Polycondensation Resins by Lignin Reaction with (Poly) amines

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Received March 06, 2017; Accepted April 13, 2017

ABSTRACT: The reaction of a desulphurized kraft lignin with hexamethylene diamine as a model of a polyamine has been investigated. For this purpose, guaiacol was also used as a lignin model compound and treated under similar conditions. Solid state CP-MAS ^{13}C NMR, FTIR and MALDI-TOF spectroscopy studies revealed that polycondensation compounds leading to resins were obtained by the reaction of the amines with the phenolic and aliphatic hydroxy groups of lignin. Simultaneously a second reaction leading to the formation of ionic bonds between the same groups occurred. These new reactions have been clearly shown to involve several phenolic and alcohol hydroxyl groups, as well as lignin units oligomerization, to form hardened resins.

KEYWORDS: Lignin-amine reactions, lignin-amine condensation, oligomer distribution, resins, MALDI-TOF, CP-MAS ^{13}C NMR, FTIR

1 INTRODUCTION

The abundance of different types of lignin as a waste product in wood pulp mills has made these materials an attractive proposition for the preparation of resins and adhesives ever since the pulping of wood to produce paper. There is a very large amount of literature on the use of lignin in the preparation of adhesives and resins and some good reviews exist for some of the relevant fields of application [1]. Contrary to the abundance of articles in the literature on this subject the corresponding industrial applications of these materials are rather scant. There are well-documented cases of the industrial utilization of lignin in adhesives for wood [1, 2] as well as in other fields, but all of these were generally discontinued after only short periods of industrial use for one reason or other. Most of these serious attempts to utilize lignin as an adhesive or a resin were based on its reaction with formaldehyde, other aldehydes, aldehyde-based resins such as phenol-formaldehyde (PF), urea-formaldehyde (UF), tannin-aldehyde, and on isocyanate resins [3–9]. Processes based on the self-coagulation of lignin [1, 5, 10], peroxide-induced gelling [1, 11] and others, although of definite interest, have always had some inherent disadvantages regarding their industrial application. One of the most evident disadvantages ever has been the low reactivity of lignin with aldehydes, aldehyde-yielding compounds and aldehyde-based resins. This was first partially overcome for some applications (i) by pre-reacting lignin with an aldehyde before adding it to a traditional resin such as a PF or UF resin [12–14], this process having been used industrially for plywood for a couple of decades in North America: and then (ii) by supporting this further by recurring crosslinking reactions not based on just the reaction of an aldehyde with phenolic nuclei of lignin but also with an isocyanate. This latter approach formed mixed networks based on methylene and urethane bridges [3, 4, 8, 9].

In the latter approach the main drawback for the use of lignin in different resins was overcome by using the alternative reaction of isocyanates with the groups formed on an aldehyde-pre-reacted lignin [3, 4, 8, 9, 15]. This indicated that to overcome the traditional low reactivity and poor crosslinking drawbacks of lignin its application must pass by reactions that are not based on the classical phenols-aldehyde approach. Polymeric isocyanates served such a purpose well, but as they are now also considered partially toxic before being neutralized in their crosslinked state, they have also become less accepted for possible use.

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DOI: 10.7569/JRM.2017.634142

It is on the basis of this background that the recent development to crosslink other polyphenols, such as tannins, by alternate polycondensation reactions [16, 17] has led to check the possibility of applying these same reactions to obtain new, hardened, crosslinked polycondensation resins based on lignin. One of these approaches and the results obtained, namely the reaction with diamines, and by inference with polyamines, of a commercial, desulfurized kraft lignin to form a hardened resin is described in this study. The reaction presented is of particular interest when applied for the rapidity of initial reaction, rendering it of interest for the preparation of non-drip coatings and for quick initial immobilization of pressure projected insulation foams.

Reactions of lignin with amines are found in the literature through the intermediate of aldehydes, particularly in formaldehyde, for example, to form asphalt emulsifiers [18, 19], or of reaction of lignin with an amine and epichloridrin [20]. However, there does not appear to be any record of direct reaction of diamines or other polyamines with lignin to form hardened crosslinked resins. Thus, in this study the reaction with diamines with lignin was investigated, first by using guaiacol as a simple model compound, followed by the same reactions on a kraft lignin by extensive MALDI-TOF spectroscopy, FTIR and solid-state CP-MAS ^{13}C NMR studies. The findings are presented in this article.

2 MATERIALS AND METHODS

2.1 Materials and Reactions

Guaiacol (purity > 98%, HPLC quality) as a simple model compound of lignin was supplied by Sigma-Aldrich. The commercial lignin used was a desulphurized softwood kraft lignin, namely Biochoice kraft lignin supplied by Domtar Inc. (Montreal, Quebec, Canada) from their Plymouth, North Carolina mill (USA).

From these two chemicals, the following experiments have been carried out. The samples were prepared as follows:

1. 0.5 g of guaiacol was mixed in equimolar amount with 0.67 g of hexamethylenediamine (HDMA) (70% solution in water) catalyzed by the addition of 1 g NaOH 33% solution in water. The sample was prepared with the proportions above, then reacted in an oven at 100 °C during 18 h.
2. 4 g of 50% water solution of Biochoice lignin at pH > 10 was mixed with 2 g of hexamethylene diamine (HMDA) (70% solution in water) + 0.8 g of NaOH 33% solution in water. Two samples were prepared with the proportions above and they were reacted in an oven at 100 °C and 180 °C during 18 h, respectively.
3. 4 g of 50% water solution of Biochoice lignin at pH > 10 was mixed with 2 g of hexamethylene diamine (HMDA) (70% solution in water) + 2 g of NaOH 33% solution in water. Two samples were prepared with the proportions above and they were reacted in an oven at 100 °C and 180 °C during 18 h, respectively.

All reactions were carried out in an oven not blanketed with inert gas using the temperatures indicated for each case and inside open containers.

Before reaction the samples were liquid solutions. After the reaction in the oven, the samples prepared from lignin at 100 °C were a paste and at 180 °C became a dry, hardened solid, while the samples prepared from guaiacol at 100 °C became a viscous liquid.

2.2 Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) Mass Spectrometry Analysis

The spectra were recorded on a KRATOS Kompact MALDI AXIMA TOF 2 instrument. The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The time period of a laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 kV acceleration voltage), 100–150 pulses per spectrum. The delayed extraction technique was used by applying delay times of 200–800 ns.

2.3 CP-MAS ^{13}C NMR

Solid-state CP-MAS (cross-polarization/magic angle spinning) ^{13}C NMR spectra of the aforementioned oven-dried solids were recorded on a Bruker MSL 300 spectrometer at a frequency of 75.47 MHz. Chemical shifts were calculated relative to tetramethyl silane (TMS). The rotor was spun at 4 kHz on a double-bearing 7 mm Bruker probe. The spectra were acquired with 5 s recycle delays, a 90° pulse of 5 ms and a contact time of 1 ms. The number of transients was 3000.

2.4 Fourier Transform Infrared (FTIR) Spectroscopy

A PerkinElmer Frontier ATR (attenuated total reflection) spectrophotometer equipped with a diamond/ZnSe crystal was used to analyze the lignin and the reaction products. About 150 mg of sample was placed on the crystal and the contact was obtained with 32 scans with the resolution of 4 cm^{-1} from 4000 to 600 cm^{-1}.

Additional samples were prepared without HMDA under the same conditions that the samples prepared in points 2 and 3 in the samples preparation section to analyze the influence of thermal degradation on the samples. The results have been presented in the supplementary material.

3 RESULTS AND DISCUSSION

3.1 MALDI-TOF

The physical state of the sample obtained by reaction of guaiacol with hexamethylene diamine (HMDA) catalyzed by NaOH was a viscous liquid. The interpretation of the peaks of the MALDI-TOF spectrum shown in Figures 1a,b and the assignment of species formed

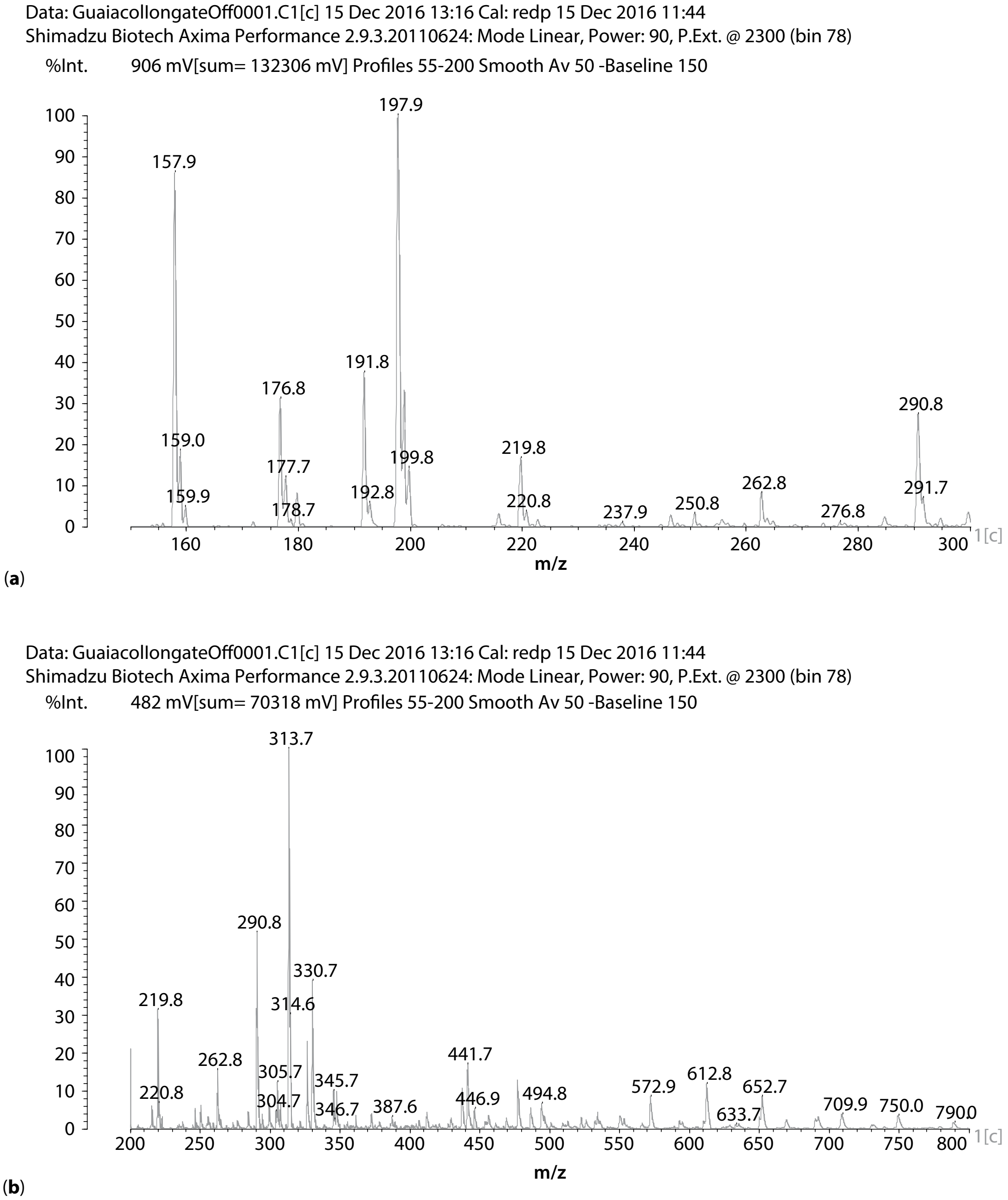
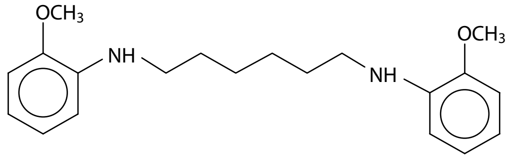


Figure 1 MALDI-TOF spectrum of the products obtained by the reaction of guaiacol with HMDA: (**a**) 50 Da–300 Da range and (**b**) 200 Da–800 Da range.

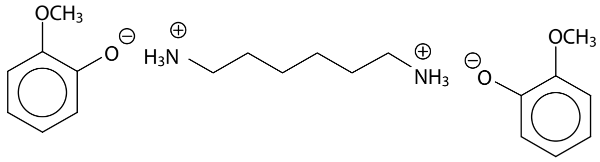
Table 1 MALDI-TOF peaks interpretation. NaOH-catalyzed reaction of guaiacol and hexamethylenediamine at 100 °C. Legend: "-" = covalent bond, "(+)(-)" = ionic bond, and "(+)(-) Na" = Na^+ linked to flavonoid units phenolic –OHs as $–O^-Na^+$.

Experimental	Calculated	Oligomer
157 Da		2,5-dihydroxybenzoic acid (DHB) (Matrix with 154 Da MW))
177 Da	177 Da	2,5-dihydroxybenzoic+Na^+
198 Da	200	2,5-dihydroxybenzoic+2x Na^+
219 Da	221 Da	Guaiacol-HMDA
246 Da	241 Da	Guaiacol-HMDA+Na^+
251 Da	251 Da	DHB-HMDA, Reaction of the amine with the matrix
263 Da	263 Da	Guaiacol(+)(-)HMDA+Na^+ Salt formation
326 Da	326 Da	Guaiacol-HMDA-Guaiacol
347 Da	349 Da	Guaiacol-HMDA-Guaiacol+ Na^+
372 Da	371 Da	HMDA-DHB-HMDA+Na^+
387 Da	387 Da	Guaiacol(+)(-)HMDA(-)(+) Guaiacol+Na^+ Double salt
446 Da	445 Da	DHB-3×HMDA
477 Da	476 Da	HMDA-DHB-HMDA-Guaiacol+Na+
495 Da	495 Da	HMDA-DHB-HMDA(-)(+) Guaiacol+Na+
572 Da	573 Da	DHB-3×HMDA-Guaiacol+Na+
653 Da	654 Da	DHB-3×HMDA-2×Guaiacol

are shown Table 1. Two types of reactions appear to occur from the calculation of the MALDI masses found, namely 1) the formation of secondary amines by reaction of the hexamethylene diamine on the free –OH groups of the guaicol units, and 2) the formation of $–O^-$ NH_3^+-ionic salt bonds between guaiacol and diamine. Thus, structures of type 1 at 347 Da such as



are present alongside structures of type 2 such as the one at 387 Da

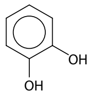


These two types of bonds are the same that have been found in the reactions of flavonoid monomers and flavonoid tannins with diamine under the same reaction conditions [17].

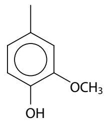
The samples obtained by reaction of lignin with HMDA at 100 °C were pastes, while those reacted at 180 °C were hardened solids.

Some of the masses found in the lignin-HMDA MALDI-TOF spectra also belong to unreacted lignin units or oligomers. The products obtained in the reactions at 100 °C with 0.8 g NaOH catalyst are shown in Figure 2a–c and in Table 2. Those obtained in the reaction at 180 °C with 0.8 g and at 100 °C and 180 °C with 2 g NaOH catalyst are shown in the figures and spectra in the Supplementary Material.

In Table 2 and Figure 2a are shown the results of the NaOH-catalyzed reaction at 100 °C. It can be seen that 5 fragments of lignin units occur as follows:



I



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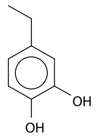

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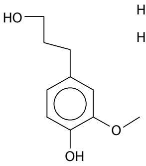

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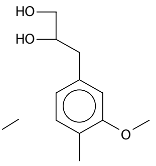
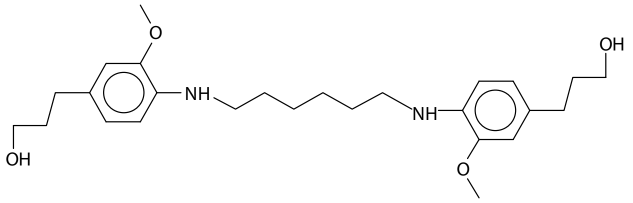


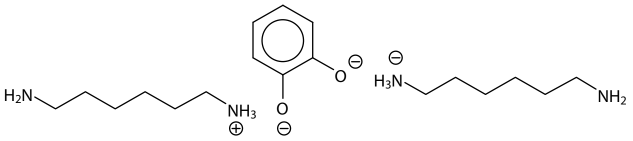
V

at 110 Da, 138.2 Da, 13.2 Da, 179.7 Da and 197.8 Da, respectively, and react and combine with HMDA to form a number of different oligomers (Table 2). Table 2 shows oligomers in which covalent bonds between the HMDA and lignin units are formed, such as those of the peaks at 205 Da, 235 Da, 441 Da, 461 Da, 463 Da, 501 Da, 541 Da, 610 Da, 685 Da, 698 Da, 712 Da and 789 Da, thus corresponding to structures of the type at 441 Da



This type of oligomer arrives at trimers of lignin reacted with HMDA (698 Da and 712 Da, Table 2).

Ionic-type salt bond species are also present as the species represented by the peaks at 255 Da and 345 Da corresponding to the structure such as the one at 345 Da shown below.



Mixed species in which HMDA moieties are linked to lignin units both by covalent and ionic bonds also

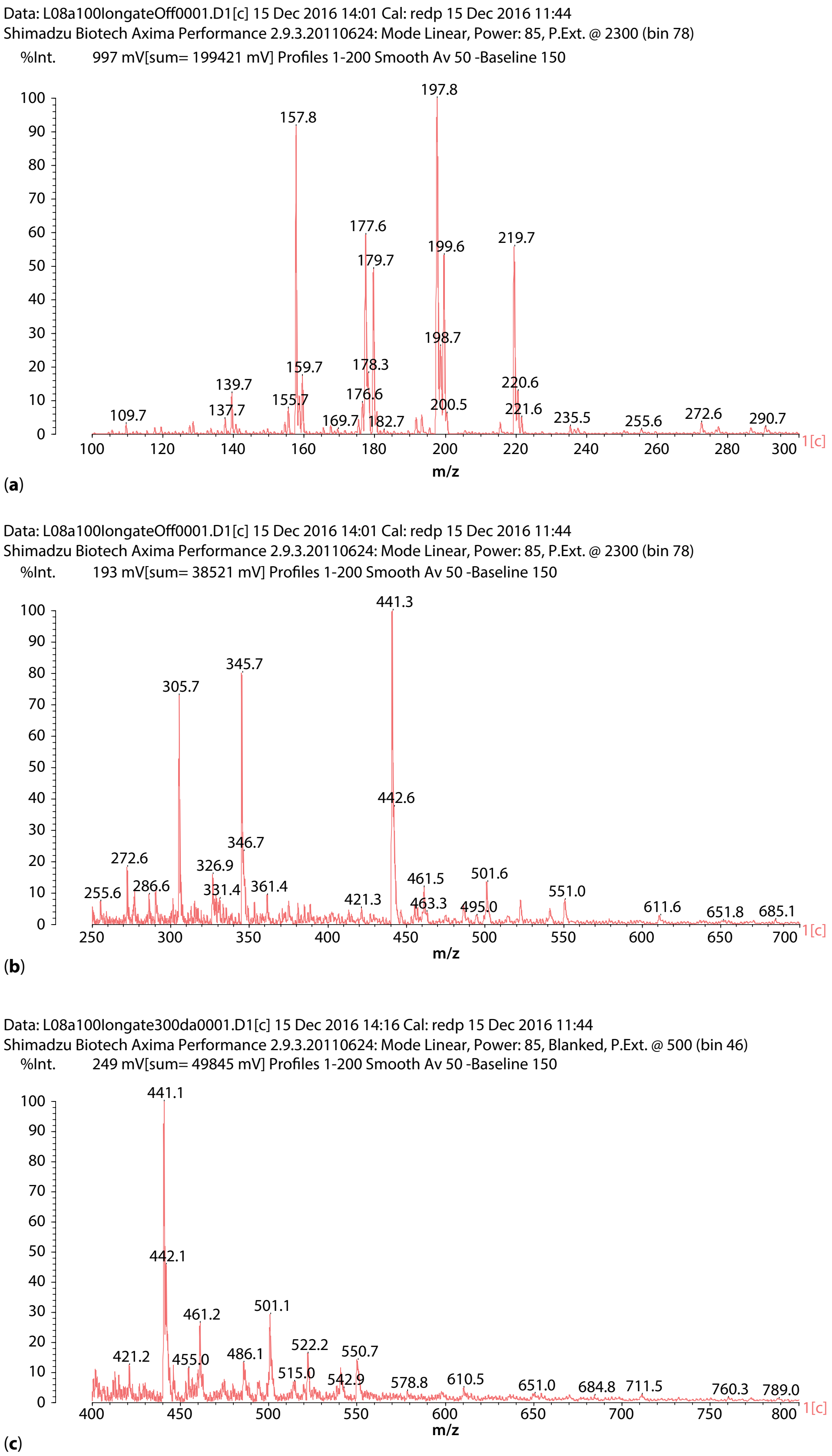
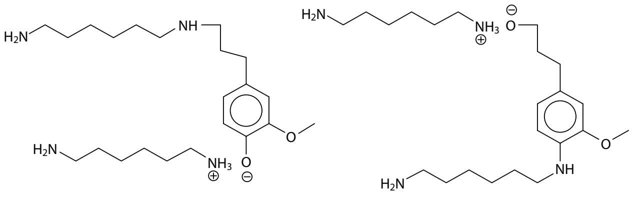


Figure 2 MALDI-TOF spectrum of the products obtained by the reaction of lignin with HMDA catalyzed by 0.8 g NaOH at 100 °C: (**a**) 100 Da–300 Da range, (**b**) 250 Da–700 Da range and (**c**) 400 Da–800 Da range.

Table 2 MALDI-TOF peaks interpretation. NaOH-catalyzed reaction of kraft Biochoice lignin and hexamethylenediamine at 100 °C catalyzed with 0.8 g NaOH solution. Legend: "-" = covalent bond and "(+)(-)" = ionic bond.

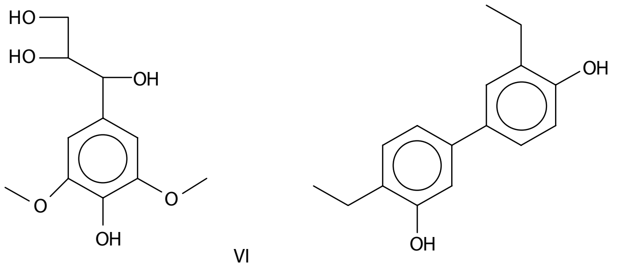
Experimental	Oligomer type
109 Da	Lignin fragment I
139 Da	HMDA+Na^+ Or lignin fragments II and III
179.7 Da	Lignin unit of type (IV)
197.8 Da	Lignin unit of type (V)
205 Da	Lignin fragment I-HMDA, 1 covalent bond
219.7 Da	Lignin unit V + Na^+
235 Da	Lignin fragment II or III-HMDA, 1 covalent bond
255 Da	Lignin fragment II or III(-)(+)HMDA, formation of salt bond
345 Da	HMDA(+)(-)(Lignin fragment III)(-)(+) HMDA, two ionic bonds
389 Da	HMDA(+)(-)Lignin unit IV-HMDA, one ionic bond and one covalent bond
441–442 Da	Lignin unit IV-(HMDA)-Lignin unit IV
461 Da	Lignin unit V-(HMDA)-Lignin unit IV
463 Da	Lignin unit IV-(HMDA)-Lignin unit V + Na^+
501 Da	Lignin unit V-(HMDA)-Lignin unit V + Na^+
539–541 Da	Lignin unit IV-(HMDA)-Lignin unit IV-(HMDA)
555.8 Da	Lignin unit IV-(HMDA)-Lignin unit IV(-)(+)HMDA, 2 covalent, 1 salt bonds
610–611 Da	Lignin unit IV-(HMDA)-Lignin unit IV-Lignin unit IV
685 Da	Lignin unit IV-(HMDA)-(Lignin unit IV)$_2$-HMDA
698–702 Da	Lignin unit IV-(HMDA)-Lignin unit IV-(HMDA)-Lignin unit IV
712 Da	Lignin unit V-(HMDA)-Lignin unit IV-(HMDA)-Lignin unit IV
789 Da	Lignin unit IV-(HMDA)-(Lignin unit IV)$_3$
959 Da	Lignin unit VI(-)(+)HMDA(+)(-)Lignin unit VI (-)(+)HMDA(+)(-)Lignin unit VI

occur, such as the peaks at 389 Da and 555.8 Da. These present two possibilities as illustrated by the chemical species at 389Da



in which the ionic salt bond can be either on the phenolic oxygen or on the alcoholic oxygen of the lignin unit. While it would appear logical that the first possibility be the most likely due to the more definite negative charge on the oxygen, the second structure is surprisingly also possible if one considers the structure of the chemical species at 555.8 Da where both types of structure definitely exist.

It must be pointed out that even higher oligomers exist, as attested by the hardened 180 °C reaction products, these species being of too high a molecular weight to be easily detected by MALDI. The species formed in the other experiments were of the same nature as described above, all the results being reported in the Supplementary Material. The higher molecular weight oligomer found was in the case of the 2 g NaOH-catalyzed at 180 °C, where an oligomer at 959 Da was detected, the species being a trimer of a lignin unit of 244 molecular weight linked through two HMDAs. Two possible structures (VI) of 244 Da molecular weight, both present in the original lignin, can possibly participate to this trimer, namely,



VI

forming an ionic salt bonded oligomer of the type Lignin(-)(+)HMDA(+)(-)Lignin(-)(+)HMDA(+)(-) Lignin (See Supplementary Material).

3.2 Fourier Transform Infrared (FTIR)

Guaiacol + HMDA

In the FTIR spectrum of the reaction product of guaiacol with HMDA one can notice the absence of the band corresponding to O-H stretching bond (cf. Figures 3 and 4). This means that reaction has occurred involving the phenolic hydroxyl group of guaiacol and HMDA. Furthermore, there are two bands at 3353 and 3290 cm^{-1} belonging to the N-H stretching bond in aliphatic primary amines, confirming that reaction has occurred. As the sample was prepared in equimolar amount, there are two amine groups for each hydroxyl group. Thus, at least half of the amine groups (primary amines) are unreacted. The first band at 3353 cm^{-1} is most probably due to the overlap of the band belonging to the aromatic secondary amine and the band corresponding to the first signal for the aliphatic primary

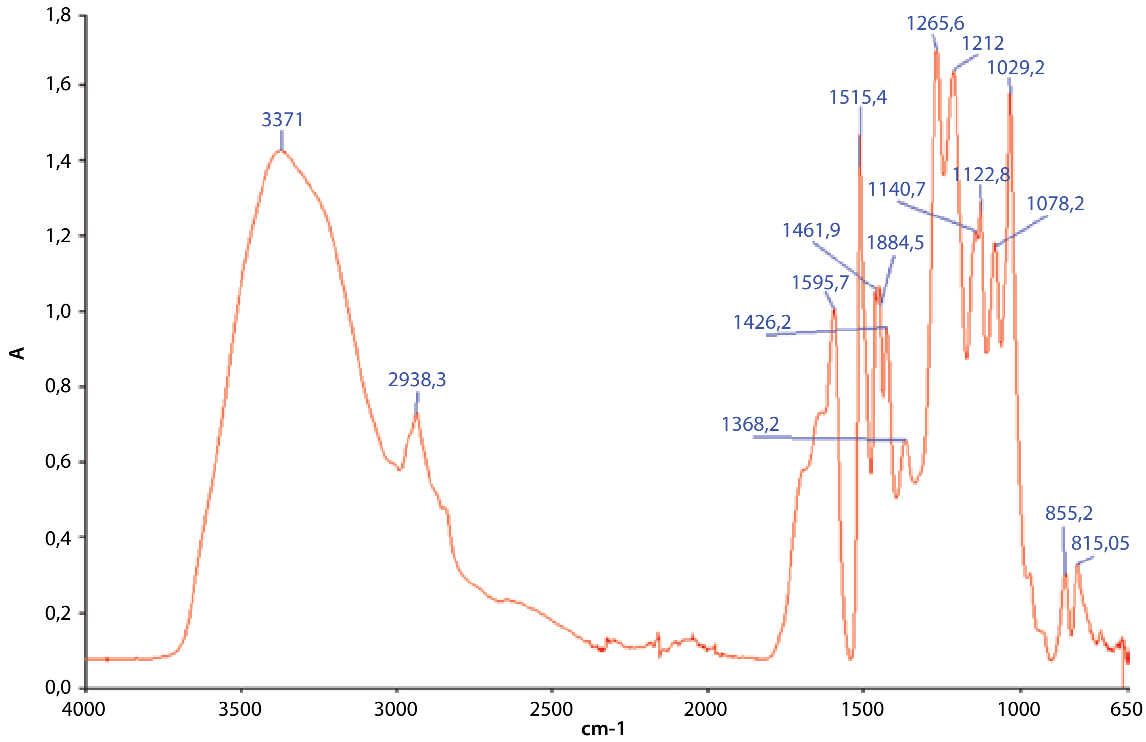


Figure 3 FTIR spectrum of unreacted lignin.

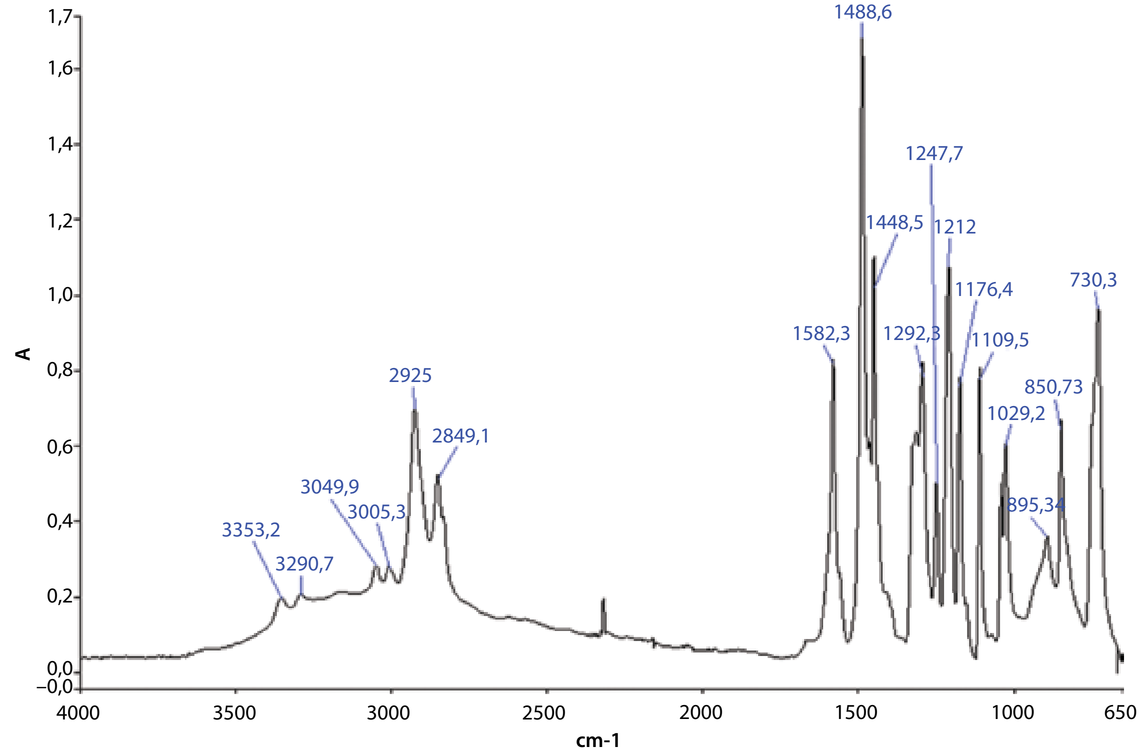


Figure 4 FTIR spectrum of the products obtained by the reaction of guaiacol with HMDA at 100 °C.

amine. The band at 1292 cm^{-1} belongs to the aromatic secondary amine. It means that substitution of the hydroxyl group on the aromatic ring by the amine group has occurred (Table 3, Figure 4).

Lignin + HMDA

The preparation of the samples under a non-inert atmosphere leads to thermal degradation of the lignin, as can be observed in the samples with and without HMDA (Figure 5 and Supplementary Material). The air oxidation effect on the lignin is especially shown in the range 1300–1000 cm^{-1} of the spectra when compared to the non-heated, unreacted lignin [21, 22]. It is also possible to observe the increase in the size of the peak at 1595 cm^{-1} due to the increase in temperature, higher than that for the non-heated, unreacted lignin. This is so because the more elevated is the temperature applied, the more significant is the effect when HMDA is added. According to Kotilainen *et al.* [23] and Li e*t al.* [21] this increase should belong to the air oxidation of a major portion of the lignin content. Conversely, the shoulders next to the peak at 1595 cm^{-1} in the lignin spectrum suggest that there should be a small proportion of structures with a ketone group in the lignin. These shoulders decrease in intensity until practically disappearing. This is true especially when the HMDA is used and when a temperature increase is used.

Table 3 FTIR assignments for the NaOH-catalyzed reaction of guaiacol with HMDA at 100 °C.

Band (cm^{-1})	Assigment
3353+3290	N-H stretching (aromatic secondary and aliphatic primary NH)
3049	C-H stretching (aromatic CH)
3005	C-H stretching (aromatic CH)
2925	C-H stretching (methylene CH asymmetric stretch)
2849	C-H stretching (methylene CH symmetric stretch and O-CH$_3$)
1582	C=C-C stretching (aromatic skeleton)
1488	C=C-C stretching (aromatic skeleton)
1448	C=C-C stretching (aromatic skeleton) with C-H bond in methylene
1292	C-N stretching (aromatic secondary CN)
1212	C-O-Ar (aromatic ether)
1176	C-H in-plane deformation (aromatic ring)
1109	C-H in-plane deformation (aromatic ring)
1029	C-O-C stretching (CO in ether)
895	C-H out-of-plane (aromatic ring)
850	C-H out-of-plane (aromatic ring)
730	Methylene –(CH$_2$)$_n$– rocking (n>3)

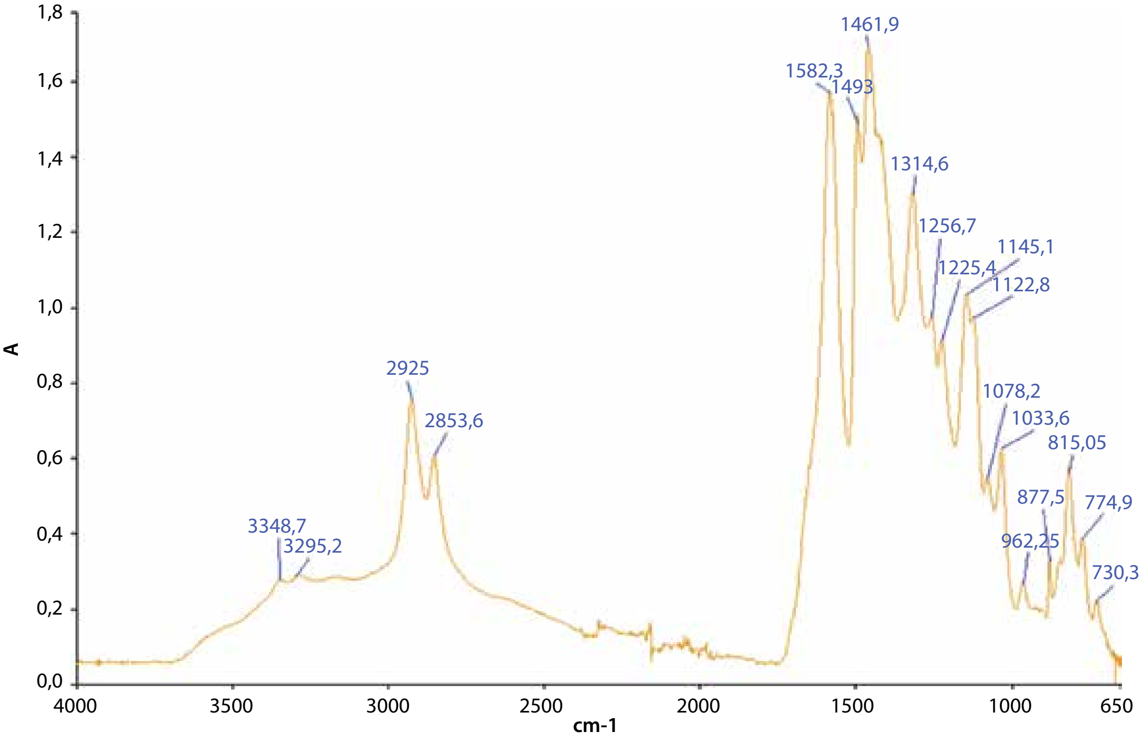


Figure 5 FTIR spectrum of the products obtained by the reaction of lignin with HMDA catalyzed by 2 g NaOH at 180 °C.

Table 4 FTIR assignments for the product of the NaOH-catalyzed reaction of lignin with HMDA at 100 °C and 180 °C [21, 24–27].

Band (cm^{-1})	Assigments	Band location (cm^{-1})		
		Lignin	**Reaction at 100 °C**	**Reaction at 180 °C**
3400		3371	–	–
~3380 + ~3325	N-H stretching (aromatic secondary and aliphatic primary NH)	–	3349+3287	3345+3282
~3130	C-H stretching (aromatic CH)	–	3167	–
2960-2925	C-H stretching (methylene CH asymmetric stretch)	2938	2922	2922
2850-2840	C-H stretching (methylene CH symmetric stretch and O-CH$_3$)	–	2850	2855
~1600	C=C-C stretching (aromatic skeleton) and C=O streching	1595	1590	1581
1513	C=C-C stretching (aromatic skeleton)	1515	1496	
1460	C-H deformation (asymmetric in –CH$_2$ and –CH$_3$)	1461	1460	1460
1445	C=C-C stretching (aromatic skeleton)	1448	-	–
1425	C=C-C stretching (aromatic skeleton) with C-H bond in methylene	1426	1421	–
1370-1365	Aliphatic C-H stretching in CH$_3$ and phenol OH	1368	–	–
1350-1280	C-N stretching (aromatic secondary CN)	–	1304	1318
1265	C-O stretching of guaiacyl unit	1265	1260	1255
~1220	C-OH+C-O-Ar (phenolic OH and ether in syringli and guaiacyl)	1212	1224	1224
1190-1130	C-N stretching (secondary amine CN)	1140	1144	1144
1115	C-H in-plane deformation (aromatic ring)	1122	1126	1122
1075	C-H in-plane deformation (aromatic ring) and C-O deformation in secondary alcohols and aliphatic ethers	1078	1077	1077
1035-1030	C-O-C stretching (CO in ether and aliphatic primary alcohol) and C-H deformation in-plane	1029	1037	1033
900-860	C-H out-of-plane (aromatic ring)	855	921	881
810-750	C-H out-of-plane (aromatic ring)	810	819	814
750-720	Methylene –(CH$_2$)$_n$– rocking (n>3)	–	725	725

This could suggest that there is reaction between keto group and diamine.

Conversely, no major differences appear to occur between the spectra due to either the difference in reaction temperature or the differences in the NaOH catalyst concentration (see Supplementary Material).

In the FTIR spectra of the reaction of lignin with HMDA the characteristic bands due to the amine reaction are several (Table 4, Figure 5). The double band at 3348 and 3295 cm^{-1} belongs to N-H stretching in aliphatic primary amines. Probably, the first band at 3348 cm^{-1} is most likely the overlap of the band belonging to the aromatic secondary amine and the band corresponding to the first signal for the aliphatic primary amine. Again, as for guaiacol, the band corresponding to O-H stretching is absent. The peak at 1515 cm^{-1} in unreacted lignin shifts to 1493-7 cm^{-1} after the reaction. Its size decreases when the temperature and the amount of catalyst increase, until being practically included in the band at 1461 cm^{-1}. The latter increases masking the peak at 1493-7 cm^{-1} for the opposite trend. Both peaks refer to the structure of the aromatic rings, thus these variations could pertain to the reaction of diamine with the aromatic rings of lignin. There are bands at 1305 cm^{-1} for the samples prepared at 100 °C and at 1314 cm^{-1} for samples prepared at 180 °C. These bands belong to the C-N bond in aromatic secondary amines. Thus, this is a further confirmation of the existence of a reaction between the aromatic ring in lignin and the amine. In addition, these bands are absent in the unreacted lignin spectrum. Moreover, the band at 1145 cm^{-1} increases its intensity with respect to the band at 1122–1126 cm^{-1}, while the opposite happens in the spectrum of unreacted lignin. The band at 1145 cm^{-1} belongs to the C-N stretch in aliphatic secondary amines; thus, it means that there is also reaction of substitution by the amine of the alcohol groups in the aliphatic chain of lignin. This confirms what was already inferred by MALDI-TOF where structures in which the alcohol hydroxyl group of the lignin units side chain have also reacted covalently with HMDA to form a secondary amine, as illustrated above for the 398 Da structure. Furthermore, the band at 1145 cm^{-1}, as the band between 1126–1122 cm^{-1}, has practically disappeared in the spectra of lignin + NaOH (see Supplementary Material), indicating that these bands show: (i) the thermal degradation suffered by the lignin, but also (ii) that their increase when HMDA is present occurs due to the interaction between the amine and the lignin.

3.3 CP MAS ^{13}CNMR

Lignin + HMDA

From the NMR spectra the reactions occurring appear to be more advanced when the temperature is higher. The corresponding CP MAS ^{13}C NMR spectrum of lignin + HMDA (case 3, see experimental part) is shown in Figure 6. The superposition of this spectrum with the spectrum of the original unaltered lignin is shown in Figure 7.

In Figure 6, first of all the aliphatic carbon in position alpha to an -NH of the diamine reacted covalently with the lignin must have a shift of 43–44 ppm while the same for an unreacted aliphatic amine should have a calculated shift of 41–42 ppm. Looking at the spectra it can be noticed that the shift is at 43.6 ppm, indicating that the amine has reacted covalently. This is confirmed by other indications. The shift for the C in β of the covalently reacted diamine should be at 30 ppm while the unreacted one is at 37 ppm and the one of the ionic salt formed one should be at 33–34 ppm. The 30 ppm peak is not visible at all as it is covered totally by the strong peak at 27–28 ppm. The 37 ppm peak has disappeared, indicating that for the lignin + HMDA + 2g NaOH at 180 °C the reaction is completed. However, a clear peak does appear at 34.8 ppm, indicating that the formation of the ionic-type salt is also significant in the reaction of the diamine with lignin.

The other clear indication of the formation of covalent and ionic bonds between the amine and the lignin –OH groups is the disappearance of the peak at 147 ppm, indicating that the lignin C4 aromatic carbons carrying the phenolic –OH groups have reacted. The species formed by this reaction are defined by the appearance of two new peaks: one at 151 ppm, characteristic of the covalent bond in which NH has substituted the phenolic –OH, and one at 43.6 ppm, characteristic of a positively charged primary amine as present in the ionic salt. These peaks belong to the

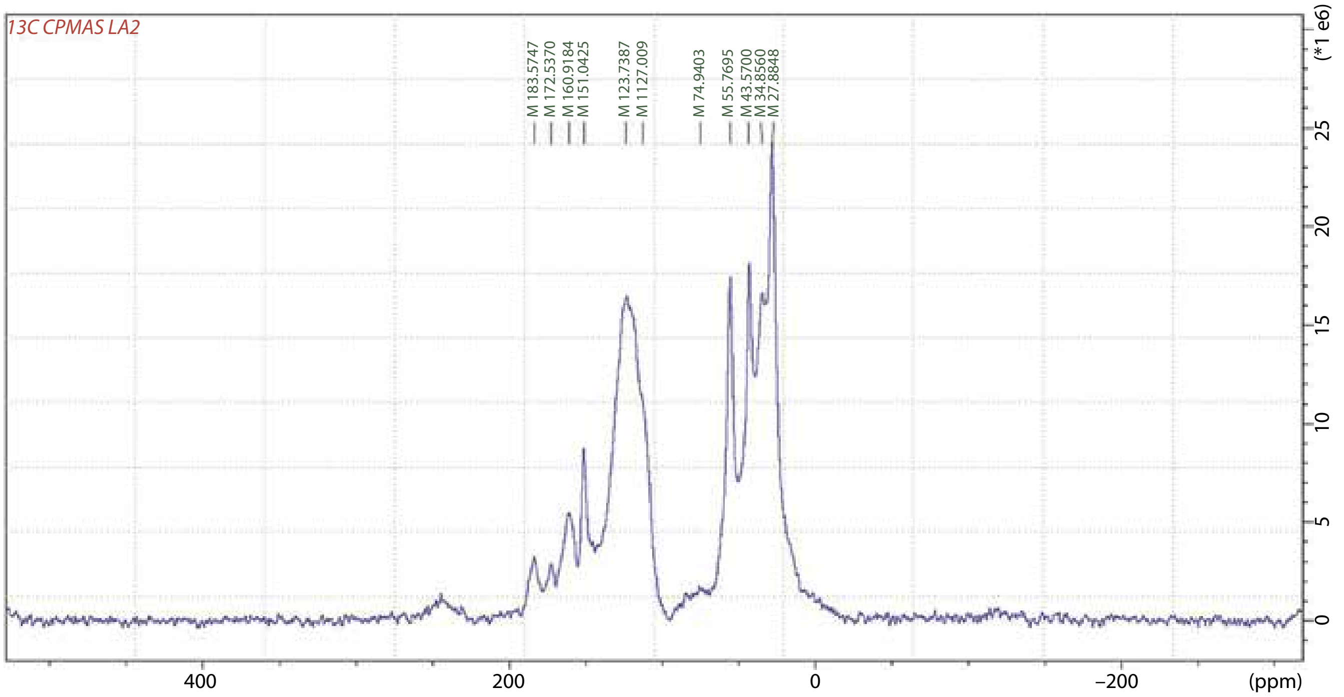


Figure 6 CP MAS ^{13}C NMR spectrum of the products obtained by the reaction of lignin with HMDA catalyzed by 2 g NaOH at 180 °C.

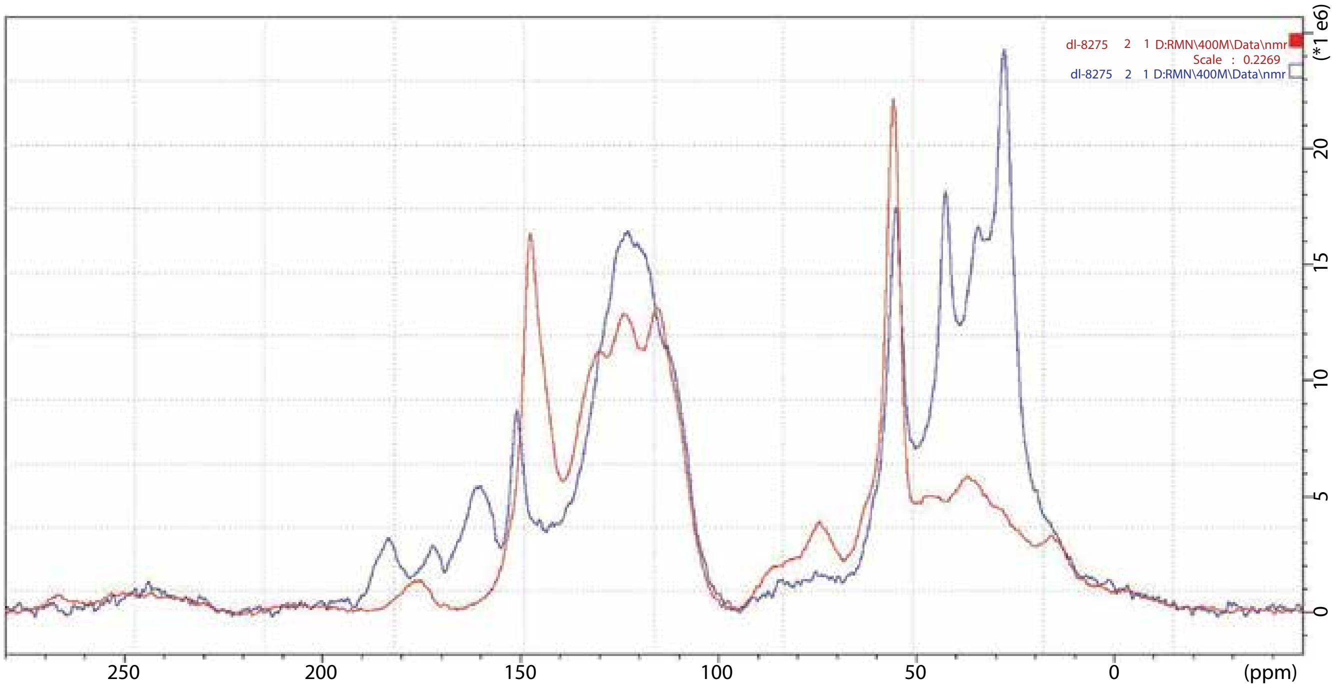


Figure 7 Superposition of the CP MAS ^{13}C NMR spectra of the unreacted lignin and of the products obtained by the reaction of lignin with HMDA catalyzed by 2 g NaOH at 180 °C.

lignin's C4 that has reacted with an amine both covalently and forming a salt. This confirms the interpretation given to the MALDI spectra

The total disappearance in the spectra of the lignin C peaks of the lignin unit's aliphatic side chains at 75 ppm and 86 ppm indicates that even the alcoholic –OH on the lignin side chain has reacted with the amine, either covalently or to form a salt, which is not evident from the spectra.

Finally, the strong peak at 27.8 ppm belongs to diamine linked either covalently or as totally ionized salts to the lignin. The unreacted diamine should present this shift at 33.8 ppm. This may be confused with the 34.8 ppm peak that is instead an indication of the shift for the amine β carbons when ionic bonds are formed.

4 CONCLUSIONS

1. Covalent bonds are formed by reaction between the amine and the aromatic rings of lignin by substitution of the lignin phenolic –OH groups.
2. Covalent bonds are formed by reaction between the amine and the aliphatic side chain of lignin by substitution of the lignin alcohol –OH groups of the lignin side chain.
3. At 180 °C and 100 °C there is a proportion of ionic bonds formed between the amine and the –OH groups both on the aromatic rings and on the aliphatic side chain of lignin units.
4. At 180 °C and to a lesser extent also at 100 °C, lignin reacted with hexamethylene diamine forms hard, condensed solids.

AKNOWLEDGMENTS

The LERMAB is supported by a grant overseen by the French National Research Agency (ANR) as part of the "Investissements d'Avenir" program (ANR-11-LABX-0002-01, Lab of Excellence ARBRE). This paper was also partially funded by King Abdulaziz University (KAU) under grant No (4-130-37-RG). The second and fifth authors acknowledge the support of KAU.

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