

CONTRIBUTION TO THE STUDY OF HYDROXYMETHYLATION REACTION OF ALKALI LIGNIN

Theodor Malutan,^{*} Raluca Nicu, and Valentin I. Popa

The hydroxymethylation of alkali lignin with formaldehyde in alkaline solution was studied. The influence of reaction conditions of the hydroxymethylation of alkali lignin was followed by modifying the temperature, time, and the ratios of NaOH to lignin and CH₂O to lignin. Three different types of alkali lignin were utilized. The reaction was followed by total consumption of formaldehyde, and the resulting products were characterized through FTIR-spectra, thermogravimetry analysis, ash and moisture contents, as well as by the amounts of OH groups.

Keywords: Lignin, Hydroxymethylation, FTIR, Thermogravimetry

Contact information: Faculty of Chemical Engineering, P.O.Box 10, postal code 700050, Bd. D. Mangeron, no. 71 A, Romania, *Corresponding author: thmalu@ch.tuiasi.ro

INTRODUCTION

Lignin is a macromolecular compound much more reactive than cellulose or other natural polymers from chemical point of view, because of its functional groups. The reactivity of lignin is determined both by its particular structure with specific functional groups and by its structural modifications induced by separation methods used for different raw materials (Popa 1983). The presence of the hydroxylic groups, both phenolic and aliphatic, in lignin has enabled its utilisation as a partial substitute for phenol in the synthesis of products with a lot of applications (Popa et al. 2003).

The substitution of phenol, particularly with kraft lignin, in the synthesis of phenol - formaldehyde (PF) resins is the most studied use of lignin (Conner 2001). Phenol-formaldehyde resins are the major adhesives used for bonding wood panels for outdoor applications. The PF adhesive resins are used primarily as a binder (Çetin 2003) in the production of softwood plywood, oriented strandboard, and waferboard. The PF resins are synthesized by the reaction of phenol with formaldehyde. By varying the reaction time, reaction temperature, catalyst type, and the ratio of formaldehyde to phenol, a number of adhesive systems with different characteristics can be produced. For the resins used in the wood industry, sodium hydroxide is the most important catalyst, although other basic catalysts such as sodium carbonate, alkaline oxides and hydroxides, and ammonia can also be used. Resole resins are formed by heating the reactive ingredients in aqueous solution at about 80-100 °C. Initially, mono-, di-, and trihydroxymethyl derivatives of phenol are formed. Further, the reaction leads to condensation of the hydroxymethyl derivatives, giving methylene or ether linkages between phenol moieties (Conner 2001)

The partial substitution of phenol by a natural polymer such as lignin, the main by-product of the pulp industry, has presented an attractive alternative (Alonso et al. 2001, Lora and Wu 2007). Lignin also represents a product obtained from renewable resources and has an aromatic and highly cross-linked structure, similar to the network of PF resins (Fig. 1) (Benar et al. 1999).

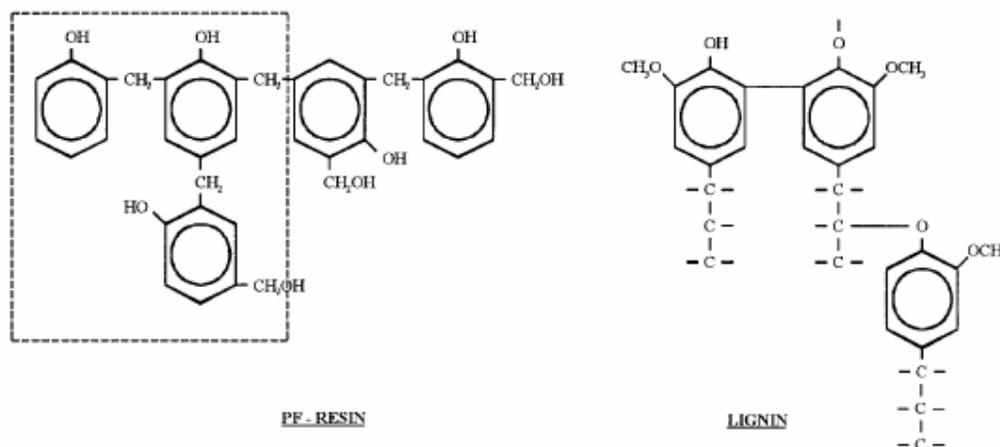


Fig. 1. Structure of PF resins and lignin

In the earlier studies, lignin has been incorporated into phenolic resins used as wood adhesives, but the current trend is to modify their chemical structure in order to increase the reactivity towards formaldehyde. The modification can be accomplished by different methods: methylation, phenolation, demethylation, and fractionation. During the methylation process, formaldehyde is added to the lignin in alkaline medium (Alonso et al. 2001).

The reactivity of lignin in hydroxymethylation depends on their sources (softwoods, hardwoods, or grass), on pulping conditions (pH, temperature, pressure), and on other reaction conditions (Peng et al. 1993). That is why the objective of this research was to study the hydroxymethylation reaction of annual plants alkali lignin (*Wheat straw* and *Sarkanda grass*) by condensation with formaldehyde in alkaline solution in order to establish optimum conditions and to characterize the resulting hydroxymethylated derivatives.

In order to prove the mechanism of interaction between lignin and formaldehyde, the modified products have been characterized by functional analysis; the amount of hydroxyl groups have been determined through a chemical method with acetic anhydride in pyridine medium (Faix et al. 1994) and by FTIR-spectra (Nada et al. 1998). Any increase in the hydroxyl content of hydroxymethylated lignin as compared to that of lignin is assumed to be due to a number of hydroxymethyl groups introduced into the lignin molecule by reaction.

The thermal stability of modified and unmodified lignin was studied by TGA.

EXPERIMENTAL

Lignin Hydroxymethylation

The experiments were carried out with different alkali lignin (offered by Granit Co.) as raw materials: L₁ (from *Wheat straw* 100-W-A), L₂ (from *Sarkanda grass* 100-S-A) and Protobind 1000 with characteristics presented in Table 1. The modification of lignin through the hydroxymethylation reaction was performed with formaldehyde - 37% solution, in alkaline medium, using NaOH solution at 3 % (w/w) concentration.

Thus, the lignin samples were dissolved in 100 mL NaOH solutions 3% (w/w) corresponding to a ratio of NaOH/L equal to 0.08 (w/w). The temperature of the lignin solution was 25 °C and the pH 9.7-9.9. The hydroxymethylation of the ionized lignin was performed by the addition of a formaldehyde 37% solution ($\rho = 1.08 \text{ g/cm}^3$) using a ratio 0.258 (w/w) of CH₂O/L, at room temperature. After that, the temperature was raised to 50 °C and subsequently to 90 °C. The total time of reaction was 3 h. The concentration of dissolved lignin in the reaction medium was nearly 280 g/L.

In parallel with the hydroxymethylated lignin a reference sample was obtained, using the same treatment without formaldehyde solution (it was replaced by distilled water). The parallel sample was analyzed using the same methods.

Precipitation of modified lignin was carried out through lowering of the solution pH value to an acid pH (1.5 - 2), using hydrochloric acid 1N solution. The obtained precipitate was centrifuged at 2500 rpm for 10 minutes, washed three times with distilled water to remove the undesired inorganic salts, unreacted aldehyde and any other residual reactants therefrom, and then dried in a vacuum oven overnight at 40 °C (Molin and Kuo 1987; Lin 1980; Marton et al. 1966).

Table 1. The Characteristics of Raw Lignin Samples

Characteristics	L1 (100-W-A)	L2 (100-S-A)	Protobind 1000
Acid insoluble lignin, %	90	87	-
Acid soluble lignin, %	1	2	-
COOH, mmole/g	3.8	3.3	2.1 – 2.3
Aromatic OH, mmole/g	1.7-1.8	1.8-1.9	1.9-2.1
OH/C9 groups chemical method	1.02	1.07	1.05
pH (10 % dispersion)	2.7	3.2	~ 3.5
Mw	3510	4310	1160
T softening, °C	170	163	200
Solubility in furfuryl alcohol, %	88.5	84	98.5
Solubility in aqueous alkali, pH 12, %	98.5	98.5	94
Ash, %	2.5	4.1	1.4-1.8

L1 – wheat straw lignin; L2-Sarkanda grass lignin.

FTIR Spectroscopy

Infrared (FTIR) spectra of the modified and unmodified lignin, pellet formed with KBr, were recorded on a Digilab FTS 2000 Fourier transform spectrometer, domain: 4000-400 cm⁻¹, resolution 4 cm⁻¹, 32 scans.

Termogravimetry Analysis

Thermal stability was studied via thermogravimetric analysis (TGA) on a METTLER TOLEDO instrument. Temperature ramps between 25 and 900°C at 15°C/min under nitrogen were performed to determine the mass loss of material as a function of temperature.

Gel Permeation Chromatography (GPC)

The molecular mass was determined by GPC (stationary phase: Sephadex LH20, mobile phase: 0.3 mL/min NaOH 0.1 N, 280 nm).

Determination of Total Hydroxyl Groups

The total OH groups content was determined by chemical method with acetic anhydride in pyridine medium (Faix 1994) and from FTIR spectral analysis (Nada et. al. 1998). The Ar-OH groups content was determined by a UV-Vis method (Gärtner et al. 1999).

RESULTS AND DISCUSSIONS

Determination of Unreacted Formaldehyde

During the lignin methylation, hydroxymethyl groups are introduced in the reactive positions of lignin, mainly in *ortho* positions (in relation to phenolic OH groups) of aromatic rings. Increasing the temperature, hydroxymethyl groups react at free positions of other lignin units or phenol to form methylene bonds (Benar et al. 1999). Under these conditions three

reactions can take place. The main one is the Lederer-Manasse reaction, where hydroxymethyl groups are incorporated in the aromatic rings of lignin, increasing the reactivity of the molecule (Fig. 2). Undesirable side reactions are the Cannizzaro reaction, in which the formaldehyde reacts with itself, and the Tollens reaction (Ayla and Nimz 1984) in which the lignin side chains are substituted by aliphatic methylol groups (Alonso et al. 2001; Zhao et al. 1994; Chen and Wu 1994).

The unreacted formaldehyde was determined during the methylation reaction through the sodium sulfite method (Walker 1975). To determine the quantity of formaldehyde which reacts with itself, a blank sample without lignin was exposed to the same conditions as those applied to the lignin. A preliminary experimental series for determination of formaldehyde consumption in secondary reactions was carried out. Finally, the values of consumption were corrected. The consumption of formaldehyde, comparing the hydroxymethylation and Cannizzaro reactions in the case of *Sarkanda grass* lignin (L_2), is presented in Table 2.

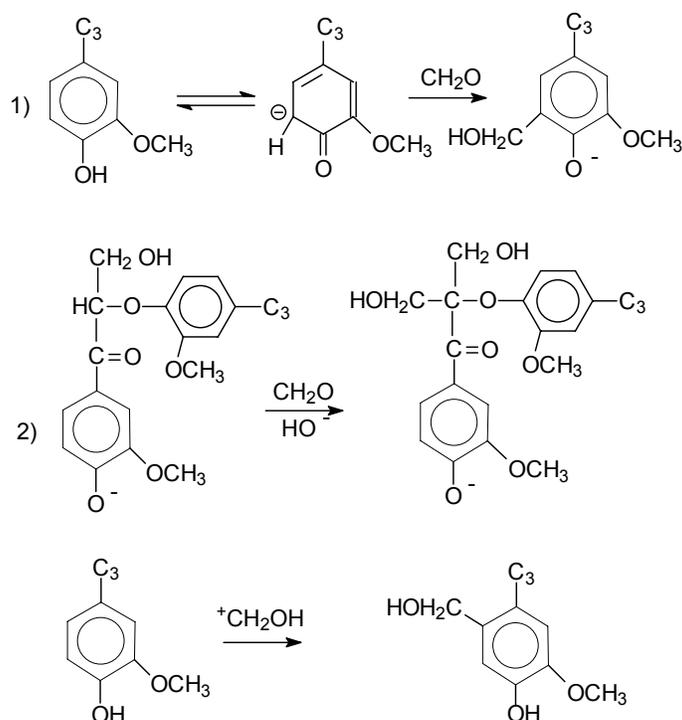


Fig. 2. Hydroxymethylation of phenolic ring of lignin units

The data presented in Table 2, show that an increase of the NaOH/L ratio from 0.04 to 0.16 (w/w) resulted in an increase in CH_2O total consumption, as well as an increase in Cannizzaro reactions. The optimal NaOH/L ratio was 0.08 (w/w). The alkali medium ensures ionization of the phenolic group of the lignin.

Table 2. The Variation of Formaldehyde Consumption in Hydroxymethylation of *Sarkanda grass* Lignin (L_2)

NaOH/L ratio, w/w	CH_2O consumption, mole	
	Total	Cannizzaro reaction
0.04	0.38	0.22
0.08	0.71	0.42
0.16	0.78	0.73

The reaction conditions were: temperature 90°C , time 180 min, $\text{CH}_2\text{O}/\text{L}$ ratio = 0.25 (w/w)

The results obtained under these conditions for hydroxymethylation of all lignin samples are presented in Table 3.

Table 3. The Formaldehyde Consumption in Hydroxymethylation of Lignin Samples

Sample	T, °C	pH	¹ Moles CH ₂ O reacted / 100 g lignin	OH/C ₉ groups chemical method	Ar-OH, mmole/ g lignin	OH/C ₉ groups FTIR	Mw
L1 (100-W-A)	initial		-	1.02	1.7-1.8	1.06	3510
	90	12.0	0.51	1.17	1.29	1.17	-
	90	10.5	0.20	1.17	1.76	1.16	-
	50	12.0	0.31	0.85	1.49	1.16	-
	50	10.5	0.20	1.03	1.66	1.24	990
L2 (100-S-A)	initial		-	1.07	1.8-1.9	1.05	4310
	90	12.0	0.35	1.64	1.53	1.19	-
	90	10.5	0.17	1.18	1.32	1.34	-
	50	12.0	0.46	1.01	1.78	1.20	-
	50	10.5	0.14	0.94	1.75	1.34	1205
Protobind 1000	initial		-	1.05	1.9-2.1	1.10	1160
	90	12.0	0.14	1.17	1.58	1.23	1325
	90	10.5	0.20	1.07	1.63	1.15	1270
	50	10.5	0.10	1.04	1.14	1.14	1080

The CH₂O/L ratio was 0.25 (w/w).

¹) The values corrected without the CH₂O consumption in Cannizzaro reactions.

The molecular mass determinations indicated a decrease of Mw during formaldehyde treatment (from 3510 to 990 for L₁, 4310 to 1205 for L₂).

By increasing the reaction temperature, the hydroxymethyl groups can react with free positions of other lignin units to form methylene bridges. Thus, in case of Protobind 1000 at temperature 90°C, the gravimetric mass increased from 1160 to 1325 (pH 12) and to 1270 (pH 10.5).

From Table 3 it can be observed that the reaction pH played an important role. At pH 12 the total formaldehyde consumption was high, and the Cannizzaro reactions were intensified. In these conditions, the lowest formaldehyde reactivity of lignin samples was observed in the case of Protobind 1000, whereas *Wheat Straw* (L₁) and *Sarkanda grass* (L₂) lignin were more reactive. This increasing of aliphatic OH is based on taking into account the methylation reaction of lignin through the Lederer-Manasse reaction.

Functional Analysis by FTIR Spectra

The FTIR spectra obtained were characterized by a broad O-H band at 3400 cm⁻¹, an intense C-H band at 2927 cm⁻¹, and another at 2854 cm⁻¹, which are typical of methoxyl groups. The aromatic skeletal vibrations occur at 1600 cm⁻¹ and 1500 cm⁻¹. These bands were used for normalization and their intensity was always set to 1.00. The C-H deformations band of asymmetric methyl and methylene appeared at 1470–1460 cm⁻¹, and carbon–oxygen ether bands at 1400–1000 cm⁻¹. The following ratios of the relative absorbance for different groups were defined:

$$\text{Mean value of OH groups} = \text{average} (A_{3430}, A_{1370}, A_{1165}, A_{1043}) / A_{1510(1600)}$$

$$\text{Mean value of phenolic OH groups} = A_{1370} / A_{1510(1600)}$$

$$\text{Mean value of OCH}_3 \text{ groups} = \text{average} (A_{2890}, A_{1460}, A_{1420}) / A_{1510(1600)}$$

$$\text{Mean value of C=O groups} = A_{1720} / A_{1510(1600)}$$

$$\text{Mean value of aromatic ring} = \text{average} (A_{1510}, A_{1600}, A_{844})$$

$$\text{Ratio of aliphatic to aromatic signals} = A_{2936} / A_{1510(1600)}$$

$$\text{S/G ratio} = A_{1330} / A_{1269}$$

The results obtained for functional groups are presented in Table 4. The ratios of absorbance of aliphatic OH and aliphatic (Ak) groups to aromatic groups can take into account the methylation reaction of lignin through the Lederer-Manasse reaction. In case of hydroxymethylation of *Sarkanda grass* lignin (L2), high values for these ratios were obtained in comparison with those of *Wheat straw* lignin (L1) or Protobind 1000. Under these reaction conditions the hydroxymethylation of Protobind 1000 lignin occurred without an important increases of the content of OH total groups and Ak/Ar ratios.

The content of Ar-OH groups was modified during the hydroxymethylation, probably because secondary reactions of condensation which can take place. The ratio of signals of phenolic OH groups indicates that during hydroxymethylation, lignin can be activated for side reaction, but these effects were very small.

A significant ratio of A_{1330}/A_{1269} (S/G) was observed, which means that there were the possibilities for substitution in 5 or 6 position due to the presence of guaiacyl or syringyl moieties in lignin structure.

Table 4. The Functional Groups of Hydroxymethylated Lignin

Sample	T, °C	pH	OH total 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
	90	12.0	1.17	0.92	1.14	1.08	0.83	0.97
	90	10.5	1.16	0.98	1.13	1.20	0.93	0.97
	50	12.0	1.16	0.99	1.09	1.08	0.89	0.93
	50	10.5	1.24	0.95	1.11	1.05	0.86	0.86
L2 (100-S-A)	-	-	1.05	0.91	0.96	0.88	0.88	0.82
	90	12.0	1.19	0.95	1.16	1.40	1.00	0.89
	90	10.5	1.14	0.95	1.10	1.11	0.92	0.85
	50	12.0	1.20	0.96	1.11	1.19	0.94	0.91
	50	10.5	1.34	0.78	1.18	3.20	0.77	0.57
Protobind 1000	-	-	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

Thermogravimetric Analysis

Thermogravimetric curves reveal the mass loss of substances in relation to the temperature of thermal degradation, while the first derivative of that curve (DTG) shows the corresponding rate of mass loss. The peak of this curve (DTG_{max}) may be expressed as a single thermal decomposition temperature and can be used to compare thermal stability characteristics of different materials.

Thermal characteristics of hydroxymethylated and unmodified lignin are presented in Table 5.

The DTG_{max} (T_m, peak 2) appeared between 370 and 381 °C, and the loss of mass was between 35 % and 52 % for all lignin samples analysed. Hydroxymethylated lignin, when subjected to thermal cure, becomes insoluble in alkali. If we compare DTA curves of alkali lignin and methylolated alkali lignin, it can be observed that in the latter case a highly exothermic reaction started around 125°C, the material became stabilized over 190°C, and it did not melt up to 190°C, where it started to soften. The endotherm change around 110°C indicates a probable loss of water, absorbed or structural. The thermal cure of methylolated lignin is a further proof of the presence of phenol alcohol structure.

Table 5. Thermogravimetry Data for Hydroxymethylated and Unmodified Lignin

Sample	Peak 1				Peak 2			
	T _{onset} , °C	T _m , °C	T _{offset} , °C	Mass loss, %	T _{onset} , °C	T _m , °C	T _{offset} , °C	Mass loss, %
L ₁	65.4	82.3	147.7	4.75	297.5	381	504.7	36.48
L ₁ H50pH10	68.0	81.7	140.0	6.64	303.2	373.4	512.8	43.74
L ₁ H50pH12	65.5	81.6	147.7	6.21	164	372.8	642	45.9
L ₁ H90pH10	58.0	79.3	126.6	5.54	220.3	371.9	688.8	48.35
L ₁ H90pH12	58.0	79.9	107.6	5.51	245.1	368.8	534.5	48.51
L ₂	58.6	82.5	140.3	4.58	290.8	373.6	489	35.16
L ₂ H50pH10	59.0	89.9	115.8	4.68	235.7	369.9	587.1	49.05
L ₂ H50pH12	58.0	78.9	108.2	6.66	248.1	372.4	557.6	48.46
L ₂ H90pH10	58.0	81.7	124.7	7.85	310.03	376.5	642.2	52.16
L ₂ H90pH12	52.0	72.4	104.1	5.37	231.6	363.1	552.24	47.63
P 1000	57.4	81.6	131	3.08	297.4	380.8	504.3	35.13
P1000H50pH10	56.8	77.4	109.2	5.05	227.1	376.7	656	52.01
P1000H90pH10	50.0	75.5	123.9	3.71	226.1	378.9	646.47	49.17
P1000H90pH12	56.0	64.8	102.6	4.95	221.9	377.5	595.2	49.12

*) Heat rate : 15 °C/min; Final temperature = 800 °C;

CONCLUSIONS

The reactivity of different kinds of lignin was studied relative to formaldehyde addition under alkaline conditions at two temperature (50°C and 90°C) and pH 10.5 and 12. The optimum conditions for methylation (reaction temperature was 50°C and pH 10.5 for lignin L₁ and L₂) depend of kind and structure of lignin. Under these conditions, the extent of the Cannizzarro reaction is low, and a substantial increase in the lignin hydroxymethyl groups is attained. The best reactivity was found for the *Sarkanda grass* lignin, in comparison with *Wheat straw* and *Protobind 1000* lignin. The aim of chemical transformation of lignin is both to enlarge its applications and to improve its product performance.

ACKNOWLEDGMENTS

The authors are grateful for the support of the CE - FP6 Program “ECOBINDERS”.

REFERENCES CITED

- Alonso, M. V., Rodríguez, J. J., Oliet, M., Rodríguez, F., Garcia, J., Gilarranz, M.A. (2001). “Characterization and structural modification of ammoniac lignosulfonate by methylation,” *Journal of Applied Polymer Science* 82, 2661-2668.
- Ayla, C., and Nimz, H. H. (1984). “Die Verwendung von Ablaugen-. lignin bei der Herstellung von Holzwerkstoffen,” *Holz Roh- Werkst.* 42, 415-419.
- Benar, P., Gonçalves, A. R., Mandelli, D., and Schuchard, U. (1999). “Eucalyptus organosolv lignins: Study of the hydroxymethylation and use in resols,” *Bioresource Technology* 68, 11-16.
- Çetin, N. S., and Özmen, N. (2003). “Studies on lignin-based adhesives for particleboard panels,” *Turk. J. Agric. For* 27, 183-189.
- Conner, A. H. (2001). “Wood: Adhesives,” *Encyclopedia of Materials: Science and Technology*, Amsterdam, New York, Elsevier Science, Ltd.
- Chen, R., and Wu, Q. (1994). “Modified lignosulfonate as adhesive,” *Journal of Applied*
- Malutan et. al. (2008). “Hydroxymethylation of alkali lignin,” *BioResources* 3(1), 13-20.

- Polymer Science* 52, 437-443.
- Faix, O., Argyropoulos, D. S., Robert, D., and Neirinch V. (1994). "Determination of hydroxyl groups in lignins," *Holzforschung*, 48 (5), 387-394.
- Gärtner, A., Gellerstedt, G., and Tamminen, T. (1999) "Determination of phenolic hydroxyl groups in residual lignin using a modified UV-method," *Nord. Pulp Pap. Res. J.* 14, 163-170.
- Lin, S. Y. (1982). "Method for polymerization of lignosulfonates," *United States Patent* 4,332,589.
- Lora, J. H., and Wu, Q. (2007) "Performance of two non-wood soda lignin derivatives in oriented strandboard powder phenolic adhesive," *Proceedings of the 8th ILI Forum Rome, May 10-12*, 213– 216.
- Marton, J., Marton, T., and Falkehag, S. I. (1966). "Alkali-catalyzed reactions of formaldehyde with lignins," *Adv. Chem. Series* 59, 125-144.
- Molin, K., Hse C.-Y, and Huang D.-H. (1991), "Alkali treated kraft lignin as a component in flakeboard resins," *Holzforschung*, 45, 47-54.
- Nada, A.-A. M. A., El-Sakhawy, M., and Kamel, S. M. (1998). "Infra-red spectroscopic study of lignins," *Polymer Degradation and Stability* 60, 247-251.
- Peng, W., Riedl, B., and Barry, A. O. (1993). "Study on the kinetics of lignin methylation," *Journal of Applied Polymer Science* 48, 1757-1763.
- Popa, V. I. (1983). *Technologies of lignin upgrading*, Polytechnic Institute Press, Iasi.
- Popa, V. I., Constantinescu, G., Lazar, N., and Popa, N. (2003). "Composites material based on lignin," *13th International symposium on Cellulose Chemistry and Technology, IVth Romanian-Italian on Pulp and Paper*, EPPIC Thematic Network - 3th Workshop, sept. 3-5, Iasi, Romania, 333.
- Rozmarin, Gh., Popa, V. I., Grovu-Ivanoiu, M., and Doniga, E. (1984). *Chemistry of Macromolecular Compounds. Chemistry of Wood - Applications*, Polytechnic Institute Press, Iasi.
- Sarghie, I., Tofan, L., Suteu, D., Bulgariu, L., and Rusu, G. (2004). Quantitative analysis - applications, Performantica Ed., Iasi.
- Zhao, L. W., Griggs, B. F., Chen, C.-L., Gratzl, J. S. and Hse, C.-Y. (1994). "Utilization of softwood kraft lignin as adhesive for the manufacture of reconstituted wood," *Journal of Wood Chemistry and Technology* 14(1), 127-145.
- Walker, J. F. (1975). *Formaldehyde 3rd ed.*, R. E. Krieger Publishers, Huntington, New York.

Article submitted: Sept. 4, 2007; First round of peer-reviewing completed: Oct. 25, 2007;
Revised version received and accepted: Nov. 12, 2007; Published: Nov. 13, 2007