LIGNIN DERIVATIVES MODIFIED BY HYDROXYMETHYLATION AND EPOXYDATION REACTIONS

DERIVAŢI LIGNINICI MODIFICAŢI PRIN REACŢIILE DE HIFROXIMETILARE ŞI EPOXIDARE

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Abstract. *Lignin derivative (the commercial product - Protobind 2000) offered by the Granit Recherche Developement S.A. company, Lausanne-Schwitzerland was synthesized from annual plants. The present study's aim was to modify commercial lignins by the reaction of hydroxymethylation (produced in alkaline medium) and epoxydation (reaction with epichlorohydrin was performed in basic catalysis, aiming at increase the functionality) and to characterize the lignin derivatives chemical, spectral (^{1}H NMR) and thermogravimetric analysis (TG). Studies have revealed some functional changes related to the difference in reactivity and reaction conditions.*
Key words: Protobind 2000, lignin, hydroxymethylation, epoxydation, spectral and thermogravimetric analysis.

Rezumat. *Lignina derivativă (produsul comercial Protobind 2000) oferită de firma Granit Recherche Developement S.A. Lausanne-Elveţia a fost sintetizată din plante anuale. Scopul prezentului studiu este a de a modifica ligninele comerciale prin reacţia de hidroximetilare (produsă în mediul alcalin) şi epoxidare (reacţie cu epiclorhidrina în cataliza bazică ce creşte funcţionalitatea) şi de a caracteriza derivaţii ligninici prin analize chimice, spectrale (^{1}H RMN) şi termogravimetrice (TG). Studiile au relevat unele modificări funcţionale legate de diferenţa de reactivitate şi condiţiile de reacţie.*
Cuvinte cheie: Protobind 2000, lignină, hidroximetilare, epoxidare, analize termogravimetrice şi spectrale.

INTRODUCTION

Lignin is a macromolecular compound, much more active than cellulose or other natural polymers, due to functional groups contained in its macromolecule, constituting the main aromatic component of vegetal tissues, representing 20-40 % of the higher plants' mass located in the cellular wall and in intercellular spaces (Benar *et al,* 1999; Ungureanu, 2011).

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It is known that lignin has a very complex structure, which varies depending on the plant species, separation method and modification reactions that may induce particular characteristics. Regarding functional groups lignin presents at least three base functional groups in its structure: methoxylic, hydroxylic (alcoholic and phenolic) and the lateral propanic chain. Alongside these functional groups, in lesser amounts, there can be found carbonylic groups (approximate 1 group of CO at 5 C9 units), most of the times, fixated at the lateral chain. In some cases, the presence of carboxylic groups into the lignin can be noticed under the form of phenol carboxylic acids or of some small quantities of lactonic groups (Ungureanu *et al,* 2009, 2016).

Lignin modification through hydroxymethylation and epoxydation offers possibilities of developing its functionality and this allows the extension of the application area for the synthesized derivatives.

Taking into account all these aspects, the objectives of this study are the modification of some lignin's from annual plants through a reaction of hydroxymethylation produced in an alkaline medium in the presence of formic aldehyde and of epoxydation effected out in an alkaline medium in the presence of epichlorhydrin and the characterization of lignin derivatives from a chemical, spectral (^{1}H NMR) and thermogravimetric methods.

MATERIAL AND METHOD

The following materials have been used:

- Protobind 2000 (Pb2000), commercial lignin offered by Granit Recherché Dévelopement Switzerland, with the following chemical characteristics presented in table 1.

Table1

The characteristics Protobind 2000

Characteristics	Protobind 2000
Solide, %	95
Ash, %	1.3
pH (10 % dispersion)	4.80
Densitatea, g/mL	~ 0.6
Aromatic OH, mmole/g	1.6-1.8
COOH, mmole/g	2.1-2.3
T softening, °C	~ 130
Solubility in furfuryl alcohol, %	41
Solubility in aqueous alkali, %	95

- Formic aldehyde (37 %);
- Dimetil sulfoxid (DMSO);
- NaOH solution 0.1 N;
- Epichlorhydrin.

Work procedure:

The hydroxymethylation reaction

The method used in the hydroxymethylation of the three lignin products was performed in a basic medium, in the presence of formic aldehyde (37 %), according to the technical literature *(*Ungureanu, 2011).

Determination of total hydroxyl groups

The total OH groups content was determined by chemical method with acetic anhidryde in pyridine medium and from FT-IR spectral analysis.The Ar-OH group's content was determined by a UV-VIS method.

The epoxidation reaction

The epoxydation method achieved in a basic medium in the presence of epichlorhydrin through which the three types of lignin studied have been modified has been effected out according to the technical literature *(*Ungureanu, 2011).

Epoxydation index

Determination of the epoxy group was effected out by HCl addition on the epoxy group and titration of the acid excess with NaOH solution 0.1 N.

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR)

Nuclear magnetic resonance (NMR) offers the richest and most complete information on the structure of organic compounds. For this purpose it was used a Bruker Avance DRX 400 MHz spectrometer.

Process: For investigation was necessary lignin acetylation and derivatives for a better dissolution in DMSO-d6. To obtain a "good" spectrum it is required to have concentrations of about 0.2 mmol/mL. Spectra processing was performed with a specialized program from SpectraManager series.

Thermogravimetry

The thermal analysis was performed using the METTLER TOLEDO derivatograph in N_2 atmosphere with a flow of 20mL/min and a heating rate of 15ºC/min, in the temperature range 25-800 °C and sample mass of 4 ÷ 6 mg.

RESULTS AND DISCUSSIONS

During the reaction of hydroxymethylation performed for lignin, the reaction conditions have been varied (50°C temperature, 90°C respectively, reaction duration of three hours and pH 10.5, pH 12 respectively) in order to obtain highly functional products.

The content of functional groups was determined according to the methods presented by different research groups. The other methods applied for chemical characterization were: the determination of carboxylic groups and of the metoxyl groups, the determination aromatic hydroxyl groups, the calculation of the fenolic groups/aliphatic groups' ratio, as well as, the determination siringyl/guaiacyl unit's ratio (S/G).

The information obtained has allowed the determination from this point of view of the optimal reaction conditions, namely: 90°C temperature, pH 10.5 and the reaction duration of three hours (tab. 2).

Table 2

The content of functional groups of modified and unmodified lignins

Sample	T, ^{O}C	pH	OH total groups	Ar-OH groups	OCH_3 groups	Ak/Ar ratio	C=O groups	S/G ratio
Pb 2000	-	-	1.11	0.89	1.05	1.17	0.89	0.83
	90	12.0	1.23	0.98	1.15	1.27	0.95	0.96
	90	*10.5*	*1.15*	*0.98*	*1.13*	*1.20*	*0.91*	*0.96*
	50	10.5	1.14	0.98	1.12	1.22	0.95	0.96
	50	12	1.16	0.99	1.14	1.21	0.94	0.96

The lignin obtained in optimal conditions there was characterized from the point of view spectral and thermogravimetric. As a consequence of the thermal analyses, it can be noticed that the modified product has a higher degradation temperature in the third stage, compared to the unmodified sample (tab. 3).

Table 3

Characteristics of the thermal degradation process of the lignin derivatives

Samples	Degradation stage	T_i (°C)	T_{max} (°C)	T_f (°C)	Mass losses (%)
Pb2000	I	205	234	326	22.78
	II	326	381	496	39.23
	III	56	79	115	5.06
Pb2000H	I	216	248	328	12.90
	II	329	3374	580	36.37
	III	205	234	326	22.78

(Ti - initial temperature at which the degradation starts; Tmax – temperature corresponding to the maximum rate of degradation, Tf –final temperature şi W – mass losses %).

The characterization of the lignin has been achieved by monitoring the influence of temperature (50°C and 70°C respectively), the mass ratio between the lignin (L) and NaOH (L:NaOH = 1:3 and 1:6) and the reaction duration (3, 5 and 7 hours respectively). It can be noticed from table 4 that the best results can be obtained when the reaction is achieved at 70°C, for a L:NaOH=1:3 ratio and a three-hour reaction duration, appreciated as being ***optimal reaction*** conditions. The reaction yield was included in the 50-90 % interval, related to the mass of the reactants and it differs according to the type of sublayer and the purification degree after washing the derivatives. It can also be noticed that along with the temperature increase and the reaction duration, from 3 to 7 hours, appear a decrease of the epoxydation number (tab. 4) (Ungureanu *et al,* 2015).

Table 4

Characteristics of the modified lignin's by epoxydation

Sample	T, ^{0}C	L:NaOH (w/w)	t, h	CE, %		η, %	U, %	Ash %	Const. f.liq, %
				f.sol.	*f.liq.*				
Pb2000E	70	1:6	3	1.20	0.21	50	5.5	8.12	16.40
	70	*1:3*	*3*	1.70	0.64	*64*	*5.1*	*2.1*	*18.20*
	50	1:3	3	1.85	0.36	60	7.2	7.85	16.25
	70	1:3	5	1.50	0.32	69	6.78	6.22	12.32
	70	1:3	7	1.63	0.40	52	6.27	5.63	15.30

For characterization by ^{1}H-NMR spectroscopy the lignin was subjected to acetylation to aid dissolution in DMSO-d6. In figures 1 and 2 are shown the ^{1}H-NMR spectra for Pb1000 lignin unmodified (Pb2000N) and hydroxymethylation

(Pb2000H), and the results were interpreted using literature data. The spectrum recorded for the two lignins weak signals in the aromatic domain at 8.64 ppm and the methoxyl groups.

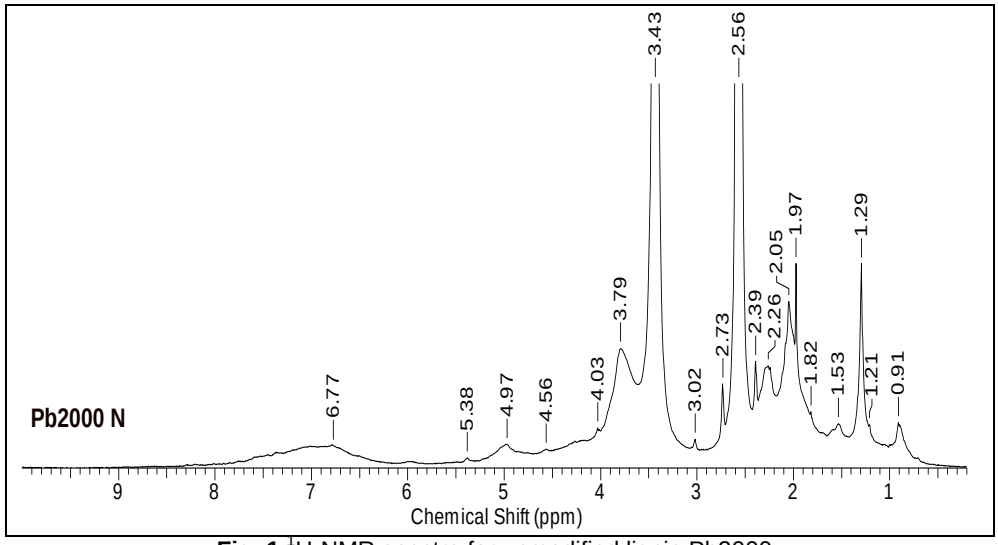

Fig. 1 ^{1}H-NMR spectra for unmodified lignin Pb2000

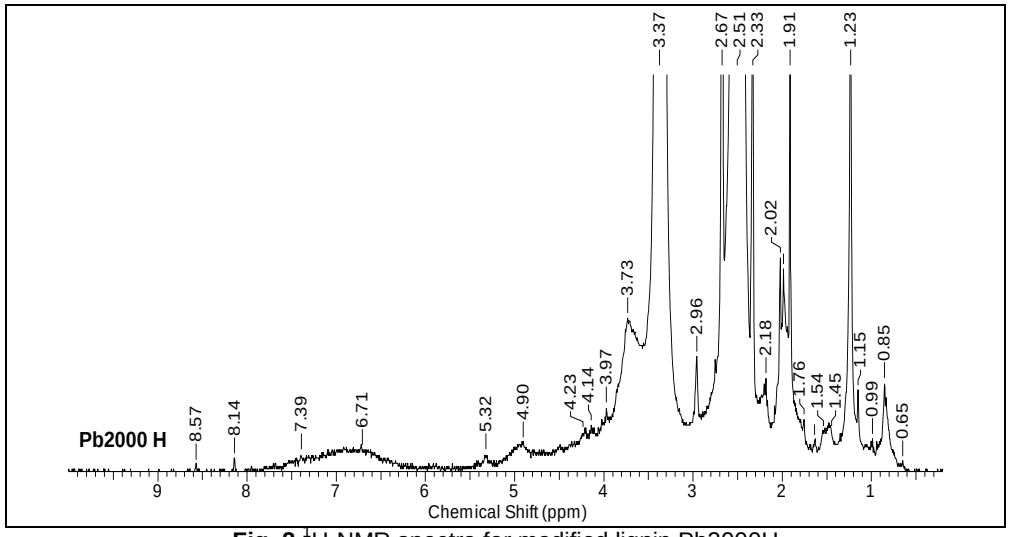

Fig. 2 ^{1}H-NMR spectra for modified lignin Pb2000H

Signals from 9.08-7 ppm confirms the presence of epoxy groups in lignin structure. Also stands out the signals of methoxyl and acetyl groups, more intense in the spectra of epoxidised lignin (fig. 3).

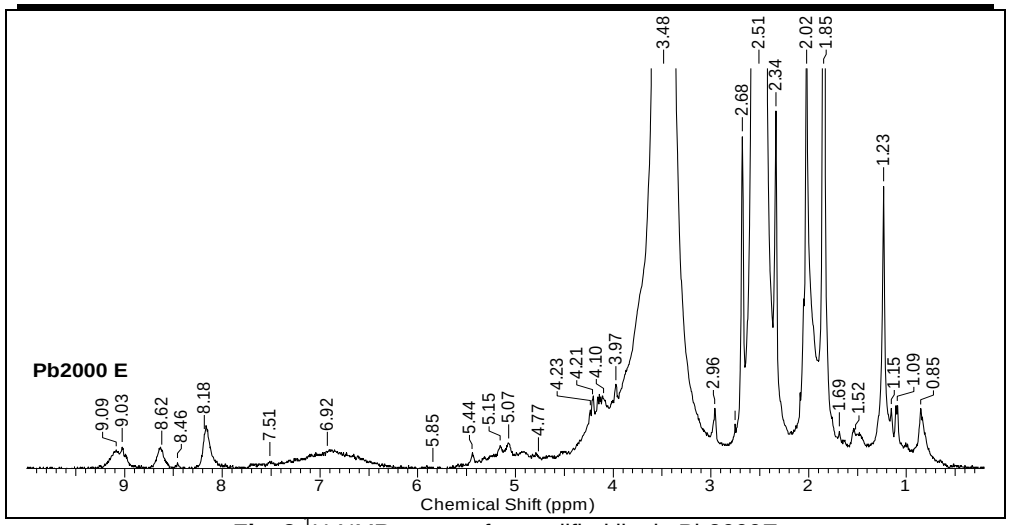

Fig. 3 ^{1}H-NMR spectra for modified lignin Pb2000E

CONCLUSIONS

1. The ^{1}H-NMR spectroscopy shows the change of functionality for lignin as a result of hydroxymethylation and epoxydation reaction.

2. The thermogravimetric analyses have proved that thermal degradation occurs in two and three stages respectively, according to the type and the degree of modification of the products tested but the hydroxymethylated/epoxydated derivatives have a higher thermostability, compared to the unmodified lignin.

REFERENCES

1. **Ariton Adina-Mirela, Creangă T., Trincă Lucia Carmen, Borş S.I., Ungureanu Elena, Măluţan Th., Popa V.I., 2015** - *Valorization of lignin modified by hydroxymethylation to ensure birch veneer bioprotection,* Cell. Chem. and Technol., 49 (9-10), p. 765-774.
2. **Benar P., Gonplves A. R., 1999** - *Principal component analysis of the hydroxymetylation of sugarcane lignin: A time-depending study by FTIR*, J. Wood Chem. Technol., 19 (1-2), p.15 1-165.
3. **Ungureanu Elena, Jităreanu Carmen Doina, Trofin Alina, Popa V.I., Sandu Tatiana, 2015** - *Chemical and spectral characterizations for some lignin products*, Lucrări Ştiinţifice, Seria Horticultură, nr.58, vol.1, p.23-28.
4. **Ungureanu Elena, 2011** - *Lignina, polimer natural aromatic cu ridicat potenţial de valorificare*, Ed. PIM, Iaşi, p. 112.
5. **Ungureanu Elena, Ungureanu O., Căpraru Adina-Mirela, Popa V.I., 2009** - *The chemical modification and the characterization the straw lignin,* Cell. Chem. and Technol., 43 (7-8), p. 263-269.
6. **Ungureanu Elena, Trofin Alina, Ariton Adina-Mirela, Jităreanu Carmen Doina, Ungureanu Ovidiu, Gîlcă Valerica, Bors S.I., Popa V.I., 2016 -** *Applications of epoxidated lignins for bioprotection of lignocellulosic materials***,** Cell. Chem. and Technol., 50 (1), p. 77-85.