CONTRIBUTION TO THE MODIFICATION AND CHARACTERIZATION OF DIFFERENT TYPES OF LIGNINS

ADINA-MIRELA CĂPRARU, VALENTIN I. POPA, TEODOR MĂLUȚAN and GABRIELA LISĂ

"Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 71, Mangeron Blvd., 700050 Iasi, Romania

Received November 2, 2009

The paper presents the results obtained in the modification and characterization of residual lignins separated from the alkaline delignification of annual plants (Sarkanda grass and wheat straw), along with some commercial products (Protobind), offered by Granit Recherche Dévéloppement S.A., Lausanne, Switzerland. To this end, the lignins were subjected to a hydroxymethylation reaction under different temperature and pH conditions and then characterized by spectroscopy (FTIR, UV-VIS and fluorescence), as well as from the viewpoint of their thermal stability. The obtained data point out that the reactivity of lignins depends on the source, while the properties of the synthesized derivatives are consistent with the changes induced in their functionality.

Keywords: wheat straw, Sarkanda grass, commercial lignin products (Protobind), hydroxymethylation, FTIR, UV-VIS, fluorescence spectroscopy, thermogravimetry

INTRODUCTION

Lignin, one of the main structures of the polymeric cell wall of higher plants, plays an important role, fulfilling a number of functions, among which mention should be made of their remarkable mechanical strength properties and protection of plant tissues against microorganisms. Although lignin has been one of the main topics of interest for chemists and biologists over the last 150 years, as regards the role it plays in the cellular metabolism of plants, many aspects of its functionality, structure and reactivity still have to be investigated. This is due to the variable composition of lignin in plants with different genetic origin and in the different tissues of the same plants, and moreover, due to the changes induced during separation. Thus, the notion of lignin does not designate a substance with a defined structure, in contrast with other natural macromolecular compounds, such as cellulose, hemicelluloses, starch or protein, but it rather refers to a group of their chemically related polymeric combinations.[1-4] Taking into account the value of lignin as a raw material for various uses, the investigations into its structure as depending on its origin, as well as into possible side changes, still continue. The research tendencies are related to the chemical and biochemical reactions applied to the residual lignocellulosic complex that consequently increase its functionality and reactivity. The initial characteristics of lignin and its derivatives can be investigated by both chemical and spectral methods, and by thermogravimetry. In this way, the functional groups and the thermal properties, which provide very useful information for predicting the behavior of the lignin derivatives and for indicating the applications and properties of the products to be obtained may be better evidenced.[5-7]

In this context, the results presented in the paper refer to the hydroxymethylation of lignins separated from annual plants (wheat straw and Sarkanda grass), along with some commercial products (Protobind), and to the characterization of derivatives synthesized through spectral methods and thermogravimetry.

EXPERIMENTAL

Materials

The following materials have been used: lignin from wheat straw (L1), lignin of Sarkanda grass, resulted from alkaline delignification, and three commercial products: Protobind 1000 (Pb1000), Protobind 2000 (Pb2000) and Protobind 3000 (Pb3000), offered by the Granit Recherche Dévéloppement S.A., Lausanne, Switzerland. The five types of lignin under study were chemically modified by the hydroxymethylation reaction.

Lignin hydroxymethylation

37 g of lignin o.d. were gradually dissolved in a 130 mL NaOH solution of 3% concentration, at room temperature, under mechanical stirring for 1 h. The pH of the solution thus obtained was checked and corrected to 10.5, using a solution of 3N NaOH. Then, a 24.1 mL solution of formaldehyde (37%) was added, while continuing stirring at a temperature of 90 °C, for 3 h. Periodically, each hour, samples were taken out of the reactor to determine the reactioned formaldehyde. After 3 h, the reaction mixture was cooled and treated with a solution of HCl lN, to obtain a pH = 2. The hydroxymethyl derivatives were separated through centrifugation at 2500 rpm for 10 min and the precipitate was washed with distilled water and dried.[8]

Analysis methods

FTIR spectroscopy

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

UV-VIS spectroscopy

The UV-VIS spectra were recorded for a solution of lignin and of its derivatives in sodium hydroxide (0.2N), 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 and 1 nm resolution. Spectra processing was carried out on a special Spectra Manager Program series.

Fluorescence spectroscopy

The fluorescence emissions of both unmodified and modified lignins were registered on a luminescence spectrometer Perkin Elmer LS 50 B, using cells with a liquid volume of 1 mL, 10 mm path length and a wavelength excitation of 350 nm, the absorptions being evaluated in the 400÷600 nm region. The lignins and their derivatives were dissolved in a sodium hydroxide solution. Spectra processing was performed with a specialized FLWinLab series program.

Thermogravimetry

Thermal analysis was performed on a METTLER TOLEDO derivatograph, in N_2 atmosphere, at a flow of 20 mL/min and heating rate of 15 ºC/min, over the 25-800 °C temperature range; sample mass = 4÷6 mg.

RESULTS AND DISCUSSION

The lignin from annual plants has a specific structure, as illustrated in Figure 1 for a typical fragment of aromatic polymer separated from wheat straw.[9]

Lignin modification through hydroxymethylation, known for quite a long time, involves the introduction of hydroxymethyl groups in the aromatic nucleus, both during alkaline and acid catalysis (Fig. 2), and allows to extend the application of the synthesized derivatives to various fields.[8]

The hydroxymethylation reaction has been applied both to lignins separated from the two annual plants and to the commercial product Protobind offered by the manufacturer. The lignin reactivity depends on its structure, if considering the introduction of hydroxymethyl groups in the guaiacyl structural units. In the following discussion, the reaction products of hydroxymethylation were designated as L1H, L2H, Pb1000H, Pb2000H and Pb3000H, their functional characteristics being presented[8] in Tables 1 and 2.

The content of functional groups was determined according to the methods presented by different research teams.[6,7,17] The determination of the total hydroxyl groups involved the comparison of the UV-VIS spectra of the samples, recorded both before and after chemical modification with acetic anhydride in pyridine medium. In the same manner, the content of phenolic OH groups was established by the UV-VIS

method; in addition, the assessment of total hydroxyl groups was performed by FTIR spectra analysis.

The other analyses carried out for the chemical characterization were determination of the carboxyl and metoxyl groups, determination of the aromatic hydroxyl groups, calculation of the phenolic groups/aliphatic groups ratio, and of the syringyl/guaiacyl units ratio.

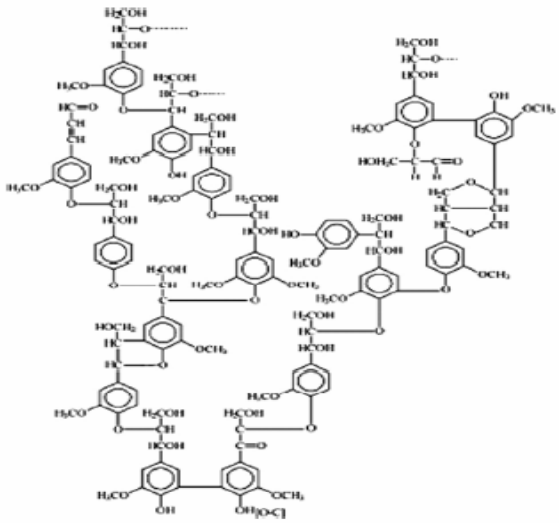

Figure 1: Structure of wheat straw lignin

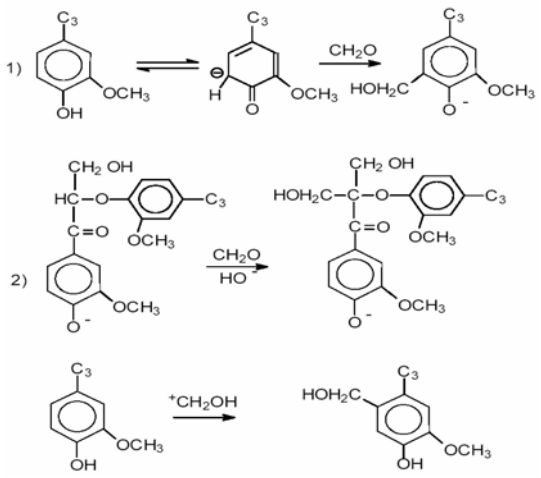

Figure 2: General scheme of the hydroxymethylation reaction of lignin during alkaline and acid catalysis

Table 1
Characteristics of unmodified and hydroxymethylated lignins

Samples	Moles CH_2O reacted/100 g lignin[1]	OH/C_9[2]	Ar-OH, mmole/g lignin[3]	OH/C_9 groups FTIR[4]
L1 (100-W-A)	-	1.02	1.7-1.8	1.06
L1H	0.23/0.20	1.17	1.76	1.16
L2 (100-S-A)	-	1.07	1.8-1.9	1.05
L2H	0.21/0.17	1.18	1.32	1.34
Protobind 1000	-	1.05	1.9-2.1	1.10
Pb1000H	0.24/0.20	1.07	1.63	1.15
Protobind 2000	-	1.08	1.8-2.0	1.12
Pb2000H	0.23/0.19	1.12	1.68	1.18
Protobind 3000	-	1.15	1.9-2.1	1.14
Pb3000H	0.25/0.21	1.19	1.65	1.19

[1] Values corrected without CH_2O consumption in Cannizzaro reactions; [2] The content of OH groups was determined by a chemical method, with acetic anhydride in pyridine medium[7,6]; [3] The content of Ar-OH groups was determined by the UV-Vis method[17]; [4] The content of OH groups was determined from FTIR spectra [7]

Table 2
Functional groups of hydroxymethylated lignins obtained under optimum reaction conditions

Sample	Total OH groups	Ar-OH groups	OCH_3 groups	Ak/Ar ratio	C=O groups	S/G ratio
L1 (100-W-A)	1.06	0.93	0.94	0.72	0.80	0.82
L1H	1.16	0.98	1.13	1.20	0.93	0.97
L2 (100-S-A)	1.05	0.91	0.96	0.88	0.88	0.82

L2H	1.34	0.95	1.10	1.11	0.92	0.85
Protobind 1000	1.10	0.89	1.05	1.17	0.89	0.83
Pb1000H	1.15	0.98	1.13	1.20	0.91	0.96
Protobind 2000	1.12	0.90	1.05	0.71	0.78	0.73
Pb2000H	1.18	0.97	1.11	0.72	0.8	0.75
Protobind 3000	1.14	0.91	1.09	0.73	0.68	0.79
Pb3000H	1.19	0.99	1.14	0.75	0.81	0.99

FTIR spectroscopy

FTIR spectroscopy permits to highlight the specific absorption characteristics of the functional groups of the initial lignin samples and those of the derivatives to be synthesized. The characteristic absorptions presented in Table 3 confirm the transformations resulted from hydroxymethylation reactions and allow the evaluation of the functional groups content.[9-12] As expected, the FTIR spectra reveal differences between each type of lignin and its synthesized derivative. The most significant of the changes include the variations in the intensities of the absorption bands, induced by the nature of the substrate and by its reactivity. Consequently, an increase, a decrease or the disappearance of bands (Table 4) may be noticed, as a function of sample reactivity.

The obtained data show that the lignin from annual plants is characterized by a high reactivity, compared to that of the commercial products, as illustrated by the variations registered in the content of the hydroxyl groups (Table 1), as well as by the hydroxyl aliphatic/aromatic (Ak/Ar in Table 2) groups ratio. Moreover, these modifications involve a molecular and structural lack of homogeneity (eventually outlined by the study of polymolecularity) in the lignin composed of fractions characterized by different functionality and reactivity, which might explain the differences observed in the content of carbonyl and metoxyl functional groups, such as the ratio of structural syringyl (S) and guaiacyl (G) units.

Table 3
Assignment of absorption bands in the FT-IR spectra of the lignin samples

Wavenumber (cm^{-1})	Type of vibration
3420-3430	Hydroxyl groups in phenolic and aliphatic structures
2938-2920	CH stretching in aromatic methoxyl groups and in aliphatic methyl and methylene groups of side chains
2850-2835	CH stretching in aromatic methoxyl groups and in methyl and methylene groups of side chains
1700-1675	C=O stretching in conjugated *p*-substituted aryl ketones
1610-1595	C=C stetching of the aromatic ring (S), CH deformation
1515-1505	C=C stretching of the aromatic ring (G), CH deformation
1470-1460	C–H asymmetric deformation in CH2 and CH3
1460-1370	Asymmetric C–H bending from methoxyl groups
1430-1422	C–H asymmetric deformation in –OCH3
1370-1355	Symmetric C–H bending from methoxyl group, O–H and C–O of phenol and tertiary alcohol
1300-1200	Aromatic C–O stretching vibrations
1268	Guaiacyl ring breathing, C–O stretch in lignin, C–O linkage in guaiacyl aromatic methoxyl groups
1235-1230	Syringyl ring breathing with C–O stretching
1160	C–H in plane deformation of G ring
1150	Aromatic C–H in plane deformation; typical of G units, whereby G condensed
1128-1115	Aromatic C–H in plane deformation (typical for S units) plus secondary alcohols plus C=O stretch
1086	C–O deformation in secondary alcohols and aliphatic ethers
1047-900	Deformation vibrations of C-O bands in primary alcohols

Table 4
Absorption bands in the FT-IR spectra of modified and unmodified lignins

Sample	3430 cm^{-1}	2938 cm^{-1}	2835 cm^{-1}	1700 cm^{-1}	1512 cm^{-1}	1460 cm^{-1}	1360 cm^{-1}	1328 cm^{-1}	1267 cm^{-1}	1219 cm^{-1}	1150 cm^{-1}	1135 cm^{-1}	1120 cm^{-1}	1035 cm^{-1}
L1	vs	m	-	m	s	s	s	m	s	m	s	s	vs	s
L1H	vs	s	-	s	-	s	-	s	s	vs	s	s	-	s
L2	vs	m	-	m	s	s	s	m	s	vs	m	s	s	s
L2H	vs	m	-	s	s	vs	-	s	s	vs	s	s	-	s
Pb1000	vs	m	s	vs	s	s	-	s	-	vs	s	s	s	s
Pb1000H	vs	-	m	m	vs	s	m	m	s	vs	s	-	s	m
Pb2000	vs	m	-	-	s	s	m	s	s	s	-	-	vs	-
Pb2000H	vs	s	-	s	s	vs	-	-	vs	s	s	-	vs	s
Pb3000	vs	-	-	-	vs	s	-	m	-	s	m	-	m	m
Pb3000H	vs	s	s	vs	s	-	m	-	s	m	-	m	m	m

vs – very strong, s – strong, m – medium

According to published data,[11] the 3700-2750 cm^{-1} region is attributed to the aromatic and aliphatic groups, while the 1800-900 cm^{-1} region is characteristic of methyl groups, represented mainly by the syringyl and guaiacyl units and by other functional groups. Table 2 indicates a higher S/G ratio for the hydroxymethylated lignins, which confirms the introduction of hydroxymethyl groups into the lignin macromolecule.

The large number of methyl and methylene groups can be correlated with the high content of syringyl units, with band intensification in the 1460 cm^{-1} region, and strains of CH bonds within the syringyl units. The 1120-1150 cm^{-1} range is attributed to the condensed guaiacyl units, the range around 1035 cm^{-1} being specific to the C-O bonds deformed by the metoxyl groups from secondary or primary alcohols and ethers.

Due to a frequent overlapping of the absorption bands in the studied lignin, the samples were analyzed in terms of intensity variations. These data suggest that the synthesized derivatives are characterized by a higher intensity of the absorption bands (s or vs), compared to that of the unmodified samples, which show a lower intensity (m or s) (Table 4). The high intensity bands appear due to a high Ak/Ar and S/G groups ratio, and also due to the presence of methoxyl (-OCH_3) and carbonyl (C=O) groups in the structure. The data presented above lead to the conclusion that, in terms of functional groups present in the lignin structure, there are at least three types of basic functional groups: methoxyl, hydroxyl (alcoholic and phenolic) and propane side chain. Along with these functional groups, several carbonyl groups were found mostly in the side chain. Sometimes, carboxyl groups are found in the lignin from annual plants as free phenolcarboxylic acid units or as minor amounts of lactonic groups.

UV-VIS spectroscopy

UV-VIS spectroscopy is one of the simplest and most commonly applied methods of quantitative analysis of lignin in solution, the position and intensity of the absorption maximum depending on the type of lignin and the solvent used. Because of its aromatic structure, lignin presents absorption bands in UV, showing that the free hydroxyl groups and the ether contribute[8] significantly to an absorption maximum around 280 nm. The results of UV-VIS spectroscopy analysis of the lignin dissolved in a 0.2N NaOH solution are shown in Table 5.

Table 5
UV-VIS characteristics of lignin samples

λ, nm	Samples									
	L1	L1H	L2	L2H	Pb1000	Pb1000H	Pb2000	Pb2000H	Pb3000	Pb3000H
u_1	245	250	246	248	242	250	240	245	241	249
u_2	285	280	285	281	288	283	288	283	288	282

u_1 – first shoulder, u_2 – second shoulder

This method was used to determine the content of carbonyl groups resulting from the reduction of the carbonyl groups from guaiacyl-propane units. It was demonstrated that the free hydroxyl and ether groups have a significant contribution to a characteristic absorption around 298 nm. Studies on lignin from wood and annual plants point out that the intensities of the absorption values vary within very close limits at 220 nm while, at 240 and 298 nm, an increased intensity, varying with the lignin type,[11] was observed. The biphenyl derivatives of unmodified lignin present absorption at 24 and 288 nm wavelength values – corresponding to the guaiacyl and syringyl units.

The higher S/G unit ratio can be correlated with the substitution degree on the guaiacyl nucleus with hydroxymethyl groups present in the synthesized derivatives. The main difference between unmodified and modified lignin is the change of absorption from 288 nm to lower wavelength values (288-280 nm), which may be caused by a higher number of substituted units (Table 4).

The hydroxymethylation reaction of lignin with formaldehyde causes the dislocation of the π electrons from the lignin macromolecule, so that the characteristic absorptions are moved from higher values of the wavelengths to lower ones, which is the result of the hypsochromic effect.

Fluorescence spectroscopy

The fluorescence phenomenon ascertained in the case of lignin was attributed to the lignin aromatic structures, such as biphenyl, phenyl coumaron and stilbene, along with carbonyl conjugated groups. The fluorescence excitation of the lignin samples was studied in a 0.2N sodium hydroxide solution. The results obtained by the deconvolution of the fluorescence spectra for the 5 lignin types under study are presented in Figures 3 to 12, the spectra being recorded with a 350 nm excitation wavelength.

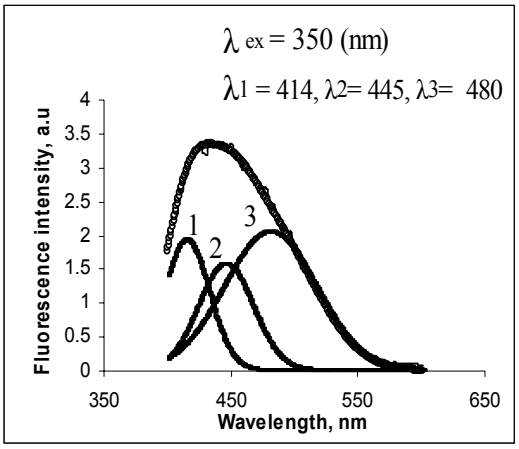

Figure 3: Fluorescence spectra for wheat straw lignin (L1)

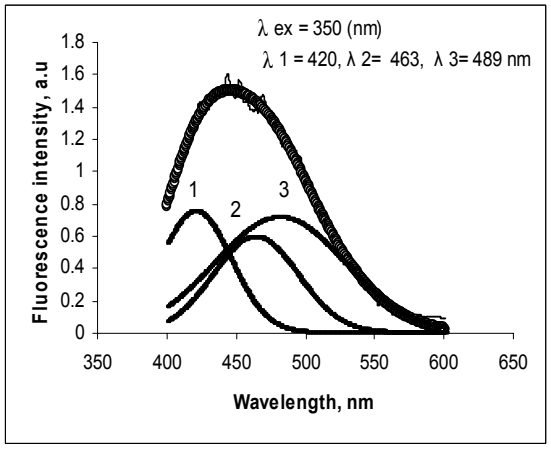

Figure 4: Fluorescence spectra for hydroxymethylated wheat straw lignin (L1H)

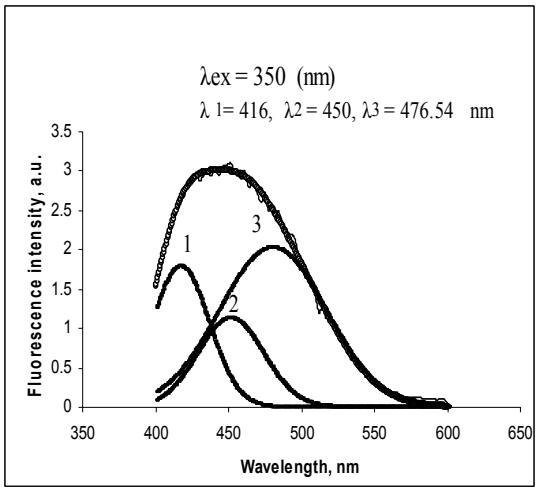

Figure 5: Fluorescence spectra for Sarkanda grass lignin (L2)

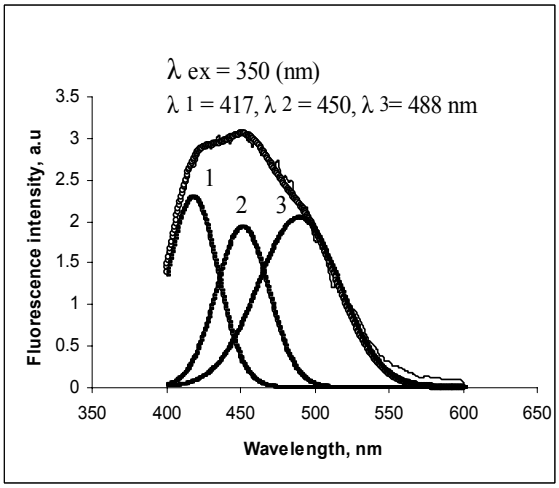

Figure 6: Fluorescence spectra for hydroxymethylated Sarkanda grass lignin (L2H)

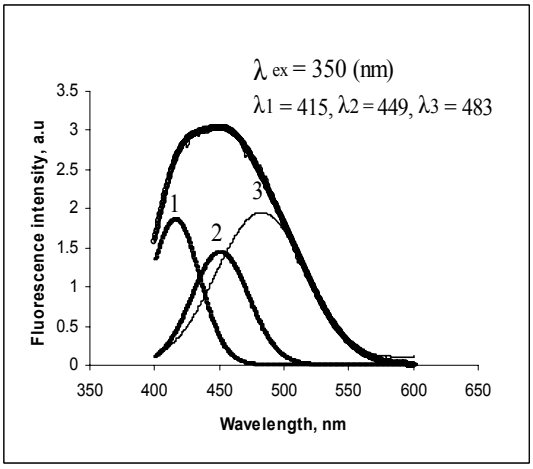

Figure 7: Fluorescence spectra for Protobind 1000 lignin (Pb1000)

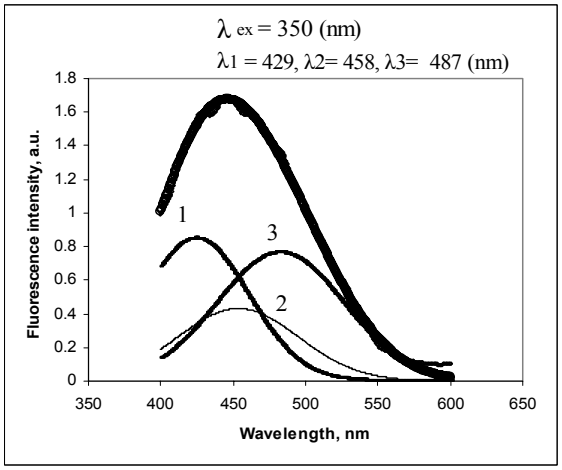

Figure 8: Fluorescence spectra for hydroxymethylated Protobind 1000 sample (Pb1000H)

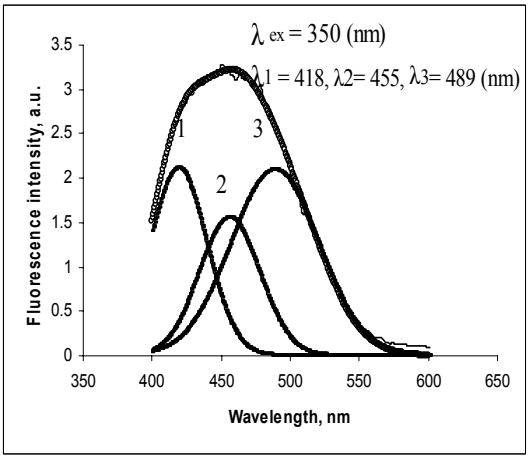

Figure 9: Fluorescence spectra for Protobind 2000 lignin (Pb2000)

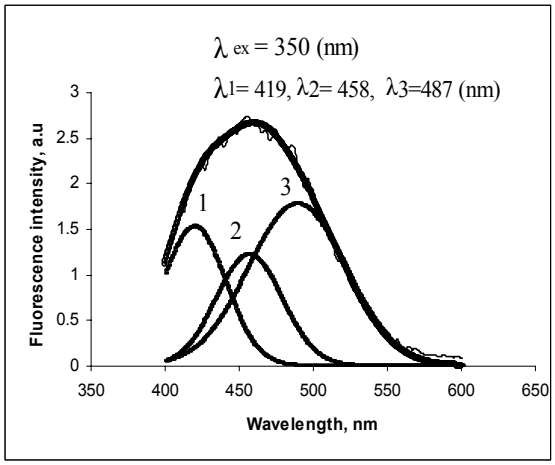

Figure 10: Fluorescence spectra for hydroxymethylated Protobind 2000 sample (Pb2000H)

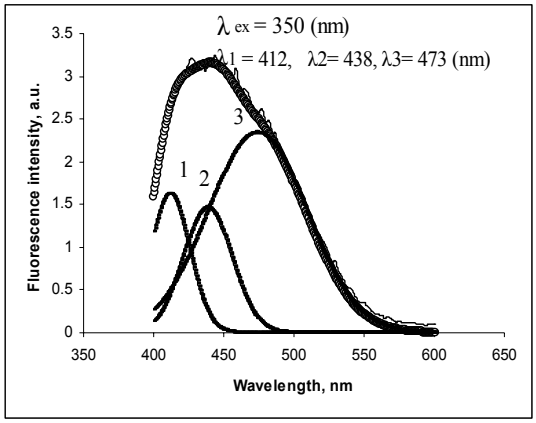

Figure 11: Fluorescence spectra for Protobind 3000 lignin (Pb3000)

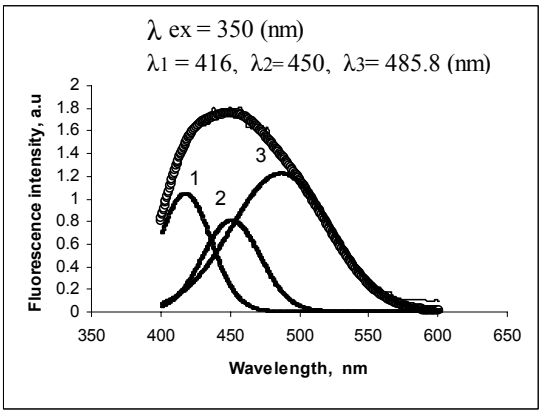

Figure 12: Fluorescence spectra for hydroxymethylated Protobind 3000 sample (Pb3000H)

The fluorescence spectroscopy method, known as highly sensitive in photochemistry, can be also applied for lignin characterization. Studies performed in different laboratories[10,12] have shown that, in the case of lignin from wood and annual plants, the outline of the emission spectra recorded in a 2.0 M NaOH solution are similar, the observed differences referring only to the intensity of the absorption bands. Thus, in the case of lignin separated from wood plants, the emission intensity is almost twice higher than that of the spectrum of lignin from annual plants. This is explained by the presence of a lower amount of carbonyl groups in the lignin from woody plants, which agrees with the information obtained from FTIR analysis.[11] On the other hand, the presence of phenyl coumaronic and stilbenic structures is viewed as responsible for the emergence of fluorescence.[13,14]

The deconvolution of the fluorescence spectra presented in this study (Figs. 3-12) offers the opportunity to remark that they are the result of several absorption peaks appearing at different wavelengths, which may be correlated with the structural changes induced by the hydroxymethylation reaction. In the case of modified lignin, a slight shift in the absorption peaks toward higher wavelength values may be noticed. These results can be correlated with the case of model compounds, for which fluorescence, recorded in the 400-600 nm range, is attributed to the hydroxyl and coumaron groups playing an acceptor role. Under these circumstances, the introduction of additional functional groups in the structure of lignin determines a characteristic behavior during excitation at a 350 nm wavelength radiation. The afore-mentioned behavior confirms that the modification by the hydroxymethylation reaction leads to different results, according to substrate reactivity.

Thermal stability

A structural characterization of the initial and hydroxymethylated lignins provides information on the thermal stability of the compounds.[15-17] Thermogravimetric analysis is known as a thermoanalytic method used to determine the rate of the chemical reactions developed under the action of the temperature necessary to assess the thermal stability of a product, which is an important characteristic for certain applications.[18-20] The recorded data show that the thermal decomposition of wheat straw lignin (L1), of grass lignin (L2) or that of lignin from commercial products Pb2000, Pb3000, and that of lignin chemically modified by the hydroxymetylation reaction, are not complete and generate an amount of approximately 40-50% residue.

The thermal degradation of lignin from wheat straw (L1) and grass (L2) occurs in two stages. In the former, humidity in the sample is diminished to approximately 4.8%, while, during the latter stage, thermal decomposition takes place.

In the case of commercial Protobind samples and of hydroxymethyl derivatives, the degradation process consists of three stages, the most significant mass loss being

recorded in the last one. The lignins modified by the hydroxymethylation reaction performed under different conditions of temperature and pH are thermally degraded in two or three steps. During the last stage of degradation, the temperature characteristic for the highest degradation rate (≈ 370 °C) is approximately the same for all analyzed samples. Additional information on the mechanism of lignin thermal degradation can be obtained from the kinetic processing of the thermogravimetric data (on a METTLER TOLEDO device equipped with a STARE SW 9.10 software). In this way, the kinetic parameters were determined by the Freemann-Caroll method, the obtained values being presented in Table 7.

Table 7
Kinetic parameters of lignin thermal degradation

Sample	Degradation stage	ln A	Ea (KJ/mol)	n
L1	II	4.83±1.67	56.48±1.67	1.08±0.005
L1H_90_pH = 10.5	II	2.48±0.21	38.55±0.85	0.59±0.0029
	III	8.98±0.26	78.11±1.34	1.78±0.0024
L2	II	4.21±0.3	52.49±1.42	1.25±0.0045
L2H_90_pH = 10.5	II	9.30±0.19	79.39±0.56	1.89±0.00225
Pb1000	II	3.81±0.18	43.85±0.75	0.76±0.0024
	III	16.76±0.25	117.43±1.27	1.52±0.016
Pb1000H_90_pH = 10.5	II	1.54±0.24	35.54±1	0.52±0.003
	III	8.80±0.39	77.54±2.03	1.74±0.0034
Pb2000	II	5.38±0.17	47.27±1.15	1.07±37.65
	III	6.31±0.14	63.31±0.73	0.83±10.39
Pb2000H_90_pH = 10.5	II	5.30±0.17	47.02±0.68	0.63±16.79
	III	10.87±0.40	87.11±2.07	1.75±33.92
Pb3000	II	1.81±0.61	29.73±2.27	0.64±65.99
	III	2.85±0.21	45.17±1.02	0.98±24.88
Pb3000H_90_pH = 10.5	II	5.63±0.26	50.62±1.09	0.66±22.95
	III	2.03±0.34	41.41±1.76	1.00±25.63

The different values of the reaction order may be explained by the possible presence of a radicalic mechanism for the thermal degradation of the studied compounds. The analysis of the apparent activation energies of the last thermal degradation stage in the samples modified by hydroxymethylation shows that the values around 70-80 kJ/mol are comparable with those recorded for unmodified lignin. The activation energy and the reaction order take lower values. Exceptions appear in the case of the Pb1000 and Pb2000H samples, where the activation energy presents the highest values of all recorded for lignins characterized by thermal analysis. The kinetic parameters of Pb1000 may be correlated with its higher content of carbonyl groups, compared with those of other types of lignin and with the high ratio of aromatic and aliphatic groups (Ak/Ar), as well as with a higher ratio of the syringyl and guaiacyl units (S/G).

CONCLUSIONS

1. Non-modified and hydroxymethylated lignin samples were characterized by spectral analysis (FTIR, UV-VIS), permitting to distinguish the functional modifications produced in the lignin derivatives after hydroxymethylation.
2. FTIR analysis demonstrates the appearance of some groups, characteristic of the C-C aromatic bonds, in the presence of the hydroxymethyl groups from the lignin macromolecule, as due to the reaction with formaldehyde.
3. The analysis of the UV-VIS absorption spectra reveals the presence of an absorption maximum at 280 nm and of a shift in the case of hydroxymethylated lignin from higher values of the absorbance wavelength to lower ones, as due to a hypsochromic effect.

4. By fluorescence spectroscopy, the absorption values were followed in the 400-600 nm range, at an excitation wavelength of 350 nm. The absorption spectra registered by fluorescence spectroscopy confirm that this method could be used to appreciate the extent of lignin modification.
5. The lignin samples modified by hydroxymethylation are characterized by different thermal stability, as appreciated from the activation energy and reaction order. The apparent activation energies calculated from the last stage of thermal degradation of the lignin samples modified by hydroxymethylation take values around 70-80 kJ/mol. In the case of the Pb1000, Pb1000H and Pb2000H samples, the activation energy has much higher values than those of the other samples submitted to thermal analysis.

ACKNOWLEDGEMENTS: The authors would like to thank the Granit Recherche Dévéloppement S.A., Switzerland, for supplying the lignin samples, and ECOBINDERS (SIXTH FRAMEWORK PROGRAMME, contract number NMP2–CT–2005–011734) for financial support.

REFERENCES

[1] Gh. Rozmarin, in "Fundamentări macromoleculare ale chimiei lemnului" (in Romanian), Ed. Tehnică, Bucureşti, 1984, p. 50.
[2] Gh. Petrovici and V. I. Popa, in "Chimia şi prelucrarea chimică a lemnului" (in Romanian), Ed. Lux Libris, Braşov, 1997, vol. 2, p. 168.
[3] Carmen G. Boeriu, Bravo Dominique Gosselink, J. A. Richard, Jan E. G. van Dam, *Ind. Crop. Prod.*, **20**, 205 (2004).
[4] N. E. E. Mansouri and J. Salvado, *Ind. Crop. Prod.*, **26**, 116 (2007).
[5] M. E. Brown, in "Introduction to Thermal Analysis, Techniques and Applications", Springer, 2001, p. 181.
[6] O. Faix, D. S. Argyropoulos, D. Robert and V. Neirinch, *Holzforschung*, **48**, 387 (1994).
[7] R. J. A. Gosselink, A. Abächerli, H. Semke, R. Malherbe, P. Käuper, A. Nadif and J. E. G. van Dam, *Ind. Crop. Prod.*, **19**, 271 (2004).
[8] Th. Măluţan, R. Nicu and V. I. Popa, *Bio/Resources*, **3**, 13 (2008).
[9] F. Le Digabel and L. Avérous, *Carbohyd. Polym.*, **66**, 537 (2006).
[10] V. I. Popa, Th. Măluţan and R. Nicu, *8th Forum ILI*, Rome, 2007, pp. 209-212.
[11] C. M. Popescu, C. Vasile, M. C. Popescu, G. Singurel, V. I. Popa and B. S. Munteanu, *Cellulose Chem. Technol.*, **40**, 597 (2006).
[12] P. Benar, G. R. Adilson, M. Dalmo and U. Schuchardt, *Bio/Resources*, **68**, 11 (1999).
[13] K. Radotič, Al. Kalauzi, D. Djikanovič, M. Jeremič, R. M. Leblanc and Z. G. Cerovic, *J. Photochem. Photobiol., B: Biology*, **83**, 1 (2006).
[14] Th. Măluţan, A. Pui, Corina Măluţan, Lucia Tătaru and Doina Humelnicu, *J. Fluoresc.*, **18**, 3, 707 (2008).
[15] E. Lopez-Capel, G. D. Abbott, K. M. Thomas and D. A. C. Manning, *J. Anal. Appl. Pyrol.*, **75**, 82 (2006).
[16] W. Hoareau, Wanderson G. Trindade, B. Siegmund, A. Castellan and E. Frollini, *Polym. Degrad. Stab.*, **86**, 567 (2004).
[17] Mansouri Nour-Eddine El and Salvadó Joan, *Ind. Crop. Prod.*, **24**, 8 (2006).
[18] Rodrigues C. Paula, Muraro Marilda, Carlos M. Garcia, Souza P. Gabriel, Abbate Miguel, Schreiner H. Wido and Gomes A. B. Maria, *Eur. Polym. J.*, **37**, 2217 (2001).
[19] A. Tejado, C. Penã, J. Labidi, J. M. Echeverria and I. Mondragon, *Bio/Resources*, **98**, 1655 (2007).
[20] Zhang Lian-hui, Dong Li, Wang Li-jun, Wang Ti-peng, Zhang Lu, Chen Xiao Dong, Mao Zhi-huai, *Bio/Resources*, **99**, 8512 (2008).