



## Hardwood and softwood kraft lignins fractionation by simple sequential acid precipitation



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### ABSTRACT

This study aimed at the fractionation of lignin by a simple acid precipitation from hardwood and softwood Kraft black liquors to propose new value-added applications. The precipitation was made sequentially by acidification at five different pHs (9, 7, 5, 3 and 1). The different lignin fractions were analyzed in terms of yield, ash content, elemental analysis, thermal analysis, FTIR, <sup>1</sup>H NMR and GPC. Hardwood lignins showed distinct relative molecular mass distributions, while softwood lignins showed similar relative molecular mass distributions in the three fractions obtained at higher pHs (pH 9, 7 and 5). This simple acid precipitation was shown to be an effective method to obtain relatively high yields of lignin. Molecular characterization by FTIR (carbonyl band) indicated that hardwood lignin was most oxidized mainly in the low pH fractions (5, 3 and 1), while the softwood lignin only presented discrete oxidized products in the lowest pHs (3 and 1). Interestingly, precipitation at pH 3 produced ash-free hardwood and softwood lignin fractions, which is a valuable product for the development of better end uses.

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### 1. Introduction

Lignin can be isolated from wood, annual plants or agricultural residues by different extraction processes. The main processes are commercial extractions by the pulp and paper industry that recover lignin through sulfur (sulfite and kraft) and sulfur-free (organosolv and soda) processes [1]. The kraft process is the main method applied for pulping [2] and has been highlighted for biorefining purposes [3]. In addition, lignin from the kraft process is a realistic prospective to produce high value-added products from biomass [4] such as chemicals, polymers, adhesives, composites and carbon fibers.

The total amount of lignin produced by the pulp industry is 60% more than what is actually needed for internal power supply [5]. Currently, 70 million tonnes of lignin are produced annually in the world and only 5% is used in commercial applications (additives, binders, surfactants or dispersants), while 95% is burned for energy production [1]. However, some studies have indicated changes in the near future [6] as efficient lignin utilization becomes economically necessary [7], and in which biorefining

concepts that consider the modification and/or incorporation of the components of lignin to obtain value-added products are an interesting alternative [6].

Research on the chemistry of lignin is not recent, but the possibility of scarcity of current raw materials used in oil exploitation [1] has generated a space for the development of new products and processes based on aromatic renewable materials, such as lignin [8]. It is well known that lignin has an amorphous and complex structure, and that its structure and properties change according to reactions during the pulping process [9,10]. However, wide molecular mass distribution [11] and wide chemical group composition may be a problem in its utilization for biorefining [12]. In this respect, a simple, easy and low cost process has been investigated in order to obtain different fractions of lignin with specific characteristics to be explored as innovative products [13].

The main fractionation methods were related to the extraction of lignin with different organic solvents [14,15], ultrafiltration by membrane technology [16,17], and fractionation by acid precipitation [18–21]. Acid precipitation is a common method that extracts lignin from black liquor, decreasing the pH gradually by the addition of a strong acid [17,22,23]. However, most acid precipitation is related to a selective pH, in which the precipitation is made by a specific pH with no sequential fractionation. More recently, a

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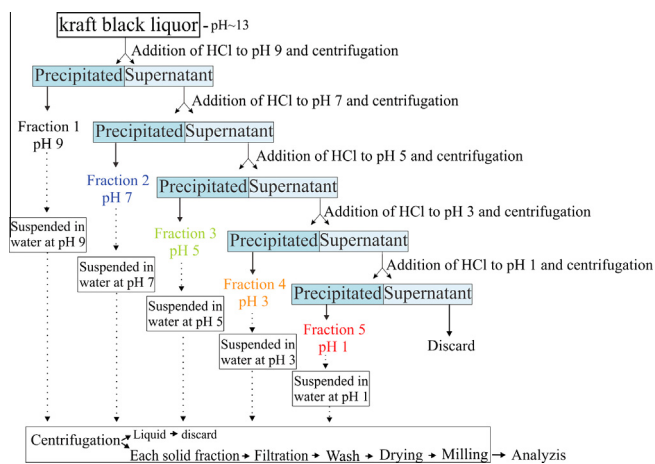


Fig. 1. Scheme of sequential lignin precipitation by acidification.

sequential precipitation at low pH (5, 4 and 2) from steam-exploded stalk was studied and, interestingly, the procedure was considered as a fractionation and purification method [19].

This work proposes a distinct fractionation approach, in which pH (9–1 pH unit) is modified sequentially from the same single sample. This allows the precipitation of a more purified fraction belonging to a specific pH, thus simplifying the process. Hardwood and softwood black liquor from the kraft process were submitted to sequential acid precipitation. The lignin fractions were physico-chemically characterized and had their thermal properties analyzed. A comparison of the softwood and hardwood lignin fractions was also depicted, in order to obtain a better understanding for eucalyptus and pine kraft lignins in the different pH extracts.

## 2. Materials and methods

### 2.1. Materials

*Eucalyptus* sp. (hardwood) kraft black liquor was provided by Suzano Pulp and Paper Industry (São Paulo, SP, Brazil) and *Pinus* sp. (softwood) kraft black liquor was given by Codelpa Pulp and Paper Industry (Curitiba, PR, Brazil).

### 2.2. Lignin precipitation

Drops of hydrochloric acid (started 12 M and followed 1 M) were added in a single sample of black liquor (~150 mL and pH ~13), until achieve pH 9, followed by centrifugation at 3500 rpm for 15 min. The precipitated fraction was reserved. The

supernatant was acidified until pH 7 adding dropwise of HCl (12 M and 1 M) under agitation. Thereafter the same method was followed to obtain fractions at pH 5, 3 and 1 sequentially (Fig. 1), in order to fractionate the lignin component.

Each reserved solid fraction was suspended in aqueous solution at the same pH of the fraction – pH's 9, 7, 5, 3, and 1 – to avoid substances belonging to the other pHs, and centrifuged again. The solution was prepared with water, and controlling the pH by adding solutions of HCl (0.1 M) and NaOH (0.1 M). Then, each precipitated fraction was filtered (the liquid was discarded), washed with acidified water (c.a. pH 2), oven-dried (50 °C) and milled in a mortar. The whole procedure was repeated in three independent replicates in order to test its repeatability.

### 2.3. Mass yield, ash content, elemental analysis and molecular mass determinations

The yield of lignin was gravimetrically determined in the three replicates and each analytical measurement was presented as the average of three independent determinations on each isolated lignin sample after all process. The ash content was determined according to Tappi T211 (1993), using 10 mg of an oven-dried lignin fraction at 100 °C. Carbon, hydrogen, nitrogen, sulfur and oxygen (by mass difference) contents were determined in a CHNS Elemental Analyzer from Vario Macro Cube using 2.5 mg of the oven-dried fractionated lignin at 50 °C.

Lignin samples were acetylated before analysis by gel permeation chromatography (GPC) in order to render them completely soluble in THF [4]: 50 mg lignin was mixed with pyridine:acetic anhydride under a nitrogen atmosphere (1:1 v/v, 1 mL, 24 h), the reaction medium was diluted with dichloromethane:methanol (9:1 v/v, 25 mL, rest for 30 min). The solution was cleaned up with HCl (2 M, 25 mL, 1×) and H<sub>2</sub>O (25 mL, 2×), the residual water of the organic phase was removed by passing the solution through a column packed with Na<sub>2</sub>SO<sub>4</sub> (c.a. 3 g), and the solvent mixture was dried by rotary evaporation. The acetylated lignin was dissolved in dichloromethane (c.a. 1 mL) and transferred to a glass vial (2 mL), and then dried in a gentle flux of nitrogen and an oven at 50 °C overnight. Gel permeation chromatography (GPC) was used to determine the lignin number-average ( $M_n$ ) and mass-average ( $M_w$ ) molecular mass as well as the sample polydispersity ( $M_w/M_n$ ). GPC analyses were performed in a Waters 1515 HPLC equipped with a Waters 2707 autosampler and a MIL-S800i-v2 interface. Two Supelco TSK-HXL columns (G2000 and G1000) and a G1000Hxl-G4000Hxl guard column were used at 40 °C under an isocratic THF flow rate of 0.8 mL min<sup>-1</sup>. Detection was carried out by differential refractometry (Waters 2414) and UV spectrophotometry at 254 nm (Waters 2487). The injection volume

Table 1

Mass yield, ash content and elemental analysis of kraft lignins obtained after precipitation at different pH.

Lignin origin	Content (%)		pH					
			9	7	5	3	1	
Hardwood	Yield		51.7 ± 13.6	33.7 ± 7.8	9.7 ± 5.3	3.4 ± 0.2	1.5 ± 0.3	
	Ash		9.5 ± 1.0	5.9 ± 4.0	3.4 ± 2.1	nd <sup>b</sup>	2.1 ± 1.5	
	Elemental analysis <sup>a</sup>	C		53.2	53.7	56.9	57.7	71.4
		H		4.9	4.8	5.3	5.4	8.6
		O		38.7	38.4	34.4	32.6	14.0
S			2.5	2.6	2.9	3.4	5.0	
Softwood	Yield		49.9 ± 0.5	37.2 ± 6.5	11.0 ± 7	0.8 ± 0.4	1.0 ± 0.4	
	Ash		11.1 ± 3.7	12.2 ± 2.9	13.3 ± 1.8	nd <sup>b</sup>	4.5 ± 0.7	
	Elemental analysis <sup>a</sup>	C		54.1	52.0	52.3	61.3	43.8
		H		5.0	4.9	4.8	5.5	4.5
		O		37.9	38.9	38.6	28.5	26.1
S			2.4	3.4	3.51	3.8	24.6	

<sup>a</sup> Nitrogen content was not considered (~1%).

<sup>b</sup> Not detected.

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