Lignins as Macromonomers for Polyurethane Synthesis: A Comparative Study on Hydroxyl Group Determination

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ABSTRACT: The hydroxyl group contents of four technical lignins [Indulin AT (Meadwestvaco), Alcell (Repap), Curan 27-11P (Borregaard LignoTech), and Sarkanda (Granit SA)] were investigated in view of their valorization as polyols in polyurethane synthesis. The different hydroxyl group contents were determined by the following methods: titration and ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR spectroscopy. The titration method chosen was on the basis of a standard method commonly used to characterize commercial polyols for polyurethanes synthesis. The values of the total and phenolic hydroxyl contents determined by the different techniques were found to be in good agreement. For the total hydroxyl contents, coefficients of variation of 5.6% (Alcell), 3.2% (Indulin AT), 2.3% (Sarkanda), and 6.2% (Curan 27-11P) were established. For the phenolic hydroxyl contents, a good correlation was observed between data obtained from ^{31}P-NMR and ^{13}C-NMR for all lignin samples, except for the Sarkanda lignin, for which a relatively high coefficient of variation (12.6%) was found. For softwood lignins (Indulin AT and Curan 27-11P), the phenolic hydroxyl content determined by ^{1}H-NMR was always lower than that deduced from ^{31}P-NMR and ^{13}C-NMR spectroscopy. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3008–3017, 2008

Key words: NMR; polyurethanes; renewable resources

INTRODUCTION

Lignin is defined as a random, amorphous, three-dimensional polymeric network that does not possess a uniform, homogeneous, well-defined structure with well-established repeating units. The major chemical functional groups in lignins include hydroxyl, methoxyl, carbonyl, and carboxyl moieties in various amounts, whose contents depend on the botanic origin and the applied extraction processes.[1] Hydroxyl groups and free positions in the aromatic ring are the most characteristic functions in lignin; they determine its reactivity and constitute the reactive sites to be exploited in macromolecular chemistry.

Nowadays, the major part of lignin is valorized in energy recovery streams by the burning of the black liquors in the pulp production industry, and only a small amount is isolated from spent pulping and commercialized (ca. 2%). However, it amounts to 1 million tons per year worldwide.[2]

Commercially available lignins are, most often, kraft or lignosulfonates associated with the corresponding most commonly used industrial processes for wood delignification and fiber isolation (kraft and sulfite, respectively). These lignins are largely used in dispersion and binding applications, and a small part is used in the production of specialty chemicals such as vanillin and dimethyl sulfoxide (DMSO).[3]

Sulfur-free lignins are becoming an emerging class of lignin products; this has been partly motivated by environmental policies but also by less capital intensive associated technologies. They can be obtained

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from three main sources: (1) biomass conversion technologies and biorefineries, (2) solvent pulping–organosolv processes, and (3) soda pulping of alternative biomass resources, such as agricultural harvesting residues and nonwood fiber crops.[4] Some examples of sulfur-free lignins are already available, as can be demonstrated by the example of Granit SA (Lausanne, Switzerland), a Swiss company, that started to commercialize sulfur-free lignins derived from nonwood fibers on the basis of a patented precipitation method [Lignin Process System (LPS)] for lignin isolation.[5] Another example, but still at a pilot level, is the company Lignol Innovations, which is producing lignin with similar characteristics to Alcell from Repap (Stamford, CT), with eastern hardwoods and fuel grade ethanol.[6] This will, undoubtedly, constitute a driving force to promote and consolidate lignin utilization in applications other than energy recovery, because sulfur-free lignins are potentially more suitable for polymeric applications than their kraft counterparts.[7]

In the last decades, considerable efforts have been directed toward the development of polymeric materials from lignin, with attempts to find new alternatives to petrochemicals and their derivatives. Lignins have been the subject of study of several research groups, and the developed applications include polyurethanes,[8–11] acrylics,[12] epoxies,[13] and phenolic resins.[14,15]

The utilization of lignin as a macromonomer in polyurethane synthesis often follows two global approaches: (1) direct utilization of lignin without any preliminary chemical modification, alone or in combination with other polyols,[7,10,16] or (2) chemical modification, such as esterification and etherification reactions, to make hydroxyl functions more readily available.[8,17,18]

A wide range of lignin-based polyurethane materials (rigid foams, elastomers, sealants) have been synthesized, and the corresponding mechanical and thermal properties have been evaluated. The exhibited properties were found promising and, in some cases, similar to those of conventional polyurethanes. The importance of these achievements has led to the appearance of some patented results.[19–21]

Despite all the research efforts made in this field and the generated knowledge, lignin is still facing some problems to be accepted as a viable and competitive monomer to substitute conventional raw materials for polyurethane and other polymeric synthesis materials. Two major difficulties are related to this situation, namely, (1) the unavailability of high-purity commercial samples and (2) the absence of normalized standard characterization protocols. An effort toward normalization has been done within the Eurolignin project (G1RT-CT-2002-0508), where some standards have been developed and tested.[22]

In what concerns polyurethane synthesis, the knowledge of the hydroxyl content is needed for formulation establishment. Several procedures are available for the determination of lignin hydroxyl groups and have been documented in the literature; two fundamental texts edited by Dence and Lin[23] and Zakis[24] are worth mentioning. The typical procedures are based on spectroscopic techniques [nuclear magnetic resonance (NMR), ultraviolet, and Fourier transform infrared (FTIR) spectroscopy], wet chemical methods (acetylation, permanganate oxidation, aminolysis, etc.), or a combination of both.

NMR spectroscopy has attained widespread application in lignin characterization, and the most commonly tested nuclei are ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR. ^{13}C-NMR spectroscopy is based on the acetylated samples and provides comprehensive structural data that lead to the determination of aliphatic (primary and secondary) and total phenolic hydroxyls. The obtained results are usually reported on the basis of the phenylpropane [C_9 (C_6–C_3)] unit.[25] Total phenolic hydroxyls can be also determined by ^{1}H-NMR spectroscopy with acetylated lignin derivatives. Recently, Tiainen et al.[26] proposed a method based on D_2O exchange of the phenolic proton that enabled the determination of the phenolic hydroxyl content without the need of acetylation. This procedure was already successfully applied to the reaction kinetics of lignin with butyric anhydride.[27] The ^{31}P-NMR spectroscopy technique was developed by Granata and Argyropoulos[28] and was found to be a very powerful tool for lignin characterization. Lignin samples were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, and from a single experiment, it was possible to discriminate between the three forms of phenolic hydroxyl groups present in the lignin (*p*-hydroxyphenyl, guaiacyl, and syringyl structures), as well as aliphatic hydroxyl groups, condensed phenol units, and carboxylic acid protons.

Among wet chemical methods, acetylation is one of the most used methods for lignin hydroxyl group determination. The total hydroxyl content can be estimated by a standard process with an acetic anhydride/pyridine mixture, followed by back-titration of acetic acid with a sodium hydroxide solution. This provides a simple tool for accessing total hydroxyl content.

The aim of this study was to carry out a detailed and reliable characterization of the different hydroxyl groups present in four commercially available technical lignins with different techniques. The hydroxyl contents were then determined by several NMR techniques, namely, ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR, and also by a titration procedure based on

a standard method commonly used to characterize commercial polyols for polyurethane synthesis.

EXPERIMENTAL

Lignin samples

The technical lignins used in this study represented three different pulping processes (kraft, soda, and organosolv) and different botanic origins, that is, softwood, hardwood, and nonwood lignin types. Thus, Indulin AT and Curan 27-11P (commercialized in the alkali form) were softwood lignins obtained by the kraft pulping process and were supplied by MeadWestvaco (Glen Allen, VA) and BorregaardLignoTech (Sarpsborg, Norway), respectively, whereas Sarkanda lignin was supplied by Granit SA. It is a nonwood lignin obtained from a soda pulping–precipitation process, patented by Granit SA. Alcell lignin of Repap Enterprises, Inc., was offered by Jairo Lora, to whom we are indebted. This lignin was extracted from mixed hardwoods (maple, birch, and poplar) by an organosolv process with aqueous ethanol. The lignins were used as received.

Ash content

The ash content was determined with a muffle furnace at 525°C over 5 h. Because of the high ash content initially obtained for Curan 27-11P, the procedure for this lignin was repeated until a constant mass of ash was achieved. All the determinations were done at least in duplicate.

Elemental analysis

Elemental analysis was carried out by the Laboratoire Centrale d'Analyse, Centre National de la Recherche Scientifique (Vernaison, France). The carbon, hydrogen, nitrogen, and sulfur contents were determined for all samples. Oxygen content was obtained by the difference after ash correction for the samples Indulin AT, Curan 27-11P, and Sarkanda. For the Alcell lignin, a high-purity lignin, the oxygen content was determined directly. All the determinations were done in duplicate.

Hydroxyl determination by titration

The methodology used followed the ISO 14900:2001(E) method[29] developed for the determination of the hydroxyl number of polyether polyols that might present steric hindrance. Briefly, the lignin and the blank samples were refluxed at 115°C in 25 mL of an acetylation reagent solution. This solution was prepared freshly daily by the mixture of 127 mL of acetic anhydride with 1000 mL of dry pyridine and 16 g of imidazole (catalyst). Additionally, lignin samples were degassed overnight *in vacuo* at 40°C before they were acetylated.

After the reflux period (1 h), the flasks were left to cool at room temperature, and thereafter, the excess of acetic anhydride was hydrolyzed with distilled water. The resulting acetic acid was subsequently titrated with sodium hydroxide (0.5*M*), and the difference between the acetic acid concentration of the blank and that of the lignin samples allowed the determination of the total hydroxyl content. The titrations were carried out in an automatic titrator (Methrom 736 GP Titrino, Courtaboeuf, France) equipped with a glass electrode. Sample size was adjusted such a way that the volume of sodium hydroxide solution used for the titration of the lignin sample was less than 80% of that required for the blank counterpart.

Sample preparation for ^{13}C-NMR analysis

^{13}C-NMR hydroxyl determination was based on acetylated lignin samples. Two different acetylation procedures were used. The first one corresponded to the procedure described in the Hydroxyl Determination by Titration section. After acetylation, the sample was recovered by precipitation with a procedure adapted from Glasser's work.[30] Briefly, the reaction mixture was precipitated in a 0.1*N* HCl solution (ca. 10 times the volume of the reaction mixture, 250 mL). Then, the acetylated lignins were filtered and washed several times with 0.1*N* HCl to remove pyridine; then, they were washed with distilled water to remove HCl. The recovered acetylated lignins were collected and freeze-dried. The final samples were stored in a desiccator at room temperature and conditioned at 0% relative humidity until analysis.

The second procedure was based on the Manson's method,[31] which was modified by Thielemans and Wool.[27] The acetylation reaction was performed without solvent with a 2:1 weight ratio of acetic anhydride to lignin and 1-methyl imidazole as a catalyst (0.05 mL/g of lignin). The reaction was conducted at 50°C under a stream of nitrogen atmosphere and vigorous stirring during 1 night. The reaction was then quenched with ethyl ether (100 mL), and the ensuing mixture was washed five times with deionized water (50 mL of each time). Cyclohexane (100 mL) was finally added to the ether phase to precipitate the derivatized lignin. The lignin was recovered by filtration and dried *in vacuo* for 24 h.

The final acetylated lignin samples (300 mg) were dissolved in 3.5 mL of DMSO-d_6. The prepared solutions were clear, and no insoluble fractions were detected. Moreover, for the used precipitation conditions, the quantity of the nonprecipitated materials was always negligible (recovered yields were close to 100%).

FTIR analysis

The completion of the acetylation reaction was checked by FTIR. FTIR spectra were collected on an Bomen FTIR instrument (model MB 104, Quebec, Canada) by the preparation of KBr pellets with a lignin concentration of 1% (w/w). Spectra were recorded between 650 and 4000 cm^{-1} at a resolution of 4 cm^{-1}, and co-adding 48 scans. To avoid pellet moisture contamination, the following procedure was followed: (1) acetylated lignin and KBr were left for 24 h at 40°C under reduced pressure before pellet preparation, and (2) pellets were subjected to the same conditions for 12 h before FTIR analysis.

Sample preparation for ^{1}H-NMR analysis

Lignin samples were prepared according to the procedure described by Tiainen et al.[26] Lignins were previously washed with a 0.004*M* HCl solution and then freeze-dried. The solutions were prepared by the dissolution of 10 mg of the resulting lignin in 0.8 mL of 99.8% DMSO-d_6 (SDS (DMSO supplier) followed by the addition of 1 μL of dimethylformamide-d_1 (DMF-d_1; reference compound). The solutions were left overnight over 4-Å molecular sieves and then transferred to an NMR tube to record the ^{1}H-NMR spectrum. Then, 20 vol % D_2O was added, and a second spectrum was recorded. The recovered washed samples were fully soluble in DMSO-d_6.

Sample preparation for ^{31}P-NMR analysis

Phosphitylation of lignin samples was performed with the method described by Hoareau et al.[32] A solvent solution of pyridine and $CDCl_3$ (1.6/1, v/v) was prepared and dried over molecular sieves. This solution was used for the preparation of the relaxation reagent solution [chromium(III) acetylacetonate, 5 mg/mL] and the internal standard solution (cholesterol, 5 mg/mL). Lignins were phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. Thirty milligrams of lignin were dissolved in 0.5 mL of DMF in a vial sealed with a Teflon-faced septum. Then, 0.3 mL of the solvent solution was added; this was followed by the addition of 0.1 mL of the internal standard and relaxation solution. The phosphitylation reagent (0.1 mL) was added, and the flask was shaken to ensure a homogeneous mixture. After derivatization, the resulting solution was transferred to a 5-mm tube, and the ^{31}P-NMR spectrum was recorded.

NMR spectrometers and procedures

^{13}C-NMR experiments were carried out on a Mercury Varian spectrometer (Palo Alto, CA) equipped with a 10-mm broad band (BB) probe operating at 100.624 MHz. Experiments were conducted at 50°C in DMSO-d_6 (99.8%; SDS). ^{13}C-NMR chemical shifts are given relative to tetramethylsilane. The positions of the peaks were referenced to the residual solvent peak of DMSO-d_6 (δ = 39.5 ppm). The spectra were quantitative (proton broad band decoupling only during the acquisition time). ^{13}C-NMR spectra were obtained with a 23-kHz (228-ppm) spectral width, 32,000 data points, and an 11-s relaxation delay and for 12 μs for a 75° pulse, zero-filling, and 10-Hz line broadening.

For the determination of the hydroxyl contents by ^{13}C-NMR, the following approximate integration limits were used: primary alcohols from 170.4 to 169.4 ppm, secondary hydroxyls from 169.4 to 168.5 ppm, and phenolic hydroxyls from 168.5 to 165.8 ppm.

^{31}P-NMR spectra were recorded on a Unity Varian spectrometer, equipped with a 5-mm inner diameter pulse field gradient (pfg) probe operating at 161.929 MHz. Experiments were recorded at 25°C in $CDCl_3$. Chemical shifts were calibrated from the sharp ^{31}P-NMR signal at 132.2 ppm arising from the reaction product between residual water and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. Spectra were quantitative (proton broad band decoupling only during acquisition time). Cholesterol was used as an internal standard for the quantitative evaluations of the lignin structural elements. Relaxation times (all < 2.5 s) were controlled with the inversion recovery sequence before any quantitative measurements. ^{31}P-NMR spectra were obtained with an 8.7-kHz spectral width, 32,000 data points, 10-s relaxation delay, and 1.8-s acquisition time and for 30 μs for a 75° pulse, zero-filling, and 1-Hz line broadening. The different hydroxyl groups were obtained by integration of the following spectral regions: aliphatic hydroxyls from 149 to 146 ppm, guaiacyl phenolic hydroxyls from 140 to 139 ppm, *p*-hydroxyphenyl phenolic hydroxyls from 138.5–137.5 ppm, syringyl phenolic hydroxyls 143–142 ppm, and carboxylic acid units from 135.5–134 ppm. The quantification of condensed phenol units resulted from the difference between the integrals of the peaks at 144–140 ppm and those at 143–142 ppm (syringyl phenolic hydroxyls).

The ^{1}H-NMR spectra of lignins were recorded on a Mercury Varian spectrometer equipped with a 5-mm quadrupole nucleus probe (QNP). Experiments were performed at 25°C. The one-pulse sequence was used with a 30°C pulse (2 μs), a relaxation delay of 4.6 s, a spectral width of 10,000 Hz, and 40,000 data points. The phenolic protons were obtained as the difference between the spectra of the samples before and after the addition of D_2O (integrals within 11–8 ppm). The integral of methyl protons in DMF-d_1 (2.9–2.6 ppm) was taken as reference.

TABLE I
Ash Content, Sugar Content, Elemental Analysis, OCH_3 Content, Empirical Formula, and Molecular Weight (M_w) of Each C_9 Lignin Unit

Lignin sample	Sugar (% w/w)	Ash (% w/w)	Elemental analysis (% w/w)					OCH_3[a]	Empirical formula	M_w (g/mol)
			C	H	N	S	O			
Alcell	0.2	0.05	65.88	5.82	<0.30	<0.20	27.69[b]	1.11	$C_9H_{7.39}O_{2.08}(OCH_3)_{1.11}$	183.08
Indulin AT	2.0	3.06	61.64	5.81	0.48	1.05	27.97[c]	0.77	$C_9H_{8.74}O_{2.56}N_{0.064}S_{0.062}(OCH_3)_{0.77}$	184.45
Sarkanda	5.0	3.26	58.84	5.86	1.14	1.01	29.89[c]	0.98	$C_9H_{8.99}O_{2.82}N_{0.16}$ $(OCH_3)_{0.98}$	194.73
Curan 27-11P	2.0	17.0	50.13	4.88	<0.30	2.30	25.69[c]	0.83	$C_9H_{8.99}O_{2.95}S_{0.17}(OCH_3)_{0.83}$	195.36

[a] Based on the C_9 unit.
[b] Direct determination.
[c] Determination by difference after ash correction.

Sugar determination

Sugar content was determined after a two-step hydrolysis procedure of lignin samples on the basis of the method documented by Lepifre et al.[33] The lignin samples (between 6 and 15 mg) were weighed directly into a screw cap tube to which 125 μL of a solution 13*M* H_2SO_4 was added. The reaction mixture was left for 1 h at 25°C and regularly crushed with a glass stick placed in the tube. A known volume (between 10 and 100 μL) of internal standard fucose solution was added (typically, 1–2 mg/mL), which was followed by the addition of 1.5 mL of deionized water to reach a 1*M* H_2SO_4 solution. The tube was closed and left at 100°C for 2 h. Finally, the solutions were left to reach ambient temperature and then filtered with a Whatman (Kent, UK) membrane filter (0.45 μm) before HPLC analysis. Sugars contents of the ensuing hydrolysates were determined by high-performance anion-exchange chromatography with pulsed amperometric detection. The chromatographic system consisted of a GP40 quaternary gradient high-pressure pump, and an ED40 pulsed amperometric detector (Dionex Corp., Sunnyvale, CA). Sugar separation was achieved with two Carbo-Pac PA1 columns (4 × 250 mm analytical column) and a guard column (4 × 50 mm) connected in series.

Sugars were analyzed in a gradient mode at a flow rate of 1 mL/min and a temperature of 30°C. Initially, 4 m*M* NaOH was used (time zero), and then, the NaOH concentration was decreased until it reached a concentration of 1 m*M* NaOH (13 min). The concentration of NaOH was then increased until it reached the initial value (4 m*M* NaOH) at the analysis time of 25 min. Pure sugar samples (glucose, mannose, xylose, galactose, and arabinose) were used to build calibration curves.

RESULTS AND DISCUSSION

Elemental analysis and methoxyl (OCH_3) group content

The OCH_3 content was determined by ^{13}C-NMR spectroscopy, with nonacetylated lignin samples, and with the signal integrated at 56 ppm. This signal corresponded to the OCH_3 group in the syringyl and guaiacyl units. As expected, the Alcell lignin presented a higher OCH_3 content. The values from elemental analysis and OCH_3 were used to establish the approximate C_9 formula. On the basis of the deduced empirical formula, the molecular weight of the C_9 unit was determined. This value can, however, only be seen as an approximation because technical lignins may have partially degraded alkyl side chains and might contain impurities (ashes and residual carbohydrates). Table I summarizes the values obtained from elemental analyses and the OCH_3 content for each lignin sample, together with the deducted C_9 formula and the corresponding molecular weights of this C_9 unit. The ash and sugar contents are also presented. The molecular weights obtained were within the range of generally reported values for lignin phenyl propane units.[34,35]

The results from elemental analysis reveal high sulfur content (1.1%) for the Sarkanda lignin. To the best of our knowledge, no sulfur containing additives were used by the soda process applied by Granit SA. Nevertheless, precipitation with sulfuric acid is a current practice for nonwood lignins, and the detected sulfur arose from inorganic origin rather than an organic counterpart. From the previous explanation, the Sarkanda sulfur content was considered as inorganic and was not included in the empirical C_9 formula. Moreover, this inorganic sulfur from the residual sulfuric acid also justified the acidic pH measured on the Sarkanda lignin aqueous suspensions. The Sarkanda lignin also presented the higher nitrogen content. This is a well-known feature of nonwood lignins from the soda pulping process.[2,36]

Total hydroxyl content

The total hydroxyl content was determined on the basis of the acetylated samples by ^{13}C-NMR and ^{31}P-NMR spectroscopy and by the titration method. For ^{13}C-NMR analysis, two different acetylation proce-

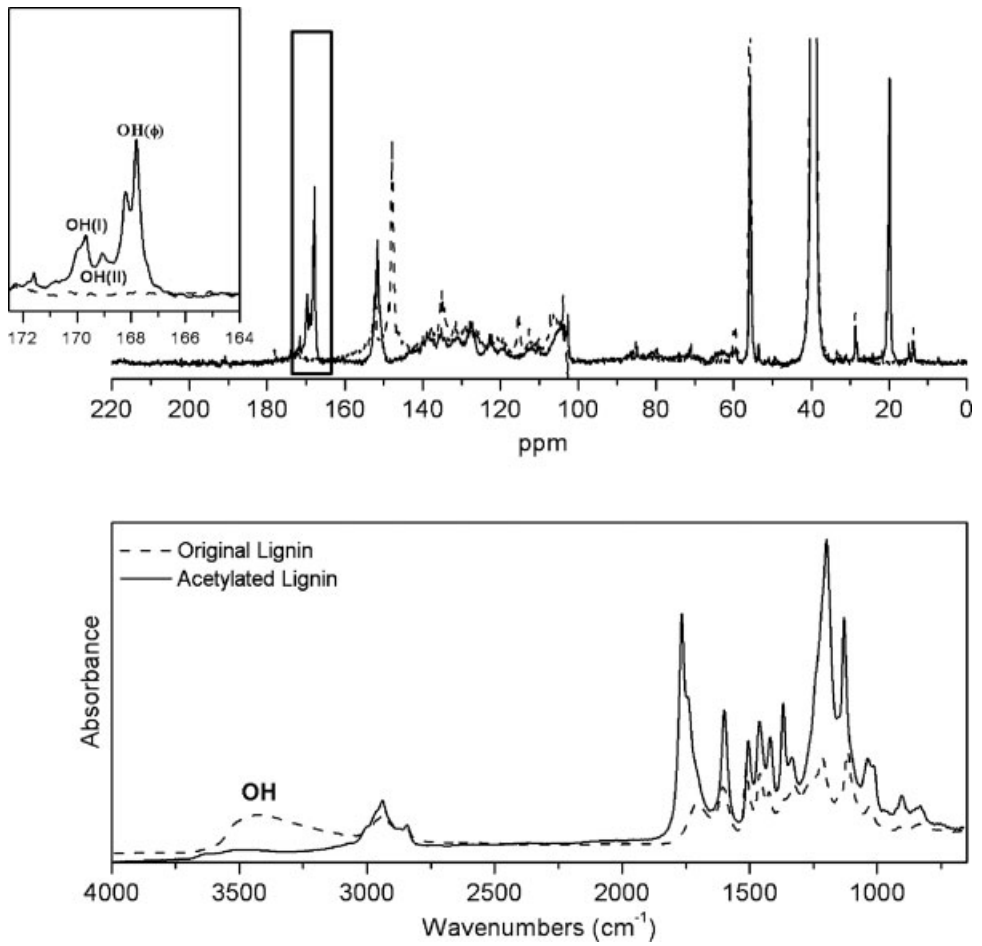

Figure 1 ^{13}C-NMR spectrum (carbonyl zone shown in detail) and the corresponding FTIR analysis for the Alcell lignin, acetylated according to the procedure described in standard method ISO 14900:2001(E).

dures were used; the first one corresponded to that reported in the ISO 14900:2001(E) method, whereas the second one followed the method improved by Thielemans and Wool. Figure 1 illustrates the ^{13}C-NMR spectrum obtained for the Alcell lignin after acetylation according to the ISO 14900:2001(E) method. The carbonyl zone is shown in detail, as well as the corresponding FTIR analysis, to check the completion of the acetylation reaction. For all the acetylated samples, the assigned hydroxyl band was always negligible, which thus confirmed that the acetylation reaction was practically complete.

The integration of the individual contributions, with the two acetylation procedures, is summarized in Table II, and the results were found to be in good agreement.

To compare the results obtained from different techniques, the previously established molecular weights of the C_9 lignin base units were used in the calculation of the total hydroxyl content in milli-

TABLE II
Number of C Atoms Associated with the OH Groups per C_9 Unit with the Two Acetylation Procedures

	Acetylation procedure 1[a]				Acetylation procedure 2[b]			
Lignin sample	OH (I)	OH (II)	OH (ϕ)	OH (total)	OH (I)	OH (II)	OH (ϕ)	OH (total)
Alcell	0.16	0.10	0.70	0.96	0.20	0.12	0.72	1.04
Indulin AT	0.33	0.22	0.72	1.27	0.35	0.22	0.70	1.27
Sarkanda	0.25	0.32	0.48	1.05	0.29	0.35	0.39	1.03
Curan 27 11P	0.29	0.19	0.69	1.17	0.31	0.21	0.65	1.17

[a] Acetylation procedure according to ISO method 14900:2001(E).
[b] Acetylation procedure according to the modified Manson method.
ϕ, phenolic hydroxyls.

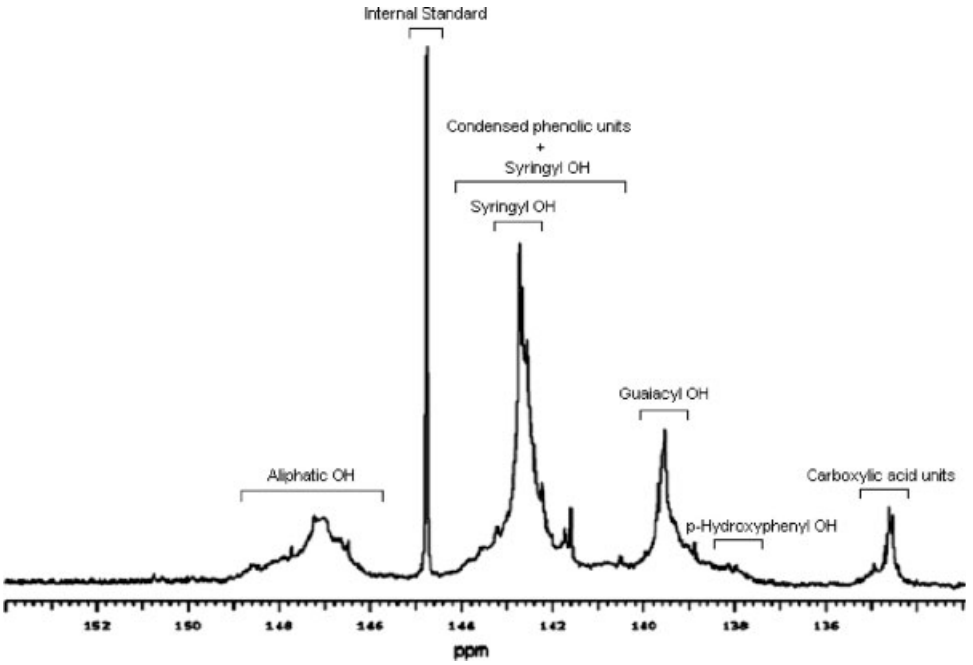

Figure 2 ^{31}P-NMR spectra of the Alcell lignin.

moles per gram from the ^{13}C-NMR data (obtained as OH/C_9 unit).

For each lignin sample, the values of the total hydroxyl content, obtained from ^{13}C-NMR (for the two acetylation procedures), ^{31}P-NMR spectroscopy (a representative sample spectrum is shown in Fig. 2), and titration were compared with their corresponding average values, as shown in Figure 3. This type of representation allows a direct and easy comparison of the results obtained for each lignin sample, as deduced from different characterization techniques. The original values of the hydroxyl content determined by titration and ^{31}P-NMR were corrected to be represented in a free ash basis. The experimentally measured values are expressed in millimoles per gram of the original sample (lignin plus ashes), which thus imposes a correction. For the ^{13}C-NMR and ^{1}H-NMR techniques, the values in millimoles per grams were calculated on the basis of the M_w of C_9 unit, which already took into account the ash correction. For the Sarkanda lignin, the original value obtained for the total hydroxyl content determined by titration was corrected because of the presence of residual sulfuric acid.

The total hydroxyl contents obtained from the three methods used (titration,^{13}C-NMR, and ^{31}P-NMR) were found to be in good agreement (Table III and Fig. 3). The coefficients of variation were 5.6, 3.2, 2.3, and 6.2% for the Alcell, Indulin AT, Sarkanda, and Curan 27-11P samples, respectively. However, the value of total hydroxyl content of the Curan 27-11P lignin obtained by titration was considerably higher than those obtained by the other methods. This result was attributed to the alkali form of this type of lignin, which interferes with the titration step and thus led to an erroneously high hydroxyl content. This value was not considered for the determination of the total average hydroxyl content. The total hydroxyl content of the Alcell and Indulin AT lignins was in close agreement with values found in the literature.[8,10,37] Within the obtained results, the highest total hydroxyl content corresponded to the softwood lignins, Indulin AT and

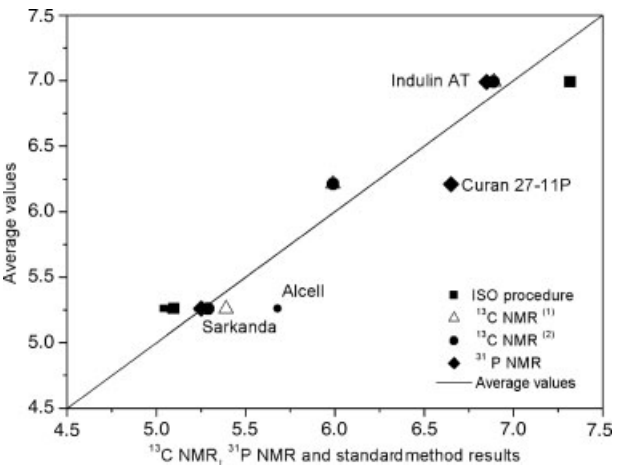

Figure 3 Comparison between the total hydroxyl contents obtained by different techniques, namely, titration with the ISO 14900:2001(E) standard procedure, ^{13}C-NMR (1: acetylation procedure according to ISO 14900:2001(E) method and 2: acetylation procedure according to the modified Manson method), and ^{31}P-NMR. To clarify the representation, the Alcell lignin is identified by smaller gray symbols.

TABLE III
Data Obtained for the Total Hydroxyl Content with Titration, ^{13}C-NMR (Two Acetylation Procedures), and ^{31}P-NMR and for the Phenolic Hydroxyl Content with ^{13}C-NMR (Two Acetylation Procedures), ^{31}P-NMR, and ^{1}H-NMR

Lignin sample	Total OH content (mmol/g)						Phenolic OH content (mmol/g)					
	^{13}C-NMR[a]	^{13}C-NMR[b]	^{31}P-NMR	Titration	Average	CV (%)[c]	^{13}C-NMR[a]	^{13}C-NMR[b]	^{31}P-NMR	^{1}H-NMR	Average	CV (%)[c]
Alcell	5.24	5.68	5.07	5.04	5.26	5.6	3.82	3.93	3.74	3.73	3.81	2.4
Indulin AT	6.89	6.89	6.85	7.32	6.99	3.2	3.90	3.83	4.11	(3.20)	3.95	3.7
Sarkanda	5.39	5.29	5.25	5.10	5.26	2.3	2.46	2.00	2.74	2.43	2.41	12.6
Curan 27-11P	5.99	5.99	6.65	(9.3)	6.21	6.2	3.53	3.33	4.02	(1.80)	3.63	9.9

The values are represented in millimoles per gram on a free ash basis.
[a] Procedure 1: acetylation procedure according to ISO 14900:2001(E) method.
[b] Procedure 2: acetylation procedure according to the modified Manson method.
[c] Coefficient of variation [$CV = (s/\bar{x}) \times 100$, where s is the standard deviation and $\bar{x}$ is average value].

Curan 27-11P, namely, 6.99 and 6.21 mmol/g, respectively. For the Alcell and Sarkanda lignins, the same value of average total hydroxyl content (5.26 mmol/g) was obtained.

Phenolic hydroxyl content

The content of phenolic hydroxyl groups was determined by quantitative ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR spectroscopy, as summarized in Table III.

The type of representation previously used to compare the total hydroxyl contents was used again to compare the phenolic hydroxyl contents obtained from the different techniques used in this study, as shown in Figure 4. The determination of the phenolic hydroxyl content of Curan 27-11P by ^{1}H-NMR showed some difficulties. Thus, the obtained spectrum displayed poorly defined peaks, and their integration was difficult to achieve properly. The obtained value was very low compared with that obtained by ^{13}C-NMR and ^{31}P-NMR spectroscopy. For Indulin AT, the same behavior was observed. The value of phenolic hydroxyl content determined by ^{1}H-NMR was found to be lower than that obtained by ^{13}C-NMR and ^{31}P-NMR. For these two lignin samples, only the phenolic hydroxyl content based on the data deduced from ^{13}C-NMR and ^{31}P-NMR spectroscopy were considered for the determination of the average phenolic hydroxyl content. The phenolic hydroxyl values determined by ^{1}H-NMR for Indulin AT and Curan 27-11P are encircled in Figure 4. Once more, the higher coefficients of variation corresponded to the Sarkanda and Curan 27-11P lignins, which were 12.6 and 9.9%, respectively.

This study showed that Indulin AT had the highest phenolic hydroxyl content (3.95 mmol/g), fol-

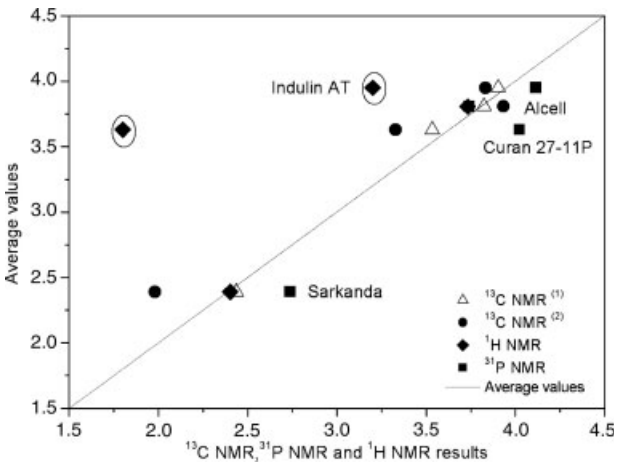

Figure 4 Comparison between the phenolic hydroxyl contents obtained by different techniques, namely, ^{13}C-NMR (1: acetylation procedure according to ISO 14900:2001(E) method and 2: acetylation procedure according to the modified Manson method), ^{31}P-NMR, and by ^{1}H-NMR.

TABLE IV
Quantification of Several Types of Hydroxyl Groups (mmol/g) by ^{31}P-NMR

Lignin sample	Aliphatic	S—OH	G—OH	5-Condensed	H—OH	Acids
Alcell	1.10	1.63	0.80	1.18	0.13	0.23
Indulin AT	2.34	0.33	1.96	1.58	0.26	0.39
Sarkanda	1.89	0.80	0.82	0.65	0.47	0.62
Curan 27-11P	2.16	0.29	2.01	1.49	0.23	0.47

The values are represented on a free ash base. S = syringyl; G = guaiacyl; H = *p*-hydroxyphenyl.

lowed by Alcell lignin, with a phenolic hydroxyl content of 3.81 mmol/g. The phenolic hydroxyl content of the Sarkanda lignin was found to be significantly lower (2.41 mmol/g). This low value was most likely a result of the pulping process (soda pulping), which produces the cleavage of aryl–ether linkages through the formation of small quantities of phenolic hydroxyls and yields a loss of primary aliphatic hydroxyl groups.[38,39]

^{31}P-NMR also allowed for a detailed quantification of the aromatic hydroxyl groups attached to the syringyl, guaiacyl, and *p*-hydroxyphenyl units. The contents of the different hydroxyl groups and carboxylic acids are presented in Table IV. As expected, the relative proportions of syringyl, guaiacyl, and *p*-hydroxyphenyl phenol structures varied according to the origin of the lignin sample. For the softwood lignins, the highest amounts of guaiacyl phenol structures and small quantities of syringyl and *p*-hydroxyphenyl phenol structures were confirmed. In the Alcell lignin, the amount of syringyl phenol structures was higher than that of guaiacyl, and only a small quantity of *p*-hydroxyphenyl structures was detected. The Sarkanda lignin, obtained from agricultural resources (wheat and hemp), presented a close proportion of guaiacyl, syringyl, and *p*-hydroxyphenyl structures (0.82/0.80/0.47 mmol/g). Another important feature related to the Sarkanda lignin was the evident presence of carboxylic acids (0.62 mmol/g). The Alcell and softwood lignins had considerably lower carboxylic acid contents.

Aliphatic hydroxyl content

The aliphatic hydroxyl contents could be directly determined by ^{13}C-NMR of the acetylated samples (sum of the primary and secondary hydroxyl contents) and ^{31}P-NMR (total aliphatic hydroxyl content). From the analysis of the results presented in Table II, we noticed that the Alcell lignin had the lowest amount of primary and secondary hydroxyl groups. Secondary hydroxyl groups were mainly present in the Sarkanda lignin (0.34/C_9). The softwood lignins had identical amounts of secondary hydroxyl groups, namely, 0.22/C_9 and 0.20/C_9 for Indulin AT and Curan 27-11P lignins, respectively.

CONCLUSIONS

The hydroxyl group content of four technical lignins was determined with several NMR techniques (^{13}C-NMR, ^{31}P-NMR, and ^{1}H-NMR) and a titration procedure on the basis of a standard method commonly used to characterize commercial polyols for polyurethane synthesis.

The values of the total and phenolic hydroxyl contents determined by the different techniques were found to be in good agreement. The titration method gave quite good results compared with the methods based on NMR spectroscopy. Limitations were observed only for the Curan 27-11P lignin, which could be associated with its isolation procedure (lignin commercially available in alkali form). Moreover, for all of the lignin samples, the hydroxyl values obtained by ^{13}C-NMR with the two different acetylation procedures were found to be in close agreement. For the phenolic hydroxyl contents, reliable results were obtained for the Alcell and Indulin AT lignins, but the Sarkanda and Curan 27-11P samples gave quite high coefficients of variance. Among the techniques used, ^{1}H-NMR spectroscopy was found to underestimate the phenolic hydroxyl contents of the softwood lignins.

A global inspection of the results showed that the Indulin AT and Curan 27-11P (softwood lignins) had the highest total hydroxyl contents. The Alcell and Sarkanda lignins had the lowest and approximately the same total hydroxyl contents. The amounts of phenolic hydroxyl groups were similar for the Indulin AT, Alcell, and Curan 27-11P lignins. The Sarkanda lignin had the lowest phenolic hydroxyl content. The Alcell lignin had the lowest aliphatic hydroxyl content (both primary and secondary hydroxyls). Identical amounts of secondary hydroxyl groups were found for the Sarkanda, Indulin AT, and Curan 27-11P lignins. The lack of accuracy in the determination of the Sarkanda phenolic hydroxyl content was attributed to the high percentage of carbohydrates (5%, w/w) together with the high car-

boxylic acid content (0.62 mmol/g by ^{31}P-NMR) present in the sample, which thus contributed to a more complex and difficult integration of the corresponding signals in the ^{13}C-NMR spectra of the acetylated lignin sample. Lignins were characterized as commercially available, and no correction was made in what concerned carbohydrate impurities. For our objective, the hydroxyls belonging to carbohydrate moieties would also contribute as reactive sites in polyurethane synthesis. Moreover, according to Singh et al.,[40] the use of lignin-containing carbohydrate moieties will improve the biodegradable characteristics of the final polymeric material, which constitutes an additional valuable feature.

For total hydroxyl content, the acetylation procedure followed by titration seemed to be an attractive procedure. It was a simple procedure and was faster than NMR-based methods. Moreover, it did not require expensive equipment and specialized technicians. For phenolic hydroxyl content, both ^{31}P-NMR and ^{13}C-NMR gave comparable results. Nevertheless, the former had the advantage of allowing quantification by discrimination of the aromatic hydroxyl groups attached to syringyl, guaiacyl, and *p*-hydroxyphenyl units.

The combination of the analytical techniques used in this study allowed for the complete characterization of hydroxyl groups present in the lignins: type and content. This detailed quantification can contribute to a better understanding of the kinetics associated with lignin-based polyurethane systems. The contribution of each hydroxyl function in the global kinetic behavior can be identified and studied independently with lignin model compounds. This study is under progress in our laboratory.

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