

Characteristics and Mechanical Potentials of Wood Adhesives Manufactured with Grasses' Lignins

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How to cite this paper: Karga, L.T., Raidandi, D., Konai, N., Pizzi, A. and Meva'a, L. (2019) Characteristics and Mechanical Potentials of Wood Adhesives Manufactured with Grasses' Lignins. *Journal of Materials Science and Chemical Engineering*, 7, 35-47.

<https://doi.org/10.4236/msce.2019.71004>

Received: November 24, 2018

Accepted: January 25, 2019

Published: January 28, 2019

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Abstract

In order to manufacture environmentally friendly particle boards and enhance local resources, the lignins of *Sorghum bicolor* and *Andropogon gayanus* characterized using RMN ¹³C and MALDI TOF have the same structures. They contents Guaiacyl (G), Syringyl (S), p-hydroxyphenylpropane (H) and functional groups of phenols, flavonoids and secondary alcohols. The total phenol content determined using Folin-Ciocalteu reagent is respectively 20.97 and 15.42 mg eqgallic acid/g of extract. The power of their adhesives is different. The Internal Bond (IB) of particleboards manufactured with these adhesives are respectively 0.37 MPa and 0.41 MPa. These lignins can be used as antioxidants.

Keywords

Lignins, *Sorghum bicolor* and *Andropogon gayanus*, Structures, Adhesives, Internal Bond, Antioxydants

1. Introduction

Plants constituents such as lignin, tannin, hemicellulose and others are interesting. Many searchers in various fields such as in the paper industry, pharmaceutical industry, bakeries, wood adhesives etc. [1]. The most quantities of lignins are used in the paper industry. Their demand is increasing today due to their uses in

the manufacturing of renewable polymers as one of the best solutions to environmental pollution [2]. In order to add value to lignins, many species have been characterized in the last decades. While Ghaffar has analyzed and characterized the structure of straw lignin [3], Gellerstedt *et al.* (2008) [4] have characterized the structures and properties of lignins for composites from renewables resources. Nadji *et al.* have done in 2009 a comparative study of lignins isolated from Alfa grass (*Stipa tenacissima* L.) [5]. Lignin is composed by three p-hydroxycinnamyl alcohol precursors: p-coumaryl, coniferyl and sinapyl alcohols [6]. Lignin has a highly complex 3D randomized structure linked to hemicelluloses. It functions as a biological barrier and as a binder holding together hemicelluloses and cellulose. Profiting from its unique structure in nature, lignin has significant potential to acquire added value to produce phenolic chemicals. Thus, lignin capability to produce high added value phenolic compounds has recently attracted a great deal of interest by the scientific community [6]. Many lignins have been used in the development of adhesives, such as Miscanthus lignin [7], wheat straw [8] and sugar maple [9]. A number of lignins have been characterized using several techniques, including Fourier transform infrared spectroscopy (FT IR), size exclusion chromatography (SEC), Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) and Nuclear Magnetic Resonance spectroscopy (NMR) [3].

This idea of upgrading local materials and replacing all synthetic resins in the wood industry with biodegradable resins made from renewable resources such as wood, grasses and bone is of economic importance particularly for African countries in development. It can be of great interest in reducing the effect of climate change in some part of this continent (the sub-Saharan Africa).

Sorghum bicolor is a cereal and forage grass which belongs to the Poaceae family and the Andropogoneae tribe. It is the world's fifth largest cereal, after maize, rice, wheat and barley [10]. It is a basic cereal plant most cultivated in sub-Saharan Africa and particularly in the Far North of Cameroon. Rich in iron, calcium and phosphorus, sorghum would be an ideal food for diabetics. In Africa, It is used as food and for treatment of various diseases such as gastrointestinal pathologies, to treat bone decalcification and to prevent gallstones. In sub-Saharan Africa, and particularly in the northern part of Cameroon, Andropogon is used as a building material. These more or less leaf-free stems are woven into mats, called "secco", and used in the construction of huts, fences, hangars, and roofs or sold in peri-urban markets while *Sorghum bicolor* stems are used in the construction of huts, Fences, sheds and manufacturing germ seed.

Despite the multiple benefits of *Andropogon gayanus* and *Sorghum bicolor* stems, these gramineae are not managed efficiently, they are waste often thrown into the wild, sometimes burned and used as firewood in households in the Northern Cameroon and they simply need to be upgraded. The Andropogon particularly is often a source of environmental hazards because it is often the source of the bush fires. Thus, the extraction of their lignins would constitute a

great economic potential for these African countries because resins and biodegradable composite materials will be manufactured locally [11].

It is in this context that the present paper responds to this approach in investigating the applicability of the lignin of *sorghum bicolor* and *Andropogon gayanus* stem. Given the importance of *sorghum bicolor* and *Andropogon gayanus* species in Africa in general, and Cameroon in particular, and that of lignin in the wood and pharmaceutical industries, a sound knowledge of the chemical structure of *sorghum bicolor* and *Andropogon gayanus* using Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) and Carbon-13 Nuclear Magnetic Resonance (^{13}C NMR) spectroscopy and the mechanical characteristics of particle board made from these lignins resins constitutes our interest center.

2. Materials and Methods

2.1. Extraction

140 g of each sample (*sorghum bicolor* and *Andropogon gayanus*) stems crushed and 980 ml of NaOH (0.7 - 1 M) were mixed in a reactor of 2 liters, and boiled at 170°C during 3 hours. After cooling the boiled content during 2 hours, it was sieved to obtain black liquor at pH = 5.5 adjusted using sulfuric acid. Then, the precipitate lignin was filtrated on the vacuum and wash with distilled water till neutral. The lignin obtained was stoved in an oven at 45°C during 48 hours [12].

2.2. Total Phenolic Content

0.0125 g extract of each sample above was diluted in 25 ml of methanol to obtain a final absorbance in the range [0, 0.5]. Portion of 2.5 mL of Folin-Ciocalteu reagent that has been pre-diluted ten times in methanol, then 2 mL of an aqueous sodium carbonate solution (75 g/L) were added to 0.5 mL of the methanolic solution of the extract. Sodium carbonate is added 30 s to 8 min after the Folin-Ciocalteu reagent. The resulting mixture was maintained during 5 min in a water bath at 50°C and then dipped in a cold water bath. The mixture was centrifuged and the absorbance of the supernatant liquid was determined at 760 nm with a Perkin-Elmer UV Lambda Spectrophotometer. The total phenolic content was calculated as gallic acid equivalent from the calibration curve of a gallic acid standard solution (0 - 25 mg/L) and expressed as milligrams of gallic acid equivalent/g of extract. All tests were repeated three times [13].

2.3. Matrix Assisted Laser Desorption Ionization Time of Light Mass Spectrometry (MALDI-TOF MS)

5 mg of each lignin extract were dissolved in 1 mL of acetone and the obtained solution was mixed with another one composed of acetone (10 mg/mL acetone) and 2,5-dihydroxybenzoic acid as matrix. Then, add the sodium chloride (NaCl) to the matrix (10 mg/mL in distilled water) to enhance the ion formation. The

resulting solutions were evaporated on the MALDI target before placing into the spectrometer. The KRATOS compact MALDI AXIMA PERFORMANCE MALDI TOF 2 instrument was used to record the spectra. The irradiation source was a pulsed nitrogen laser (wave-length: 337 nm, laser pulse length 3 ns, and target type: ground steel).

2.4. Solid State Carbon-13 Nuclear Magnetic Resonance (¹³C NMR)

A Bruker MSL spectrometer (Bruker Biospin, Wissembourg, France) was used to analyze the Carbon-13 Nuclear Magnetic Resonance (¹³C NMR). The spectra were acquired with 5 s recycle delays, a 90° pulse of 4.2 μs and a contact time of 1 ms. The number of transients used was 3000 [14].

2.5. Adhesives Development and Particleboards Manufacture and Testing

A water solution containing 35% lignin extract was mixed with 5% paraformaldehyde powder and pH was adjusted to 10 adding sodium hydroxide solution (NaOH). All components weight are on solids lignin. The components of each formulation was mixed in a beaker at 25°C temperature, process was stopped when viscosity reached 750 mPas using Brookfield viscometer RV. Spindle Nr, 27 at 25°C. Two formulations of adhesives with those lignins extract where developed. These adhesives were used to manufacture particle boards.

Two particleboards of 350 × 300 × 14 mm³ dimension were prepared using particles of *Sorghum bicolor* and *Andropogon gayanus* (moisture content = 2%) at 28 kg/cm² maximum pressure and 190°C - 200°C press temperature during 7.5 min. The total adhesive resin solids load on dry wood was 10% w/w of the total mix of different lignin. The particleboards were tested for dry internal bond (IB) strength in accordance with the standard EN312.

3. Results and Discussion

3.1. Total Phenol Content

The total phenolic content of *Sorghum bicolor* lignin and *Andropogon gayanus* in the solvent measured by the Folin-Ciocalteu method are respectively 20.97 and 15.42 mg eqgallic acid/g of extract. The possibility to uses this lignin as adhesive is showed by the existence of phenol in this extract [15].

3.2. Matrix Assisted Laser Desorption Ionization Time of Light Mass Spectrometry (MALDI-TOF MS)

The examination of the MALDI TOF spectra of *Sorghum bicolor* and *Andropogon gayanus* lignin in **Figure 1** and **Figure 2** in the range 200 to 699 Da and 100 to 4000 Da respectively, shows the 3 most common monomers participating in the formation of the lignin oligomers: G (guaiacyl), S (syringyl) and H (p-hydroxyphenylpropane). The MALDI-TOF spectrum between 20 and 200 Da was recorded but is not reported here. The molecular weight corresponding to

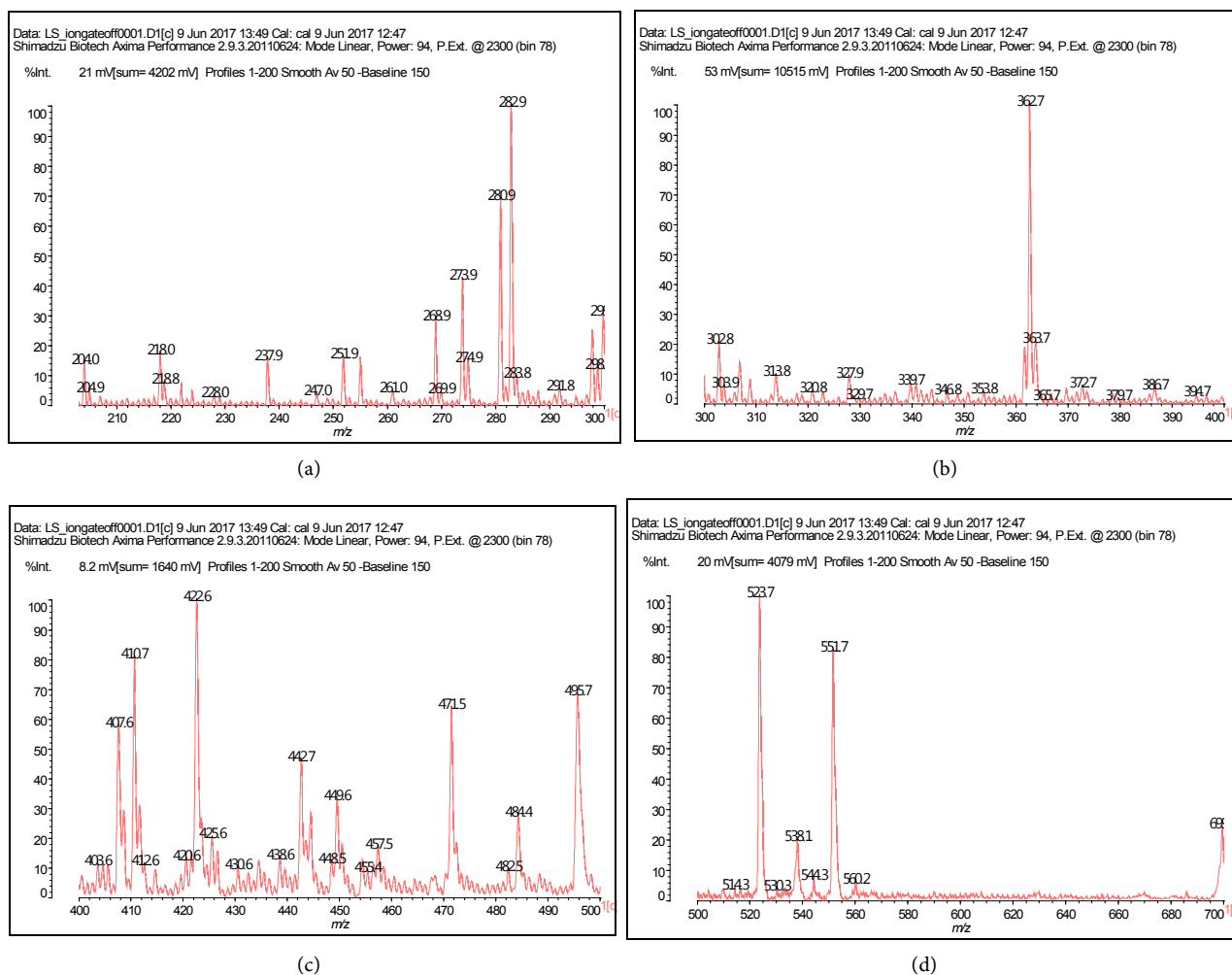


Figure 1. (a) MALDI-TOF spectrum of *Sorghum bicolor* lignin in the a 200 - 300 Da range; (b) MALDI-TOF spectrum of *Sorghum bicolor* lignin in the a 300 - 400 Da range; (c) MALDI-TOF spectrum of *Sorghum bicolor* lignin in the a 400 - 500 Da range; (d) MALDI-TOF spectrum of *Sorghum bicolor* lignin in the a 500 - 700 Da range.

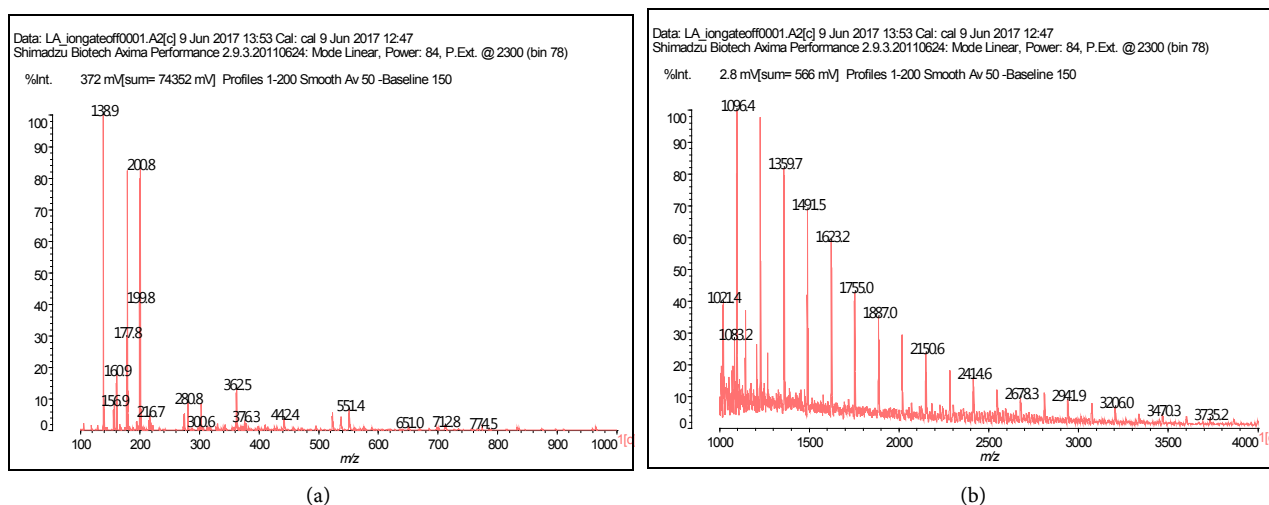


Figure 2. (a) MALDI-TOF spectrum of *Andropogon gayanus* lignin in the a 100 - 1000 Da range; (b) MALDI-TOF spectrum of *Andropogon gayanus* lignin in the a 1000 - 4000 Da range.

these monomers are: 94; 139 Da (for H); 151; 182 and 197 Da (for G) and 210 (for S) Da (**Table 1** and **Table 2**) [16]. The linkages between them are indicated by the “classical” nomenclature such as β -O-4, α -O-4, β - β , β -5, 5-5' [13]. The peak 430 Da correspond to the G- β -O4-S or G- α -O4-S structures. The values in Da of the structures corresponding to these peaks must be subtracted of 23 Da to obtain the value of their molecular weight from the peaks of the MALDI spectrum due to the NaCl matrix enhancer used. During the formation of oligomers, the loss of either a hydrogen atom or the protonated form [17] and the loss of a hydroxyl group [18] of the monomer units must be taken into account if they are not the terminal units of the oligomers. The loss of the water molecules must be taken into consideration, since water molecule will be eliminated (1 water molecule for every 2 monomers) from the oligomer during the condensation. The spectra of each lignin grasses revealed the presence Protonated or multi-protonated (with Na⁺) oligomers and there are some oligomers which have lost or acquired an OH group [17] (**Table 2** and **Table 3**). There are some signals in the range of 482–700 Da confirming the presence of trimers S- β O4-H- β 5-G, G- β O4-G- β 5-G and S- β O4-S- β β -S. Regarding the molar masses of these twolignins, namely 4000 Da for andropogon and 700 Da for *Sorghum bicolor*, we deduce that the degree of polymerization of andropogon lignin is greater than that of *Sorghum bicolor* lignin.

3.3. Solid State Carbon-13 Nuclear Magnetic Resonance (¹³C NMR)

Further information on the chemical structure of lignin extracts of *Andropogon gayanus* (LA) and lignin *sorghum bicolor* (LS) was obtained by ¹³C NMR. The peaks of the spectra in **Figure 3** and **Figure 4** show the shifts of the components or functional groups of the monomers present in the lignin extract of *Andropogon gayanus* and bicolor sorghum. Each peak is associated with either a functional group or a monomer present in these lignin extracts. The attributions of the different peaks of these lignins extracts are listed in Table 4 according to the literature [19]. The Analysis of the ¹³C NMR spectra in **Figure 3** and **Figure 4** shows that peaks 152.75; 148.23 133.63; 102.59 ppm for LS and 153.37; 148.03; 134.04; 102.38 ppm for LA indicate the presence of syringyl units (S) while the signals at 148.23; 115.54 ppm indicate the presence of a guaiacyl unit (G). The peaks 115.54 ppm for LS and 114.92 ppm for LA can also be attributed to C5 in p-hydroxyphenyl (H) or in guaiacyl unit (G) [20]. The peak 128.08 is assigned to C2/C6 in p-hydroxyphenyl (H). These peaks confirm that the lignin extract can be an herbaceous lignin (HGS) as indicated by MALDI TOF analysis. In addition, the ¹³C NMR spectra of lignin extracts of *Andropogon gayanus* and bicolor sorghum are similar to those of herbaceous crops [20]. The very high intensity of the peak at 73.60 ppm for LS is associated with the C α in β -O-4 shows that the β -O-4 bond is the most abundant in the lignin extract of *Sorghum bicolor*. Signals at 82.23; 82.65 ppm are associated with C- α and C- β in β -O-4/ α -O-4 and C- α in β 5 and β β . Peaks 63.73 and 63.94 ppm are attributed to C-Y in β -5 side chain carbons. The peaks at 55.92 and 55.71 ppm correspond to the methoxyl

Table 1. Monomers and oligomers present in *Sorghum bicolor* lignin extract.

structure		Calculated M.W	Calculated M.W +Na	Experimental peak	Peak relative proportion (%)
G 1H	monomer	181	204	204	15
G-2H	monomer	195	218	218	20
S-5H	monomer	205	228	228	5
S + 4H	monomer	214	237	237	18
S + 6H	monomer	224	247	247	5
H-G-OH	dimer	228	251	251	15
H-G-7H	dimer	238	261	261	8
H-G	dimer	245	268	268	28
H-G + 1H	dimer	246	269	269	5
H-G + 5H	dimer	250	273	273	37
S-S-CH ₃	dimer	251	274	274	15
G-H-2OH	dimer	257	280	280	65
S-S-7H	dimer	259	282	282	97
G-H + 6H	dimer	260	283	283	10
S-S + 2H	dimer	268	291	291	5
S-S + 3H	dimer	279	302	302	21
G-G + 4H	dimer	280	303	303	15
G-H	dimer	290	313	313	10
G-H + 7H	dimer	297	320	320	5
H-S G-G	dimer	304	327	327	10
H-S G-G + 2H	dimer	306	329	329	5
H-S G-G-CO ₂	dimer	316	339	339	9
S-H-CH ₂	dimer	323	346	346	5
G-G + 2OH	dimer	330	353	353	5
H-G + 3H	dimer	339	362	362	100
H-G-2H	dimer	340	363	363	3
G-H-H ₂ O S-H	dimer	342	365	365	3
H-S G-H-CH ₃	dimer	345	368	368	12
S-H	dimer	349	372	372	5
H-G-1H	dimer	356	379	379	4
G-G S-H + 3H	dimer	363	386	386	5
G-G-2H	dimer	371	394	394	4
G-G-2H	dimer	380	403	403	12
G-G-H ₂ O	dimer	384	407	407	68

Continued

G-G + 2H	dimer	387	410	410	82
G-S-H ₂ O	dimer	389	412	412	15
G-G-2H	dimer	397	420	420	16
G-G-4H	dimer	399	422	422	100
G-S-5H	dimer	402	425	425	22
G-S	dimer	407	430	430	12
G-S + 8H	dimer	415	438	438	15
S-S-OH	dimer	419	442	442	42
G-S + H ₂ O	dimer	425	448	448	13
S-S-11H	dimer	426	449	449	32
S-S-5H	dimer	432	455	455	12
S-S-3H	dimer	434	457	457	18
S-S + H ₂ O	dimer	448	471	471	62
S-H-G-4H	trimer	459	482	482	10
S-H-G-2H	trimer	461	484	484	28
H-H-G-3H	trimer	472	495	495	65
S-H-G	trimer	491	514	514	5
S-H-G	trimer	500	523	523	100
S-H-G + 7H	trimer	507	530	530	5
S-S-H + 2H	trimer	515	538	538	20
S-S-H-2H	trimer	521	544	544	7
S-S-H-1H	trimer	528	551	551	82
G-G-G-3H	trimer	537	560	560	8
S-S-S + CH ₃ O	trimer	676	699	699	5

group OCH₃ in the syringyl and guaiacyl units. The very high intensity of the signal at 75.04 ppm corresponds to the aliphatic group -CH₂OH of the side chain of the lignin unit. The signal associated with the α and β -methylene group on the n-propyl side chains appears at 31.25 and 30.42 ppm [21]. Peaks 177.22 and 176.60 ppm are attributed to the non-conjugated CO₂H carboxyl group in this lignin [22]. All information from these ¹³C NMR spectra confirms the presence of guaiacyl, syringyl units, a small amount of p-hydroxyphenyl units and phenols, as shown by the MALDI TOF. The presence of phenols and flavonoids in these lignins extracts show that they can be used as wood adhesives and can also be used as antioxidants.

3.4. Adhesives Development and Particleboards Manufacture and Testing

Particleboards manufactured with the two formulations of lignin resins of Andropogon (LPA4055) and Sorghum (LPS4055) had good IB strength. Result

Table 2. Monomers and oligomers present in *Andropogon gayanus* lignin extract.

structure		Calculated M.W	Calculated M.W +Na	Experimental peak	Peak relative proportion (%)
G-5H	Monomer	177	200	200	85
G-4H	Monomer	193	216	216	8
H-G + 12H	dimer	257	280	280	12
G-H + 1H	dimer	277	300	300	5
S-H-10H	dimer	339	362	362	18
S-H +4H	dimer	353	376	376	5
S-S-OH	dimer	419	442	442	5
S-S-H-1H	trimer	528	551	551	10
S-S-S-2H	trimer	628	651	651	3
H-G-H-G + 11H	tetramer	689	712	712	3
G-G-G-S + 1H	tetramer	751	774	774	65
S-S-S-S-S	hexamer	998	1021	1021	45
S-H-S-H-S-H-1H	hexamer	1060	1083	1083	28
S-H-S-H-S-H-4H	hexamer	1073	1096	1096	100
S-H-S-H-S-H-S-H-4H	octamer	1336	1359	1359	82
S-S-S-S-S-S-S-2H	heptamer	1468	1491	1491	70
S-H-S-H-S-H-S-H-S-H	decamer	1600	1623	1623	60
G-S-G-S-G-S-G-S -CH ₃ -OH	octamer	1732	1755	1755	42
G-G-G-G-G-G-G-G-G + H ₂ O	decamer	1864	1887	1887	35
H-S-H-S-H-S-H-S-H-S-H-S-H-S-1H	pentadecamer	2127	2150	2150	22
H-G-H-G-H-G-H-G-H-G-H-G-H-G + H ₂ O	tetradecamer	2391	2414	2414	18
G-G-G-G-G-G-G-G-G-G-G-G-G-G-G-G	octadecamer	2655	2678	2678	10
S-S-S-S-S-S-S-S-S-S-S-S + CH ₃	tetradecamer	2918	2941	2941	10
S-H-S-H-S-H-S-H-S-H-S-H-S-H-S-H-S-H + 6H	octadecamer	3183	3206	3206	8
G-S-G-S-G-S-G-S-G-S-G-S-G-S-G-S-OH	hexadecamer	3447	3470	3470	3
G-S-G-S-G-S-G-S-G-S-G-S-G-S-G-S + Na ⁺	octadecamer	3712	3735	3735	5

satisfied the dry IB strength requirement of the standard NF EN 312-2 (1996). Dry IB strength of particle boards manufactured with particles of *Andropogon gayanus* and the LPA4055 formulation was 0.37 MPa (**Figure 5**) and those manufactured particles of *Sorghum bicolor* and the LPS4055 formulation was 0.41 MPa (**Figure 6**). These two IB values are higher the standard Norm NF EN 312-2 (1996) (0.37 > 0.35 MPa and 0.41 > 0.35 MPa).

4. Conclusion

MALDI-TOF MS and 13°C NMR analysis were used for the characterization of lignin extracted from the stem of *Sorghum bicolor* and *Andropogon gayanus*.

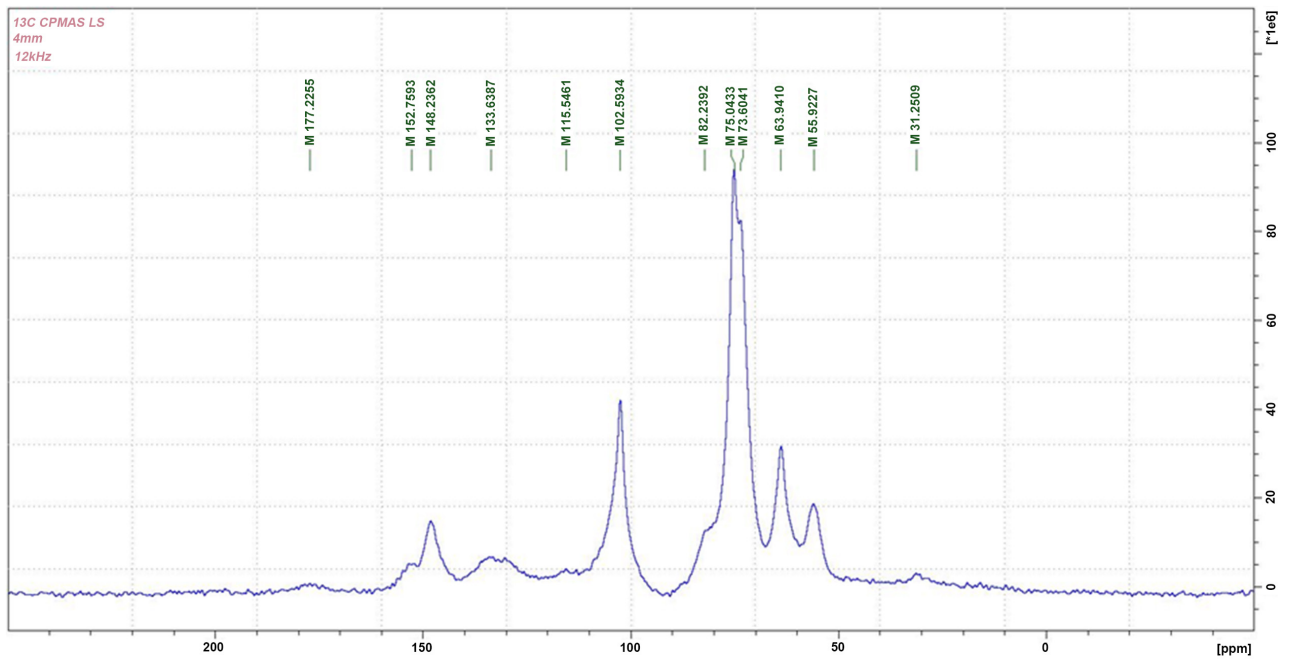


Figure 3. ^{13}C NMR Spectrum of *Sorghum bicolor* lignin extract (LS).

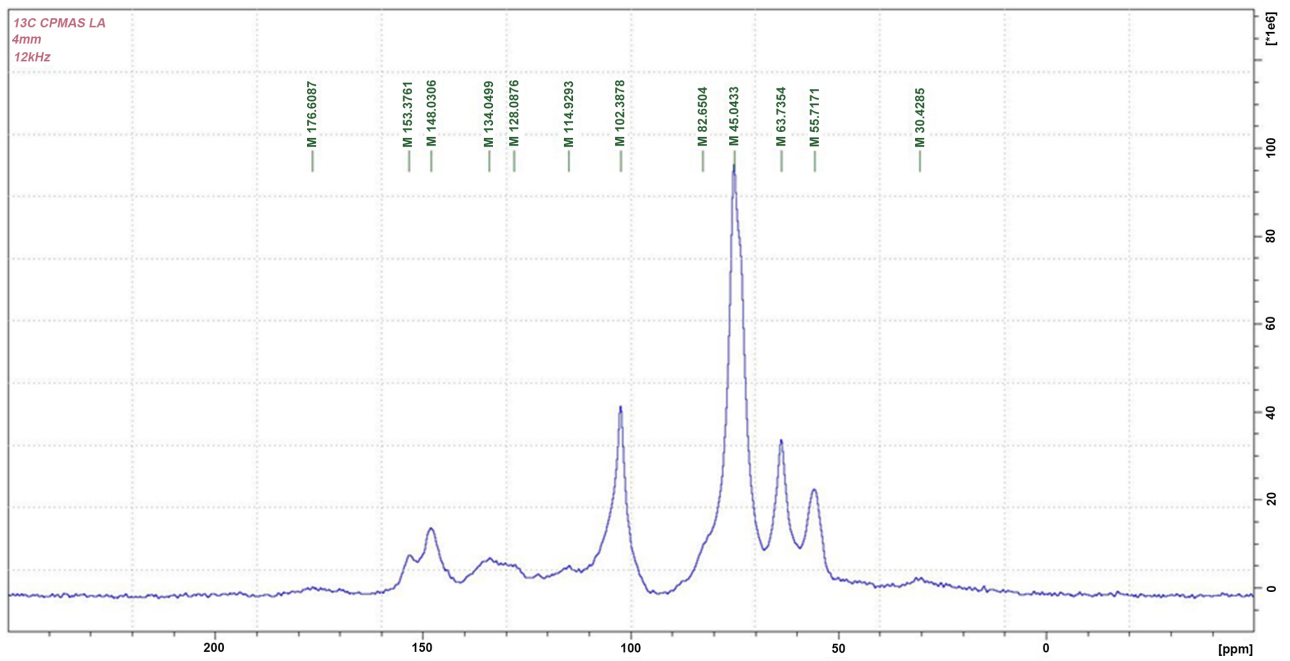


Figure 4. ^{13}C NMR Spectrum of *Andropogon gayanus* lignin extract (LA).



Figure 5. Particleboard of *Andropogon gayanus*.



Figure 6. Particleboard of Sorghumbicolor.

Table 3. Carbon chemical shifts (δ , ppm), intensity and assignment of the lignin preparation LS and LA in ^{13}C NMR spectrum.

Peak (ppm) LS	Intensity %	Peak (ppm) LA	Intensity %	Peak (ppm)	Assignments
177.22	2	176.60	2	178.0 - 167.5	Unconjugated-CO ₂ H
152.75	10	153.37	10	154 - 152	C3/C5 S etherified
148.23	15	148.03	15	148 - 147	C4 G etherified, C3C5 S non etherified
133.63	5	134.04	5	134	C1 S or C1 in G β -O-4
		128.08	3	128	C2/C6 H
115.54	3	114.92	5	115	C5 G
102.59	38	102.38	38	105 - 104	C2/C6 S
82.23	10	82.65	5	89 - 78	C β in β -O-4, C α in β 5 and $\beta\beta$ C α and C β in β -O-4/ α -O-4 units
75.04	95	75.04	100		Aliphatic-CH ₂ OH
73.60	80			73 - 71	C α in β -O-4
63.94	30	63.73	30	64	C γ in β 5, C γ with C α = O, C γ -O PC ester
55.92	18	55.71	25	56	OCH ₃ in G and S
31.25	2	30.42	2	31 - 29	α , β méthylène groups

H = Hydroxyphenyl; S = Syringyl; G = Guaiacyl; LS = *Sorghum lignin*; LA = *Andropogon lignin*

The analysis carried out had shown that these lignins consist of Guaiacyl (G), Syringyl (S), p-hydroxyphenylpropane (H) units and of phenolic, flavonoid and secondary alcohols functional groups. It is mainly composed of Guaiacyl (G) and Syringyl (S) units β -O-4 linked. The presence of phenols and flavonoids in this lignin extract shows that it could be used as wood adhesives and as antioxidant. They are good for wood adhesive because IB for their particleboards is respectively 0.37 and 0.41 MPa. A study aimed at increasing the mechanical characteristics of these bio-based panels by combining for example tannin and lignin in the elaboration of bioadhesives since tannin and lignin form the essential of polyphenols present in the plant species.

Acknowledgements

The authors acknowledge Dr. FRANCISCO JOSE SANTIAGO MEDINA for his valuable support during laboratory experimentation carried out at the LERMAB, at the University of Lorraine (France), Pr NTEDE Head of the Laboratory of

Chemistry of Higher National School of Engineering, University of Yaoundé 1, Dr. CHEMENI the Head of the Assistant Laboratory of Macromolecular Chemistry at the University of Yaoundé 1, Dr. Jean-Bosco Saha Tchinda, Mr. FokoStephan, Mr Agueda Fabrice and Mr. Njom Abel for their assistance.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Berrima, B. (2015) Etude structurale et chimique de la lignine d'Alfa et sa valorisation comme macromonomère et/ou précurseur du charbon actif. Génie des procédés. Université Grenoble Alpes, Français.
- [2] Thakur, V., Raghavan, P. and Kessler, M.R. (2014) Progress in Green Polymer Composites from Lignin for Multifunctional Applications: A Review. *ACS Sustain Chem Eng*, **2**, 1072-1092. <https://doi.org/10.1021/sc500087z>
- [3] Ghaffar, S.H. and Fan, M. (2013) Structural Analysis for Lignin Characteristics in Biomass Straw. *Biomass Bioenergy*, **57**, 264-279. <https://doi.org/10.1016/j.biombioe.2013.07.015>
- [4] Gellerstedt, G. and Henriksson, G. (2008) Lignins: Major Sources Structures and Properties. In: Belgacem, M.N. and Gandini, A., Eds., *Monomers Polymers and Composites from Renewables Resources*, 201-224.
- [5] Nadji, H., Diouf, P., Benaboura, A., Bedard, B., Riedl, T. and Stevanovic (2009) Comparative Study of Lignins Isolated from Alfa Grass (*Stipa tenacissima* L.). *Bio-resource Technology*, **100**, 3585-3592. <https://doi.org/10.1016/j.biortech.2009.01.074>
- [6] Ragauskas, A.J., Beckham, G.T., Bidy, M., Richard, C., Fang, C., Mark, F., Davis, H. and Davison (2014) Lignin Valorization: Improving Lignin Processing in the Biorefinery. *Science*, **344**, 709-719.
- [7] El Hage, R., Brosse, N., Navarrete, P., *et al.* (2011) Extraction, Characterization and Utilization of Organosolv Miscanthus Lignin for the Conception of Environmentally Friendly Mixed Tannin/Lignin Wood Resins. *Journal of Adhesion Science and Technology*, **25**, 1549-1560. <https://doi.org/10.1163/016942410X524110>
- [8] Feng, X., Sun, J.X., Sun, R.C., *et al.* (2006) Comparative Study of Organosolv lignins from Wheat Straw. *Industrial Crops and Products*, **23**, 180-193. <https://doi.org/10.1016/j.indcrop.2005.05.008>
- [9] Dongre, P., Driscoll, M., Amidon, T., *et al.* (2015) Lignin-Furfural Based Adhesives. *Energies*, **8**, 7897-7914.
- [10] Jacques, C., Jean-François, C., Alain, R. and Gilles, T. (2013) Le sorgho, Éditions Quæ, CTA, Presses agronomiques de Gembloux, 267 p.
- [11] Noel, K., Raidandi, D., Pizzi, A., *et al.* (2016) Thermogravimetric Analysis of Anningre Tannin Resin. *Maderas. Ciencia y Tecnología*, **18**, 245-252.
- [12] Mousavioun, P. and Doherty, W. (2010) Chemical and Thermal Properties of Fractionated Bagasse Soda Lignin. *Industrial Crops and Products*, **31**, 52-58.
- [13] Huang, Z., Hashadi, K., Makino, R., Kawamura, F., Kuniyoshi, S., Ryuichiro, K. and Ohara, S. (2009) Evaluation of Biological Activities of Extracts from 22 African Tropical Wood Species. *Journal of Wood Science*, **55**, 225-229.

- <https://doi.org/10.1007/s10086-008-1024-y>
- [14] Navarrete, P., Pizzi, A., Pasch, H. and Delmotte, L. (2012) Study on Lignin-Glyoxal Reaction by MALDI-TOF and CP-MAS ^{13}C -NMR. *Journal of Adhesion Science and Technology*, **26**, 1069-1082.
- [15] Zhao, M.Z., Jing, J.L., Zhu, Y.C., Yang, X.M., Wang, X.F. and Wang, Z.C. (2016) Preparation and Performance of Lignin-Phenol-Formaldehyde Adhesives. *International Journal of Adhesion & Adhesives*, **64**, 163-167.
- [16] Navarrete, P., Mansouri, H.R., Pizzi, A., et al. (2010) Wood Panel Adhesives from Low Molecular Mass Lignin and Tannin without Synthetic Resins. *Journal of Adhesion Science and Technology*, **24**, 1597-1610.
<https://doi.org/10.1163/016942410X500972>
- [17] Konai, N., Pizzi, A., Raidandi, D., Lagel, M.C., L'Hostis, C., Saidou, C., Hamido, A., Abdalla, S., Bahabri, F. and Ganash A. (2015) Anigre (*Aningeria* spp.) Tannin Extract Characterization and Performance as an Adhesive Resin. *Industrial Crops and Products*, **77**, 225-231. <https://doi.org/10.1016/j.indcrop.2015.08.053>
- [18] Pizzi, A., Pasch, H., Rode, K. and Giovando, S. (2009) Polymer Structure of Commercial Hydrolysable Tannins by Matrix-Assisted Laser Desorption Ionization-Time-of-Light Mass Spectrometry. *Journal of Applied Polymer Science*, **113**, 3847-3859. <https://doi.org/10.1002/app.30377>
- [19] Pan, X., Lachenal, D., Neirinck, V. and Robert, D. (1994) Structure and Reactivity of Spruce Mechanical Pulp Lignins: ^{13}C -NMR Spectral Studies of Isolated Lignins. *Journal of Wood Chemistry and Technology*, **14**, 483-506.
<https://doi.org/10.1080/02773819408003109>
- [20] Catherine, L. and Bernard, M. (1987) RMN ^{13}C Bidimensionnelle des lignines de peuplier: Etude des Corrélations entre Atomes de Carbone et Réexamen par la Méthode INADEQUATE des Attributions des Signaux du Spectre. *Holzforshung*, **41**, 51-58. <https://doi.org/10.1515/hfsg.1987.41.1.51>
- [21] Wang, K., Xu, F. and Sun, R. (2010) Molecular Characteristics of Kraft-AQ Pulping Lignin Fractionated by Sequential Organic Solvent Extraction. *International Journal of Molecular Sciences*, **11**, 2988-3001. <https://doi.org/10.3390/ijms11082988>
- [22] Tian, X., Fang, Z., Smith Jr., R.L., Wu, Z. and Liu, M. (2016) Properties, Chemical Characteristics and Application of Lignin and Its Derivatives. In: Fang, Z. and Smith Jr., R.L., Eds., *Production of Biofuels and Chemicals from Lignin*, Springer, Berlin, 3-33. https://doi.org/10.1007/978-981-10-1965-4_1