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P. R. Bonelli<sup>ab</sup> & A. L. Cukierman<sup>abc</sup>

<sup>a</sup> Programa de Investigación y Desarrollo de Fuentes Alternativas de Materias Primas y Energía (PINMATE)—Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina

<sup>b</sup> Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Buenos Aires, Argentina

<sup>c</sup> Cátedra de Farmacotecnia II. Departamento de Tecnología Farmacéutica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Buenos Aires, Argentina

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# Physico-chemical Characteristics and Pyrolysis Behavior of Klason Lignins Isolated from Agro-industrial Biomass

P. R. Bonelli<sup>1,2</sup> and A. L. Cukierman<sup>1,2,3</sup>

<sup>1</sup>*Programa de Investigación y Desarrollo de Fuentes Alternativas de Materias Primas y Energía (PINMATE)—Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina*

<sup>2</sup>*Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Buenos Aires, Argentina*

<sup>3</sup>*Cátedra de Farmacotecnia II. Departamento de Tecnología Farmacéutica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Buenos Aires, Argentina*

Klason lignins lab-isolated from two lignocellulosic biomasses emerging from the processing of agro-industrial products, *Aspidosperma australe* wood sawdust and *Bertholletia excelsa* nutshells, with different contents of lignin (27 and 57 wt%, respectively), are characterized. Characterization includes determination of ash content, elemental composition, Fourier-transform infrared spectra, and surface morphological features by scanning electronic microscopy. Pyrolysis behavior of the isolated lignins as well as of the parent biomasses from which they are extracted is comparatively examined by non-isothermal thermogravimetric analysis from room temperature up to 1000°C. The lignins exhibit different ash contents and elemental compositions, as well as noticeable differences in their pyrolytic behavior depending on the botanical origin of the bio-resource and with respect to that determined for the untreated parent biomasses. Overall, the lignin isolated from the nutshells is more resistant to degrade than the sawdust-derived lignin, likely due to a more condensed chemical structure.

*Keywords:* bio-energy, biomass, Klason lignins, pyrolysis

## 1. INTRODUCTION

Pyrolysis of lignin is complex, since it depends on lignin composition and process conditions (Brodin et al., 2010; Yang et al., 2007; Ferdous et al., 2002). Lignins are complex racemic polymers derived mainly from three hydroxycinnamyl alcohol monomers that differ in their degree of methoxylation: p-coumaryl, coniferyl, and sinapyl alcohols, which have the amino acid phenylalanine as their bio-synthetic precursor. These species, known as monolignols, produce p-hydroxyphenyl, guaiacyl, and syringyl phenylpropanoid units, respectively, which are the main building blocks of the lignin polymer (Faravelli et al., 2010).

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Address correspondence to Dr. A. L. Cukierman, Programa de Investigación y Desarrollo de Fuentes Alternativas de Materias Primas y Energía (PINMATE)—Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Intendente Güiraldes 2620, Ciudad universitaria, Buenos Aires C1428BGA, Argentina.  
E-mail: [analea@di.fcen.uba.ar](mailto:analea@di.fcen.uba.ar); [anacuki@ffyb.uba.ar](mailto:anacuki@ffyb.uba.ar)

Various methods have been developed to separate the macromolecular bio-polymeric components in lignocellulosic biomass. However, the recovery of lignin from lignocellulosic materials is generally difficult due to condensation and oxidation reactions taking place during the isolation processes (Haykiri-Acma et al., 2010). Despite the fact that several studies exploring different aspects on lignin pyrolysis have been reported, a thorough knowledge on the pyrolytic behavior of lignin has not been attained and it is still difficult to predict pyrolysis characteristics for a particular lignin due to uncertainties about lignin structure and to the difficulty in its isolation (Wang et al., 2009; Baptista et al., 2006). In particular, studies concerned with the pyrolytic behavior of lignins isolated from lignocellulosic biomasses are still restricted. Low molecular weight model compounds related to structural elements of lignin polymers and/or commercial samples have been mostly employed, even though they are far from representing the real scenario (Haykiri-Acma et al., 2010).

Within this context, the present work deals with characterization and pyrolytic behavior of Klason lignins lab-isolated from two unexplored lignocellulosic biomasses with different contents of lignin, generated in large quantities from the processing of agro-industrial products. The pyrolytic behavior of the lignins, as determined by thermogravimetric analysis, is examined and compared with those assessed for the whole biomasses from which they are obtained.

## 2. EXPERIMENTAL

### 2.1. Materials and Isolation of Lignins

Lignocellulosic wastes emerging from the processing of two agro-industrial products were employed for lab-isolation of lignin samples: sawdust from *Aspidosperma australe* wood (AWS) and shells from Brazil nuts (BNS). *Aspidosperma australe*, commonly known as Guatambú, is a tree species indigenous to South America, found in Argentine, Brazil, and Paraguay. The wood has many uses in carpentry, owing to its good characteristics, and it is also employed as fuel in some regions. Brazil nut is the fruit of the *Bertholletia excelsa* tree. It belongs to the Lecythidaceae family and grows in a vast zone of South America, mostly in the region of Pará (Brazil). Industrial shelling of the nuts generates huge amounts of shells as waste material (Bonelli et al., 2001).

The Klason method was applied to isolate lignin from the biomasses. This procedure has become one of the standard methods for the determination of lignin in wood (Jiang et al., 2010). Table 1 reports the contents of lignin and holocellulose for both wastes. It also includes ash contents and elemental compositions. The former were determined according to ASTM standards, whereas the latter ones were assessed using a Carlo Erba EA 1108 elemental analyzer. As seen in Table 1, the content of lignin in the nutshells is remarkably higher than that in wood sawdust. It is similar to the one recently reported for hazelnut shells (Haykiri-Acma et al., 2010) on the same basis. Besides, the lignin content of the wood sawdust is comparable to values earlier reported for other species (Cukierman, 2007).

### 2.2. Characterization of Lignin Samples

Ash content and elemental composition of the lab-isolated Klason lignins were assessed according to ASTM standard and using a Carlo Erba Model EA 1108 instrument, respectively. Results are reported as average values of triplicate determinations, where the standard error did not exceed 5%. In addition, Fourier transform infrared (FT-IR) spectroscopy was applied to characterize the lignins and the biomasses used for isolation of the Klason lignins. The spectra were recorded using a Nicolet Magna IR 550 spectrometer within the wavenumber range of 400–4000  $\text{cm}^{-1}$ . The transmission method and pellets of KBr containing 1% of the sample were used. Surface

TABLE 1  
Chemical Characteristics of the Parent Lignocellulosic Biomasses and of the Lab-isolated Klason Lignins

<i>Characteristic/Sample</i>	<i>AWS</i>	<i>BNS</i>	<i>AWL</i>	<i>BNL</i>
Biopolymer content (wt%) <sup>a</sup>				
Lignin	27	57	—	—
Holocellulose	73	43	—	—
Proximate analysis (wt%) <sup>b</sup>				
Volatile matter	72.7	76.1	—	—
Ash	1.0	1.7	0.1	6.0
Fixed carbon <sup>d</sup>	26.3	22.2	—	—
Elemental analysis (wt%) <sup>c</sup>				
Carbon	48.2	50.0	58.9	52.7
Hydrogen	5.6	5.8	6.0	4.7
Nitrogen	0.9	0.7	0.6	0.5
Sulfur	—	—	0.2	1.4
Oxygen <sup>d</sup>	45.3	43.5	34.3	40.7

<sup>a</sup>Dry and extractive-free basis.

<sup>b</sup>Dry basis.

<sup>c</sup>Dry and ash-free basis.

<sup>d</sup>Estimated by difference.

morphology of the lignins was examined by field emission scanning electron microscopy (SEM), using a FE-SEM Carl Zeiss, Supra 40 microscope. Before the measurements, all of the samples were attached to mounting stubs, dried under vacuum, and sputter coated with Au.

### 2.3. Thermogravimetric Measurements for the Pyrolysis of Lignins

Pyrolytic behavior of the Klason lignins and of the whole lignocellulosic biomasses from which they were isolated, was examined by non-isothermal thermogravimetric (TG) analysis. For all of the samples, an average particle diameter lower than 44  $\mu\text{m}$  was employed. Measurements were carried out from ambient temperature up to 1,000°C operating under flowing  $\text{N}_2$ . A TA Instruments SDT Q600 thermogravimetric balance equipped with a  $\text{N}_2$  mass flow controller and a data acquisition system was used to carry out the measurements.

Preliminary experiments were first conducted in order to assess operating conditions for which diffusional effects were negligible. Accordingly, masses of 10 mg,  $\text{N}_2$  flow rates of 400 mL/min, and a heating rate of 10°C/min were employed. Further details of the different experimental procedures employed may be found in previous works (Kim et al., 2010; Bonelli et al., 2007).

## 3. RESULTS AND DISCUSSION

Ash content and elemental composition determined for the Klason lignins extracted from wood sawdust and nutshells are reported in Table 1. The data in the table show that the lignin isolated from the nutshells possesses lower contents of elemental carbon and hydrogen, and higher amounts of ash and sulphur than the one extracted from the wood sawdust. Major contents of the former are close to those reported for other samples isolated via acid hydrolysis of softwood (Nowakowski et al., 2010). Overall, elemental compositions point to different chemical structures of the lignin samples.

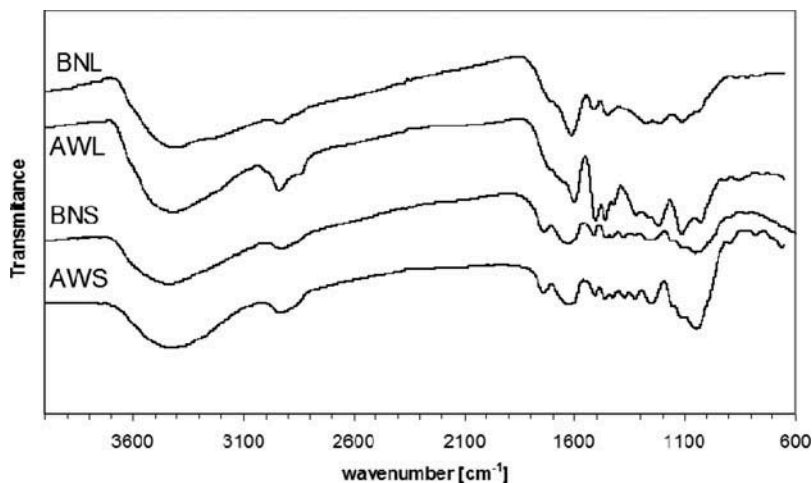


FIGURE 1 Fourier-transform infrared (FT-IR) spectra for the Brazil nutshells (BNS), sawdust from *Aspidosperma Australe* wood (AWS), and for the Klason lignins lab-isolated from the wood sawdust (AWL) and nutshells (BNL).

FT-IR spectra for the Klason lignins and the parent biomasses are comparatively shown in Figure 1. As may be appreciated, all of the spectra display a broad band at 3,600–3,000  $\text{cm}^{-1}$  assigned to –OH groups in aliphatic and phenolic structures. Characteristic bands are mainly found at 1,500–1,600  $\text{cm}^{-1}$  and at ca. 1,450  $\text{cm}^{-1}$  arising from deformations and aromatic ring vibrations. Below 1,400  $\text{cm}^{-1}$ , spectral analysis becomes more difficult, with the complex bands observed probably arising from contribution of various vibration modes (Boeriu et al., 2004). Besides, as seen in Figure 1, the spectrum for the nutshells with a preponderantly high content of lignin (57 wt %), as reported in Table 1, is not substantially different from that determined for the derived lignin in the region of 800–1,200  $\text{cm}^{-1}$ . On the contrary, differences in the same region are more noticeable between the wood sawdust and the lignin extracted from this biomass. They may be related to C–O, C–C, and C–OH bonds, which are characteristic of polysaccharides. As shown in Table 1, the content of lignin composing the sawdust is lower than that of holocellulose. The main differences between the lignins extracted from both biomasses may be noticed in the peaks at 1,550 and 1,450  $\text{cm}^{-1}$ .

SEM images of both lignins are shown in Figures 2a–2d, at two different magnifications (2,000 $\times$  and 40,000 $\times$ ). As can be seen, their surfaces look rough and show cavities and/or cracks, likely due to the extraction method applied, which involves hydrolysis of cellulose and hemicellulose in strong acid conditions, leaving lignin as an acid-insoluble residue. Likewise, differences between the lignins depending on the biomass botanical origin may be noticed.

Typical TG and DTG curves determined for the thermal degradation of the lignins isolated from the wood sawdust and the nutshells and normalized by the ash content, are illustrated in Figures 3 and 4, respectively. In each figure, TG-derivative thermogravimetric (DTG) curves determined for the pyrolysis of the whole biomasses are also included for comparison. As may be appreciated, small changes in weight fractions for all of the samples take place at temperatures lower than 100 $^{\circ}$ C, attributable to moisture evolution. Both biomasses start to decompose at around 160–170 $^{\circ}$ C, releasing volatile matter. The TG curves show two major weight loss stages, between  $\sim$ 200 and 400 $^{\circ}$ C and above 400 $^{\circ}$ C, with the slope of the curves changing between these two temperature intervals. The slope between 200 and 400 $^{\circ}$ C is higher than that for the higher temperature range.

In agreement with other reported results, distinct weight loss zones may be associated with degradation dynamics of main constituents composing lignocellulosic biomasses. Since the

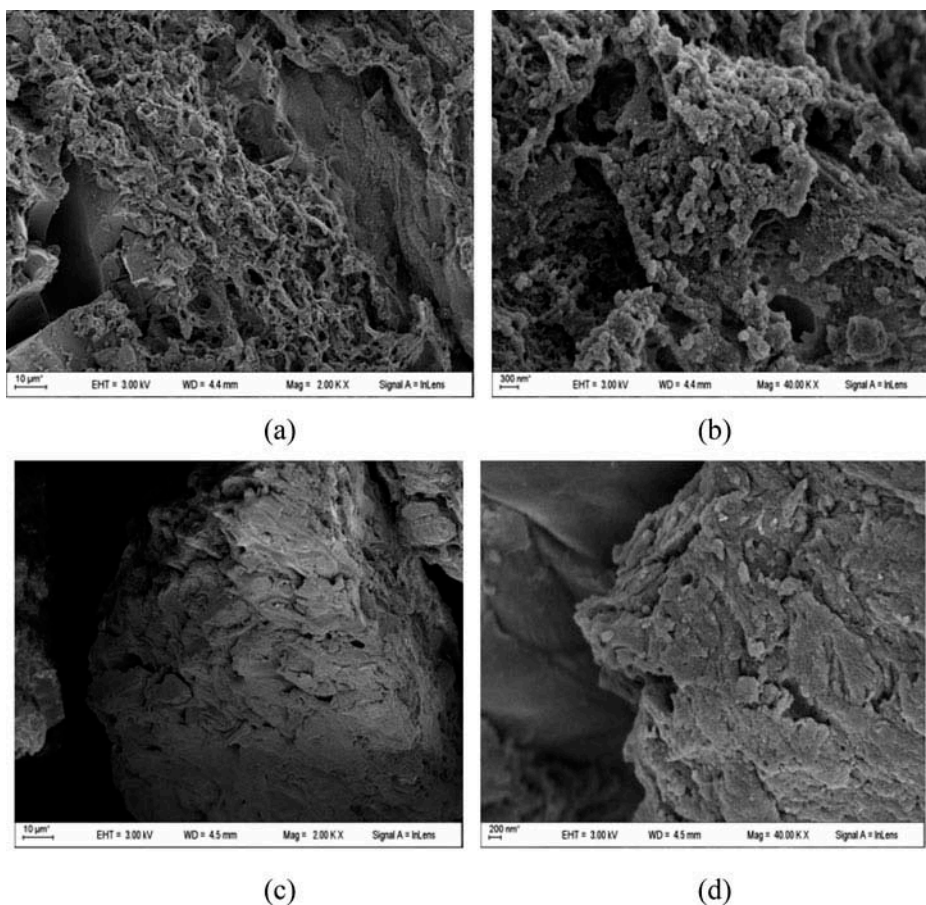


FIGURE 2 SEM micrographs of the Klason lignins extracted from: (a) wood sawdust at 2,000 $\times$ , (b) wood sawdust at 40,000 $\times$ , (c) nutshells at 2,000 $\times$ , and (d) nutshells at 40,000 $\times$ .

biomasses are mostly composed by cellulose, hemicellulose, and lignin, decrease in weight fractions at around 225–325 $^{\circ}\text{C}$  is generally attributed to the onset of hemicellulose degradation, while contribution of cellulose decomposition to pyrolysis is considered to predominate in the range between 325 and 375 $^{\circ}\text{C}$ . Lignin has a broad decomposition temperature range at temperatures higher than 250 $^{\circ}\text{C}$ . Hence, degradation of cellulose and hemicellulose composing the biomasses, possessing a polysaccharide structure relatively easy to break down, should predominantly take place at the lower temperatures. At higher temperatures, decomposition of lignin, which is more resistant to degrade than the other two major biopolymers composing the biomasses, due to its cross-linked aromatic structure, appears to become predominant inducing pyrolysis of biomass to slow down (Haykiri-Acma et al., 2010; Wongsiriamnuay and Tippayawong, 2010; Basso et al., 2005).

On the other hand, the results (Figures 3 and 4) also show that thermal degradation of the lignins proceeds steadily almost throughout the temperature range in comparison with the pyrolysis of the whole biomasses from which they were isolated. For temperatures above 200 $^{\circ}\text{C}$ , weight fractions for the lignins are pronouncedly higher than those for the whole biomasses. Likewise, the maximum degradation rates are lower for the lignins than for the biomasses and the degradation profiles are shifted to higher temperatures. As expected, higher residual weight fractions are



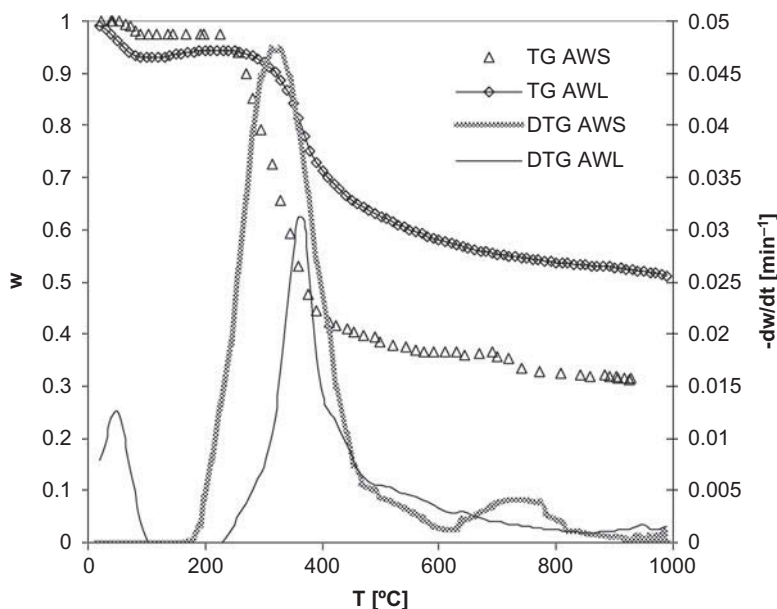


FIGURE 3 TG-DTG curves for the pyrolysis of the sawdust from *Aspidosperma australe* wood sawdust (AWS) and of the lab-isolated Klason lignin (AWL).

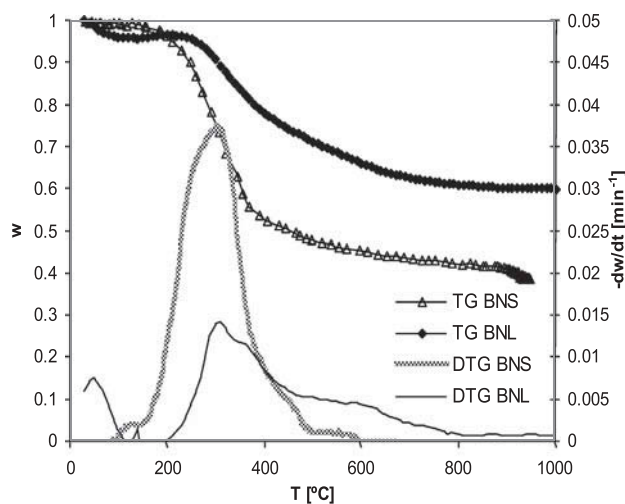


FIGURE 4 TG-DTG curves for the pyrolysis of the Brazil nutshells (BNS) and of the lab-isolated Klason lignin (BNL).

attained for the lignins. Accordingly, comparison of the thermal degradation behavior for the lignins with that for the biomasses clearly evidences the effect of the other major biopolymers, i.e., cellulose and hemicellulose, and minor constituents on thermal degradation.



Furthermore, noticeable differences in the pyrolytic behavior between the Klason lignins may be appreciated. The onset of degradation for the lignin extracted from the wood sawdust takes place at a relatively higher temperature (179°C) than for the sample obtained from the nutshells (160°C). The maximum reaction rate and the corresponding peak temperature are also higher for the former. However, residual weight fractions at 950°C ( $w_r$ ), namely, char yields attained for the pyrolysis of the investigated lignins, indicate that the sample extracted from the nutshells ( $w_r = 0.62$ ) offers a higher resistance to thermal degradation compared to the wood sawdust-derived lignin ( $w_r = 0.38$ ). Since the Klason method reportedly favors condensing reactions (Faravelli et al., 2010; Jakab et al., 1997), the results suggest a more condensed structure of the lignin isolated from the nutshells than that of the sawdust-derived lignin. Hence, differences in composition and chemical structures of the lignins related to the different botanical origin of the biomasses from which they were extracted should be responsible for the degradation behaviors observed.

#### 4. CONCLUSIONS

The Klason isolation method applied to *Aspidosperma australe* wood sawdust and *Bertholetia excelsia* nutshells, with pronouncedly different lignin contents, lead to lignin samples characterized by different ash contents and elemental compositions. In agreement, noticeable differences in their thermal degradation behavior depending on the parent biomass are found. Thermal degradation of the wood-derived lignin starts at a relatively higher temperature than that of the lignin isolated from the nutshells. The maximum reaction rate and the peak temperature are also higher for the former, whereas char yields as judged by the residual weight fractions attained at 950°C indicate that the lignin derived from the nutshells is more resistant to degrade than that extracted from the wood sawdust. The behavior could be due to a more condensed structure for the former.

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