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Abstract
Kraft (LN-T-CO_2-2) and wheat straw (CIMV) glyoxalated lignin mixed with mimosa tannin and hexamine as a hardener were used as wood adhesive resins in particleboard fabrication. The adhesive systems proportion used were 40/60 and 50/50 w/w for lignin and tannin, respectively. The gel time test was determined by knowing the polymerization time between the different mixes under the controlled conditions. The results showed a slower polymerization with the kraft lignin/mimosa tannin blending than with the wheat straw lignin/mimosa tannin one. Thermomechanical analyses (TMA) tests were carried out as an indication of the final strength of the adhesive systems revealed by the elasticity modulus (MOE). The MOE results have demonstrated the best mechanical resistance values in 40/60 lignin/mimosa tannin proportion with respectively 3.422 and 3.347 (MPa), for CIMV and LN-T-CO_2-2, and 2.122 (MPa) for 50/50 proportion. Particleboards were prepared and the internal bond (IB) tests were carried out according to the European Standard EN 312. The IB tests confirmed the TMA results. The higher mechanical results of the IB were 0.43 and 0.53 (MPa), for CIMV and LN-T-CO_2-2 lignin in a 40/60 lignin/mimosa tannin proportion. They were classified as interior panel P2 in according with the standard request EN-312. Free-formaldehyde was

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determined through the flask method EN 717-3. Particleboards prepared with these natural adhesive resins registered emissions at least 87 and 75% lower than the commercial UF and MUF adhesive resins. The panels were classified as E0.

1. Introduction

The main stimulus for today's renewed interest in bio-based adhesives is the acute sensitivity of the general public toward anything concerning the environment and its protection [1]. However, use of synthetic resins limits somewhat the environmental attractiveness of such adhesives based on purely natural materials, while the use of some natural materials such as tannins alone is currently limited by the relatively low supply of these materials [1].

Wood biomass primarily consists of hemicellulose, cellulose and lignin with lignin being the second most abundant and important natural product derived from plant material [2]. When plants need to develop mechanical support for their fibrous tissues, they produce lignin, and deposit it as a reinforcing agent. In addition, lignin performs as a sealant and decay retarder, to name only a few of its many service functions to woody plants [3]. Lignin is a polymer synthesized from phenolic compounds of phenylpropane type and occurring under well defined molecular associations [4]. Understanding the structure of lignin has been a great challenge because of: its heterogeneous and complex molecular structure; its deficiency of stereo regularity; and its molecular weight depends of the species of the plant and the sample origin [5]. Lignin is a three-dimensional natural polymer highly ramified with a very large number of functional groups that provide active centres for chemical and biological interactions [6]. The main functional groups in lignins include phenolic hydroxyls, aliphatic hydroxyls, metoxiles, carbonyls, carboxyles and sulfonates [6]. The amount of lignin in wood depends on several factors, including tree species, climate and soil conditions [2]. Typically it represent between 19 and 40% of the dry wood weight [7]. Lignin is a low cost waste product available in relatively large amounts [6]. Different waste lignins produced in pulp mills have made such materials an attractive proposition in converting it to phenolic precursors for phenol-based resins [6], and for the preparation of natural adhesives [8]. The motivation for this development is largely due to the readily available waste from the debarking of wood performed by many panel manufactures, and also due to the relatively high lignin and phenolic extractives available in the bark [6]. Much has been written about and many studies have been made regarding the use of lignin for wood panel adhesives; with some of them based simply on the substitution of phenol in phenol-formaldehyde (PF) resins [9]. Some researchers have demonstrated that natural phenols sources can be an alternative to replacing phenol [10], but always together with some synthetic products or polymeric diphenyl methane

diisocyanate (pMDI) combinations [8, 11] in order to obtain a more reactive and resistant adhesive, or to produce a more reactive phenolic precursor to lignin that can be processed prior to resin synthesis [12, 13].

Formaldehyde emission is an important factor when evaluating the environmental and healthy effects of wood based board materials [14]. This chemical is the most abundant [15] and the most important carbonyl compound in the atmosphere [16]. It is a ubiquitous gas which reaches high concentrations in polluted areas and can have great impact on human health [15]. The main sources of formaldehyde include burning processes, chipboards production and the chemical industry [17]; formaldehyde is one of the two short chain aldehydes emitted by industrial plants, but its origin within these plants remains unclear [18].

To reduce formaldehyde emission, several studies have been carried out. The possibility of using replacement materials for urea-formaldehyde (UF) and PF adhesives has been studied for a long time [19]. One alternative is tannin, which gives very good properties and lower emissions even when substituted in small proportions in normal synthetics resins [20]. However, the hardeners used, can cause formaldehyde emissions even when tannin adhesives are used [21, 22]. This does depend on the wood extractives composition, and, hence, this implies that the different natural raw materials used to prepare adhesives resins must be studied individually.

In this work, the goal was to use mixtures of mimosa tannin and glyoxalated lignin from the kraft and organosolv process (from wheat straw) for the preparation of low cost wood panel adhesives which performed well and did not require any fortification using synthetic resins. These natural resins emit lower levels of free formaldehyde than commercial synthetic resins-adhesives. The adhesive resins formulations we used were between 40 and 50% of kraft and wheat straw glyoxalated lignin and between 60 and 50% of mimosa tannin in the adhesive formulation.

2. Experimental

2.1. Lignin and Tannin Preparation

Wheat straw lignin was obtained industrially as a by-product of pulp and paper manufacture using an acetic acid based organosolv process [23]. This lignin was supplied by the industrial manufacturer, CIMV (Compagnie Industrielle de la Matiere Vegetale, Reims Factory, France). A second type of lignin was obtained as a by-product of the production of pulp and paper (black liquor ligni) from a factory at Tembec Tarascon (Forêt Cellulose Bois-Construction Ameublement, France, FCBA). The lignin was precipitated using CO_2 and then washed several times in acid until at pH 2–4. This second type of lignin, called LN-T-CO_2-2, has a lower molecular weight because of the rupturing of the polymers which takes place in the saw mill process. This lignin often has an ortho carbon ring which is not occupied and can react with formaldehyde [10].

Both lignins were subjected to glyoxalation according to the procedure described by El Mansouri [8]. A quantity of 295 parts by mass of this lignin powder (96% solid) was slowly added to 477 parts of water while sodium hydroxide solution (30%) was added from time to time keeping the pH of the solution between 12 and 12.5. This, together with vigorous stirring with an overhead stirrer facilitated the dissolution of the lignin powder. A total of 141 parts by mass of 30% sodium hydroxide aqueous solution were added.

A 2-liter flat bottom flask equipped with a condenser, a thermometer and a magnetic stirrer bar was charged with the above solution and heated to 58°C. A quantity of 17.5 parts by mass glyoxal (40% in water) were added and the lignin solution was then continuously stirred with a magnetic stirrer/hot plate for 8 h. The final pHs of the glyoxalated lignins were 6.6 and 12.3 for CIMV and LN-T-CO$_2$-2, respectively.

Glyoxal was used because it is an aldehyde that has been tested in lignin [8, 24], tannin [25] and other adhesives, such as soy [1, 26] for use in wood panels such as particleboards. Glyoxal is a non-toxic (LD50 rat $\geqslant$ 2960 mg/kg; LD50 mouse $\geqslant$ 1280 mg/kg) [27], non-volatile aldehyde but less reactive than formaldehyde which is toxic (LD50 rat $\geqslant$ 100 mg/kg; LD50 mouse $\geqslant$ 42 mg/kg) [28].

Mimosa tannin extract (origin: Tanzania. Supplied by: Silva, S. Michele Mondovi', Italy) of Stiasny value of 92.2 [29, 30] was used. The tannin solution (45% concentration) in water was prepared and its pH adjusted to 10 with a 33% aqueous solution of NaOH. A high pH (pH: 10) was used as the hardener performed best best under such conditions [31, 32].

The glue-mix was composed of: the tannin extract solution to which was added a hardener of 6% hexamethylenetetramine (calculated on the tannin solids basis) as a 30% hexamine solution in water, and the glyoxalated lignin solution. The proportions of tannin solids/glyoxalated lignin were 60:40 and 50:50 w/w (%).The initial lignin glyoxalated and tannin solutions conditions are shown in Table 1 and the adhesives specifications and the viscosity are shown in the Table 2.

2.2. Gel Time

Gelation is defined as the point at which the resin ceases to be a viscous liquid and become a soft, elastic, rubbery solid [33, 34]. Triplicate samples from each adhesive resins system were prepared. Gel time tests were conducted at 100°C. An amount

Table 1.

Initial lignin glyoxalated and tannin solutions conditions

Solution	Total solids percentage (%)	Viscosity (spin 27, 20 rpm, 25°C) (cp)	pH
LN-T-CO$_2$-2: Tarascon lignin	35.28	362	12.3
CIMV: Wheat straw lignin	31.42	100	6.6
MIMOSA: Mimosa tannin	45	1100	10

Table 2.
Adhesives specifications

Formulation	Specifications	Viscosity (spin 27, 20 rpm, 25°C) (cp)
40%LN-T-CO$_2$/60%MIM	40% lignin LN-T-CO$_2$-2/60% mimosa tannin	3100
40%CIMV/60%MIM	40% lignin CIMV/60% mimosa tannin	613
50%CIMV/50%MIM	50% lignin CIMV/50% mimosa tannin	325

of 5 g of each mixture was weighed in a glass test tube, and then placed in a boiling water bath. The wire spring was manually moved rapidly upward and downward, and the time for gelation was measure using a stopwatch.

2.3. Thermomechanical Analysis (TMA)

The hardening reaction of a single resin system or mixtures was evaluated by TMA, by monitoring the rigidity of a bonded wood joint as a function of temperature. In this way the, glue-mixtures of glyoxalated lignin and tannin/hexamine were analysed by TMA. All experiments were conducted under the same conditions: heating rate = 10°C/min, 30 mg resin, in the temperature range 25–250°C.

Triplicate samples of beech wood, and of two beech wood plies each 0.6 mm thick bonded with each adhesive system, for sample dimensions of 21 mm × 5 mm × 1.2 mm were used in a three-point bending mode on a span of 18 mm. A force varying continuously between 0.1 N, 0.5 N and back to 0.1 N was applied on the specimens with each force cycle of 12 s (6 s/6 s). The classical mechanics relation between force and deflection $E = [L^3/(4bh^3)][\Delta F/(\Delta f)]$ (where L is the sample length, b and h are the sample width and thickness, ΔF is the variation of the force applied and Δf is the deflection obtained) was applied in calculating the the modulus of elasticity (MOE) E for each case tested. The thermomechanical analyzer used was a Mettler Toledo TMA40. The software used for the data treatment was STARe. Deflection curves that allow modulus of elasticity (MOE) to be determination were obtained in the three-point bending TMA mode. The MOE of the wood joints bonded with different resin systems gave a good indication of the final strength of the adhesive system tested.

2.4. Wood Panels Manufacture and Internal Bond

One-layer laboratory particleboards of dimensions 350 × 300 × 14 mm were prepared using a mixture of core particles of beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) woods. The wood particles, before resin addition, had a moisture content of 2%. The resin solids loading on the dry wood were maintained at 10% of the total mixture of glyoxalated lignin and tannin/hexamine. The operational conditions were composed of three stages of different pressures applied to the panel: 35 kg/cm^2, 12 kg/cm^2 and 7 kg/cm^2. The total press time was maintained at 7.5 min, and the press temperature was 195°C. The panels, after sandpapering the

surfaces, were cut out in samples of $50 \times 50 \times 13$ mm. All the particleboards were tested for dry internal bond (IB) strength, and after two hours in boiling water, were tested dry [35–37].

2.5. CP-MAS ^{13}C NMR Spectroscopy

The glyoxalated organosolv (CIMV) and kraft lignin resins in the solid state were prepared for NMR analysis. The hardened lignin resins were analyzed by solid state CP-MAS ^{13}C NMR. Spectra were obtained on a Bruker AVANCE II 400 MHz spectrometer at a frequency of 100.6 MHz and a sample spin of 12 kHz, using a recycling delay time of 1 s and a contact time of 1 ms. The number of transients was about 15 000, and the decoupling field was set at 78 kHz. Chemical shifts were determined relative to tetramethyl silane (TMS) used as control sample. The spectra were accurate to 1 ppm. The spectra were recorded with suppression of spinning side bands.

2.6. MALDI-TOF

Since its introduction by Karas and Hillenkamp in 1987 [38], matrix-assisted laser desorption/ionization (MALDI) mass spectrometry has greatly expanded the use of mass spectrometry towards large molecules and has proved to be a powerful method for the characterization of both synthetic and natural polymers [39–44]. Fragmentation of analyte molecules upon laser irradiation can be substantially reduced by embedding them in a light absorbing matrix. As a result intact analyte molecules are desorbed and ionized along with the matrix and can be analysed in a mass spectrometer. This soft ionization technique is mostly combined with time-of-flight (TOF) mass analysers. In this way the TOF-MS provides a complete mass spectrum of each event, with its virtually unlimited mass range, for a small amount of analyte and at a e relatively low cost for the equipment.

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

For the sample preparation, the lignin water solution samples were dissolved in acetone (4 mg/ml, 50/50 vol. %) and mixed with an acetone solution (10 mg/ml in acetone) of the matrix which was 2,5-dihydroxy benzoic acid. For the enhancement of ion formation, NaCl was added to the matrix (10 mg/ml in water). The solutions of the sample and the matrix were mixed in the proportion 3 parts matrix solution + 3 parts sample solution + 1 part NaCl solution, and 0.5 to 1 µl of the resulting solution mixture were placed on the MALDI target. After evaporation of the solvent the MALDI target was introduced into the spectrometer. The dry droplet sample preparation method was used.

2.7. Free-Formaldehyde

Over the past years, several approaches to produce wood-based panels with low formaldehyde emission using these wood adhesives have been developed and several different methods have been used [19]. Formaldehyde emission is an important factor in the evaluation of the environmental, health and comfort issues concerning wood-based board materials [14, 45]. Formaldehyde is a gas at room temperature. It can be transformed into paraformaldehyde through polymerization and readily form methylenglycol through dissolution in water [46].

In this work, the free-formaldehyde was determined by the flask method [47]. This method developed by Roffael, is based on storing one to three board pieces with a total mass of about 20 g in a close polyethylene or glass bottle [48], with 50 ml distilled water and under a constant temperature of 40°C for 180 min. The formaldehyde released by the test samples during this period of time was absorbed by the water. Then, the formaldehyde content in water photo metrically was determined by the acetilcetone method (Hantzsch's reaction) at 412 nm.

A total of three natural adhesives from lignin/tannin base, and two synthetic (UF and MUF) adhesive resins were analyzed. The goal was to compare the formaldehyde emissions of theses resins, taking the synthetic resins as a reference.

3. Results and Discussion

3.1. Gel Time

The gel time results are showed in Table 3. The gel times reported for the natural resins was always higher than for the traditional urea formaldehyde adhesives which registered a value of 127 s. Comparing the same proportions in each adhesive system to 40/60 (w/w), the CIMV/MIM tannin formulation was more reactive than the LN-T-CO_2-2/MIM, with a gel time of 507 and 700 s, respectively. The blended system with a higher CIMV proportion (50%), gave a gel time of 480 s.

In general the gel time measured for the CIMV/MIM mixture was shorter because the CIMV lignin had a lower pH than the LN-T-CO_2-2 lignin. The mixture of CIMV lignin (pH = 6) with mimosa tannin solution and hexamine (pH = 10) reduced the final adhesive system pH. The hexamine is a monoprotic base and to react it has first of all to decompose. This decomposition is more difficult at high pHs,

Table 3.
Gel time results

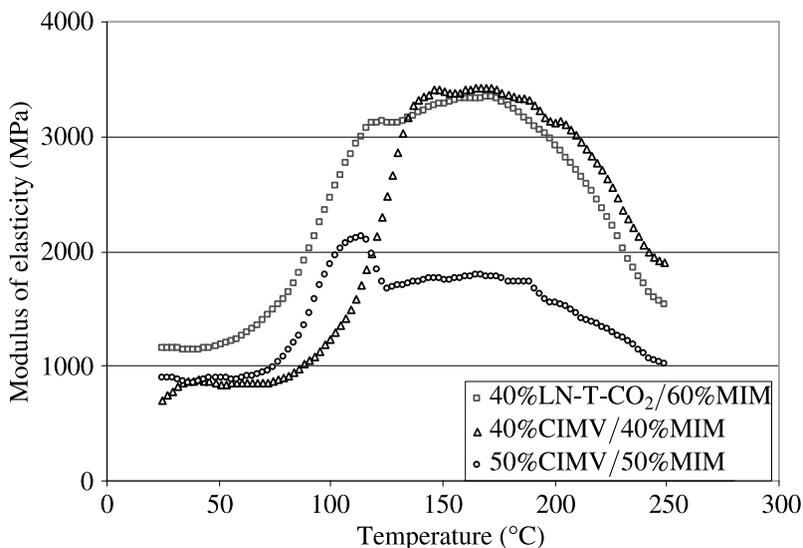| Adhesive formulations	Gel time (min/s)
40%LN-T-CO_2/60%MIM	11′40″
40%CIMV/60%MIM	8′27″
50%CIMV/50%MIM	8′
Reference: Urea formaldehyde	2′07″

Figure 1. Thermomecanical resistance.

thus, it is slower and, as a consequence, there is time availability for the reactive species to cross-link with the tannin. The hardening time of the mimosa tannin with hexamine lengthened with increasing pH [49, 50]. In our case, the system pH decreased as a consequence of the lower CIMV glyoxalated lignin pH. This condition made the gel times shorter than if the kraft glyoxalated lignin had been used.

3.2. Thermomechanical Analysis TMA

The thermomechanical analysis (TMA) results are shown in Fig. 1. The 40/60 CIMV/MIM and the LN-T-CO$_2$-2/MIM formulations showed very similar MOE values. There were no significant difference between the two cases. The maximum MOE values were 3422 and 3347 (MPa), for the CIMV/MIM and LN-T-CO$_2$-2/MIM blends, respectively. In the second case, the polymerization starts at a lower temperature (around 60°C) than it does in the first case (around 80°C) before reaching a maximum value. The results were the lowest for the 50/50 CIMV/MIM blend, with a MOE of 2122 (MPa). This was expected because the mimosa tannin was more reactive than the lignin and in this case there was a lower tannin proportion in the adhesive system blend.

3.3. Internal Bond Strength (IB) and Swelling

TMA tests results were confirmed by the internal bond strength results (Table 4). High values were obtained for the formulations containing 40% lignin. All the formulations tested achieved the standard requirements.

The IB results obtained in this work showed that the best mechanical resistance values were found for the kraft lignin LN-T-CO$_2$/MIM adhesive 40/60 (w/w) with a value of 0.53 MPa, while the wheat straw lignin CIMV/MIM adhesive, with the

Table 4.
Internal bond and swelling results

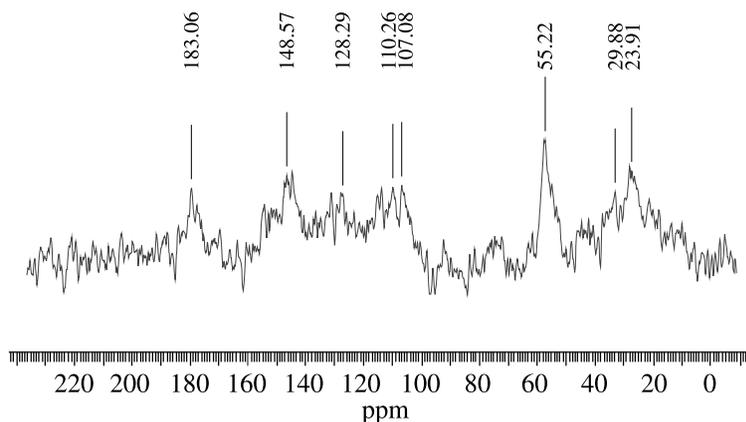| Adhesives	Density (kg/m^3)	IB strength dry (MPa)
40%LN-T-CO$_2$/60%MIM	712	0.53 ± 0.10
40%CIMV/60%MIM	708	0.43 ± 0.06
50%CIMV/50%MIM	707	0.39 ± 0.04

Figure 2. ^{13}C NMR lignin CIMV pH 6.6.

same proportions, had a value of 0.43 MPa. An increase of the wheat straw lignin proportions — to 50/50 (w/w) — resulted in a decreased value of 0.39 MPa.

A comparison of our CIMV/MIM 50/50 (w/w) results with those obtained by Mansouri [51] for the same proportions, showed that our results were lower. The reason is twofold; firstly, our glyoxalated lignin pH was much lower and secondly this condition makes the final mimosa tannin pH low, resulting in a lower mechanical resistance [32]. On the another hand the ^{13}C NMR results showed the presence of unreacted lignin in the wheat straw.

None of these formulations was able to resist the drastic conditions of the boiling water, and all formulations showed very high water absorption and swelling. The high pH level would most likely increase the water absorption and, hence, the swelling [32]. Therefore, and in accordance with the IB results, the particleboards prepared with kraft and wheat straw lignin were classified as boards type P2.

3.4. CP-MAS ^{13}C NMR Spectroscopy

The ^{13}C NMR results for the glyoxalated lignins showed some functional groups that confirmed the lignin–glyoxal reaction. The results for the CIMV and LN-T-CO$_2$-2 do show some similarities and some differences which could explain the mechanical results (Figs 2 and 3). In both cases bands at 183–182, 148–151, 125–
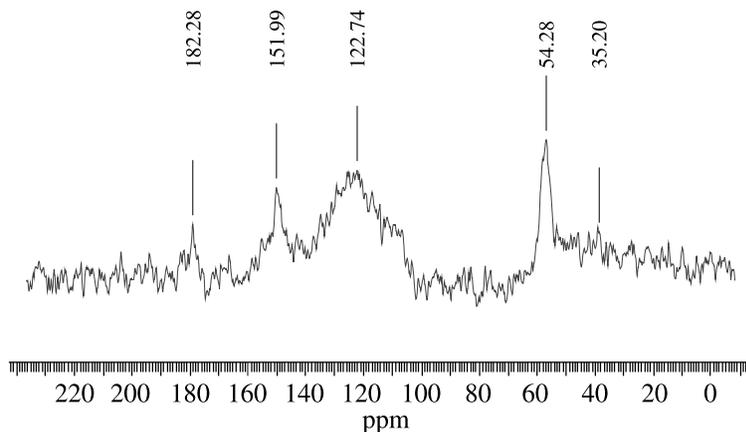
Figure 3. ^{13}C NMR lignin LN-T-CO$_2$-2.

135 and 54–55 ppm were present in the lignins. The 183–181 ppm peaks belongs to the aromatics quinones generated by oxidation in the site of phenolic hydroxyl groups of the lignin. The peaks between 148–151 ppm relate to the aromatic carbons which are linked to phenolic hydroxyl groups. The results indicate that the reactivity of the aromatic nuclei of lignin are slightly greater in the case of the LN-T-CO$_2$-2 lignin than it is for the CIMV lignin. The 125–135 ppm peaks indicate ArC-C linkages which form from the methylene and methylene ether bridges. Between 54 and 55 ppm the peaks are due to –OCH$_3$ groups on the aromatic nuclei of lignin which are coupled with the peaks at 148–151 ppm.

There is no peak at 120 ppm which is an indication that the ArC-H has disappeared indicating an extensive introduction of substituted groups on the aromatic rings of the phenyl propane lignin units [9].

In the LN-T-CO$_2$-2 there is no peak at 105–115 ppm as there is in the CIMV case; this implies that in the second case there is unreacted lignin present at *ortho* and *para* sites on the aromatic lignin [9, 52]. This could be a consequence of the low pH in the CIMV glyoxalated lignin. Equally noticeable is the presence of the band between 54.2–55.2 ppm characteristic of the metoxy groups (–OCH$_3$) on the aromatic nuclei of lignin coupled with of the 148.5–151.9 ppm band of aromatic carbons linked to phenolic hydroxyl groups due the reactivity of the aromatic nuclei of lignin.

The peak at 181.8 ppm is also of interest. This band belongs to aromatic quinones generated by oxidation on the site of phenolic hydroxyl group of lignin.

Results for the CIMV lignin shows a peak at 29.88 ppm; this is due to –CH– groups of the glyoxylene bridges linking the two aromatic rings in a structure given in Fig. 4. There is an absence of a peak at 84.5 ppm in both lignins; this implies that there is no formaldehyde in the glyoxalated lignin [9].
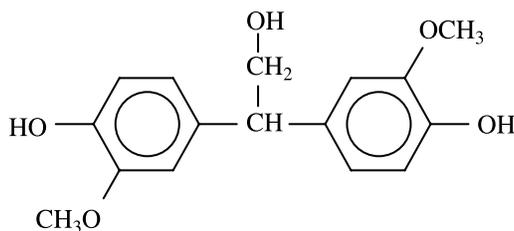
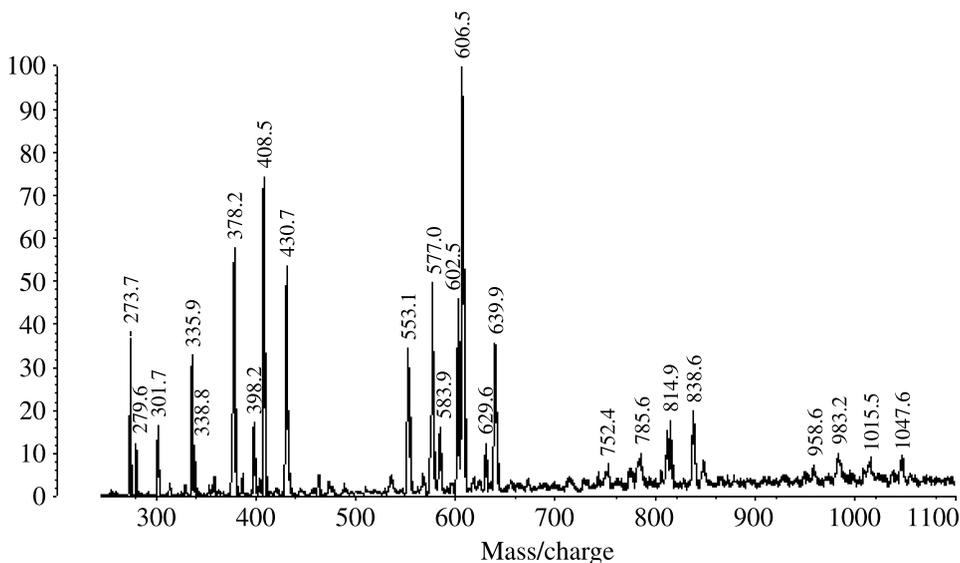**Figure 4.** Glyoxylene bridge linking the two aromatic rings in structure.

Figure 5. MALDI-TOF glyoxalated lignin LN-T-CO_2-2.

3.5. *MALDI-TOF Analysis*

The glyoxalated lignin showed internal rearrangements of the lignin itself and evidence of glyoxal reactions (Figs 5 and 6). The interpretation assignments of the compounds involved in the glyoxalated lignin are indicated as G for guaiacyl units, S for siringyl units and H for phenolic units (Tables 5 and 6). In Fig. 7, H_F, G_F and S_F fractions appear, indicating demethylation of methoxy groups as well as cleavage of the aliphatic C3 chain from aromatic ring. The $-\beta 1-$ linked dimmers, in which one of three fractions H_F, G_F and S_F (Fig. 6) are linked to an uncleaved lignin, were observed. This type of rearrangement is well known in lignin chemistry and is one of the main mechanisms for the cleavage and recombination of such polymers [7]. As regards the lignin alone, the heat treatment also leads to further types of recombination by autocondensation. Thus, compounds such as G-G-G-G, a tretramer at 750 Da appears to have been formed by this route [52].

As a consequence of glyoxalation, a number of different condensates seem to have been formed. The simple phenol represented by structures H_F, G_F and S_F have
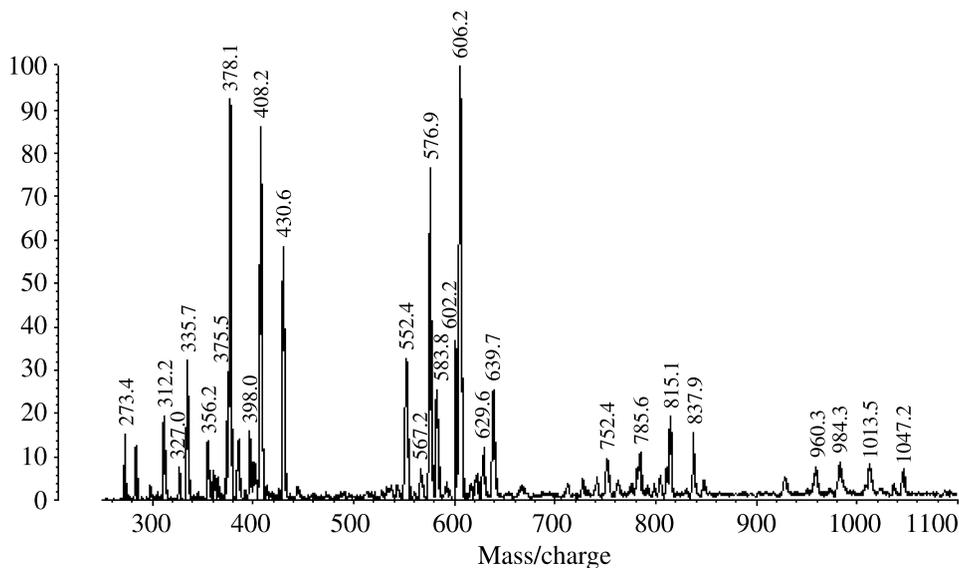
Figure 6. MALDI-TOF glyoxalated lignin CIMV pH 6.6.

easily reacted with the aldehyde to give a variety of different compounds. Some of these compounds still contained a reactive hydroxyglyoxyl group which appeared to have been formed in abundant proportions. Oligomers were also present; these included the hydroxyglyoxylated trimers and tetramers in different proportions (Tables 5 and 6). Similar oligomers were found in both lignins.

3.6. Formaldehyde Emissions

The formaldehyde emission test showed a great difference between the natural and the traditional commercial synthetic adhesives resins used in this work (Fig. 8). These results were different from some of the results reported in other publications. There are several reasons for this but in all cases the natural adhesives showed lower values of released formaldehyde. Different methods and different adhesive resins systems formulations have been studied. For example, Sukhbaatar *et al.* [10] determined free formaldehyde in phenol-formaldehyde adhesive resins in which a part of phenol had been replaced by lignin. Their results indicated that the amounts of formaldehyde used in resins synthesis were not in excess and no formaldehyde odour problem would result in using the resins in board manufacturing, but in this case, the test was made directly on the resins and not in the panels prepared with lignin phenol-formaldehyde resin.

Another example, this time from the work of Mansouri *et al.* [51]; they reported zero emission by the dessicator method using glyoxalated lignin and tannin blend as adhesives. Also Pichelin *et al.* [32] did not find formaldehyde emission in panels bond with mimosa tannin adhesives using hexamine. However, Ballerini *et al.* [25]

Table 5.
LN-T-CO_2-2 glyoxalated lignin interpretation

Experimental M+Na+. (Da)	Calc.		Peak intensity (%)	Interpretation
	M+NA	M+NA+ (PM23)		
273.7	248	271	38	G-H$_F$
279.6	261	284	12	H-G$_F$
301.7	274	297	16	H-G$_F$ or/and G-H$_F$
335.9	313	336	32	H-G$_F$ (minus a CH$_3$) = H-H$_F$ -OH
338.8	318	341	8	G-glyox-H$_F$
378.2	348	371	57	S-glyox-H$_F$
398.2	373	396	16	S-H$_F$ –OH and/or HO-H$_F$ -H–glyox-OH[**]
408.5	382	405	73	H-H$_F$-glyox-H$_F$
430.7	406	429	53	G-glyox-G and/or S-glyox-S$_F$, and/or G-βO4-S, and/or G-βO4-S
553.1	529	552	34	G-glyox-G-G$_F$ and/or G-S-glyox-S$_F$
577	551	574	50	G-G-glyox-H
583.9	566	589	18	H$_F$-G-glyox-H-H$_F$
602.5	579	602	46	G-S-H$_F$ –OH and/or HO-H$_F$ –H-G–glyox-OH[**]
606.5	584	607	100	G-G-glyox-G
629.6	607	630	12	S-G-glyox-H
639.9	614	637	32	G-G-glox-S or S-S-glox-H
752.4	728	751	8	G-G-G-G and/or S$_F$ -S-S-S$_F$
785.6	764	787	9	G-G-glyox-G-G or S-H-glyox- H-S or G-G-glyox-G-G
814.9	791	814	16	[**](HO-glyox-)G-H-S-H$_F$ –OH and/or HO-H$_F$ –H-H-G(–glyox-OH)$_2$[**]
838.6	808	831	20	S-H-glyox-H-S-glyox
958.6	928	951	6	S-S-glyox-S-S-glyox
983.2	962	985	6	G-G-glyox-G-G-glyox-S$_F$
1015.5	988	1011	10	S-G-glyox-G-S-glyox-S$_F$
1047.6	1022	1045	6	S-G-glyox-G-S-glyox-S$_F$

found very small emissions with glyoxal in radiate pine tannin adhesive using the same method.

In this work our comparison of particleboards prepared with UF and with the natural adhesives, showed at least seven times higher emissions of formaldehyde than did the particleboards prepared with lignin and tannin. The melamine-urea-formaldehyde (MUF) particleboards registered more than four times higher formaldehyde emissions than did the natural adhesives. The highest values found for the natural adhesive blends was 1.12 mg formol/kg panel in the case of CIMV/MIM (40/60 (w/w)) and the lowest value was 0.92 mg formol/kg panel for LN-T-CO_2/MIM (40/60 (w/w)). All the results with natural adhesive resins obtained in this work could be classified as E0 panels [14]. The formaldehyde

Table 6.
CIMV glyoxalated lignin interpretation

Experimental M+Na+. (Da)	Calc.		Peak intensity (%)	Interpretation
	M+NA	M+NA+ (PM23)		
273.7	248	271	38	G-H_F
312.2	290	313	20	G_F -glyox-G_F and/or 327 (minus1x-CH_3)
327	304	327	6	H-S_F and/or G-G_F and/or S-H_F, and/or H-β1-S, and/or G-β1-G, and/or S-β1-H
335.7	313	336	32	H-G_F (minus a CH_3) = H-H_F –OH
356.2	334	357	14	G-S_F
375.5	350	373	28	S_F -glyox-S_F
378.2	348	371	57	S-glyox-H_F
398	373	396	15	S-H_F –OH and/or HO-H_F -H–glyox-OH[**]
408.2	382	405	85	H-H_F-glyox-H_F
430.6	406	429	58	G-glyox-G and/or S-glyox-S_F, and/or G-βO4-S, and/or G-βO4-S
552.4	529	552	32	G-glyox-G-G_F and/or G-S-glyox-S_F
567.2	540	563	6	G-G-G
576.9	551	574	76	G-G-glyox-H
583.8	566	589	24	H_F-G-glyox-H-H_F
602.2	579	602	46	G-S-H_F –OH and/or HO-H_F –H-G–glyox-OH[**]
606.2	584	607	100	G-G-glyox-G
629.6	607	630	11	S-G-glyox-H
639.7	614	637	25	G-G-glox-S or S-S-glox-H
752.4	728	751	10	G-G-G-G and/or S_F -S-S-S_F
785.6	764	787	11	G-G-glyox-G-G or S-H-glyox-H-S or G-G-glyox-G-G
815.1	791	814	18	[**](HO-glyox-)G-H-S-H_F –OH and/or HO-H_F –H-H-G(–glyox-OH)$_2$[**]
837.9	808	831	14	S-H-glyox-H-S-glyox
960.3	928	951	6	S-S-glyox-S-S-glyox
984.3	962	985	6	G-G-glyox-G-G-glyox-S_F
1013.5	988	1011	6	G-G-glyox-G-G-glyox-G
1047.2	1022	1045	6	S-G-glyox-G-S-glyox-S_F

present in the particleboards prepared with lignin and tannin could be the natural formaldehyde from the wood. The ^{13}C NMR results at 84.5 ppm peak showed no formaldehyde emission from glyoxalated lignins. Furthermore, the hexamine used as the hardener for the tannins has been accepted by JIS A5908 as not being a formaldehyde source in the presence of polyflavonoid condensed tannins.

We found similar results to that found by Eom *et al.* [19], in their study of natural adhesives as used in particleboard preparation. Although different methods were used in the evaluations, the natural adhesives always showed lower formalde-
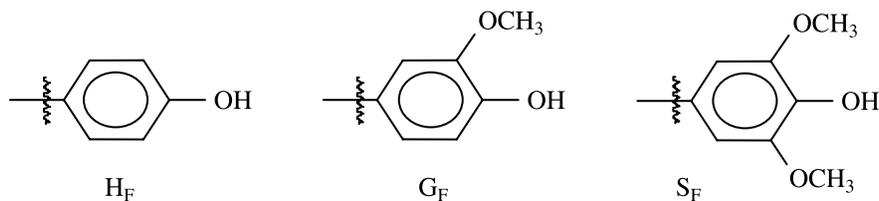
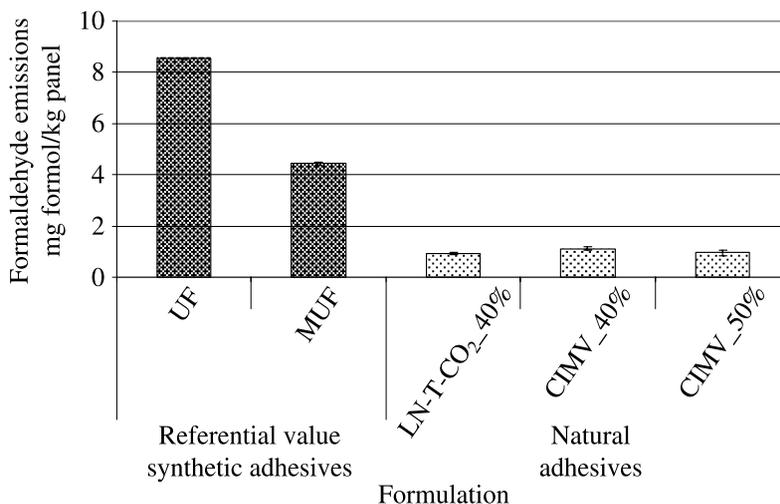**Figure 7.** H_F, G_F and S_F fractions appear.

Figure 8. Formaldehyde emissions by EN-717-3 standard method.

hyde emission than did the commercial synthetics adhesives such as as UF and melamine-formaldehyde (MF) resins. The formaldehyde presence in the natural material could be explained as being due to the natural emissions of volatile organics compounds which starts in the forest [53]. Wood is a natural source of formaldehyde and is due the lignin decomposition [48]. These emissions are low as it has been demonstrated by some researchers [48]. The natural oxidation of terpene compounds produces simple aldehydes such as formaldehyde [53], which are then directly released into the atmosphere. There are a great many direct and indirect factors involved in formaldehyde emissions and in general the emission of volatile organic compounds (VOCs) have multiple atmospheric implications [18].

Finally, it is worth mentioning that according to work by Schäfer and Roffael [54] extractives play a dual role — on the one hand they release formaldehyde and on the other hand they — the extractives — react with formaldehyde and, hence, act as formaldehyde scavengers. The dependance of the wood extractives on chemical composition, pH, and this type of scavenger behaviour, make it necessary for each type of natural raw material to be studied individually.

4. Conclusions

1. The ^{13}C NMR and MALDI-TOF results in this work showed that the kraft and wheat straw organosolv lignin showed very similar chemical structures. Both showed similar internal rearrangements and glyoxal reactions. The simple phenol represented by structures H_F, G_F and S_F had readily reacted with the aldehyde to give a variety of different compounds, resulting in oligomers such as the hydroxyglyoxylated trimers and tetramers which were present in different proportions.

2. The different formulations of lignin and mimosa tannin studied in this work have performed well and could readily be used for interior-grade applications in accordance with the standard EN 312 directive. The internal bonds obtained were 0.53 MPa for LN-T-CO_2/MIM at 40/60 (w/w) and 0.43 MPa for CIMV/MIM in the same proportions. At 50/50 proportion the internal bond decreased to 0.39 MPa. All of samples tested were within the specifications necessary for a P2 grade (EN 312). That implies that the lignin from mills and the wheat straw used here with mimosa tannin have a great potential to be used in producing natural adhesives for the panel industry. The different IB results found in this work, between the kraft and wheat straw lignin was due to a proportion of wheat straw lignin not react with the glyoxal under low pH conditions as did the kraft lignin. This wasc shown by the MALDI-TOF results.

3. The formaldehyde released from boards prepared with the different natural adhesives must each be studied. In our case, a great difference between the natural and the traditional commercial synthetic adhesives resins was found. The free-formaldehyde emissions from particleboards prepared with lignin and tannin were very low. According to the flask method (EN 717-3), the particleboards could be classified as E0 with a formaldehyde release of between 0.92–1.12 mg formol/kg panel. The free-formaldehyde found could be due to the formaldehyde released from wood because the ^{13}C NMR at 84.5 ppm peak showed no formaldehyde emission from glyoxalated lignins and the hexamine using with tannin has been accepted by JIS A5908 as not being a formaldehyde source in presence of polyflavonoid condensed tannins.

References

1. A. Pizzi, *J. Adhesion Sci. Technol.* **20**, 829–846 (2006).

2. A. Effendi, H. Gerhauser and A. V. Bridgwater, *Renewable and Sustainable Energy Reviews* **12**, 2092–2116 (2008).

3. H. Lei, Ecole Nationale Supérieure des Technologies et Industries du Bois, Université Henri Poincaré-Nancy 1, Thesis in cosupervision China — France to obtain the degree of Doctor (2009).

4. C. Jolivet, B. Guillet, M. Karroum, F. Andreux, M. Bernoux and D. Arrouays, *C. R. Acad. Sci. Paris, Sciences de la Terre et des planètes/Earth and Planetary Sciences* **333**, 651–657 (2001).

5. F. Ysambertt, T. González, N. Delgado, B. Bravo, G. Chávez, A. Cáceres, N. Márquez and J. Bullón, *Revista cubana de química* (2009).

6. N.-E. El Mansouri, Memoria presentada para optar el titulo de Doctor en Ingenieria Quimica y de Procesos, Terragona, España (2006).
7. D. Fengel and G. Wegener, *Wood: Chemistry, Ultrastructure, Reactions*. Walter de Gruyter, Berlin, Germany (1983).
8. N.-E. El Mansouri, A. Pizzi and J. Salvado, *Holz Roh Werkst.* **65**, 65–70 (2007).
9. A. Pizzi, *Advanced Wood Adhesives Technology*. Dekker, New York (1994).
10. B. Sykhbaartar, P. H. Steele and M. G. Kim, *Bioresources* **4** (2), 789–804 (2009).
11. H. Lei, A. Pizzi and G. Du, *Journal of Applied Polymer Science* **107**, 203–209 (2008).
12. G. Doering and G. Harbor, US Patent 5,202,403, Georgia Pacific Resins Inc. (1993).
13. S. Chen, *Holzforch Holzverwert* **4**, 58–60 (1996).
14. M. Risholm-Sundman and N. Wallin, *Holz Roh Werkst.* **57** (5), 319 (1999).
15. R. Seco, J. Peñuelas and I. Filella, *Atmospheric Environment* **42**, 7907–7914 (2008).
16. P. S. Muir and A. M. Shirazi, *Environmental Pollution* **94** (2), 227–234 (1996).
17. S. Smidt, H. Bauer, O. Pogodina and H. Puxbaum, *Atmospheric Environment* **39**, 4087–4091 (2005).
18. R. Seco, J. Peñuelas and I. Filella, *Atmospheric Environment* **41**, 2477–2499 (2007).
19. Y. G. Eom, S. Kim, I.-Ch. Baek and H.-J. Kim, *Mokchae Konghak.* **33** (2), 29–39 (2005).
20. S. Kim, *Bioresource Technology* **100** (2), 744–748 (2009).
21. A. Trosa and A. Pizzi, *Holz als Roh-und Werkstoff* **59** (40), 266–271 (2001).
22. S. Kim and H.-J. Kim, *J. Adhesion Sci. Technol.* **17** (10), 1369–1383 (2003).
23. G. Avignon and M. Delmas, US patent 7,402,224 (2000).
24. L. Lorenz, C. R. Frihart and J. M. Wescott, in: *Proceedings of Wood Adhesives*, Forest Products Society, Madison, Wisconsin, pp. 501–506 (2006).
25. A. Ballerini, A. Despres and A. Pizzi, Non-toxic, zero emission tannin-glyoxal adhesives for wood panels, *Holz Roh Werkst.* **63**, 477–478 (2005).
26. G. A. Amaral-Labat, A. Pizzi, A. R. Goncalves, A. Celzard and S. J. Rigolet, *Journal of Applied Polymer Science* **108**, 624–632 (2008).
27. NIOSH, National Institute for Occupational Safety and Health, The Registry of Toxic Effects of Chemical Substances (2000).
28. NTIS, National Technical Information Service, Springfield, VA 22161, Formerly U.S. Clearing House for Scientific & Technical Information, AD-A125-539 (2005).
29. E. Stiasny, *Der Gerber* (740), 186; (775), 347 (1905).
30. L. Suomi-Lindberg, *Paperi Ja Puu* **67** (2), 65–69 (1985).
31. W. E. Hillis and G. Urbach, *J. Appl. Chem.* **9**, 665–673 (1959).
32. F. Pichelin, M. Nakatani, A. Pizzi, S. Wieland, A. Despres and S. Rigolet, *Forest Prod. J.* **56**, 31–36 (2006).
33. A. Pizzi and A. Stephanou, *Holzforschung* **47**, 439–445 (1993).
34. A. Pizzi and A. Stephanou, *Holzforschung* **47**, 501–506 (1993).
35. European Standard EN 312, Wood particleboard — specifications (1995).
36. European Standard EN 317, Particleboards and fibreboards — determination of swelling in thickness after immersion in water (2003).
37. European Standard EN 319, Particleboards and fibreboards — determination of tensile strength perpendicular to the plane of the board (1993).
38. M. Karas, D. Bachmann, U. Bahr and F. Hillenkamp, *Int. J. Mass Spectrom. Ion Proc.* **78**, 53–58 (1987).
39. U. Bahr, A. Deppe, M. Karas, F. Hillenkamp and U. Giessmann, *Anal. Chem.* **64**, 2866–2869 (1992).

40. H. Ehring, M. Karas and F. Hillenkamp, *Org. Mass Spectrom.* **27**, 472–480 (1992).
41. P. O. Danis, D. E. Karr, F. Mayer, A. Holle and C. H. Watson, *Org. Mass Spectrom.* **27**, 843–846 (1992).
42. P. O. Danis and D. E. Karr, *Org. Mass Spectrom.* **28**, 923–925 (1993).
43. H. Pasch and F. Gores, *Polymer* **36**, 1999–2005 (1995).
44. H. Pasch, A. Pizzi and K. Rode, *Polymer* **42**, 7531–7539 (2001).
45. S. Kim, J.-A. Kim, H.-J. Kim and S.-D. Kim, *Polymer Testing* **25**, 605–614 (2006).
46. B. Meyer and C. Boheme, *Forest Prod. J.* **47** (5), 45–48 (1997).
47. European Standard EN 712-3, Wood-based panels — determination of formaldehyde release — Part 3: Formaldehyde release by the flask method (1996).
48. T. Salthammer, S. Mentese and R. Marutzky, *Chem. Rev.* **110**, 2536–2572 (2010).
49. A. Pizzi, *Holzforschung Holzverwertung* **31** (4), 86–87 (1979).
50. F. Pichelin, *PhD thesis*, University of Hamburg, Hamburg, Germany (1999).
51. H. R. Mansouri, P. Navarrete, A. Pizzi, S. Tapin-Lingua, B. Benjelloun-Mlayah and S. Rigolet, *Eur. J. Wood Prod.* **69**, 221–229 (2011).
52. P. Navarrete, H. R. Mansouri, A. Pizzi, S. Tapin-Lingua, B. Benjelloun-Mlayah, H. Pasch and S. Rigolet, *J. Adhesion Sci. Technol.* **24**, 1597–1610 (2010).
53. E. Roffael, *Holz als Roh-und Werkstoff* **64**, 144–149 (2006).
54. M. Schäfer and E. Roffael, *Holz als Roh-und Werkstoff* **58**, 259–264 (2000).