



## Characterisation of Kraft lignin separated by gradient acid precipitation



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### ABSTRACT

Lignin is considered the second most abundant organic natural compound in the world. Lignin represents a promising source of new materials based on renewable resources. Currently the lignin is used in low value-added applications and for energy production and chemical recycling for industrial process itself in production of pulp and paper. Only a small amount is being used for other applications. The aim of this study was to analyze the effects of precipitation on the composition of lignin extracted from black liquor produced in industry CMPC Celulose Riograndense. For this, lignins were precipitated at different pH conditions, with various acids. Obtained lignin samples were characterized by various analytical techniques such as FTIR, GPC, HPLC and XRD. Furthermore, the quantity of carboxyl groups was also analyzed. The antioxidant activity of the analyzed lignins was evaluated by the radical ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) assay. Total phenolic content was evaluated by Folin-Ciocalteu method while the antioxidant potential of lignins was measured by DPPH. The lignins showed a variable composition according to the acid used for its precipitation; the lignin precipitated with sulphuric acid presented Na<sub>2</sub>SO<sub>4</sub> salts while with hydrochloric acid, NaCl was found. In addition, a change in lignin composition was observed at different pH.

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### 1. Introduction

After cellulose, lignin is the organic component most abundant in the environment. The annual production of lignin on earth has been estimated in the range of 5–36 × 10<sup>8</sup> tons (Lin and Dence, 1992; Gellerstedt and Henriksson, 2008). Lignin is an amorphous polyphenolic material created through enzymatic polymerisation of three monomers, coniferyl, sinapyl and *p*-coumaryl alcohol. Maziero et al. (2012) affirmed that the monomers forming lignin (*p*-hydroxyphenyl (H), guaiacyl alcohol (G) and syringyl alcohol (S)) differ only in the degree of substitution on the phenolic ring. Lignins are a promissory source of new materials; Jin et al. (1990) used the lignin as a phenolic resin, Park et al. (2008) as a substitute of phenol in phenol formaldehyde (PF) and Boeriu et al. (2004) as an emulsifier. Toledano et al. (2012) reported the potential use of fractionated lignins by selective precipitation as a dispersant or as a chelating agent. According to Rojas and Salager (1994), the dispersant activity of lignin increases as the pH used for its precipitation. Otherwise, due to the high content of diverse functional

groups (phenolic and aliphatic hydroxyls, carbonyls, carboxyls, etc.) and its phenylpropanoic structure, lignin can serve as a neutralizer or inhibitor in oxidation processes, stabilizing reactions induced by oxygen radicals and their derived species (García et al., 2010). Nevertheless, this antiradical activity greatly depends on lignocellulosic material from which lignin is obtained, the method used for its extraction, and the treatments applied during its isolation and purification.

Technical lignins are obtained from industrial process; Kraft pulping is by far the most important industrial method for chemical pulps production (Gellerstedt et al., 2004), and many tons of lignin are generated as by-product. Kraft process is characterised for accepting any type of wood and forest species, and chemical products from inorganic process can be recovered and reused efficiently. Kraft pulp represents approximately 90% of chemical pulp, and about 130 million tons of cellulose per year in the world (Tran and Vakkilainen, 2007). However, volume of residues generated during the pulp production is preoccupant for the environment because currently the finality of these residues is for recycling the chemical agents and for energy production to supply the industry.

New researches are needed to increase utilisation of the lignin as a raw material. According to Lora and Glasser (2002), only a small quantity (<2%) of the lignin worldwide produced is used

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in different applications for production of value-add, renewable and eco-friendly materials. In this study, Kraft lignin produced by CMPC-Celulose Riograndense pulp and paper industry was precipitated at different pH in order to analyze the effect of the process and the precipitation technique on lignin composition. Changes on composition were determined using ATR-IR, XRD, HPLC and GPC. The carboxyl groups and antioxidant power of lignin were measured by ABTS and Folin–Ciocalteu techniques. Lignin composition recovered with this study would be useful in order to evaluate its potential for further applications like source of bulk chemicals by its depolymerisation.

## 2. Materials and methods

### 2.1. Lignin precipitation

The acid precipitation of lignins from black liquor from Kraft pulp of CMPC-Celulose Riogrande pulp and paper industry located in Southern Brazil (30°08'56.85"S 51°18'49.51"O) was performed at different pH (2, 4 and 6) using a method described by Alriols et al., 2009. To achieve this, sulphuric acid (98%, w/w) and hydrochloric acid (37%, w/w) were used. Samples were referenced as follows: lignin precipitated with sulphuric acid at pH 2 LKS 2, at pH 4 LKS 4 and at pH 6 LKS 6 while lignin samples precipitated with hydrochloric acid LKH 2, LKH 4 and LKH 6.

### 2.2. Composition of lignins

Yield of Kraft lignin (g/L) was determined by gravimetric method, based on total dry solid of black liquor. Analysis of main sugars content was performed in HPLC equipment using the filtrated liquid obtained from Klason lignin measurements (TAPPIT222 om-98). Insoluble lignin content was measured using a method described by Toledano et al. (2012). Acid-soluble lignin was measured in a Jasco V-630 spectrophotometer UV–vis. To achieve this, an aqueous solution containing H<sub>2</sub>SO<sub>4</sub> 1 M of the filtrated material previously obtained was done until the absorption of the samples was between 0.1 and 0.8, at 205 nm.

The antioxidant power of lignins samples as the lignin capacity to reduce ABTS radical was measured through spectrophotometric method described by García et al. (2012) using a UV–vis spectrophotometer.

### 2.3. Carboxyl groups and antioxidant power of lignin

Carboxyl groups were determined by aqueous titration as described by Toledano et al. (2012). The antioxidant activity in Kraft lignins was determined using a method described by Dizhbite et al. (2004). Spectrophotometric method based on the use of the free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) using a spectrophotometer Jasco V-630. Extracted samples dissolved in dioxane/water (90:10, v/v) at a concentration of 1 g/L, the 0.1 mL were mixed with

3.9 mL of a  $6 \times 10^{-5}$  M DPPH solution, and the absorbance at 518 nm of the mixture was measured at different times, 15 min and 30 min.

The total phenols content of lignins samples were determined using a method described by García et al. (2012) To achieve this, a volume of 2.5 mL Folin–Ciocalteu reactive and 5 mL of 20% Na<sub>2</sub>CO<sub>3</sub> solution was mixed with 0.5 mL of lignin solution (20 mg in 10 mL of DMSO). The mixture was kept for 30 min at 40 °C before measuring the absorbance at 750 nm. The intensity of blue colour was measured at 750 nm in a UV–vis spectrophotometer, and the total phenols content was determined using a standard curve with gallic acid solutions.

### 2.4. Molecular weight distribution

Molecular weight of lignins was analyzed through gel permeation chromatography (GPC) technique using a JASCO instrument equipped with an interface (LC-NetII/ADC) and a reflex index detector (RI-2031Plus). Two PolarGel-M columns (300 × 7.5 mm<sup>2</sup>) and PolarGel-M guard (50 × 7.5 mm<sup>2</sup>) were employed. Dimethylformamide + 0.1% lithium bromide was the eluent. The flow rate was 0.7 mL/min and the analyses were carried out at 40 °C. Calibration was made using polystyrene standards (Sigma-Aldrich) ranging from 70,000 to 266 g/mol.

### 2.5. X-ray diffraction

X-ray diffraction was performed in order to study the crystallinity of lignins. For this propose, a Shimadzu XRD-6000 X-ray diffractometer equipped with a copper anode lamp ( $\lambda = 0.154$  nm) was used.

### 2.6. Infrared spectroscopy (ATR-IR)

The attenuated total reflectance infrared spectroscopy (ATR-IR) by direct transmittance in a single-reflection ATR System was performed in the lignins. The equipment was configured for 32 scans in a range of 4000–600 cm<sup>-1</sup> and resolution of 4 cm<sup>-1</sup>. Moreover, the salts presented in the lignins sample were precipitated after addition of 25 mL of absolute ethanol in 0.5 g of lignin, constant agitation for 24 h, filtration and drying. The precipitated material was analyzed by ATR-IR and was compared with the commercial salts of Na<sub>2</sub>SO<sub>4</sub> and NaCl.

## 3. Results and discussion

### 3.1. Composition and characterisation of lignins

Table 1 shows the results for analysis of lignin content and elemental sugars of lignins precipitated with different pH. The lignin precipitation could be explained by its colloidal behaviour. Marton (1964) found that the lignin behaves as a hydrocolloid that is precipitated with low pH due to the effect of protonation of acid groups in the lignin.

**Table 1**  
Chemical characterisation of lignins from different pH.

Parameter (%)	LKS 2	LKS 4	LKS 6	LKH 2	LKH 4	LKH 6
Glucose	0.0027 ± 0.0001	0.0019 ± 0.0003	0.0013 ± 0.0005	0.0008 ± 0.0003	0.0021 ± 0.0002	0.0027 ± 0.0001
Xylose	0.027 ± 0.0023	0.0314 ± 0.0004	0.0104 ± 0.00009	0.00066 ± 0.0001	0.0175 ± 0.0001	0.0219 ± 0.0006
Arabinose	ND	0.0006 ± 0.000072	ND	ND	ND	ND
Insoluble lignin	40.93 ± 0.79	41.97 ± 2.09	26.88 ± 3.05	57.11 ± 1.07	30.02 ± 3.33	35.59 ± 7.17
Soluble lignin	1.59 ± 0.20	2.16 ± 0.09	1.49 ± 0.03	1.90 ± 0.11	2.07 ± 0.10	1.71 ± 0.62
Total lignin	42.52 ± 0.91	44.10 ± 2.06	28.38 ± 3.09	59.01 ± 1.18	32.12 ± 3.24	37.30 ± 6.78
Total salts	57.45 ± 0.99	55.83 ± 2.18	71.62 ± 3.08	40.99 ± 1.18	67.89 ± 3.43	62.67 ± 7.79
Yield of solids (g/L)	100.01	123.23	107.41	75.63	93.61	78.13

ND= no detectable.

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