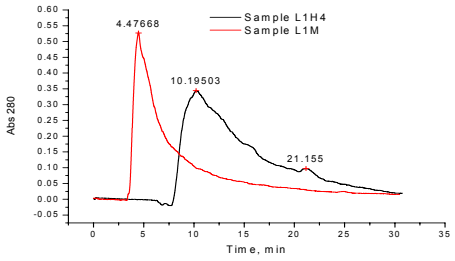

Figure 4: Chromatogram of unmodified L_1 (1) and modified L_1H_4 (2) lignin obtained by HPLC

Additional processes of condensation or even cross-linking of the different molecular fractions are assumed to take place during the thermal treatment which, in the end, determines the formation of a larger quantity of residue.

Thermal degradation, occurring in two or three stages, is accompanied by endo- and exothermic effects, depending on the chemical structure. It has been noticed that the thermal degradation of wheat straw lignin L_1 takes place in two stages. In the former stage, the humidity of the sample is removed in a percentage of about 4.8%, while, in the latter, the thermal decomposition of lignin occurs. In the last degradation stage of the

samples under analysis, the temperature at which the degradation rate is the highest is approximately the same for both samples: $T_{max} \approx 370$ ºC.

The study has been extended with a kinetic processing of the gravimetric data by the Freeman-Caroll method.[14] The analysis of the apparent activation energies in the last stage of the thermal degradation of the samples modified through hydroxymethylation shows that they are situated around the value of 60-70 KJ/mol.

Figure 4 shows that non-modified lignin L_1 reveals just a single peak, whereas for modified lignin L_1H_4 two peaks are visible, which confirms that hydroxymethylation contributes to creating some modifications in lignin polymolecularity, as a consequence of the different reactivity of the lignin fractions or of some condensation reactions.

The results of UV-VIS spectroscopy are presented in Figure 5.

Compared to the simple model compounds, for biphenyl derivatives, the maximum absorption is shifted to a wavelength of 240 nm, while, at 280-288 nm, it gives signals from the non-conjugate phenolic group structure of lignin. Following the hydroxymetylation reaction of lignin with formaldehyde, the dislocation of the π electrons from the lignin molecule occurs, such characteristic absorptions being shifted from higher to lower wavelength values, following the hypsochromic effect.

The results of fluorescence spectroscopy are plotted in Figures 6 and 7.

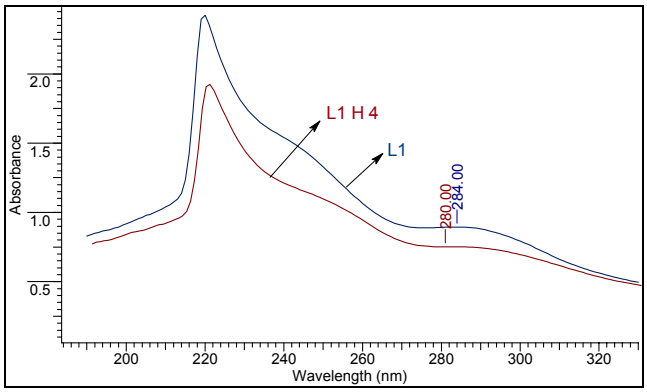

Figure 5: UV-VIS spectra for L_1 and L_1H_4 lignins

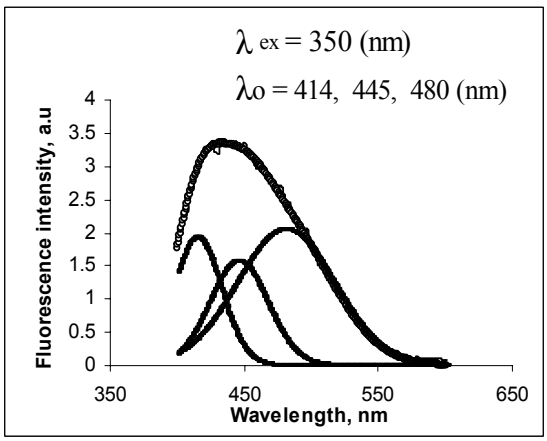

Figure 6: Fluorescence spectra for wheat straw lignin (L_1)

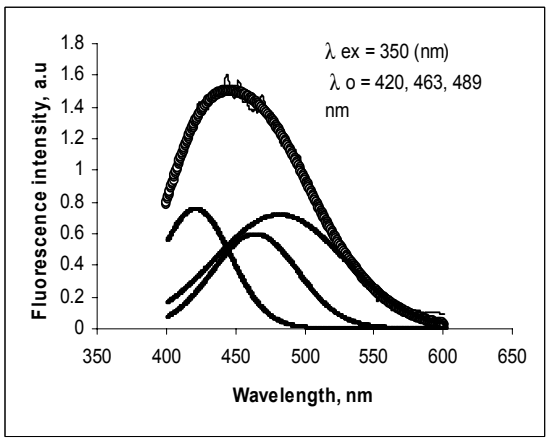

Figure 7: Fluorescence spectra for hydroxyl-metylated wheat straw lignin (L_1H_4)

The deconvolution of the fluorescence spectra here presented (Figs. 6 and 7) offers the opportunity to ascertain that they are the result of several absorption bands appearing at different wavelengths, which may be correlated with the structural changes induced by the hydroxymetylation reaction. In the case of modified lignin, one may observe a slight shift of absorption to higher wavelength values. Under such circum-

stances, the introduction of additional functionalities in the lignin structure determines a special behavior, following the excitement of the 350 nm wavelength radiation, which confirms that, as a function of the substrate reactivity, the reaction leads to different results.

CONCLUSIONS

1. The chemical modification of wheat straw lignin through hydroxymethylation has been studied for possible new practical applications of this natural aromatic polymer.
2. The two types of lignin (modified and non-modified) have been characterized by thermogravimetric (TG and DTG) and spectral analyses (FTIR, UV and flourescence), as well as by high performance liquid chromatography (HPLC), to evidence the transformations occurring in the lignin macromolecule. The experimental data show that the hydroxymethylation reaction allows the modification of lignin functionality, an increase in the content of the OH-alcohol and carbonyl groups and a decrease in the content of the OH-phenol ones being noticed.
3. The activation energy of the thermal degradation of modified lignin increases compared to that recorded for the non-modified lignin, so that the thermal stability of the hydroxymethylated lignin is improved.
4. HPLC analysis indicates that hydroxymethylation contributes to some modifications in lignin polymolecularity, as a result of the different functionalization of the lignin fractions or of the occurrence of some condensation reactions.
5. The derivative of lignin and the non-modified sample are recommended to be tested in adhesive systems and wood bioprotection.

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REFERENCES

[1] A. Abaecherli and V. I. Popa, *EEMJ*, **4**, 273 (2005).
[2] E. Ungureanu, V. I. Popa and T. Todorciuc, *Celuloză şi Hârtie*, **55**, 5 (2006).
[3] E. Ungureanu, *Ph.D. Thesis*, "Gh. Asachi" Polytechnic University of Iasi, Romania, 2008, pp. 69-78.
[4] L. H. Zhang, L. Dong, L. J. Wang, T. P. Wang, L. Zhang, D. X. Chen and Z. H. Mao, *Bioresource Technol*., **99**, 8512 (2008).
[5] F. Digabel and L. Averous, *Carbohyd*. *Polym*., **66**, 537 (2006).
[6] U. Buranov and G. Mazza, *Ind. Crop*. *Prod*., **28**, 237 (2008).
[7] V. I. Popa, "Tehnologii de valorificare a ligninei" (in Romanian), "Gh. Asachi" Polytechnic University of Iasi, Romania, 1984, p. 11.
[8] V. I. Popa, E. Ungureanu and T. Todorciuc, *Cellulose Chem*. *Technol*., **41**, 119 (2007).
[9] Th. Măluţan, R. Nicu and V. I. Popa, *Bio/Resources*, **3**, 13 (2008).
[10] C. M. Popescu, C. Vasile, M. C. Popescu, G. Singurel, V. I. Popa and B. S. Munteanu, *Cellulose Chem*. *Technol*., **40**, 597 (2006).
[11] Th. Măluţan, A. Pui, C. Măluţan, L. Tătaru and D. Humelnicu, *J*. *Fluoresc*., **18**, 707 (2008).
[12] E. Lopez-Capel, G. D. Abbott, K. M. Thomas and D. A. C. Manning, *J*. *Anal*. *Appl*. *Pyrol*., **75**, 82 (2006).
[13] C. Boeriu, G. Bravo Dominique Gosselink, J. A. Richard and E. G. Jan van Dam, *Ind*. *Crop*. *Prod*., **20**, 205 (2004).
[14] E. S. Freeman and B. Carroll, *J*. *Phys*. *Chem*., **62**, 314 (2006).