

# Mild chemical modification of acetosolv lignin from several Chilean sources

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## Abstract

Lignin is the most abundant aromatic bio-polymer in nature. However, applications of lignin as building-blocks in material science is affected by several drawbacks. In order to tailor selected properties a mild modification at room temperature (22 °C) was carried out. Acetosolv lignin from *Pinus sp.*, *Triticum sp.*, and *Eucalyptus sp.* were modified with propylene oxide for 24 hours in alkaline media (pH: 12). Physico-, chemical-, and biological-properties were evaluated. Regardless lignin source hydroxypropyl-lignin (HPL) were synthesized in a high yield (87-96%). Strong structure-property relationship was established in function of monolignol units. <sup>1</sup>H-NMR provide valuable insight regarding reaction efficiency ratio associated to the Syringyl/Guaiacyl ratio. Hydroxypropylation affects solubility, antioxidant activity, and the thermal behaviour. However, changes upon derivatization were related to the specific source and composition. Modified Acetosolv lignin from Chilean sources possess properties that are expected to enhance their role in new polymerization pathways for material engineering.

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## Introduction

Lignin are the most abundant phenolic bio-polymer in vascular plants, and comprises a wide group of molecules with a very heterogeneous chemical structure based on three monomer units (H: hydroxyphenyl, G: guaiacyl, S: syringyl). Lignin exhibit physicochemical limitations for polymer formulation. Drawbacks such as low solubility, limited compatibility in binary and ternary polymer-systems, as well as a challenger recalcitrant behavior are recognized (Kumar *et al.*, 2014). In order to tailor properties chemical modification is an useful strategy. Among several pathways, O-alkylation with propylene oxide (PO) in alkaline medium has been successfully utilized.

Considering the interest to developing new routes for lignin valorization, the aim of this work deals about the mild modification of several Acetosolv lignin feedstocks with PO. Lignins as well as modified derivatives were characterized by several methods and structure-properties relationship was established.

## Experimental

Lignin from *E. globulus* (hard-wood), *P. radiata* (soft-wood), and *Triticum sp.* (non-wood) were isolated by the Acetosolv process in acid media (Berg *et al.*, 2013).

**Monolignol composition.** Lignin monomer-(C<sub>9</sub>) composition was determine by nitrobenzene oxidation/HPLC technique.

**Acetyl-content.** Acetate-content was determined by titration (ISI, 1999).

**Carboxylic group-content.** NIR-FTR spectra were collected using a Perkin Elmer System 2000R spectrometer.

**Hydroxypropyl lignin (HPL).** Lignin (100 g, ca. 80 mmol) were dissolved in 500 mL aq. 2N NaOH and the pH was adjusted to 12. One-third, each, was combined with different molar equivalents (PO/C<sub>9</sub>) in order to establish three degree of substitution (DSHPL: 0.5, 1.0, 1.5). The reaction was carried out for 24 h while stirring at room temperature (~22 °C). Adjusting the pH to 2 using conc. HCl (40%, v/v) produced a precipitate that was centrifuged. The induced precipitate was collected and washed three times with cold distilled water (5 °C) and oven-dried (40 °C, 72 h).

**Total phenols content (TP).** Lignin and lignin-derivatives were dissolved in methanol (1 gL<sup>-1</sup>) and 0.5 mL of Folin-Ciocalcu reagent added (Sigma Aldrich).

**Antioxidant activity (AA).** Free radical scavenging power was assessed by DPPH (2,2-diphenyl-1-picrylhydrazyl) assay (Brand-Williams *et al.*, 1995).

**Proton Nuclear Magnetic Resonance (<sup>1</sup>H-NMR).** <sup>1</sup>H-NMR spectra were used in order to gain insight regarding chemical structure and substitution patterns. (García *et al.*, 2013).

**Solubility testing.** The procedure was based on dissolving HPL-samples in solvents at room temperature (21 °C) with vigorous mechanical stirring for 24 h (García *et al.*, 2014).

**Thermal stability (TGA).** Thermogravimetric analysis was performed on a Pyris 1 TGA instrument (TG 209 F3 Tarsus, Germany). Approximately 6 ±2mg of sample was heated at 10 °Cmin<sup>-1</sup> to 600 °C under 20 mLmin<sup>-1</sup> N<sub>2</sub> flow.

## Results and Discussion

### Characterization of pilot-plant feedstocks

The functional group content of the Acetosolv lignin subjected to chemical modification is provided in Table 1.

Table 1. Chemical composition of Acetosolv lignin subjected to chemical modification.

Variable	Lignin			
	LE	LPT	LPR	
Monolignol (%) <sup>1</sup>	H	4 ± 0.1	13 ± 0.6	3 ± 0.1
	G	21 ± 0.8	72 ± 1.3	65 ± 1.3
	S	75 ± 1.2	15 ± 0.9	33 ± 1.1
S/G ratio	3.6	0.2	0.50	
-COCH <sub>3</sub> (%) <sup>2</sup>	8.8 ± 0.4	3.2 ± 0.1	7.1 ± 0.3	
-COOH (%) <sup>3</sup>	0.3 ± 0.01	0.4 ± 0.01	0.8 ± 0.02	

Average ± standard deviation, <sup>1</sup>monolignol unit (H: p-hydroxyphenyl, S: syringyl, G: guaiacyl) based on nitrobenzene assay/GC-MS, <sup>2</sup>by NaOH titration (ISI, 1999), <sup>3</sup>by 1FT-IR determination (Kihara *et al.*, 2002).

As expected chemical features in term of monolignol reveals notable differences between procedences. All Acetosolv lignin show low H- content (3-13 %), while G- and S- content was strongly related to the source. LPT exhibited the lowest S/G ratio, LE show the highest S- content, while LPR reveals notable content of carboxylic acid moieties.

Results confirm the differentiated monolignol composition of hard-, soft, and non-wood sources.

### Synthesis of HPLs

Lignin modification exhibited yields ranging between 87 and 96 %. Supernatand evaporation revealed low HPT-content.

Lignin derivatization showed high yields regardless the procedence, and the PO-charge. The collected HPL-precipitable fraction seems to be favored by the low solubility of derivatives in aqueous solutions at pH 2.

In addition, the isolation procedure enables an easy recovering of quantitative fractions of modified Acetosolv lignin with a minimum work-up.

### Total phenols (TP) content and antioxidant capacity

Hydroxyl-content reveals the availability of -OH groups prone to react in accordance with the monolignol composition (Fig. 2).

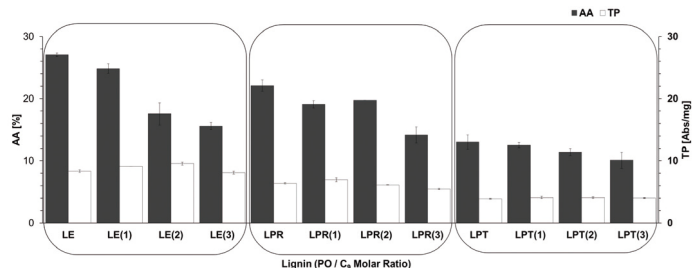


Fig. 2. Polyphenolic content (TP) and antioxidant activity (Antiox. Act.) of lignin, and lignin derivatives.

TP content reveals negligible differences in function to the PO/C<sub>9</sub> equivalent. The result surprising because hydroxypropylation replaces aromatic by aliphatic -OH groups. However, the behavior may be explained based on the chemical structure of lignin-monomers in term of hydroxylation pattern.

Lignins and HPLs antioxidant-capacity oscillated between 10 and 29 %. The antiradical power was negative related to the PO-charge (Fig. 2). The range of activity correlated to several reports based on stilbenes, flavonoids, and procyanidins considered as the most active scavenger polyphenols (Stanković *et al.*, 2011).

### Reaction efficiency ratio (<sup>1</sup>H-NMR)

<sup>1</sup>H-NMR spectroscopy is an accurate technique for determining structural features in polyphenols. However, peracetylated derivatives spectra with a well-separated baseline acetates signals is required (Glasser *et al.*, 1984). Spectra of native lignin reveals common aliphatic and aromatic signals, slight differences mainly for aliphatic protons signals in term of multiplicity and intensities between 0.5-1.5 ppm is noticed (data not-shown).

Differences in hydroxypropylation efficiency was noticed in function of the PO/C<sub>9</sub> ratio (Fig. 3, bottom).

Lignin with the highest S/G content (LE, and LPR) show certain chemical resilience to be modified at room temperature. Additionally, LE (S/G: 3.6) exhibited significant content of aromatic -OH even at the highest PO/C<sub>9</sub>.

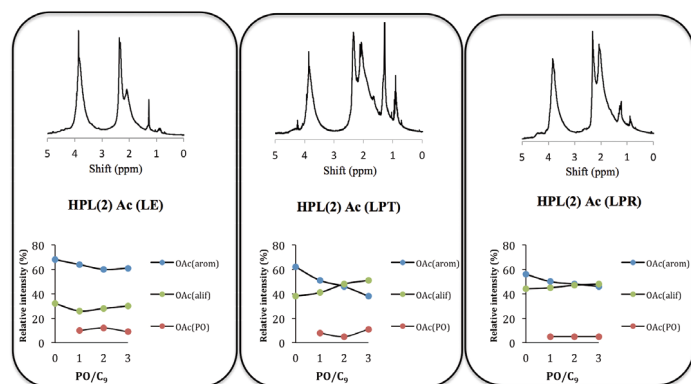


Fig. 3. (A) <sup>1</sup>H-NMR spectra of hydroxypropyl Acetosolv lignin acetates illustrating aromatic and aliphatic signal features. (B) evolution of acetoxy groups of acetylated Organosolv hydroxypropyl lignin in function of molar equivalent. Note: Relative intensity is based on acetate signals.

### Solubility test

Solubility of HPL samples shows dramatical changes in selected solvents (Fig. 4). In general, lignin modification decrease solubility in MeOH and acetic acid, while solubility increase slight in water/NaOH. HPL solubility virtually is less affected in protic than aprotic solvents. Surprising LE- exhibited the highest solubility changes.

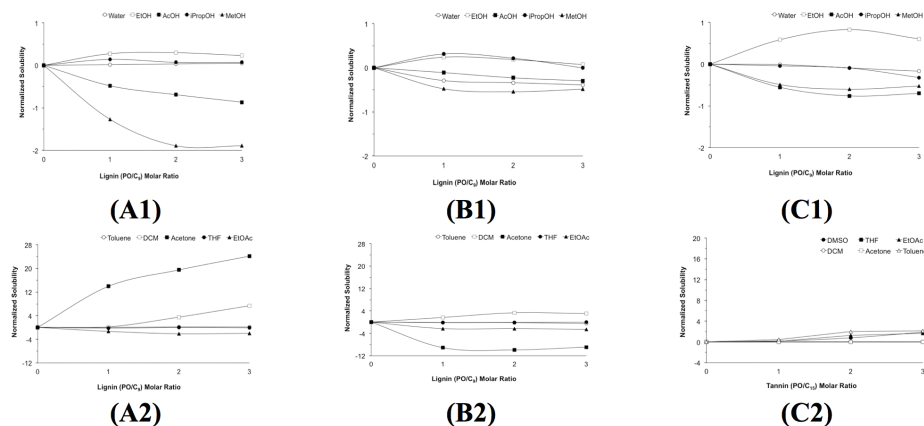


Fig. 4. Normalized solubility of HPL in different solvents at 21 °C using the native lignin solubility as reference. (1) Protic solvents and (2) aprotic solvents. (A) LE-. (B) LPR-. (C) LPT-.

General trends show that hydroxypropylation decreases the solubility in polar solvents to increase the solubility in acetone and DMSO. Considering the solubility behavior, and the composition of the tested lignin, specific site of derivatization in term of aliphatic or aromatic -OH seems to affect the interaction of lignin derivatives with organic solvents.

### Thermogravimetric analysis

Changes in thermal resistance of lignin in function to PO-charge was noticed (Fig. 5).

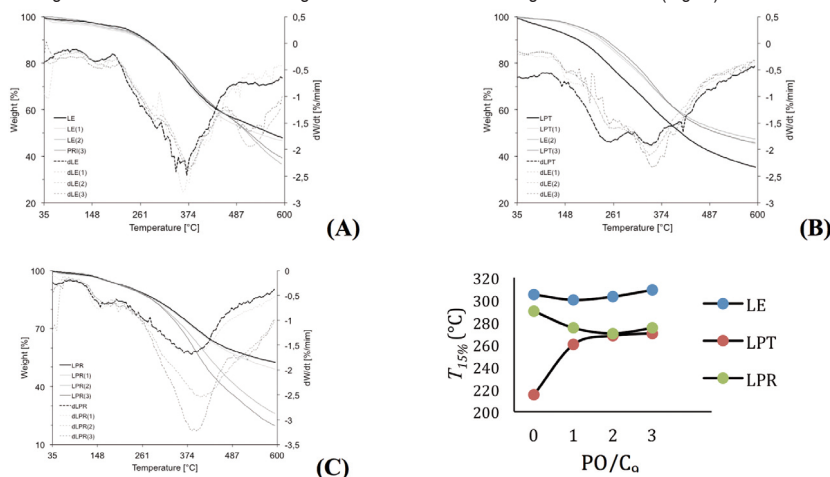


Fig. 5. Thermal decomposition of native lignins and HPL at 5 °Cmin<sup>-1</sup> in N<sub>2</sub> atmosphere.

Thermal resistance of LPT-based derivatives was improved in the entire range of temperature. However, negligible differences between LE-based derivatives stability were observed. In contrast, derivatization decreased the thermal stability of LPR-based HPL at high temperature (300 and 600 °C). Considering the results the highest PO-uptake the highest thermal resistance regardless the lignin-type.

### Conclusions

Oxypropylation at room temperature of several Acetosolv lignin from *Eucalyptus sp.*, *P. radiata*, and wheat straw obtained under pilot-plant conditions were performed for a first time. Spectroscopic and functional-group analysis provides valuable insight regarding reaction efficiency ratio and structural-properties relationship. A varied range of derivatization efficiency in function of the chemical structure were established. Lignin from wheat straw showed the best performance in term of enhanced properties. The highest S/G ratio favors the maximum hydroxypropylation efficiency at room temperature.

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