

CHEMICAL AND PHYSICO-CHEMICAL CHARACTERIZATION OF LIGNINS OBTAINED FROM ETHANOL-WATER FRACTIONATION OF BAGASSE

María E. Vallejos,^{a,b} Fernando E. Felissia,^a Aprigio A.S. Curvelo,^{c,d} Marcia D. Zambon,^c Luis Ramos,^c and María C. Area,^{a,b,*}

Organosolv lignins can replace petroleum chemicals such as phenol either partially or totally in various applications. Eight lignins, seven of which corresponded to the ethanol-water fractionation of bagasse and the other to a reference lignin (Alcell®) were analyzed with the aim to evaluate their chemical and physicochemical characteristics. The purity of the lignin fractions was determined by high pressure liquid chromatography (HPLC) and by ash content. Fourier Transform-Infrared Spectroscopy (FTIR) techniques and differential UV spectroscopy were applied to identify the chemical groups in the lignin samples. The molecular weight distribution was determined by size exclusion chromatography (HPSEC). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques were used to determine the mass loss due to the high temperature treatment. The lignins studied showed the presence of p-hydroxyphenyl (H unit) and a greater proportion of guaiacyl (G unit) moieties, lower purity, similar or greater amount of phenolic hydroxyl groups, and higher degradation temperatures, than the Alcell® lignin.

Keywords: Lignin; Ethanol-Water Fractionation; HPSEC; Infrared spectroscopy; Thermal analysis

Contact information: a: Programa de Celulosa y Papel - FCEQyN – Universidad Nacional de Misiones - Félix de Azara 1552, (3300) Posadas, Misiones, Argentina. mariaxvallejos@hotmail.com; b: Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET); c: Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, 13560-970, São Paulo, Brazil; d: Laboratório Nacional de Ciência e Tecnologia do Bioetanol – CTBE; Corresponding author: *m_c_area@fceqyn.unam.edu.ar

INTRODUCTION

Almost all lignins used nowadays in industrial applications are obtained as by-products from the pulp and paper industry. However, the major part is burned, as an energy source, in the chemical recovery system (Lora 2008). Lignin presents diverse functional groups depending on its genetic origin, the applied pulping sequences, and the extraction processes. The reactions involved in the pulping processes modify the properties of the native lignin and determine its potential applications. Most applications of commercial lignins require high-purity, homogeneity, and the absence of smell and color.

Organosolv pulping is an alternative pretreatment for the production of ethanol from lignocellulosic biomass. The organosolv lignins are characterized by their high purity, low molecular weight, narrow molecular weight distribution, low glass transition temperature, high solubility in organic solvents, and water insolubility (Pye et al. 2000;

Lora 2008). Extensive research activities have been focused on the replacement of phenol by lignins in the production of phenol-formaldehyde (PF) resins and also in the production of biodegradable polyurethanes, replacing petroleum chemicals, in view of their similar phenolic structure. Structurally, they have a strong chemical similarity to phenol-formaldehyde resins (PF), and, like PF resins, they condense to form high molecular weight structures at high temperatures. However, unlike PF resins, lignins are not produced in the presence of formaldehyde, and as a consequence, they do not release formaldehyde during condensation at high temperatures. In fact, it has been shown that when organosolv lignins are mixed with PF resins to form thermoset materials, they prevent the release of formaldehyde of PF resins during the pressing of the panels. This is a desirable attribute from the perspective of industries that use PF thermosetting resins. The main applications of these resins are in particle boards and for plywood industry applications. They are also used as thermal and acoustic insulation materials and electrical insulators, and as matrix for friction materials (Pye et al. 2000; Wang et al. 2009).

Fractionation can be used to separate the principal components of a fibrous raw material: cellulose, hemicelluloses, and lignin. This study analyzed organosolv lignins obtained by different fractionation processes, with the aim to evaluate their chemical and physicochemical characteristics. Eight lignins, including a commercial lignin of reference (Alcell®), were analyzed. The recovery of lignins from spent liquor first requires their separation from dissolved sugars. The purity of the recovered lignin fractions was determined by quantification of substances commonly found in these samples (sugars, organic acids, ethanol, and inorganic substances) by high pressure liquid chromatography (HPLC). Fourier Transform-Infrared Spectroscopy (FTIR) techniques were applied to identify the characteristic absorption bands of the chemical groups in lignin, and differential UV spectroscopy to determine the content of phenolic-OH, as an indicator of their potential reactivity. The molecular weight distribution of lignin, the number average molecular weight (M_n), the weight average molecular weight (M_w), and polydispersity (M_n/M_w) were determined by size exclusion chromatography (HPSEC). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques were used to determine the mass loss of samples due to the temperature treatment, as indicative of thermal stability and thermal decomposition of a compound. In addition, the pyrolysis behavior of lignin is important to evaluate the possibility of converting them into fuels or high-value chemicals. In DSC, the differences in heat flow are recorded as a function of temperature and depend on the behavior of the sample as a result of endothermic or exothermic events during the treatment.

This work is part of a project whose general aim is to study the technical and economic feasibility of production of unconventional derivatives of sugarcane, using environmentally compatible and economically competitive technologies. In previous works, we presented the results of the ethanol-water fractionations of sugarcane bagasse catalyzed with acetic acid and sulfuric acid at moderate temperatures (Area et al. 2009), as well as methodologies for the separation and recovery of lignins from the fractionation of spent liquors (Felissia et al. 2008).

EXPERIMENTAL

The Alcell® lignin, evaluated as reference, was produced from organosolv pulping of mixed hardwoods (birch, maple, and poplar) by Repap Technologies Inc. (Valley Forge, U.S.).

Bagasse fractionations were carried out by an organosolv (ethanol-water) process, using a 7 L MK digester (M/K Systems, Inc., Maryland) with liquor circulation, under different conditions. The ratios of liquor/bagasse and ethanol/water remained constant at 14/1 (v/w) and 50% (% v/v), respectively. The time to reach the maximum temperatures was 30 min. The variables involved were: maximum temperature, time at maximum temperature, and acid presence or concentration. Acetic acid (2 g/L) and sulfuric acid (0.5, 1.0 and 2.0 g/L) were used as catalysts. The characterization of bagasse and a detailed description of the ethanol-water organosolv fractionations, as well as of the lignin separation methods, have been presented in previous works (Area et al. 2009; Felissia et al. 2008). Fractionation conditions are given in Table 1.

Table 1. Levels of the Variables in the Fractionations Performed

Fractionation	F 1	F 2	F 3	F 4	F 5	F 6	F 7
Time at maximal temperature (min)	240	240	240	240	240	120	120
Maximal temperature (°C)	175	175	180	180	175	150	160
Catalyst	Acetic acid	Without catalyst	Acetic acid	Without catalyst	Sulfuric acid	Sulfuric acid	Sulfuric acid
Catalyst conc. (g L ⁻¹)	2.0	0	2.0	0	2.0	0.5	0.5

Lignin samples were obtained from the spent liquors by dilution with acidic aqueous solution (dilution factor 1:2) at room temperature and pH 2.7. The experimental methodology followed in the lignin recovery and the characterization procedures applied to the obtained fractions are shown in Fig. 1.

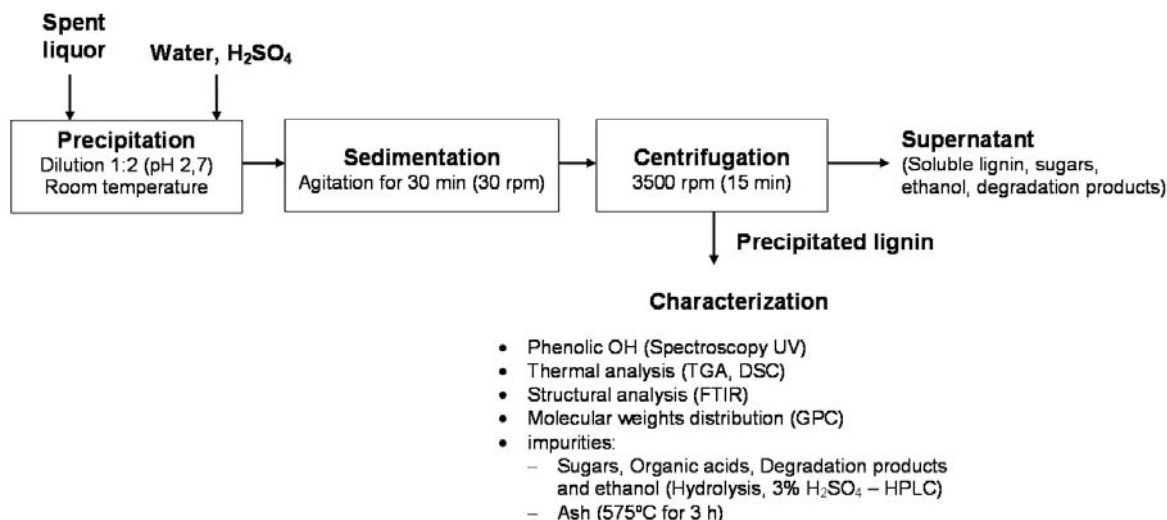


Fig. 1. Scheme of the experimental methodology

The precipitated lignins were separated by centrifugation (3500 rpm, 15 min) and then dried in a vacuum oven at 50°C to constant weight. The recovered lignins were hydrolyzed with 3% sulfuric acid to determine monosaccharides, organic acids, and ethanol by HPLC chromatography. The ash content was determined by incineration at 575°C for 3 hours. The purity of the lignin samples was determined as the ratio between the weight of precipitate free of impurities, and the precipitate as it is.

Chromatographic determinations were performed using an Aminex HPX87H column (BIO-RAD), with 4 mM H₂SO₄ as eluent, a flow of 0.6 mL.min⁻¹, at 35°C, and with Refraction Index (RI) and Diode Array (DA) as detectors.

FTIR spectra were obtained from samples of lignin in KBr (1% by weight and dried in vacuum oven at 50 °C), between 400 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹ and 32 scans.

The determination of the phenolic hydroxyl groups was performed by UV spectroscopy, based on the absorption difference of phenolic units in neutral and alkaline solutions at 300 and 360 nm (Zakis 1994).

The molecular weight determination was carried out by HP-SEC in a Shimadzu Liquid Chromatograph, using a PLgel guard column and a series of three Plgel columns (Polymer Laboratories - 500 Å, 1000 Å and 10000 Å) each 7.5 mm x 300 mm, gel-filled poly (styrene/divinylbenzene) - PS / DVB (10μ or 6μ). The columns were calibrated in the range of 106-770000 Dalton. The eluent was THF, the flow rate 1.0 mL min⁻¹, and the detectors IR and UV/254nm.

A TA-50WSI Shimadzu Thermal Analyzer, equipped with TGA-50 and DSC-50 modules was used for thermal analysis. The conditions of TGA analysis were: N₂ atmosphere, flow rate of 20 mL.min⁻¹, heating rate of 10 °C.min⁻¹, and temperature range from ambient to 900 °C. The same conditions were used for DSC analysis, with a temperature range from ambient to 500 °C.

The results were analyzed with Statgraphics software using ANOVA, Multiple Range, and correlation tests.

RESULTS AND DISCUSSION

Precipitation yields ranged between 50 and 55% by weight of precipitate, calculated as the ratio of the amount of precipitate and the lignin content in the liquor. Results of the purity of lignins are shown in Table 2.

Table 2. Impurities in Lignins (% by weight of dry solids)

Lignin	Glucose	Xylose	Arabinose	Total sugars	Formic acid	Acetic acid	Ethanol	Purity
Alcell	0.090	0.285	0.003	0.378	0.036	0.135	0.549	98.9
F1	0.682	0.898	0.539	2.119	0.147	0.464	1.921	95.4
F2	0.694	0.913	0.503	2.109	0.153	0.406	1.512	95.8
F3	0.695	0.332	0.312	1.339	0.151	0.276	2.387	95.8
F4	0.650	0.499	0.376	1.526	0.175	0.305	2.225	95.8
F5	0.731	0.077	0.007	0.815	0.197	0.106	2.239	96.6
F6	0.809	4.012	2.320	7.140	0.193	1.085	3.340	88.2
F7	0.695	1.239	2.036	3.970	0.176	0.413	3.114	92.3

The ash content of all samples was less than 0.05%. Alcell lignin presented the highest average purity (98.9% by weight), while lignins from fractionations F1, F2, F3, F4 and F5 showed no significant differences between them, with averages between 96.6% and 95.4% by weight. F6 (fraction obtained from precipitation with 0.5 gL^{-1} of sulfuric acid, shorter times and moderate temperatures) presented the lowest purity (88.2%). Lignin F5 treated at more severe conditions presented higher purity. Lignins F6 and F7 contained the highest amount of xylose and arabionose, suggesting the presence of lignin-carbohydrate complexes. The main impurities in all lignins, total sugars and ethanol were positively correlated ($R = 0.80$, $p = 0.003$).

The results of the FTIR spectra are shown in Fig. 2 and their analysis in Table 3.

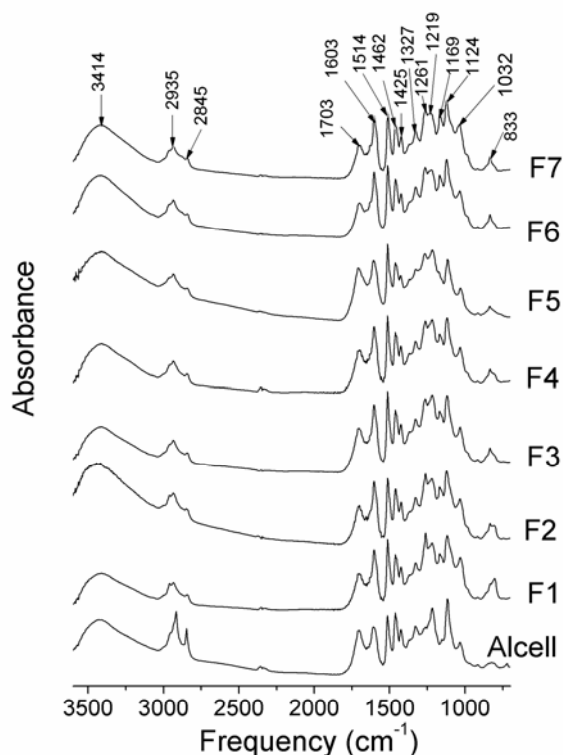


Fig. 2. FTIR spectra of the studied lignins

The bands were normalized as the ratio of each absorbance to the absorbance at 1514 cm^{-1} (according to the methodology followed by Sarkanen et al. 1967a, 1967b, 1967c; Singh et al. 2005, and Gonçalves et al. 1999). This band, typical of the stretching of aromatic rings, was selected as an internal reference, as it has a relatively constant intensity (Roof et al. 2007; Faix 1992). All the lignins studied presented other typical bands of vibrations of the aromatic ring at $1425\text{--}1427 \text{ cm}^{-1}$ (Sarkanen et al. 1971); at 1462 cm^{-1} , combined with C-H deformations in the plane (Singh et al. 2005; Boeriu et al. 2004) related to $-\text{CH}_3$ + $-\text{CH}_2$ groups (Tejado et al. 2007; Faix 1992); and at $1603\text{--}1605 \text{ cm}^{-1}$, where C=C (Singh et al. 2005) and C-C stretching (Tejado et al. 2007) are evidenced in the aromatic ring, plus C=O stretching in S> G: condensed G > etherified G (Faix, 1992; Singh et al. 2005).

Table 3. FTIR Bands, Normalized as the Ratio of each Absorbance to the Absorbance at 1514 cm^{-1}

(cm^{-1})	AlIcel	F1	F2	F3	F4	F5	F6	F7
824-835	0.45	0.45	0.48	0.36	0.43	0.38	0.45	0.41
1032-1037	0.69	0.74	0.76	0.60	0.66	0.57	0.85	0.68
1117-1125	1.20	1.03	1.08	0.96	0.98	0.85	1.16	1.04
1169	0.00	0.83	0.90	0.78	0.81	0.00	0.98	0.87
1217-1222	1.09	0.95	1.00	0.96	0.96	0.94	0.00	0.95
1261-1265	0.00	1.03	1.05	0.92	0.94	0.91	1.03	0.97
1327-1329	0.87	0.71	0.78	0.69	0.73	0.75	0.77	0.75
1425-1427	0.83	0.67	0.73	0.63	0.67	0.69	0.71	0.66
1462	1.03	0.82	0.88	0.79	0.82	0.82	0.86	0.83
1603-1605	0.87	0.88	0.96	0.85	0.88	0.84	0.96	0.91
1705-1709	0.83	0.59	0.69	0.58	0.63	0.76	0.58	0.55
2841-2849	0.85	0.39	0.65	0.30	0.38	0.56	0.43	0.45
2916-2937	1.05	0.54	0.83	0.45	0.52	0.70	0.58	0.61
3414-3429	0.95	0.73	1.18	0.60	0.70	0.93	0.86	0.90

Aromatic C-H deformations in the plane ($G > S$), C-O deformation in primary alcohols (Roof et al. 2007; Faix 1992; Singh et al. 2005; Sarkanen et al. 1971), plus stretching of non-conjugated C=O (Roof et al. 2007; Faix 1992) were observed at the 1032-1037 cm^{-1} band.

C-C and C-O stretching vibrations associated with C=O stretching (Faix 1992; Boeriu et al. 2004), in G condensed > G etherified (Faix 1992), stretching of C-O (H) + C-O (Ar), phenolic OH + ether (Roof et al. 2007), secondary OH and deformation C-H in the plane, typical of G units (Singh et al. 2005), were observed at the 1217-1222 cm^{-1} band.

All OH stretching, in phenolic and aliphatic units of lignin (Singh et al. 2005; Roof et al. 2007; Faix 1992; Boeriu et al. 2004; Sarkanen et al. 1971) were observed at the 3414-3429 cm^{-1} band.

The peak at 1169 cm^{-1} involves C-O stretching in conjugated ester groups in HGS lignins, typical of monocots (Faix 1992), and certainly represented the bagasse HGS lignin. Breathing and stretching on C-O of guaiacyl rings (Roof et al. 2007; Faix 1992) plus stretching of C=O groups in G lignins appeared at 1261-1265 cm^{-1} (Faix 1992; Singh et al. 2005; Boeriu et al. 2004). Alcell lignin did not show an absorption band at this frequency, because the number of guaiacyl units in GS lignin is, in general, much lower than in HGS lignin (Ragauskas ca. 2008). There were no significant differences between the lignins obtained in this work. C-H deformations of the aromatic group of units S (Roof et al. 2007; Singh et al. 2005), plus C-O deformations in secondary alcohols, C-O stretching (Singh et al. 2005; Faix, 1992), and aliphatic ethers (Singh et al. 2005) appeared at the 1117-1125 cm^{-1} C-H.

The band at 1327-1329 cm^{-1} is typical of syringyl ring breathing (Faix 1992; Sarkanen et al. 1971), C-O stretching (Faix 1992; Sarkanen et al. 1971), S and G rings condensed (Boeriu et al. 2004) with G substituted at position 5 (Faix 1992; Singh et al. 2005), stretching of C-C and C-O, in G condensed > G etherified (Singh et al. 2005). F2 and F6 lignins had values close to those of Alcell lignin.

At $1705\text{--}1709\text{ cm}^{-1}$, the stretching vibration of carbonyl and unconjugated carbonyl/carboxyl groups (Boeriu et al. 2004), is clearly identified. There was no absorption band at 1653 cm^{-1} , attributed to the stretching of carbonyl groups conjugated with aromatic rings in organosolv lignins (Xu et al. 2006).

The C-H stretch of methyl and methylene groups in aliphatic chains of lignin (Faix 1992; Sarkanen et al. 1971; Boeriu et al. 2004), and the C-H stretching in aromatic methoxyl groups (Boeriu et al. 2004) appeared at $2841\text{--}2849\text{ cm}^{-1}$. The stretching of methyl and methylene groups also appeared at the $2916\text{--}2937\text{ cm}^{-1}$ band of lignin (Roof et al. 2007; Sarkanen et al. 1971), involving symmetric and asymmetric signals.

Based on the analysis of FTIR spectra of lignins obtained by different fractionations it can be concluded that there were no significant differences between the lignin structures obtained in this work.

The lignin appends different substituents to the aromatic ring by selecting the appropriate reagents and conditions. In the case of the synthesis of phenol-formaldehyde resins, the polymerisation reactions take place by electrophilic substitution of formaldehyde at a free position of the aromatic ring. The free positions in the ring (C3-C5 and C5, respectively) are susceptible to reacting with formaldehyde. The S-type units both C3 and C5 positions are linked to a methoxy group, resulting in low reactivity with formaldehyde. From this point of view, lignins with H and G groups must be a priori more suitable for phenol-formaldehyde formulations (Tejado et al. 2007).

The chemical reactivity of lignin in various modification processes is profoundly influenced by its phenolic hydroxyl content, e.g. in the reaction with formaldehyde for the production of lignin adhesives (Gilarranz et al. 2001). Lignin's patterns can be characterised by the phenolic functionality, and many lignin modifications are based on the phenolic character, a property that is not easily quantified in a complex material. The phenolic hydroxyl groups may promote the formation of condensed structures via phenoxy radicals (Tiainen et al. 1999). The presence of this group therefore tends to increase the reactivity of lignin towards formaldehyde when lignin is used for phenolic resin formulation (El Mansouri et al. 2006).

UV-spectroscopic methods are based on the wavelength shift between ionised and protonated phenolic hydroxyl groups. The intensities of the absorbances in the ionisation difference spectrum are proportional to the content of phenolic hydroxyl groups. The method is based on the difference in absorption at 300 and 360 nm between phenolic units in neutral and alkaline solutions. The content of ionizing phenol hydroxyl groups can be quantitatively evaluated by comparing the $\Delta\epsilon$ values of substances studied at certain wavelengths to the values of $\Delta\epsilon$ of the respective model compounds (I, II, III, IV types), as shown in Fig. 3.

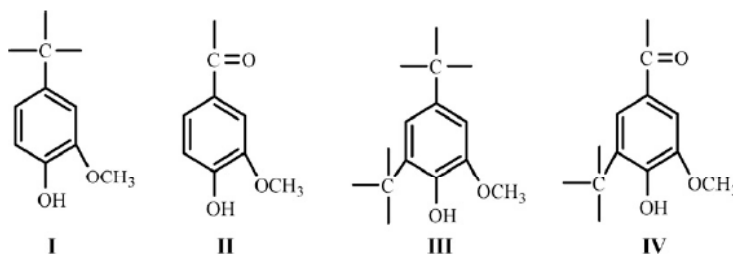


Fig. 3. Types of phenolic structures determined by the UV method (Zakis 1994)

EI Mansouri and Salvadó (2007) compared the content of various phenolic units in different lignin samples by several methods: aminolysis, UV spectroscopy, ^1H NMR, ^{13}C NMR, and non-aqueous potentiometric titration. The statistical comparison of the methods has shown that the methods used are not fully comparable. This variability in results was attributed by the authors to an incomplete acetylation in the case of methods based on lignin acetylation, such as ^1H NMR, ^{13}C NMR, and aminolysis, due to steric hindrance by the methoxyl groups present in lignins. Moreover, NMR-spectroscopy is characterized by an overlapping signal that lowers the accuracy of these techniques. They concluded that UV spectroscopy is an easy method to quickly estimate some phenolic hydroxyl structures. Results obtained by the UV method have been shown to correlate well with those obtained by ^1H NMR (Tiainen et al. 1999), as well as by aminolysis (Gartner et al. 1999). UV spectroscopy has also been used as the calibration method for the determination of phenolic hydroxyl groups by FTIR (Gilarranz et al. 2001).

The phenolic hydroxyl contents determined for the studied lignins are presented in Table 4.

Table 4. Mean Values of Phenolic OH in Lignins, % (w/w) of Lignin

	OH _I	OH _{II}	OH _{III}	Total OH *
Alcell	2.48	0.53	0.98	4.01
F1	1.37	1.30	2.00	4.67
F2	0.87	1.29	1.90	4.06
F3	1.66	1.12	1.70	4.47
F4	1.59	1.18	1.76	4.54
F5	4.11	0.82	1.51	6.45
F6	0.51	1.34	1.85	3.70
F7	1.05	1.31	1.85	4.19

* Note: No OH IV groups were present in these lignins.

The phenolic OH content in lignins referred by other authors for the ethanol water process are very variable, ranging from 3.8% w/w (2.21 mmol/g, NMR method) and 8.2% w/w (4.83 mmol/g), (Pan et al. 2006). Results in Table 4 are somewhat higher than those obtained by EI Mansouri and Salvadó (2007) with ethanol process lignin from *Populus* wood pretreated by steam explosion and the simultaneous saccharification and fermentation process (OH_I: 1.43; OH_{III}: 0.68; OH_{II}: 0.14; OH_{IV}: 0.05).

The highest value of OH_I corresponded to F5 (4.11%), followed by the Alcell lignin (2.48%). The OH_{II} correlated with the absorbance band at 1261-1265 cm^{-1} , indicative of G groups ($R=0.863$, $p=0.001$). The highest value of OH_{II} corresponded to condition F6 (1.36%). Similarly, the OH_{III} correlated strongly with G groups, at 1261-1265 cm^{-1} ($R=0.935$, $p=0.000$). F5 lignin presents a significantly lower value of OH_{III}.

F5 lignin, obtained with the most severe conditions, presented the highest amount of total phenolic-OH, even though the aromatic hydroxyl groups increase rather rapidly in the initial stages and then tended to level off (Goyal et al. 1992). No lignins exhibited OH_{IV}.

The reactivity and physicochemical properties of lignins are partly governed by their molar mass distribution. The usual method to its determination using size-exclusion

chromatography (SEC). The molecular weights and polydispersity of lignins are presented in Table 5.

Table 5. Molecular Weights, Mn, Mw, and Polydispersity (Mw / Mn).

Lignin	Mw	Mn	Mw/Mn
Alcell	1324	608	2.18
F1	1466	773	1.90
F2	1692	909	1.86
F3	1436	732	1.96
F4	1436	742	1.93
F5	932	562	1.66
F6	1331	794	1.68
F7	1420	901	1.58

All lignins showed low molecular weights compared with the values reported for ethanol-water processes at high temperatures (Glaser et al. 1993; Roof et al. 2007) and for soda process (Hoareau et al. 2004), but similar to those found by other authors (Sarkanen 1981), when working at moderate temperatures (Mw: 1800, Mn: 824), indicating a lower condensation between lignin fragments.

There were significant negative correlations between molecular weights and phenolic OH, i.e., Mw and Total OH ($R = -0,745$, $p = 0,034$), Mw and OH_I ($R = -0,816$, $p = 0,014$), and Mn and OH_I ($R = -0,868$, $p = 0,005$).

The F5 fractionation (240 min, 175° C, and 2.0 g L⁻¹ sulfuric acid) produced a lignin with a Mn and Mw significantly lower than the others (564 and 932, respectively), whereas the F2 process (240 min, 175° C, without the addition of acid (autocatalyzed) produced a lignin with a significantly higher Mw (1692). Therefore, this last process produced the highest molecular weights, with a high purity. The lowest polydispersity Mw/Mn corresponded to the lignin obtained from the F7 fractionation, but it formed a homogeneous group with F5 and F6 lignins. The lignins obtained in this work had values of Mw and Mn similar to or higher than Alcell lignin. On the other hand, these lignins showed polydispersity values lower than Alcell lignin. These results agree with those of Olier et al. 2001.

The multifactorial ANOVA test showed that the presence and the acid concentration, and the temperature and time of the treatments, significantly affected Mw ($p = 0.006$ and 0.025 respectively) and Mn ($p = 0.025$ and 0.021 respectively), whereas only the acid affected polydispersity ($p = 0.047$). More aggressive fractionation conditions (presence of sulfuric acid and high temperature) generate lignins of lower molecular weights.

Thermal decomposition of lignin was determined by thermogravimetric analysis (TGA) under N₂ atmosphere. DTG (rate of weight loss) and TG (weight loss) curves are presented in Fig. 4. Table 6 gives the degradation onset temperature (T_{onset}), maximum degradation temperature (T_{max}), and the correspondent weight loss. Maximum degradation temperature (T_{max}) may be expressed as a thermal decomposition temperature and can be used to compare thermal stability characteristics of different materials.

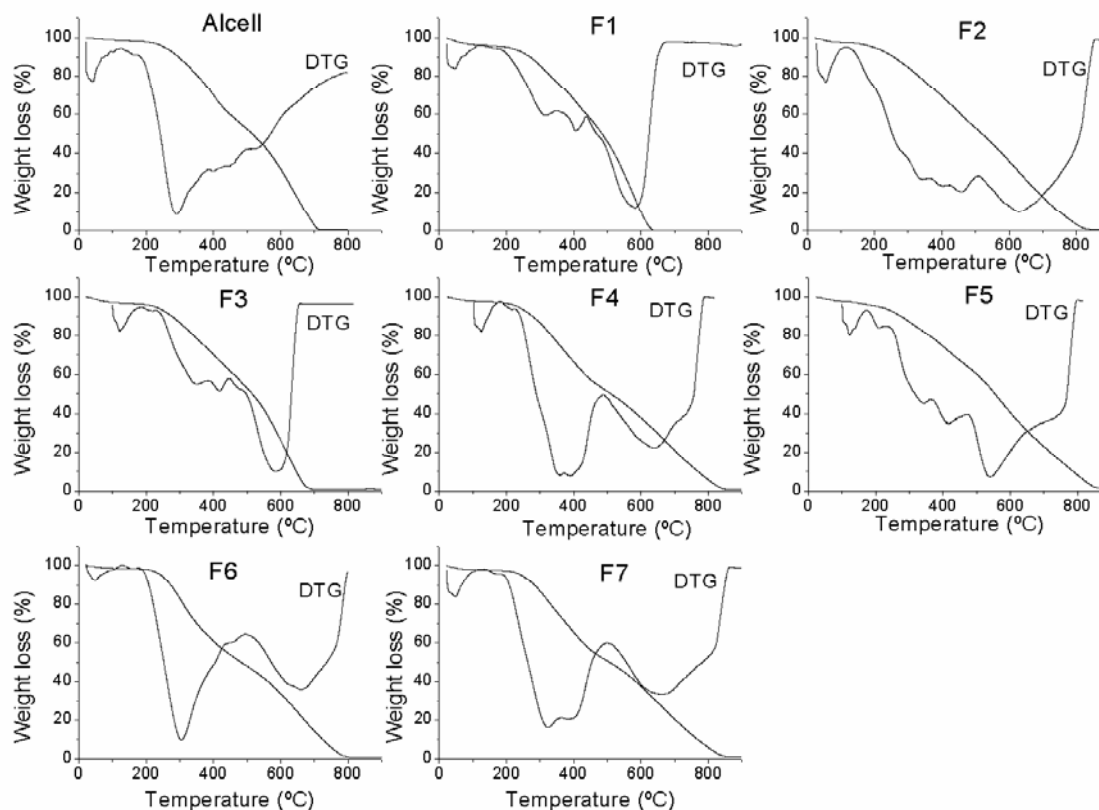


Fig. 4. Thermal analysis of lignins (TG and DTG)

Table 6. Thermal Analysis of Lignins (TGA)

Lignin	Temperature to 5% weight loss (°C)	1 st thermal event				2 nd thermal event				Residue at 700°C (%)
		T_{onset} (°C)	Weight loss (%)	$T_{max.}$ (°C)	Weight loss at $T_{max.}$ (%)	T_{onset} (°C)	Weight loss (%)	$T_{max.}$ (°C)	Weight loss at $T_{max.}$ (%)	
Alcell	255	270	35.4	394	28.5	-	-	-	-	0.0
F1	200	265	47.4	415	35.5	510	41.3	583	83.2	0.0
F2	203	238	42.6	435	35.4	526	46.6	630	68.4	18.8
F3	226	252	49.7	410	31.5	546	40.7	616	79.2	0.9
F4	233	254	32.3	376	28.7	563	42.5	681	75.7	21.1
F5	209	272	31.2	408	26.7	506	30.6	560	51.0	23.1
F6	245	246	28.2	308	18.4	570	37.7	650	77.5	12.4
F7	239	249	23.0	321	18.0	533	43.5	619	82.8	4.0

Moisture loss of the material (< 5% of mass loss) is not considered a thermal event (Singh et al. 2005; Sun 2001a). The results indicate that thermal degradation of these lignins began above 240 °C (T_{onset}). This means that these lignins are thermally stable until about 240 °C; therefore, the processing temperature could be raised to about this temperature without serious lignin degradation. Two thermal events can be identified

(Sun 2001b; Xu et al. 2006; Domínguez et al. 2008): in the first step, large amounts of volatiles (H_2O , CO , and CO_2) generated by the breaking of the side chains are released, whereas in the second one, CO , CO_2 , and CH_4 (Yang et al. 2007; Liu et al. 2008) are released primarily.

Maximum DTG of the first thermal event appeared between 308 and 435 °C. Both events would correspond to the breaking of the bonds between the monomeric units of lignin, generating the release of phenols. The decomposition of aromatic rings occurs above 400 °C (Hoareau et al. 2004), and demethoxylation or demethylation of the aromatic ring do not occur above 450° C (Meier et al. 1999). The Alcell, F2, F4, F5, F6, and F7 lignins formed a homogeneous group, showing lower weight loss than the F1 and F3 group (treated with acetic acid). DTG curves of the F6 and F7 lignins (treated with acetic sulfuric) showed similar behavior during thermal decomposition, however, F5 showed an own behavior. Also F1 and F3 lignins (treated with acetic acid) presented similar behavior, and this behavior is different than that of F2 and F4 lignins.

Weight loss at maximum temperature in the first thermal event showed significant differences ($p = 0.003$) between lignins, being lower in the F7 and F6 lignins, and higher in F3. The highest value corresponded to the homogeneous group formed by F1 and F2 (both 35.4%). Lignins from the fractionations made with acetic acid or without acid showed higher maximum degradation temperature (T_{max}) than PF resins (approximately 345 °C) (Tejado et al. 2007), so that their incorporation could broaden the application temperature range of resins. The second thermal event occurred at temperatures between 560 and 659° C (Fig. 4).

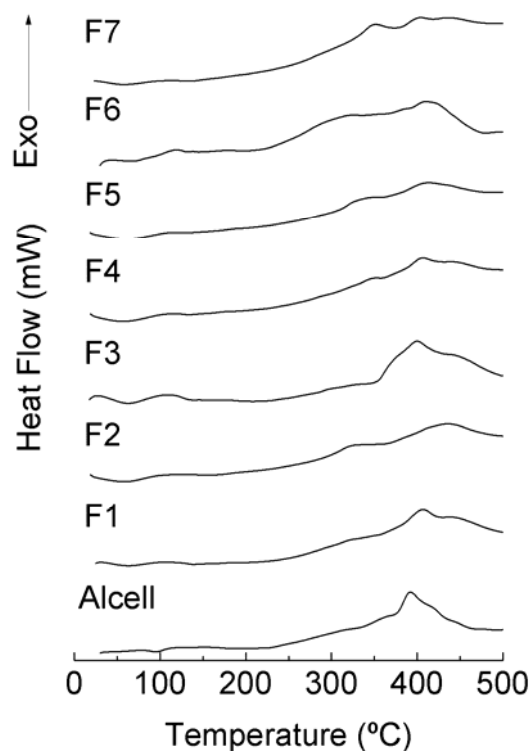


Fig. 5. Thermal analysis (DSC) of the studied lignins

Differential scanning calorimetry (DSC) is a thermoanalytical technique used to measure the thermal properties of a sample, as phase transition and glass transition temperature. The thermal analysis (DSC) of the studied lignins is shown in Fig. 5. All lignins showed a small endothermic peak below 100 °C, which corresponded to the removal of moisture. DSC curves showed a broad exothermic peak with maximum peaks between 350 and 450° C, where also occurs the maximum DTG of the first thermal event.

CONCLUSIONS

1. Lignins from the ethanol-water fractionations of bagasse with acetic acid or without acid showed purity values higher than those obtained using moderate temperatures and a low concentration of sulfuric acid.
2. Based on the analysis of FTIR spectra of lignins can be concluded that there were no significant differences between the lignin structures obtained in this work.
3. All the lignins exhibited relatively low molecular weights, indicating a lower condensation than a reference commercial lignin sample (Alcell®).
4. The TGA and DSC thermograms of the lignins studied presented two main thermal events: the first between 310 and 435°C, and the second between 560 and 659 °C. The degradation of all lignins began above 235 °C (T_{onset}).
5. All the studied lignins showed: p-hydroxyphenyl (H) groups and a greater proportion of guaiacyl (G) groups, with free positions in the ring (C3-C5 and C5, respectively) than the Alcell® lignin, favoring the electrophilic aromatic substitution reactions. These lignins showed lower purity, similar or greater amount of phenolic hydroxyl, and higher degradation temperatures, than the Alcell® lignin.
6. The results are promising to explore the technical and economic feasibility of bagasse derivatives, mainly lignins for the production of phenol–formaldehyde (PF) resins and biodegradable polyurethanes, replacing petroleum chemicals.

REFERENCES CITED

- Area, M. C., Felissia, F. E., and Vallejos, M. E. (2009). "Ethanol-water fractionation of sugar cane bagasse catalyzed with acids," *Cell. Chem. Technol.* 43, 269-277.
- Boeriu, C. G., Bravo, D., Gosselink, R. J. A., and van Dam, J. E. G. (2004). "Characterisation of structure-dependent functional properties of lignin with infrared spectroscopy," *Ind. Crop.Prod.*20, 205-218.
- Domínguez, J. C., Oliet, M., Alonso, M. V., Gilarranz, M. A., and Rodríguez, F. (2008). "Thermal stability and pyrolysis kinetics of organosolv lignins obtained from *Eucalyptus globulus*," *Ind. Crop. Prod.*27, 150-156.
- El Mansouri, N. E. E., and Salvado, J. (2006). "Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins," *Ind. Crop. Prod.* 24, 8-16.
- El Mansouri, N. E. E., and Salvado, J. (2007). "Analytical methods for determining functional groups in various technical lignins," *Ind. Crop. Prod.* 26, 116-124.

- Faix, O. (1992). "Fourier transformed infrared spectroscopy," in: *Methods in Lignin Chemistry*, Lin, S.Y., Dence, C.W. (eds.), Springer-Verlag, Berlin-Heidelberg, pp. 93.
- Felissia, F. E., Vallejos, M. E., and Area, M. C. (2010). "Lignin recovery from spent liquors from ethanolwater fractionation of sugar cane bagasse," *Cellulose Chem. Technol.* 44(9), 311-318.
- Gartner, A., Gellerstedt, G., and Tamminen, T. (1999) "Determination of phenolic hydroxyl groups in residual lignin using a modified UV-method," *Nord. Pulp Pap. Res. J.* 14, 163-170.
- Gilarranz, M. A., Rodríguez, F., Oliet, M., García, J., and Alonso, V. (2001). "Phenolic OH group estimation by FTIR and UV spectroscopy. Application to organosolv lignins," *J. Wood Chem. Technol.* 21(4), 387-395.
- Glasser, W. G., Davé, V., and Frazier, C. E. (1993). "Molecular weight distribution of (semi-) commercial lignin derivatives," *J. Wood Chem. Tech.* 13, 545-559.
- Gonçalves, A., and Schuchardt, U. (1999). "Oxidation of organosolv lignins in acetic acid: Influence of oxygen pressure," *Appl. Biochem. Biotech.* 77, 127-132.
- Goyal, G. C., Lara, J. H., and Kendall Pye, E. (1992). "Autocatalyzed organosolv pulping of hardwoods: Effect of pulping conditions on pulp properties and characteristics of soluble and residual lignin," *Tappi J.* 75, 110-116.
- Hoareau, W., Trindadea, W. G., Siegmund, B., Castellana, A., and Frollini, E. (2004). "Sugar cane bagasse and curaua lignins oxidized by chlorine dioxide and reacted with furfuryl alcohol: Characterization and stability," *Polym. Degrad. Stab.* 86, 567-576.
- Lora, J. (2008). "Industrial commercial lignins: Sources, properties and applications," in: *Monomers, Polymers and Composites from Renewable Resources*, Belgacem, M., and Gandini, A. (eds.), Elsevier, Oxford, UK, pp. 225-241.
- Liu, Q., Wang, S. R., Zheng, Y., Luo Z. Y., and Cen, K. F. (2008). "Mechanism study of wood lignin pyrolysis by using TG-FTIR analysis," *J. Anal. Appl. Pyrol.* 82, 170-177.
- Meier, D., and Faix, O. (1999). "State of the art of applied fast pyrolysis of lignocellulosic materials - A review," *Bioresource Technol.* 68, 71-77.
- Oliet, M., Rodríguez, F., García, J., and Gilarranz, M. A. (2001). "The effect of autocatalyzed ethanol pulping on lignin characteristics," *J. Wood Chem. Tech.* 21(1), 81-95.
- Pan, X., Kadla, J. F., Ehara, K., Gilkes, N., and Saddler, J. N. (2006). "Organosolv ethanol lignin from hybrid poplar as a radical scavenger: Relationship between lignin structure, extraction conditions, and antioxidant activity," *J. Agric. Food Chem.* 54, 5806-5813.
- Pye, E. K., and Katzen, R. (2000). "Recovery of co-products from nonwood organosolv pulping," *TAPPI Pulping/Process & Product Quality Conference Proceedings*, Boston, MA, TAPPI Press.
- Ragauskas, A. J. (ca. 2008). "Typical H:G:S Ratio for Lignin from Biomass," *Technical reviews: Lignin*, Institute for Paper Science and Technology (IPST) http://www.ipst.gatech.edu/faculty/ragauskas_art/technical_reviews/lignin%20HGS.pdf (consulted 10/02/2011)
- Sarkanen, K. V., Chang, H. M., and Allan, G. G. (1967c). "Species variation in lignins. III. Hardwood lignins," *Tappi J.* 50, 587-590.

- Sarkanen, K. V., Chang, H. M., and Allan, G. G. (1967b). "Species variation in lignins. II. Conifer lignins," *Tappi J.* 50, 583-587.
- Sarkanen, K. V., Chang, H. M., and Ericsson, B. (1967a). "Species variation in lignins. I. Infrared spectra of guaiacyl and syringyl models," *Tappi J.* 50, 572-575.
- Sarkanen, K. V., and Ludwig, C. H. (1971) (eds.). *Lignins: Occurrence, Formation, Structure and Reactions*, John Wiley & Sons, Inc., New York.
- Sarkanen, S., Teller, D. C., Hall, J., and McCarthy, J. L. (1981). "Lignin. 18. Associative effects among organosolv lignin components," *Macromolecules* 14, 426-434.
- Singh, R., Singh, S., Trimukhe, K. D., Pandare, K. V., Bastawade, K. B., Gokhale, D. V., and Varma, A. J. (2005). "Lignin-carbohydrate complexes from sugarcane bagasse: Preparation, purification, and characterization," *Carbohydr. Polym.* 62, 57-66.
- Sun, R. C., Sun, X. F., and Wen, J. L. (2001a). "Fractional and structural characterization of lignins isolated by alkali and alkaline peroxide from barley straw," *J. Agric. Food Chem.* 49, 5322-5330.
- Sun, R. C., Lu, Q., and Sun, X. F. (2001b). "Psycho-chemical and thermal characterization of lignins from *Caligonum monogolicum* and *Tamarix* spp. Polym," *Degrad. Stab.* 72, 229-238.
- Tejado, A., Pena, C., Labidi, J., Echeverria, J. M., and Mondragon, I. (2007). "Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis," *Bioresource Technol.* 98, 1655-1663.
- Tiainen, E., Drakenberg, T., Tamminen, T., Kataja, K., and Hase, A. (1999). "Determination of phenolic hydroxyl groups in lignin by combined use of ^1H NMR and UV spectroscopy," *Holzforschung* 53(5), 529-533.
- Wang, M., Leitch, M., and Xu, C. (2009). "Synthesis of phenol-formaldehyde resol resins using organosolv pine lignins," *Eur. Polym. J.* 45, 3380-3388.
- Xu, F., Sun, J. X., Sun, R. C., Fowler P., and Baird, M. S. (2006). "Comparative study of organosolv lignins from wheat straw," *Ind. Crop. Prod.* 23, 180-193.
- Yang, H., Yan, R., Chen, H., Lee, D. H., and Zheng, C. (2007). "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel*. 86, 1781-1788.
- Zakis, G. L. (1994). *Functional Analysis of Lignins and Their Derivatives*, TAPPI Press, Atlanta, GA.

Article submitted: November 25, 2010; Peer review completed: January 15, 2011;
Revised version received: February 16, 2011; Accepted: February 19, 2011; Published:
February 21, 2011.