JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

ARTICLE

pubs.acs.org/JAFC

Preparation of Lignopolyols from Wheat Straw Soda Lignin

Behzad Ahvazi,*[,†] Olivia Wojciechowicz,[†] Tan-Minh Ton-That,[‡] and Jalal Hawari[†]

[†]Biotechnology Research Institute, National Research Council of Canada, 6100 Royalmount Avenue, Montréal, Québec, Canada H4P 2R2

[‡]Industrial Materials Institute, National Research Council of Canada, 75 Mortagne Boulevard, Boucherville, Québec, Canada J4B 6Y4

ABSTRACT: Wheat straw soda lignin was modified and characterized by several qualitative and quantitative methods such as ^{31}P NMR spectroscopy to evaluate its potential as a substitute for polyols in view of polyurethane applications. Chemical modification of the lignin was achieved with propylene oxide to form lignopolyol derivatives. This was performed by a two-step reaction of lignin with maleic anhydride followed by propylene oxide and by direct oxyalkylation under acidic and alkaline conditions. The physical and chemical properties of lignopolyols from each method and the subsequent chain-extended hydroxyl groups were evaluated. Direct oxyalkylation of lignin under alkaline conditions was found to be more efficient than acidic conditions and more effective than the two-step process for preparing lignopolyol with higher aliphatic hydroxyl contents.

KEYWORDS: wheat straw, soda lignin, oxyalkylation, propylene oxide, lignopolyl, characterization, ^{31}P NMR spectroscopy, FTIR

INTRODUCTION

Modification and characterization of biobased polymers for preparation of higher valued green chemicals[1] and biobased products favor the future use of lignin biomass components with substantial environmental and economical benefits.[2]

Lignin is the second most naturally abundant biopolymer substance in plant cell walls, exceeded only by cellulose. It is an amorphous, highly branched polyphenolic macromolecule with a complex structure and high molecular weight. The chemical structure of lignin is highly irregular and extremely challenging. Lignin consists primarily of phenylpropanoic units cross-linked together in three dimensions via a radical coupling process during its biosynthesis.[3] Its physical and chemical properties are highly dependent on the wood species, botanic region, and isolation processes.[4]

The overall reactivity of different lignins depends on their chemical structures and functional groups. Softwoods contain almost exclusively guaiacyl (G) units, whereas hardwoods contain both syringyl (S) and guaiacyl units. Lignin contains several important functional groups[5] including *p*-hydroxyphenyl (H), aliphatic hydroxyl, and carboxylic acid groups. In particular, lignin contains a considerable amount of aliphatic hydroxyl groups on the propanoic side chain of its several different monomeric units. These units contain both primary and secondary hydroxyl groups with properties similar to those of polyols. Lignin samples contain different types and quantities of these functional groups that could be utilized in making and/or replacing a majority of petroleum-based products in the manufacture of industrial biomaterials and biocomposites[6,7] such as polyurethanes.[8,9]

Lignin incorporation in polyurethane production has been one of the most intensively investigated applications.[7−12] In some cases, its presence modifies the polyurethane cure rate by contributing aromatic groups and increasing the degree of cross-linking. Lignin acts as a reinforcing agent, which adds rigidity to the polymeric matrix.[9] Several studies have suggested that the solubility and the uniformity of the lignin are the foremost key parameters affecting its reactivity for polyol substitution in polyurethane production.[12,13] This in turn is directly dependent upon different classes of hydroxyl groups that may be present in lignin causing both electronic and steric factors affecting the lignin reactivity[14] in the polyurethane network. Lignin substitution in polyurethane could be achieved either by direct substitution, in combination with polyols,[10,11,15] or through chemical modification.[8,16,17]

The objective of lignin modification is to increase the reactivity of specific functional groups in lignin and enhance the polycondensation process during the production of biobased polyurethanes.[16,17] For example, free phenolic −OH groups are found to be more reactive[18] than benzylic −OH except toward diisocyanates.[19] It has been reported that lignin can react with an alkene oxide to yield lignin-based polyol, which in turn improves the solubility and uniformity of lignin.[18,20] Chemically modified lignins provide several advantages in replacing conventional polyols used in polyurethane fabrication. During lignin modification, the majority of phenolic hydroxyl groups are converted to aliphatic hydroxyl units, leading to readily available and more reactive hydroxyl groups. In addition, the chain extension of these hydroxyl groups can reduce the steric and/or electronic constraints.

The procedure for lignin modification can be achieved either by direct oxyalkylation[18,20] or by a two-step reaction of lignin with maleic anhydride[21,22] followed by oxyalkylation.[23] Oxyalkylation is more reactive with alcohols than with phenol and less so with carboxylic acids, in accordance with the order of

Received: June 8, 2011
Revised: August 18, 2011
Accepted: August 19, 2011
Published: August 19, 2011

nucleophilicity. During oxyalkylation, the reaction of lignin with an alkene oxide would lead to chain-extended hydroxypropyl lignin and the formation of lignin polyol derivatives.[18,20] The resulting lignopolyols were expected to be more fluid, possessing secondary hydroxyl groups suitable for reaction with isocyanate-terminated prepolymer to form urethane. In the other lignin modification method, maleic anhydride is utilized to convert phenolic hydroxyl groups to their corresponding aliphatic carboxylic acids, which are subsequently subjected to oxyalkylation. The overall modification would lead to a longer branched polyether with hydroxyl groups at the end.

Although the oxyalkylation of various types of lignins including kraft, sulfite, organosolv, and alkali lignin has been documented, no reports are currently available on the oxyalkylation of lignin from agricultural residues. Among various agricultural byproducts, wheat straw is one of the most abundant materials in the world. The annual worldwide production of wheat straw was estimated to be 686×10^6 tonnes in 2009.[24] Depending on the source, genetics, and growth conditions, the lignin content of wheat straw varies from 16 to 23% by weight.[25]

The objective of this study was to elucidate the physical and chemical characteristics of wheat straw lignin before and after oxyalkylation. In particular, several important functional groups in lignin containing hydroxyl groups such as phenolic and aliphatic groups as well as carboxylic acid groups were classified, and their contents were quantified by employing novel ^{31}P NMR spectroscopy. Characterization and modification of wheat straw soda lignin as sustainable biomass would then pave the way toward preparing biobased materials, which are compatible with the conventional petroleum-based polyols, as substitutes in polyurethane applications.

MATERIALS AND METHODS

Lignin Sample and Reagents. A sample of commercially available lignin extracted from wheat straw by the soda process was provided by GreenValue (Lausanne, Switzerland) for this study. All of the chemicals and reagents utilized in this study were purchased from Sigma-Aldrich Chemicals (Oakville, ON, Canada).

Characterization of Lignin. Lignin moisture and ash contents were determined gravimetrically according to the ASTM D 2974-87 Standards Test Methods. The elemental analyses of lignin samples were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Oxyalkylation of Lignin. Wheat straw soda lignin (1 g) was first esterified with an excess (10:1 mol) of maleic anhydride (MA) in 1,4-dioxane. A total of 2 mL of 0.5 g of 1-methylimidazole in 10 mL of 1,4-dioxane was added to the reaction. The reaction mixture was kept overnight under nitrogen atmosphere, with vigorous stirring at 70 °C. The mixture was brought to room temperature and transferred to a 250 mL round boiling flask, and its volume was reduced by using a rotary evaporator. Ethyl ether anhydrous (2×200 mL) was used to precipitate the lignin. The maleated lignin was washed and centrifuged with (4×20 mL) deionized water. The isolated product was dissolved in a mixture of dioxane/water (3:1 v/v) and freeze-dried under reduced pressure. The resulting maleated lignin was suspended at 1% consistency in 0.1 N HCl solution under gentle agitation for 1 h. The sample was filtered and the procedure repeated. After thorough washing with deionized water, the sample was dispersed in 400 mL of a 37% (w/w) of propylene oxide in water and allowed to react at room temperature under constant agitation for 7 days. Excess propylene oxide was removed under reduced pressure, and the remaining materials were washed with deionized water and centrifuged three times. The isolated product was then dissolved in a mixture of dioxane/water (3:1 v/v) and freeze-dried under reduced pressure.

Alternatively, wheat straw soda lignin (200 mg) was dispersed in 100 mL of a 37% (w/w) solution of propylene oxide in water under constant agitation for 30 min. To this mixture were added 5 mL of 0.1 N NaOH under alkaline and 5 mL of 1 M H_2SO_4 under acidic conditions and allowed to react at room temperature under constant agitation for 7 days. The reaction was stopped, and excess propylene oxide was removed under reduced pressure. Ethyl ether anhydrous (2×200 mL) was used to precipitate the lignin. The lignin was isolated by centrifugation and subsequent washing with (4×20 mL) deionized water three times. The isolated product was dissolved in a mixture of dioxane/water (3:1 v/v) and freeze-dried under reduced pressure.

^{31}P NMR Spectroscopy. Quantitative ^{31}P NMR spectra of all lignin preparations were obtained using published procedures.[26,27] Approximately 30−40 mg of dry lignin was dissolved in 500 μL of anhydrous pyridine and deuterated chloroform (1.6:1, v/v) under stirring. This was followed by the addition of 200 μL of *N*-hydroxynaphthalimide (*N*-HNI; 11.4 mg/mL in anhydrous pyridine and deuterated chloroform 1.6:1, v/v) or 100 μL of cyclohexanol (22.01 mg/mL), as an internal standard, and 50 μL of chromium(III)acetylacetonate solution (5.6 mg/mL in anhydrous pyridine and deuterated chloroform 1.6:1, v/v), as relaxation reagent. Finally, the mixture was treated with 100 μL of phosphitylating reagent I (2-chloro-1,3,2-dioxaphospholane) or reagent II (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, TMDP) and was transferred into a 5 mm NMR tube for subsequent NMR analysis.

All NMR experiments were carried out at 298 K on a Bruker Avance 500 NMR spectrometer operated at a ^{1}H frequency of 500.13 MHz and equipped with a 5 mm broadband inverse probe. ^{31}P NMR spectra were recorded with 32768 data points and a spectral width of 60606.06 Hz. A relaxation delay of 5 s was used, and the number of scans was 512. The ^{31}P chemical shifts were referenced with respect to water signals at 132.2 and 121.1 ppm corresponding to reagents II and I, respectively. Spectra were processed and analyzed using the Bruker Topspin 1.3 software package. All chemical shifts are reported relative to the product of TMDP with *N*-hydroxynaphthalimide, which has been observed to give a sharp signal at 153.7 ppm for reagent II referenced from the water signal at 132.2 ppm and at 138.2 ppm for reagent I referenced from the water signal at 121.1 ppm. The content of hydroxyl groups for reagent I was obtained by integration of the following spectral regions: *erythro* (136.7−134.5 ppm), *threo* (134.5−133.8 ppm), primary hydroxyl units (133.7−132.4 ppm), syringyl phenolic units (132.0−131.4 ppm), guaiacyl phenolic units (130.6−129.1 ppm), *p*-hydroxyphenyl phenolic units (128.9−127.8 ppm), and carboxylic acids (127.6−126.6 ppm). The content of hydroxyl groups for reagent II was obtained by integration of the following spectral regions: aliphatic hydroxyls (149.1−145.0 ppm), condensed phenolic units (DPM, 144.6−143.3; and 5-5′, 142.0−141.2 ppm), syringyl phenolic units (143.3−142.0 ppm), guaiacyl phenolic hydroxyls (140.5−138.6 ppm), *p*-hydroxyphenyl phenolic units (138.5−137.3 ppm), and carboxylic acids (135.9−134.0 ppm).

FTIR. Fourier transform infrared (FTIR) spectra were obtained for powdered solid lignin on KBr disks using a Bruker Tensor Series FT-IR spectrometer in the transmittance (TR) analysis mode. Spectra were collected from 4000 to 400 cm^{-1} with 64 scans and a 4 cm^{-1} resolution.

Maleated soda lignin: −OH, 3300−3600 cm^{-1}; C−H stretch (methylene and methyl), 2800−3100 cm^{-1}; −C═CH$_2$ and −C═CH, 3092, 3071, 3057, 3024, 2990 cm^{-1}; −CH$_2$ and −C—H, 2849 cm^{-1}; carboxylic −OH, 2918 cm^{-1}; carboxylic acid (high concentration), 2397−2670 cm^{-1}; unconjugated −C═O stretch, 1710−1742 cm^{-1}; −C═O, 1771 cm^{-1} (aromatic) and 1722 cm^{-1} (aliphatic); aromatic skeletal vibrations, 1452, 1493, 1512, 1601 cm^{-1}; ether C—O, 1213 cm^{-1}; alcohol C—O, 1028 cm^{-1} (primary) and 1121 cm^{-1} (secondary); guaiacyl C—H, 1090 cm^{-1}; C—H out of plane

(aromatic), 934 cm^{-1}; C—H out of plane (guaiacyl, syringyl, and *p*-hydroxyl phenolic), 824−752 cm^{-1};[28] and Ph—O—C, 698 cm^{-1}.

Propylation of maleated soda lignin: −OH, 3100−3600 cm^{-1}; C—H stretch (methylene and methyl), 2800−3100 cm^{-1}: −C═CH_2 and −C═CH, 3101, 3080, 3059, 3024, 2960 cm^{-1}; −CH_2 and −C—H, 2851 cm^{-1}; carboxylic −OH, 2918 cm^{-1}; carboxylic acid (high concentration), 2467−2627 cm^{-1}; unconjugated −C═O stretch, 1709−1755 cm^{-1}; −C═O, 1720 cm^{-1} (aliphatic); aromatic skeletal vibrations, 1452, 1493, 1510, 1601 cm^{-1}; −CH_3 of propylated, 1375 cm^{-1}; ether C—O, 1205 cm^{-1}; alcohol C—O, 1045, 1060 cm^{-1} (primary) and 1118 cm^{-1} (secondary); guaiacyl C—H, 1061 cm^{-1}; aliphatic ether, 930 cm^{-1}; C—H out of plane (aromatic), 839 cm^{-1}; C—H out of plane (guaiacyl, syringyl, and *p*-hydroxyl phenolic), 754 cm^{-1}; and Ph—O—C, 698 cm^{-1}.

Propylated soda lignin: −OH, 3100−3600 cm^{-1}; C—H stretch (methylene and methyl), 2800−3100 cm^{-1}; −C═CH_2 and −C═CH, 3076, 3059, 3018, 2966 cm^{-1}; carboxylic −OH, 2916, 2920 cm^{-1}; −CH_2 and −C—H, 2870, 2849 cm^{-1}; carboxylic (high concentration), 2467−2627 cm^{-1}; unconjugated −C═O stretch, 1701−1728, 1707 cm^{-1} (aliphatic); aromatic skeletal vibrations, 1458, 1508, 1591 cm^{-1}; −CH_3 of propylated, 1375 cm^{-1}; ether C—O, 1242 cm^{-1}; alcohol C—O, 1026 cm^{-1} (primary) and 1124 cm^{-1} (secondary); aliphatic ether, 930 cm^{-1}; C—H out of plane (aromatic), 856 cm^{-1}; C−H out of plane (guaiacyl, syringyl, and *p*-hydroxyl phenolic), 756 cm^{-1}; and Ph—O—C, 698 cm^{-1}.

Size Exclusion Chromatography. Gel permeation chromatography (GPC) analysis was performed using a multidetection system from Agilent Technologies (model 1200, 76337 Waldbronn, Germany) consisting of a high-performance liquid chromatography system equipped with a solvent tray, degasser, quaternary pump, autosampler, column heating module, UV diode array detector, and LC 3D software. The additional detectors were a Wyatt (Santa-Barbara, CA) Dawn Heleos II multiangle laser light scattering (MALLS) detector equipped with fluorescence filters on even-number detectors and a Wyatt Optilab rEX refractive index detector. Astra 5.3.4 software from Wyatt was used for data collection and calibration. Separation was performed with dry BHT-stabilized tetrahydrofuran (THF) by injecting 75 μL of acetobrominated lignin solutions in THF. Each sample was prepared by dissolving 1.0 mg/mL and filtering through a 0.2 μm membrane before injection into the thermostatically (25 °C) controlled columns (300 mm × 7.8 mm) of Styragel HR4, HR4E, and HR1 (Waters, Milford, MA). The flow rate was 1 mL/min. Molar masses of the samples were determined with the MALLS even-number detector signals using the specific refractive index increments (d*n*/d*c*) of each sample from the refractive index detector. A calibration curve was based on polystyrene standards from Polymer Laboratories (Amherst, MA) and Sigma-Aldrich using the molar masses determined by the manufacturers for the determination of molar mass based on the elution time from the Agilent UV detector signal at 254 nm.

Glass Transition Temperature (T_g) and Differential Scanning Calorimetry (DSC). The lignin samples were heated in a Perkin-Elmer Pyris 1 DSC instrument (Woodland, CA) using nitrogen atmosphere at temperatures ranging from −40 to 200 °C at 20 °C/min.

Scanning Electron Microscopy (SEM). SEM images were obtained using a Hitachi scanning electron microscope (S-2600 N, Tokyo, Japan) operating in high-vacuum mode at acceleration voltages of 5−16 KV and working distances of 5−20 mm. A 30−50 nm thin layer of Pd/Au was deposited using a Cressington Sputter Coater, model 108, on the samples prior to the SEM analysis to minimize the charge effect due to the insulating properties of the samples.

Transmission Electron Micrographs (TEM). TEM images were recorded using a Philips CM20 200 kV electron microscope (Eindhoven, The Netherlands) equipped with a Gatan UltraScan 1000 CCD camera and an energy dispersive X-ray spectrometer INCA Energy TEM 200. Samples for TEM analysis were prepared by suspending the lignin in ethanol and sonicating for several minutes. One drop of the suspension was placed onto a 300 mesh carbon-coated TEM copper grid and dried in air. The dried specimen was loaded into the specimen holder and examined with the equipment under 200 kV. Bright field images were taken with the CCD camera at different magnifications on different areas of the specimen.

Table 1. Characterization of Wheat Straw Soda Lignin by Quantitative ^{31}P NMR Spectroscopy, Elemental Analysis, and Size Exclusion Chromatography

parameter	wheat straw soda lignin (L)
^{31}P NMR analysis	
COOH	0.97 mmol/g
noncondensed phenolic −OH	
G[a]	0.79 mmol/g
S[b]	0.82 mmol/g
H[c]	0.45 mmol/g
condensed phenolic −OH	0.48 mmol/g
aliphatic −OH	
primary	1.61 mmol/g
secondary (*erythro* and *threo*)	0.51 mmol/g
total phenolic −OH	2.54 mmol/g
total −OH	5.63 mmol/g
elemental analysis	
elemental unit	
C	59.75%
H	6.16%
N	3.10%
O	28.60%
S	<0.5%
OCH_3	11.20%
C9 structural unit	$C_9H_{9.86}O_{2.78}N_{0.432}(OCH_3)_{0.703}$
molecular weight	190.38 g/mol
size exclusion chromatography (GPC)	
M_w	229.8 × 10^3 Da
M_n	136.9 × 10^3 Da
polydispersity	
M_w/M_n	1.68
d*n*/d*c*	0.151

[a] Guaiacyl −OH. [b] Syringyl −OH. [c] *p*-Hydroxyphenyl −OH.

RESULTS AND DISCUSSION

Wheat straw lignin isolated by the soda process was characterized by employing different qualitative and quantitative methods. Moisture and ash contents were determined gravimetrically to be 6.45 and 2.12%, respectively. ^{31}P NMR spectroscopy[26,27] was employed for classification and quantitative determination of several different classes of hydroxyl groups in lignin. In this study, two different phosphitylating reagents were utilized to monitor and obtain more in-depth information about the content of hydroxyl groups before and after oxyalkylation. The phosphitylating reagent (2-chloro-1,3,2-dioxaphospholane, reagent I) provides essential information about primary hydroxyl groups along with both *erythro* and *threo* diastereomers of the arylglycerol-β-aryl ether structures. However, the second phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, TMDP; reagent II) is a powerful analytical tool for distinguishing between different phenolic condensed units in lignins. Throughout this

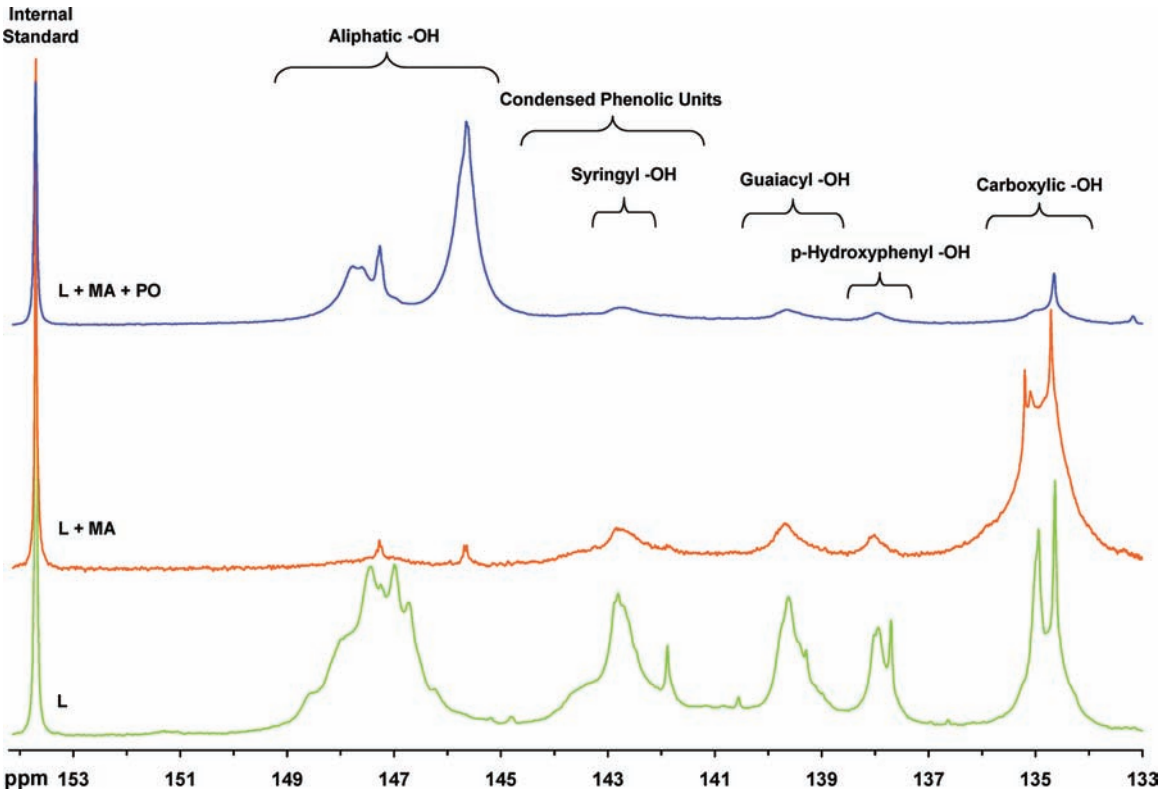

Figure 1. ^{31}P NMR spectra and signal assignments of wheat straw lignin (L) derivatized with maleic anhydride (L + MA) followed by propylene oxide (L + MA + PO) with TMDP.

Table 2. Characterization of Modified Wheat Straw Soda Lignin with the Two-Step Oxyalkylation Method

parameter	L	L + MA	L + MA + PO
^{31}P NMR analysis			
COOH	0.97 mmol/g	2.87 mmol/g	0.18 mmol/g
noncondensed phenolic −OH			
G[a]	0.79 mmol/g	0.28 mmol/g	0.13 mmol/g
S[b]	0.82 mmol/g	0.23 mmol/g	0.16 mmol/g
H[c]	0.45 mmol/g	0.16 mmol/g	0.06 mmol/g
condensed phenolic −OH	0.48 mmol/g	0.13 mmol/g	0.18 mmol/g
aliphatic −OH			
primary	1.61 mmol/g	0.07 mmol/g	0.72 mmol/g
secondary (*erythro* and *threo*)	0.51 mmol/g	0.01 mmol/g	1.18 mmol/g
total phenolic −OH	2.54 mmol/g	0.80 mmol/g	0.53 mmol/g
total −OH	5.63 mmol/g	3.75 mmol/g	2.61 mmol/g
size exclusion chromatography (GPC)			
M_w	229.8 × 10^3 Da	237.7 × 10^3 Da	309.4 × 10^3 Da
M_n	136.9 × 10^3 Da	90.51 × 10^3 Da	260.1 × 10^3 Da
polydispersivity			
M_w/M_n	1.68	2.36	1.19
dn/dc	0.151	0.150	0.102
differential scanning calorimetry			
ΔC_p	1.258 J/g·°C	2.322 J/g·°C	0.986 J/g·°C
T_g	104.39 °C	89.22 °C	59.00 °C

[a] Guaiacyl −OH. [b] Syringyl −OH. [c] *p*-Hydroxyphenyl −OH.

study, quantitation of all hydroxyl groups was obtained from the integration of ^{31}P NMR spectra of lignin after derivatization with TMDP reagent. Distinction between the primary and secondary aliphatic hydroxyl groups was obtained from the integration of ^{31}P NMR spectra of phosphitylated lignin with reagent I (Table 1).

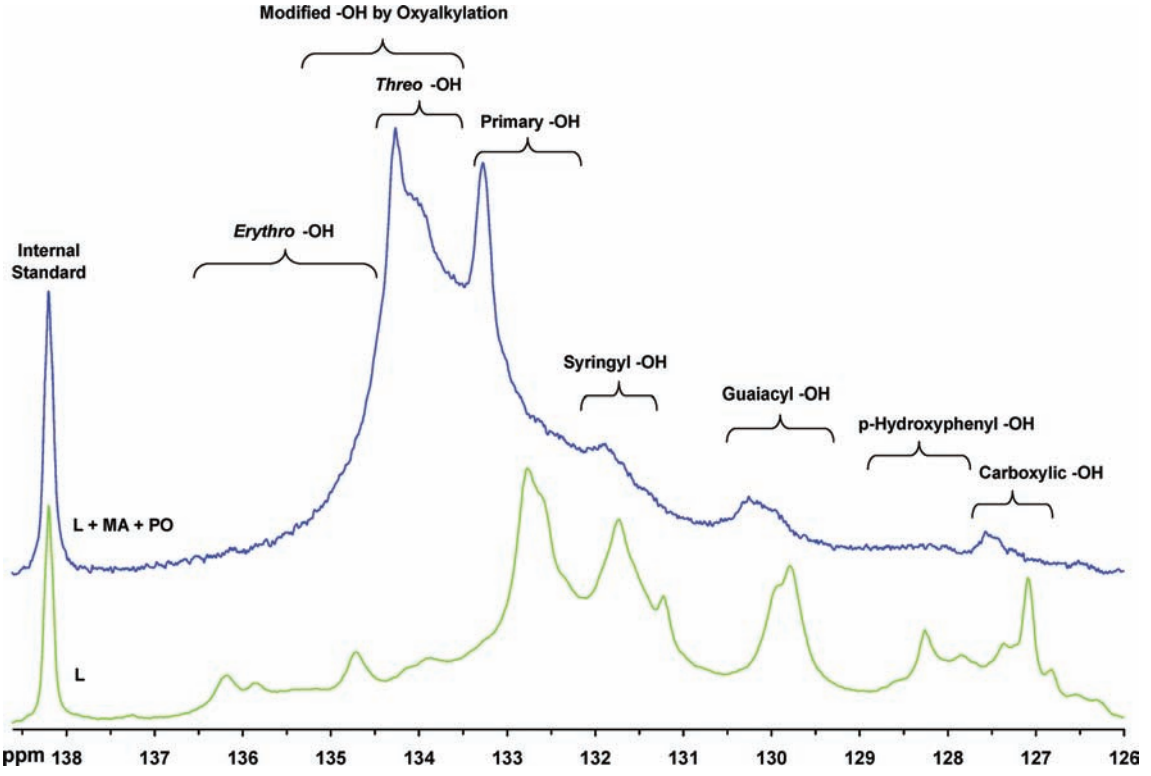

Figure 2. ^{31}P NMR spectra and signal assignments of wheat straw lignin before (L) and after modification with maleic anhydride and propylene oxide (L + MA + PO) with reagent I.

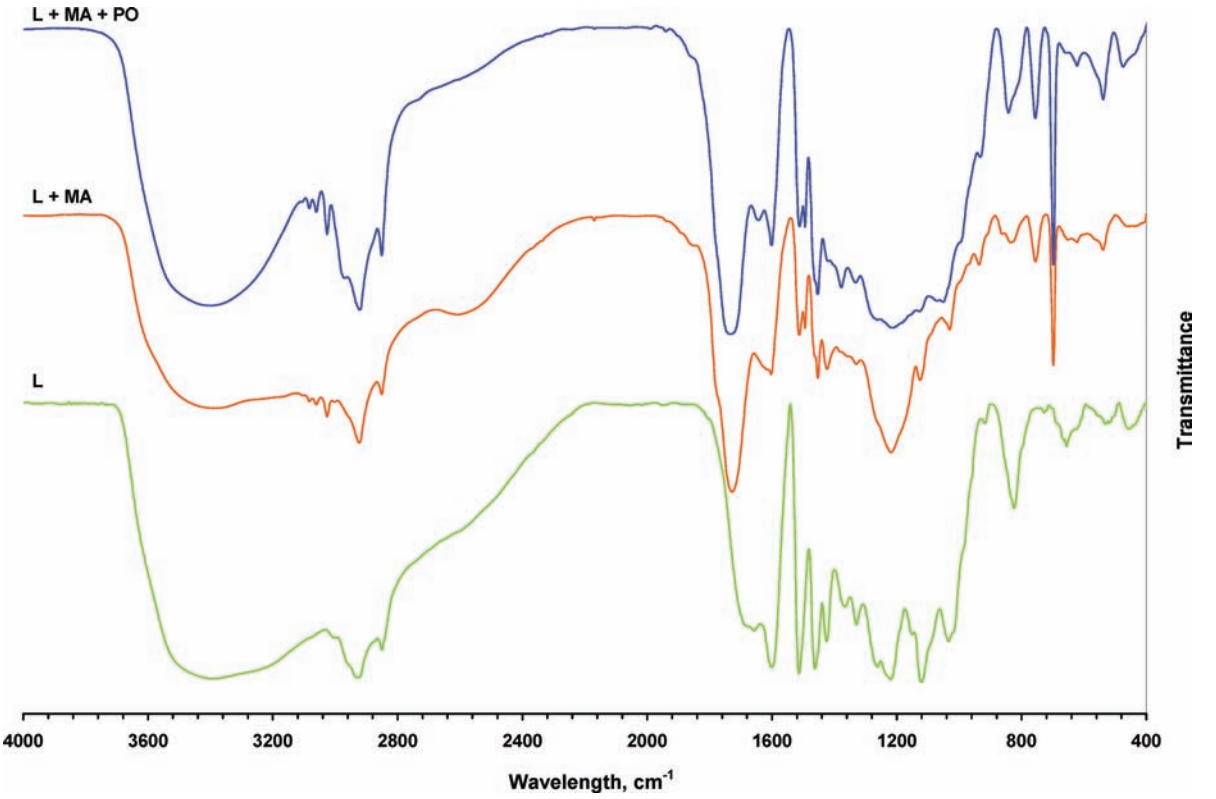

Figure 3. FTIR spectra of wheat straw lignin (L) derivatized with maleic anhydride (L + MA) followed by propylene oxide (L + MA + PO).

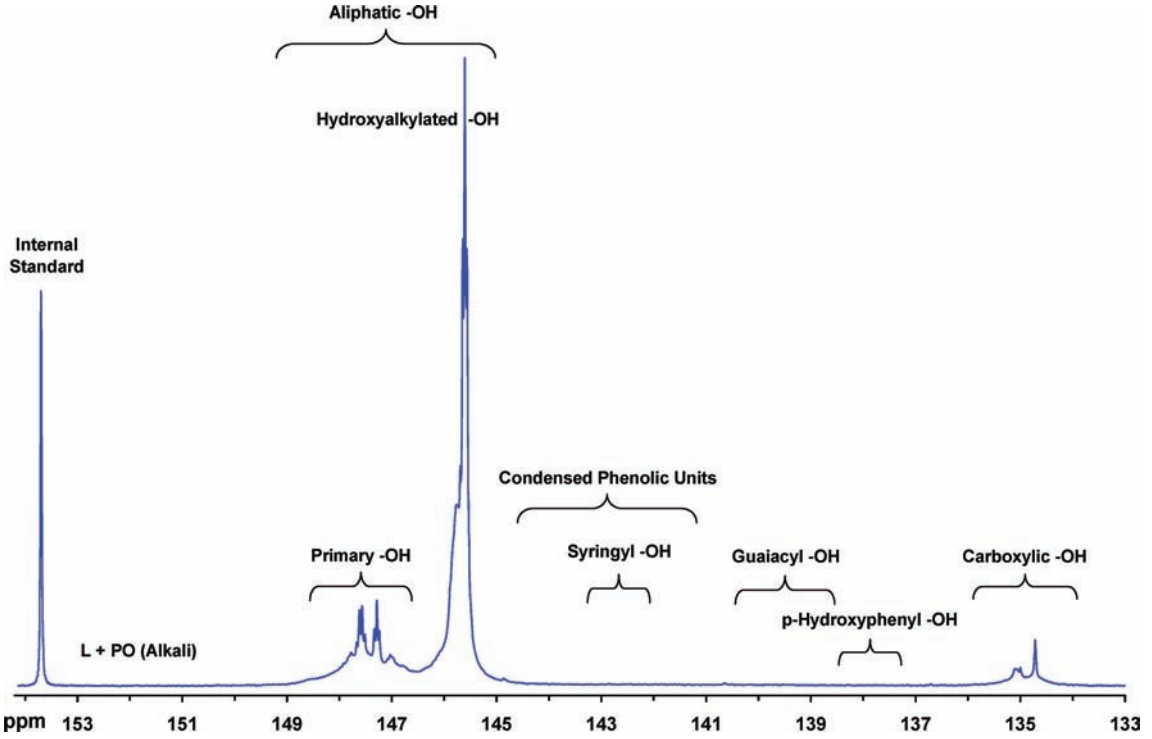

Figure 4. ^{31}P NMR spectrum and signal assignments of modified lignin with propylene oxide (L + PO) under alkaline conditions with TMDP.

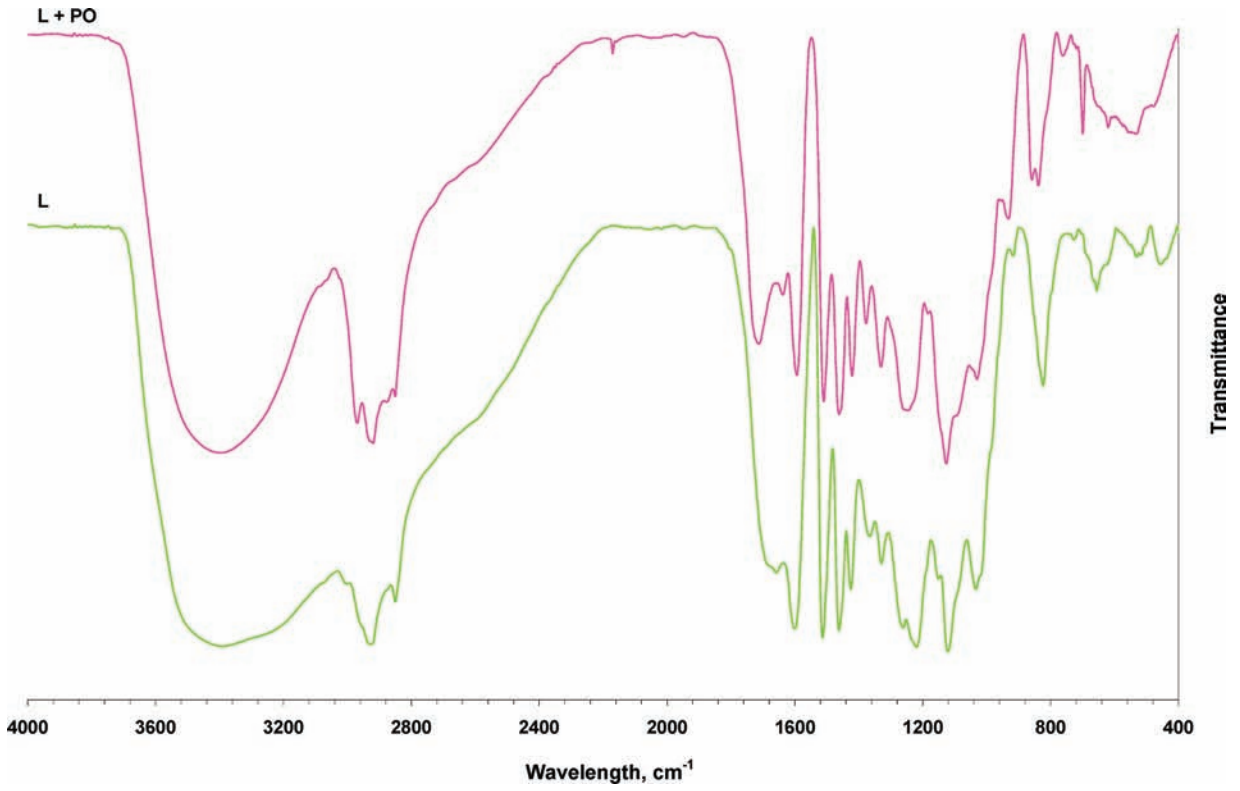

Figure 5. FTIR spectra of wheat straw lignin (L) and modified lignin with propylene oxide (L + PO) under alkaline conditions.

The examination of the ^{31}P NMR spectrum (Figure 1-L) of wheat straw soda lignin reveals two significant features. Unlike softwood lignin, which is exclusively guaiacyl, and hardwood lignin, which contains both guaiacyl and syringyl units, the soda lignin from agro-residues showed distinct signals corresponding to the presence of all three major (G:S:H) monomeric components of lignin. The second feature was the presence of several sharp signals appearing in different regions of *p*-hydroxyphenyl,

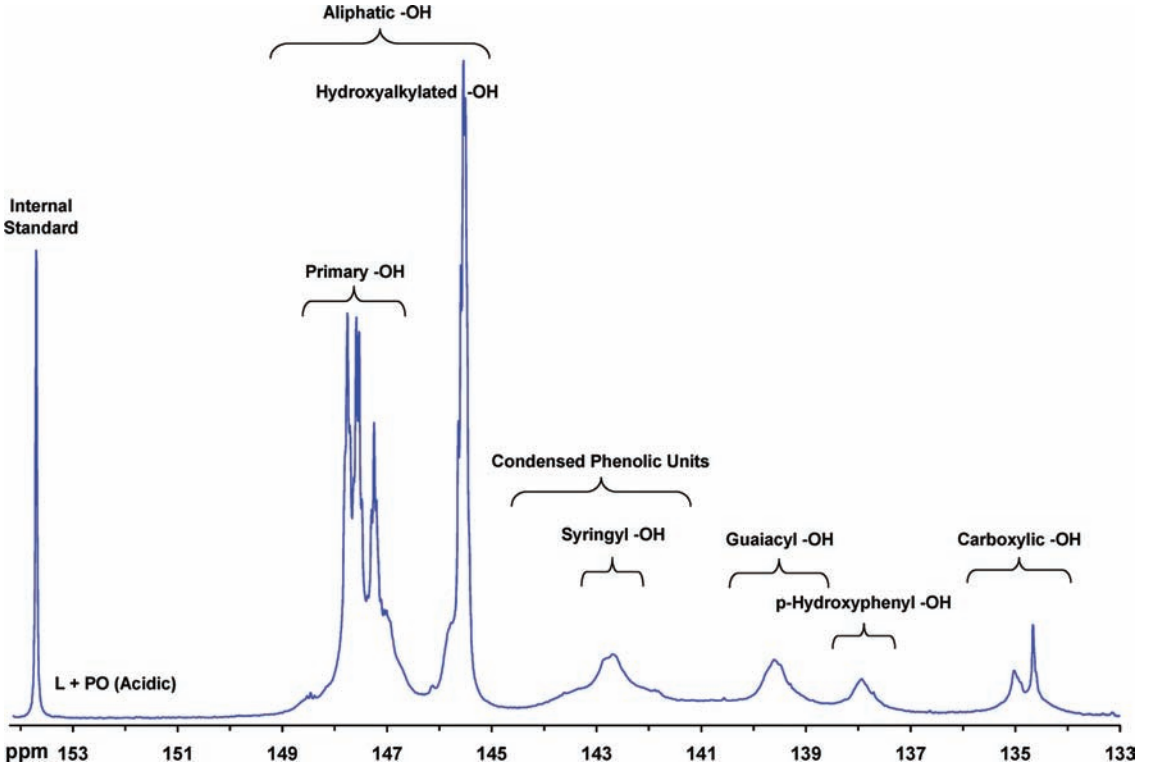

Figure 6. ^{31}P NMR spectrum and signal assignments of modified lignin with propylene oxide (L + PO) under acidic conditions with TMDP.

guaiacyl, and syringyl. The presence of these signals, which generally are not detected in a typical technical lignin, may be attributed to some type of lignin moieties either from the feedstock or created during the isolation processes.

Wheat straw soda lignin was chemically modified by both direct and two-step oxyalkylation processes. During the chemical modification, the lignin was first treated with maleic anhydride followed by propylene oxide to derivatize phenolic groups to yield terminal aliphatic hydroxyl groups, hence increasing the compatibility of lignin with polyols. Then, in a separate experiment, the wheat straw soda lignin was hydroxypropylated directly with propylene oxide under two separate alkaline and acidic conditions.

Two-Step Oxyalkylation of Lignin. The ^{31}P NMR spectra of wheat straw soda lignin (L) treated with maleic anhydride (L + MA) followed by propylene oxide (L + MA + PO) with TMDP are presented in Figure 1. The comparison between the ^{31}P NMR spectra of the starting material (L) and the maleated lignin (L + MA) shows that almost all of the hydroxyl groups were esterified with maleic anhydride and converted to their corresponding aliphatic carboxylic acids. However, the reactivity of maleic anhydride toward phenolic hydroxyl groups was found to be relatively low. The degree of substitution (DS) was calculated on the basis of the formula

$$DS_{NMR} = \frac{C_f - C_i}{C_i}$$

where C_f and C_i are the final and initial concentrations of hydroxyl units in the starting material and the modified lignin, respectively.

Accordingly, the DS of the subsequent chain extension of different hydroxyl groups during the esterification of the lignin with maleic anhydride was determined to be 1.96. The significant increase of carboxylic acid content from 0.97 mmol/g in the wheat straw lignin to 2.87 mmol/g in the maleated lignin confirms the efficiency of maleic anhydride with several classes of hydroxyl groups and particularly with the aliphatic hydroxyl units (Table 2).

Table 3. Characterization of Modified Wheat Straw Soda Lignin with the Direct Oxyalkylation Method under Alkaline and Acidic Conditions

parameter	L + PO (alkali)	L + PO (acidic)
^{31}P NMR analysis		
COOH	0.33 mmol/g	0.35 mmol/g
noncondensed phenolic −OH		
G[a]	0.00 mmol/g	0.56 mmol/g
S[b]	0.00 mmol/g	0.65 mmol/g
H[c]	0.00 mmol/g	0.24 mmol/g
condensed phenolic −OH	0.00 mmol/g	0.35 mmol/g
aliphatic −OH		
primary	1.85 mmol/g	3.07 mmol/g
secondary (*erythro* and *threo*)	4.79 mmol/g	1.96 mmol/g
total phenolic −OH	0.00 mmol/g	1.80 mmol/g
total −OH	6.97 mmol/g	7.18 mmol/g
size exclusion chromatography (GPC)		
M_w	165.8 × 10^3 Da	N/A
M_n	72.39 × 10^3 Da	N/A
polydispersivity		
M_w/M_n	2.29	N/A
dn/dc	0.13	N/A

[a] Guaiacyl −OH. [b] Syringyl −OH. [c] *p*-Hydroxyphenyl −OH.

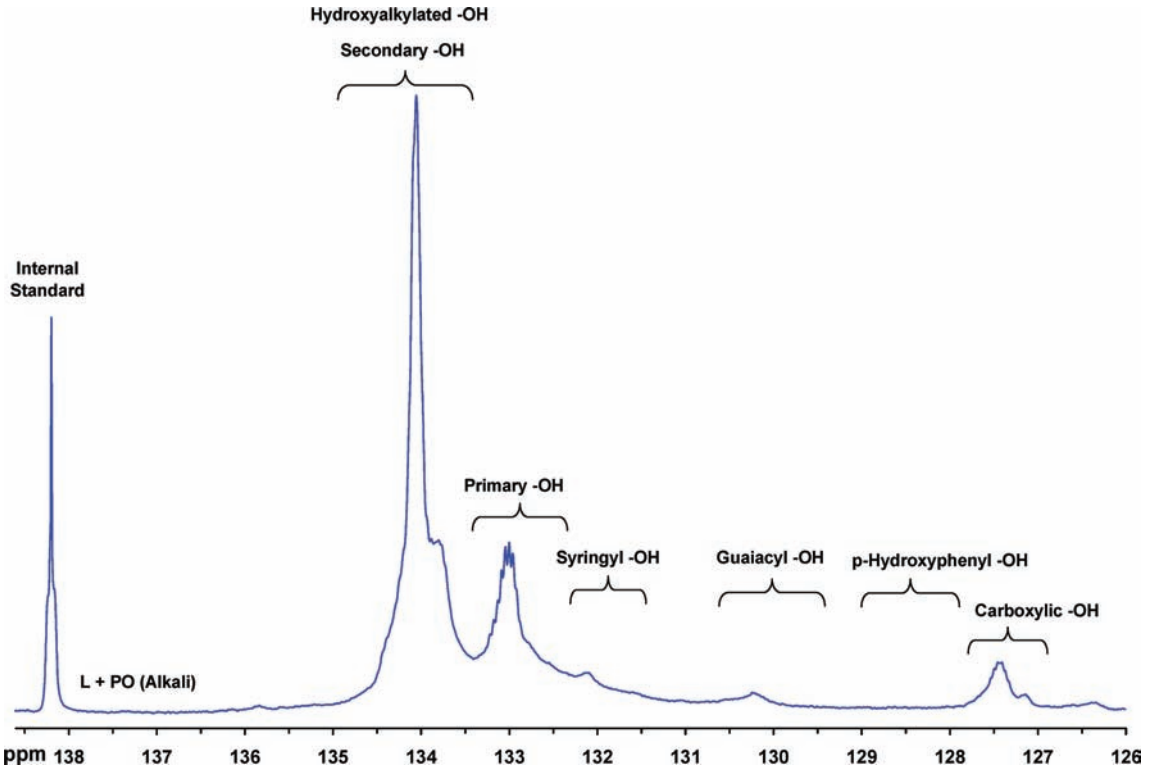

Figure 7. ^{31}P NMR spectrum and signal assignments of modified lignin with propylene oxide (L + PO) under alkaline conditions with reagent I.

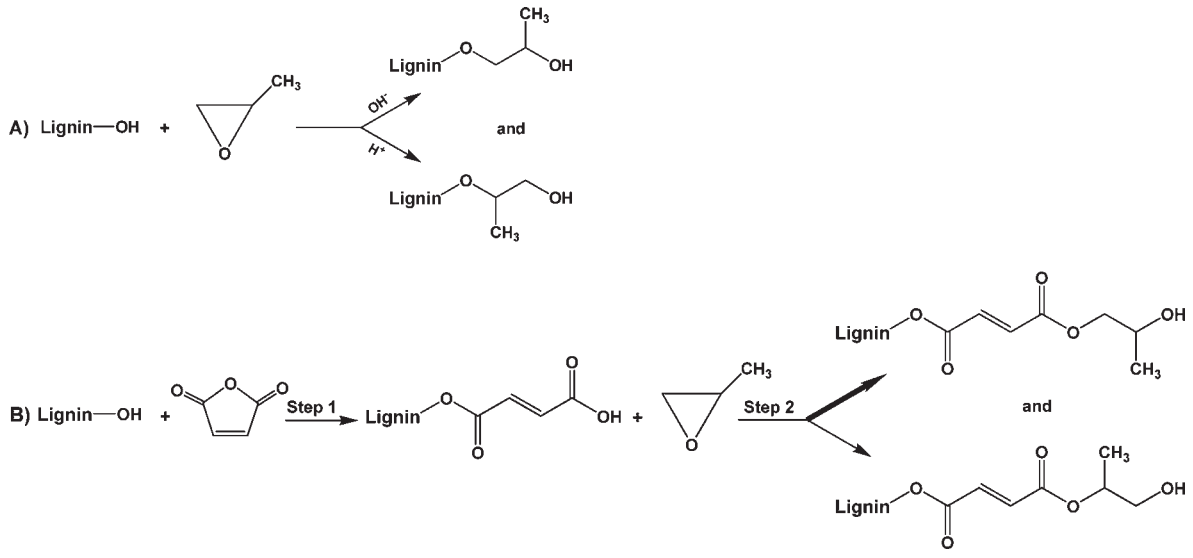

Figure 8. Schematic diagrams of direct and two-step oxyalkylation methods of hydroxyl groups in lignin.

Furthermore, the comparison of ^{31}P NMR spectra of L + MA + PO to the starting material and the maleated lignin demonstrates two significant phenomena. First, the L + MA + PO spectrum coupled with the quantitation data of Table 2 indicates that carboxylic acids did not completely undergo transformation to their corresponding aliphatic groups during hydroxypropylation. This is expected because oxyalkylation is less reactive with carboxylic acids than the other functional groups, as 0.18 mmol/g or 6.9% of carboxylic acids remained unreacted. Indeed, the signal assignment of remaining terminal carboxylic acids recorded at 134.6 ppm in the ^{31}P NMR spectrum (Figure 1) shows that among the two types of carboxylic acid groups, the benzylic type was more reactive than the terminal type toward subsequent chemical modification with propylene oxide.

The other phenomenon was the appearance of two different and distinct broad signals in the aliphatic region of ^{31}P NMR spectra recorded between 149.5 and 146.7 ppm and between 146.5 and 144.1 ppm. The signal recorded between 149.5 and 146.7 ppm appears in the same region as the aliphatic hydroxyl groups of the starting material. However, the signal recorded

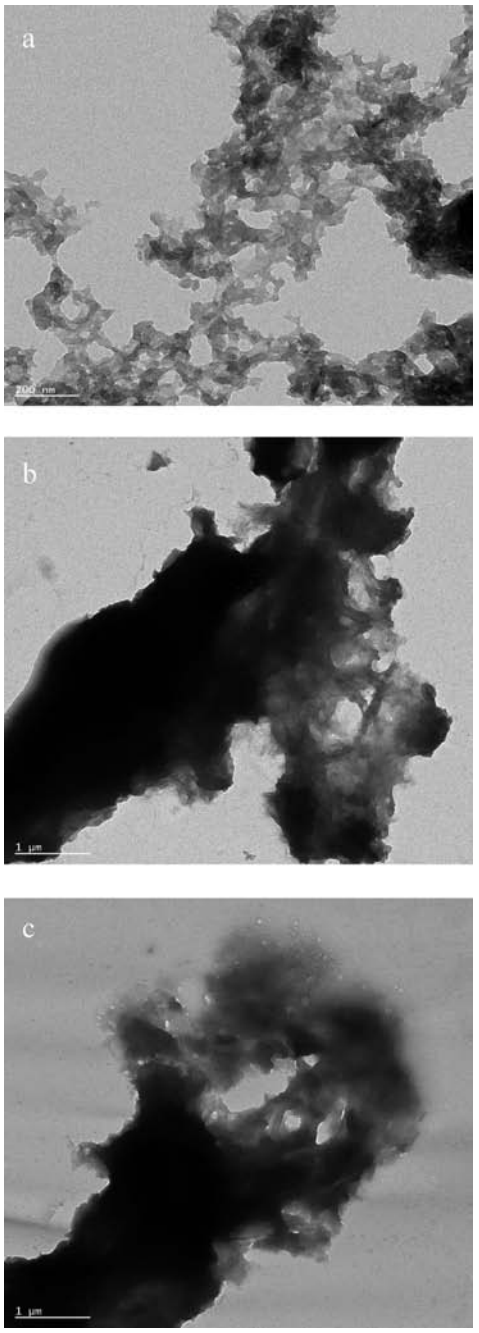

Figure 9. TEM images of (a) wheat straw lignin, (b) derivatized with maleic anhydride (L + MA), and (c) followed by propylene oxide (L + MA + PO).

between 146.5 and 144.1 ppm was shifted upfield from the aliphatic region, and it is seemingly attributed to the hydroxypropylation reaction. To further help identify and classify these two signals, L + MA + PO was examined with reagent I and compared to the spectrum of the starting material as presented in Figure 2.

The ^{31}P NMR spectral analysis of L + MA + PO with reagent I clearly reveals the presence of two distinct signals in the aliphatic region. The signal recorded between 133.6 and 132.1 ppm (primary −OH) appears in the same region as the aliphatic hydroxyl groups of the starting material. However, the other signal recorded between 136.6 and 133.6 ppm indicates the formation of new hydroxyl groups recorded in the area that is designated only to the secondary alcohols and assigned to both *erythro* and *threo* diastereomers of the arylglycerol-β-aryl ether structures (C_α-aryl) in lignin.[29]

In support of ^{31}P NMR spectroscopic analysis, the FTIR spectra of the starting material, L + MA, and L + MA + PO are presented in Figure 3. Comparison of the subsequent modified lignins to the starting material (L) exhibits significant changes. Some IR characteristics remain the same for both modified samples such as the formation of new C−H stretch bands for methylene and methyl groups and carbonyl units, as well as esterified phenols. However, other IR bands are more specific as per modification. For example, the broad band of L + MA centered at 2590 cm^{-1} is an indication of the hydroxyl groups of the carboxylic acids due to the carboxylation, whereas the bands at 1045 and 1060 cm^{-1} of the L + MA + PO sample belong to the alcohol of C−O due to the hydroxypropylation.

Direct Oxyalkylation of Lignin. Chemical modifications of wheat straw lignin were carried out by a one-step oxyalkylation method. In the first experiment, the starting material was hydroxypropylated with propylene oxide under alkaline conditions, and the isolated modified lignin was examined by ^{31}P NMR spectroscopy as illustrated in Figure 4.

^{31}P NMR spectral analysis shows that both condensed and noncondensed phenolic units were efficiently hydroxypropylated. However, much like the original observations for hydroxypropylation of maleated lignin (L + MA + PO) in Figure 1, the carboxylic acids did not react completely toward propylene oxide even at elevated temperature, as some remained unreacted. Furthermore, similar to L + MA + PO spectra, two distinct and well-resolved signals were also detected between 148.8 and 146.5 ppm and between 146.4 and 144.8 ppm in the aliphatic region.

The signal between 148.8 and 146.5 ppm was assigned exclusively to the primary hydroxyl groups. Closer examination of this region shows two separate signals recorded between 147.7 and 147.4 ppm and between 147.4 and 147.1 ppm with J couplings of 0.053 and 0.046 Hz, respectively. The former was assigned to the presence of γ-OH in β-O-4 units, and the latter was assigned to either γ-OH in α-carbonyl-containing units or cinnamyl alcohol units in lignin.

The signal between 146.4 and 144.8 ppm was assigned to the secondary hydroxyl groups. The nature, chemical shift, and intensity of this signal in ^{31}P NMR spectra strongly suggest the formation of secondary alcohols attributed dominantly by the one-step hydroxypropylation reaction. In fact, the signal is almost identical to the one recorded between 144.1 and 146.5 ppm in the L + MA + PO spectrum after the hydroxypropylation step.

The FTIR spectra of the starting material and the hydroxypropylated lignin (L + PO) are presented in Figure 5. The modified hydroxypropylated lignin exhibits new bands at 2870, 1375, 1026, 1124, and 698 cm^{-1} corresponding to −C−H, −CH_3, primary −OH, secondary −OH, and Ph−O−C, respectively.

In the second experiment, the starting material was hydroxypropylated under acidic conditions at pH 1.5−2. The isolated products were subjected to ^{31}P NMR analysis and presented in Figure 6. ^{31}P NMR spectral analysis suggests that several different lignin monomeric components containing hydroxyl groups were less amenable to hydroxypropylation under acidic conditions than their counterparts under alkaline conditions. Comparison between the ^{31}P NMR spectra (Figures 4 and 6) as well as their hydroxyl contents (Table 3) indicates that in addition to carboxylic acids, *p*-hydroxyphenyl, guaiacyl, and syringyl units did not react significantly with propylene oxide at lower pH.

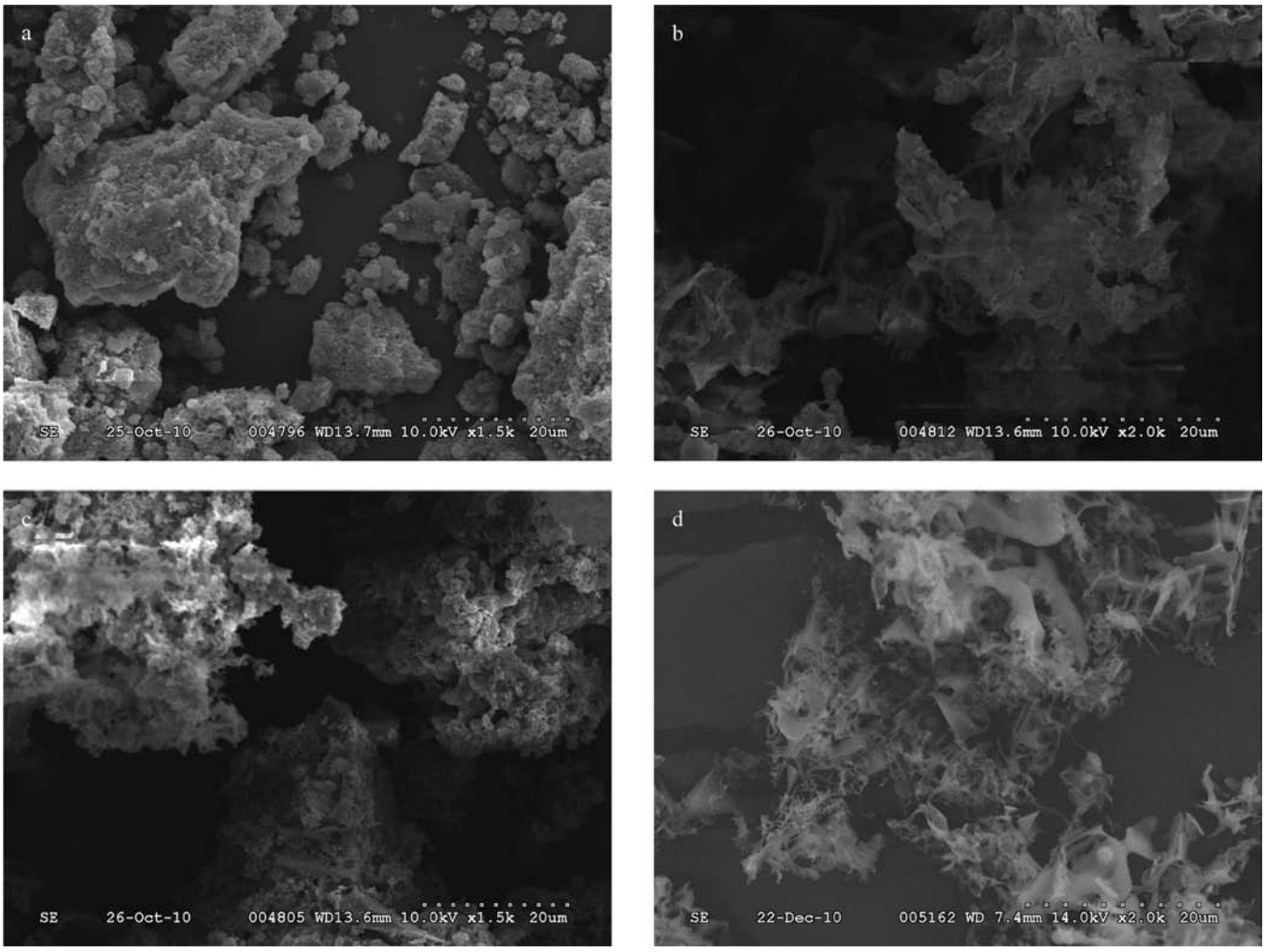

Figure 10. SEM images of (a) wheat straw lignin, (b) derivatized with maleic anhydride (L + MA), (c) followed by propylene oxide (L + MA + PO), and (d) modified lignin with propylene oxide (L + PO) under alkaline conditions.

However, the hydroxypropylated aliphatic signals in both spectra were recorded in the same ^{31}P NMR region with similar chemical shifts.

To classify these aliphatic hydroxyl groups formed during both alkaline and acidic oxyalkylation reactions, the hydroxypropylated lignin under alkaline conditions was examined with reagent I and is presented in Figure 7. The ^{31}P NMR spectrum unequivocally shows that the oxyalkylated hydroxyl signal belongs to secondary hydroxyl groups.[29] The DS values of the subsequent chain extension of aliphatic hydroxyl groups during hydroxypropylation of lignin under acidic and alkaline conditions were determined to be 1.37 and 2.13, respectively. The significant increase of aliphatic groups confirms the hydroxypropylation efficiency for several classes of hydroxyl groups under alkaline conditions.

With regard to the regioselectivity of the direct conversion of lignin with propylene oxide,[30] it seems that under alkaline conditions the reagent is attacked at the sterically less hindered CH_2 carbon, resulting in the formation of predominantly secondary alcohols. In accordance with the reaction mechanism for the opening of epoxides under acidic conditions, more primary than secondary hydroxyl groups were detected in the hydroxyalkylated lignin at pH 1.5−2, as presented in Figure 8A. The higher efficiency of the alkaline over the acidic conditions is reflected in the complete consumption of phenolic groups in alkaline medium, whereas at lower pH some phenolic groups remained unreacted. Therefore, in accordance with Figure 8B, under mild acidic conditions, the hydroxypropylation reaction of maleated soda lignin generated primary and predominantly secondary aliphatic hydroxyl groups as shown in Figure 1.

The morphology of wheat straw soda lignin after each modification was examined by TEM and SEM and is presented in Figures 9 and 10, respectively. TEM revealed little information about the morphology of modified lignin. Images taken by TEM show lignin agglomerates as hydroxyl groups are modified by the two-step oxyalkylation.

The SEM image of wheat straw soda lignin (Figure 10a) shows the submicrometer porous powder which agglomerates anywhere from 2 to 20 μm granules. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) distributions were determined by MALLS to be 229.8 and 136.9 kDa, respectively. Esterification of the wheat straw lignin by maleic anhydride (Figure 10b) increased its M_w to 237.7 kDa and reduced its T_g by 15.2 °C. The original shape was also altered into plate-like flakes, staggered over a void volume measuring >20 μm in size. Subsequent modification by hydroxypropylation of the maleated lignin (Figure 10c) further converted the

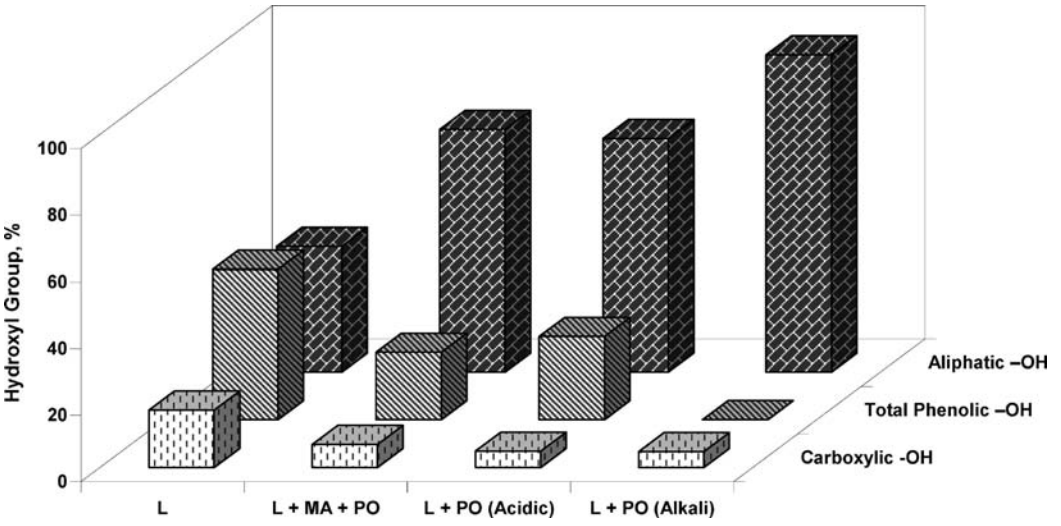

Figure 11. Distribution of hydroxyl groups in wheat straw lignin (L), derivatized with maleic anhydride followed by propylene oxide (L + MA + PO) and modified lignin with propylene oxide under acidic L + PO (acidic) and alkaline L + PO (alkali) conditions.

morphology into densely packed microparticles with a sponged-shaped structure, which are the largest by far from its predecessors, and may exhibit some porosities as well. The M_w and M_n were measured to be the highest, corresponding to 309.4 and 260.1 kDa, respectively. The T_g for L + MA + PO decreased further by 30.2 °C from that of L + MA and by 45.4 °C from that of the starting material.

The SEM image of the one-step hydroxypropylated soda lignin (L + PO) under alkaline conditions (Figure 10d) is significantly different from the SEM image of the two-step oxyalkylation lignin (L + MA + PO). Comparison between the two sets of images indicates that direct hydroxypropylation altered the lignin structure toward polymer-like agglomerates, with decreased porosity and smoother morphology. The M_w and M_n for hydroxypropylated lignin were determined to be 165.8 and 72.39 kDa, respectively.

Figure 11 represents the percent distribution of hydroxyl groups of three major lignin functional groups by quantitative ^{31}P NMR spectroscopy and compares their contents before and after each modification. The experimental data have shown that direct oxyalkylation of wheat straw lignin with propylene oxide under alkaline conditions was more efficient than that under acidic conditions and also more economically feasible than the two-step oxyalkylation. This method generated >95% aliphatic hydroxyl, predominantly secondary alcohols, leading to the formation of lignopolyol, which is compatible with polyols in view of polyurethane applications.

AUTHOR INFORMATION

Corresponding Author

*Phone: (514) 283-7212. Fax: (514) 496-6265. E-mail: behzad.ahvazi@cnrc-nrc.gc.ca.

ACKNOWLEDGMENT

We are grateful for the support of the National Bioproduct Programs at the National Research Council of Canada. We also gratefully acknowledge Dr. Jairo H. Lora at Green Value for providing the lignin sample, Dr. Ping Xu at BRI for accommodating us with NMR facilities, Dr. Hannes Leisch at BRI for useful discussion, Dr. Dashan Wang at ICPET for acquiring TEM, and Sabahudin Hrapovic for acquiring SEM and discussing the analysis.

REFERENCES

(1) Kleinert, M.; Barth, T. Towards a lignincellulosic biorefinery: direct one-step conversion of lignin to hydrogen-enriched biofuel. *Energy Fuels* **2008**, *22*, 1371–1379.

(2) Glasser, W. G.; Barnett, C. A.; Muller, P. C.; Sarkanen, K. V. The chemistry of several novel bioconversion lignins. *J. Agric. Food Chem.* **1983**, *31*, 921–930.

(3) Wardrop, A. B. Occurrence and formation in plants. In *Lignins. Occurrence, Formation, Structure and Reactions*; Sarkanen, K. V., Ludwig, C. H., Eds.; Wiley Interscience: New York, 1971; pp 19−41.

(4) Gross, G. G. Biosynthesis of lignin and related monomers. In *The Structure, Biosynthesis and Degradation of Wood*; Recent Advances in Phytochemistry; Loewus, F. A., Runeckles, V. C., Eds.; Plenum Press: New York, 1977; Vol. 11, pp 141−184.

(5) Adler, E. Structural elements of lignin. *Ind. Eng. Chem.* **1957**, *49*, 1377–1383.

(6) Feldman, D. Lignin and its polyblends − a review. In *Chemical Modification, Properties, and Usage of Lignin*; Hu, T. Q., Ed.; Kluwer Academic/Plenum Publishers: New York, 2002; pp 81−99.

(7) Wang, J.; St. John Manley, R.; Feldman, D. Synthetic polymer-lignin copolymers and blends. *Prog. Polym. Sci.* **1992**, *17*, 611–646.

(8) Hatakeyama, H. Polyurethanes containing lignin. In *Chemical Modification, Properties, and Usage of Lignin*; Hu, T. Q., Ed.; Kluwer Academic/Plenum Publishers: New York, 2002; pp 41−56.

(9) Feldman, D.; Lacasse, M.; St. John Manley, R. Polyurethane-based sealants modified by blending with Kraft lignin. *J. Appl. Polym. Sci.* **1988**, *35*, 247–257.

(10) Vanderlaan, M. N.; Thring, R. W. Polyurethanes from Alcell lignin fractions obtained by sequential solvent extraction. *Biomass Bioenergy* **1998**, *14*, 525–531.

(11) Cateto, C. A.; Barreiro, M. F.; Rodrigues, A. E. Monitoring of lignin-based polyurethane synthesis by FTIR-ATR. *Ind. Crop Prod.* **2008**, *27*, 168–174.

(12) Saraf, V. P.; Glasser, W. G.; Wilkes, G. L.; McGrath, J. E. Engineering plastics from lignin. VI. Structure property relationship of PEG-containing polyurethane networks. *J. Appl. Polym. Sci.* **1985**, *30*, 2207–2224.

(13) Rials, T. G.; Glasser, W. G. Engineering plastics from lignin − XIII. Effect of lignin structure on polyurethane network formation. *Holzforschung* **1986**, *40*, 353–360.

(14) Kelley, S. S.; Glasser, W. G.; Ward, T. C. Multiphase materials with lignin. IX. Effect of lignin content on interpenetrating polymer network properties. *Polymer* **1989**, *30*, 2265–2268.

(15) Yoshida, H.; Mörck, R.; Kringstad, K. P.; Hatakeyama, H. Kraft lignin in polyurethanes II. Effects of the molecular weight of the Kraft lignin on the properties of polyurethanes from Kraft lignin-polyether triol-polymeric MDI system. *J. Appl. Polym. Sci.* **1990**, *40*, 1819–1832.

(16) Gandini, A.; Belgacem, M. N.; Guo, Z.-X.; Montanari, S. Lignin as macromonomers for polyesters and polyurethanes. In *Chemical Modification, Properties, and Usage of Lignin*; Hu, T. Q., Ed.; Kluwer Academic/Plenum Publishers: New York, 2002; pp 57−80.

(17) Nadji, H.; Bruzzèse, C.; Belgacem, M. N.; Benaboura, A.; Gandini, A. Oxypropylation of lignins and preparation of rigid polyurethane foams from the ensuing polyols. *Macromol. Mater. Eng.* **2005**, *290*, 1009–1016.

(18) Wu, L. C.-F.; Glasser, W. G. Engineering plastics from lignin. I. Synthesis of hydroxypropyl lignin. *J. Appl. Polym. Sci.* **1984**, *29*, 1111–1123.

(19) Pizzi, A.; Walton, T. Non-emulsifiable, water-based, mixed diisocyanate adhesive systems for exterior plywood − Part I. Novel reaction mechanisms and their chemical evidence. *Holzforschung* **1992**, *46*, 541–547.

(20) Hornof, V.; Hombek, R. Surface-active agents based on propoxylated lignosulfonate. *J. Appl. Polym. Sci.* **1990**, *41*, 2391–2398.

(21) Feldman, D.; Luchian, C.; Banu, D.; Lacasse, M. Polyurethane-maleic anhydride grafted lignin polyblends. *Cellul. Chem. Technol.* **1991**, *25*, 163–180.

(22) Thielemans, W.; Wool, R. P. Lignin esters for use in unsaturated thermosets: Lignin modification and solubility modeling. *Biomacromolecules* **2005**, *6*, 1895–1905.

(23) Glasser, W. G.; Hsu, O. H.-H. Polyurethane intermediates and products and methods of producing same from lignin. U.S. Patent Application 4,017,474, 1977.

(24) Food and Agriculture Organization of the United Nations. http://faostat.fao.org/ (accessed May 19, 2011).

(25) Mckean, W. T.; Jacobs, R. S. *Wheat Straw as a Paper Fiber Source*; The Clean Washington Center: Seattle, WA, June 1997.

(26) Granata, A.; Argyropoulos, D. S. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholate, a reagent for the accurate determination of the uncondensed and condensed phenolic moieties in lignins. *J. Agric. Food Chem.* **1995**, *43*, 1538–1544.

(27) Argyropoulos, D. S. Quantitative phosphorus-31 NMR analysis of lignin: a new tool for the lignin chemist. *J. Wood Chem. Technol.* **1994**, *14*, 45–63.

(28) Faix, O. Fourier transform infrared spectroscopy. In *Methods in Lignin Chemistry*; Lin, S. Y., Dence, C. W., Eds.; Springer-Verlag: Berlin, Germany, 1992; Chapter 4.1, pp 83−110.

(29) Argyropoulos, D. S. ^{31}P NMR in wood chemistry: a review of recent progress. *Res. Chem. Intermed.* **1995**, *21*, 373–395.

(30) Pandey, K. K.; Vuorinen, T. Study of kinetics of reaction of lignin model compounds with propylene oxide. *Holzforschung* **2008**, *62*, 169–175.