

## Characterization of Kraft Lignin Precipitated with Different Alcohols

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Lignin is the second major component of lignocellulosic biomass and represents the most important source of aromatics in nature. However, traditionally lignin has been considered as a waste or used for energy generation in pulp and paper mills. Lignin can be used in a wider range of fields, among all applications, small aromatic building blocks from lignin will be needed in order to satisfy the enormous and diverse industrial demand for aromatics.

The problem is that the lignin has different structure and composition depending on used raw material and the extraction process.

This study was aimed to characterize the composition and structure of precipitated Kraft lignin using different organic alcohols such as methanol, n-propanol, butanol and ethanol in the presence or absence of CaCl<sub>2</sub>, being an alternative to acid precipitation. Moreover, the influence of calcium chloride salts addition and alcohol/liquor ratios were assessed. Lignin samples were characterized by FTIR. Furthermore, the amount of carboxyl groups and also the antioxidant potential of lignin using ABTS techniques and Folin-Ciocalteu, DPPH were determined. Lignin showed variable composition according to the process used for precipitation.

### 1. Introduction

Lignin is renewable materials, is the second biopolymer most abundant on Earth. The molecule is an amorphous, aromatic polymer composed of phenylpropano units, and cross-linked. According to Lora and Glasser (2002), only a small quantity about 2 % of the lignin produced worldwide is used in different applications, not for production of energy, but for materials value-add and renewable materials.

The lignin can be extracted from lignocellulosic materials by different methods, like Kraft process, and others (Erdocia et al., 2012). The Kraft process is the most important industrial process of chemical pulps production (Gellerstedt et al., 2004), which can use any type of wood and forest species. According to Tran and Vakkilainen (2008), the Kraft pulp represents approximately 90 % of chemical pulp produced in world and about 167 million tons of cellulose per year in all world were produced (Bracelipa, 2014).

For the recovery of Kraft lignin, acidic precipitation with sulphuric acid or hydrochloric acid is the most used technique (Dos Santos et al., 2014). According to Dos Santos et al. (2014), the yield of lignin recovery about 30 %, could be reached at pH 2 with HCl.

Moral et al. (1993) have showed that Kraft lignin could be precipitated from black liquor by adding different alcohols such as: methanol, ethanol and isopropanol.

The objective of this work was to obtain of lignin by precipitation, using different alcohol such as methanol, n-propanol, butanol and ethanol in the presence or absence of CaCl<sub>2</sub>, being an alternative to acid precipitation. Moreover, the influence of calcium chloride salts addition and alcohol/liquor ratios were assessed. Furthermore, the lignin samples were characterized by FTIR. The amount of carboxyl groups, the power

antioxidant by ABTS and DPPH and also the total phenols content by Folin-Ciocalteu techniques were determined.

## 2. Materials and methods

### 2.1 Lignin precipitation

The Kraft lignin was isolated from original Kraft liquors provided by CMPC-Celulose Riograndense Pulp and Paper, located in Southern Brazil (30°08'56.85"S 51°18'49.51"O), from different species of Eucalyptus. The Kraft lignin was precipitated using different organic alcohols in the presence or absence of CaCl<sub>2</sub>, with different relations of Kraft liquors and solvent (1:4 and 1:6) according to a method similar to the described by Moral et al. (1993). Thereafter, the precipitated lignin was separated by filtration, washed with acidified water and then vacuum dried at 50 °C until constant weight.

### 2.2 Characterization of lignin

The yield of Kraft lignin in g/L was determined by gravimetric method, based on total dry solid of black liquor. The insoluble lignin content was measured using a method described by Toledano et al. (2013). Acid-soluble lignin was measured in a Jasco V-630 spectrophotometer UV-VIS.

The carboxyl groups were determined by aqueous titration using the method described by Toledano et al. (2013). The carboxyl groups were calculated as the difference between the aggregate and the consumed NaOH.

The total phenols content were characterized to quantitatively assess the total phenols content in lignin samples were determined using a method described by García et al. (2012) using a UV-VIS spectrophotometer. The total phenols content was determined using Gallic acid as standard.

The antioxidant power of lignin was determined using two different methods using a UV-VIS spectrophotometer. The first method, using the radical 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) described by García et al. (2012). The antioxidant activity of lignin was also determined using the radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) method described by Dizhbite et al. (2004) using different reduction times (18, 36 and 54 min).

The attenuated-total reflectance infrared spectroscopy (ATR-IR) was measured by direct transmittance in a single-reflection ATR System with an MKII Golden Gate SPECAC instrument. Spectrums data was configured for 32 scans in a range of 4000-600 cm<sup>-1</sup> and resolution of 4 cm<sup>-1</sup>.

## 3. Results and discussion

### 3.1 Chemical characterisation of Kraft lignin

The yields of Kraft lignin, content of lignin soluble and insoluble, ash and carboxyl groups, are presented in Table 1. Lignin yield (based on total dry solid of black liquor) was determined by weighing oven-dried lignin.

Table 1: Chemical characterisation of Kraft Lignin Precipitated with Different Alcohols

Name	KLET 1:6	KLET 1:6	KLET 1:4	KL BUT 1:4	KL BUT 1:6	KL MET 1:4	KL PROP 1:4	KL PROP 1:6
Parameter (%)	—	CaCl <sub>2</sub>	CaCl <sub>2</sub>	CaCl <sub>2</sub>	CaCl <sub>2</sub>	CaCl <sub>2</sub>	CaCl <sub>2</sub>	CaCl <sub>2</sub>
Insoluble lignin	31.4 ± 4.5	12.0 ± 1.6	15.9 ± 1.6	17.6 ± 4.5	16.5 ± 1.0	23.2 ± 1.9	19.2 ± 3.6	17.0 ± 4.5
Soluble lignin	9.3 ± 1.7	6.8 ± 0.05	7.8 ± 0.3	8.5 ± 1.3	9.3 ± 0.8	11.5 ± 0.3	7.6 ± 0.5	9.4 ± 0.1
Total lignin	40.7 ± 2.8	18.8 ± 1.6	23.7 ± 1.9	29.3 ± 5.8	25.9 ± 0.2	34.7 ± 1.7	26.8 ± 4.1	26.4 ± 4.6
Ash	60.9 ± 0.5	62.5 ± 0.3	57.4 ± 0.5	71.3 ± 0.2	69.0 ± 0.9	51.0 ± 0.05	52.0 ± 0.3	64.5 ± 0.3
Carboxyl groups	23.9 ± 0.13	12.1 ± 0.2	22.2 ± 0.3	22.9 ± 0.3	23.3 ± 1.4	22.8 ± 0.3	23.6 ± 0.3	23.2 ± 0.4
Yield of lignin* (g/L)	68.7 ± 3.1	203.2 ± 16.4	151.0 ± 13.1	103.2 ± 24.3	131.1 ± 12.6	100.3 ± 2.7	130.5 ± 3.9	120.8 ± 0.7

\* Based on total dry solid of black liquor.

The results reported in Table 1 showed the differences between the yield of the lignin, the samples that showed the highest and the lowest yields were precipitated with ethanol (68.7 and 203.2) and both with the same ratio of black liquor: solvent. 1: 6, but the sample without the presence of CaCl<sub>2</sub> had a lower yield of approximately 67 % over the ethanol precipitated samples with CaCl<sub>2</sub>, meaning that the CaCl<sub>2</sub> had a positive influence on lignin precipitation. The same behaviour was observed by Moral et al. (1993), who reported that

the addition of calcium salts is very effective, in some cases, the yield could reach about 100 % of precipitated lignin.

For the results insoluble lignin, soluble and method using the total solution in 72% H<sub>2</sub>SO<sub>4</sub>, it can be seen that the presence of CaCl<sub>2</sub> interfere in the proportion of pure lignin, which makes believe that the high yield of precipitated lignin is caused by the addition calcium salts in the sample. The precipitated samples had higher yields with lower lignin contents (soluble, insoluble and total), with high value of impurities.

The result of ash is very high, because in all samples more than half of the precipitated material is considered as ash or inorganic material.

It is worth mentioning that lignin precipitated with different alcohols, presented similar behaviour in analysis of carboxylic groups, with exception of lignin precipitated with ethanol and CaCl<sub>2</sub> 1:6 liquor: solvent ratio. This result was expected, because this sample presented low total lignin content and then would have less carboxylic groups.

### 3.2 Total phenol content

Figure 1 shows the results for chemical analysis of Kraft lignin for total phenol content in the samples was not influenced by the addition of CaCl<sub>2</sub>. A slight decrease of GAE content in comparison to samples precipitated with ethanol for the ratio 1:4 liquor/solvent and CaCl<sub>2</sub> higher percentage, 1:6 liquor/solvent and CaCl<sub>2</sub> and 1:6 liquor/solvent and without the presence of CaCl<sub>2</sub> (10.5 %, 9.4% and 8.2 %).

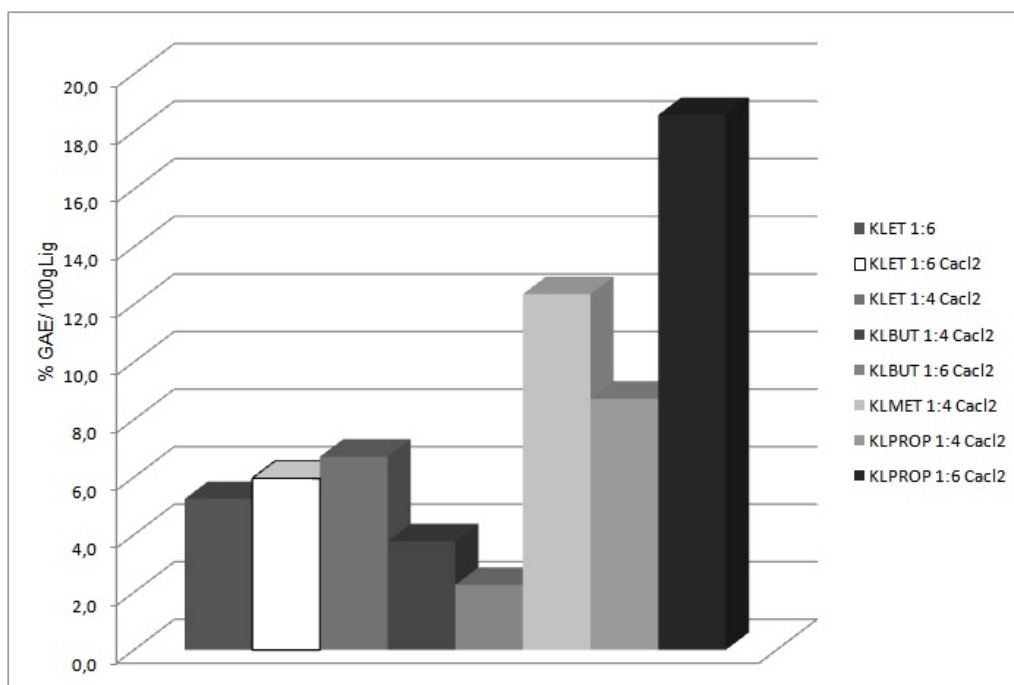


Figure 1: Average values of % of GAE, for the Kraft Lignin precipitated with different alcohols.

Total phenolic content (GAE) of the Kraft lignin varies with the used alcohol, the lignin precipitated with KL<sub>PROP</sub> 1:6 liquor: solvent CaCl<sub>2</sub> showed the best results (29.2 % GAE/ 100gLig), followed by lignin KL<sub>MET</sub> and KL<sub>PROP</sub> both with ratio of 1:4 liquor: solvent and CaCl<sub>2</sub>.

### 3.3 Antioxidant power

Due to the high complexity of the reaction mechanisms, is a low correlation between the antioxidant capacity between and different radicals ABTS and DPPH (Lopez-Alarcon and Denicola, 2013).

#### • DPPH radical

Regarding the ability to inhibit the DPPH radical, it was observed that after 18 min of Kraft lignin with different alcohols showed a variable behaviour, resulting higher for lignin with n-propanol (Figure 2), specially for the lignin (KL<sub>PROP</sub>) with 1: 4 and 1:6 that showed the highest percentage of inhibition of DPPH about (98 %), after 54 min of exposure.

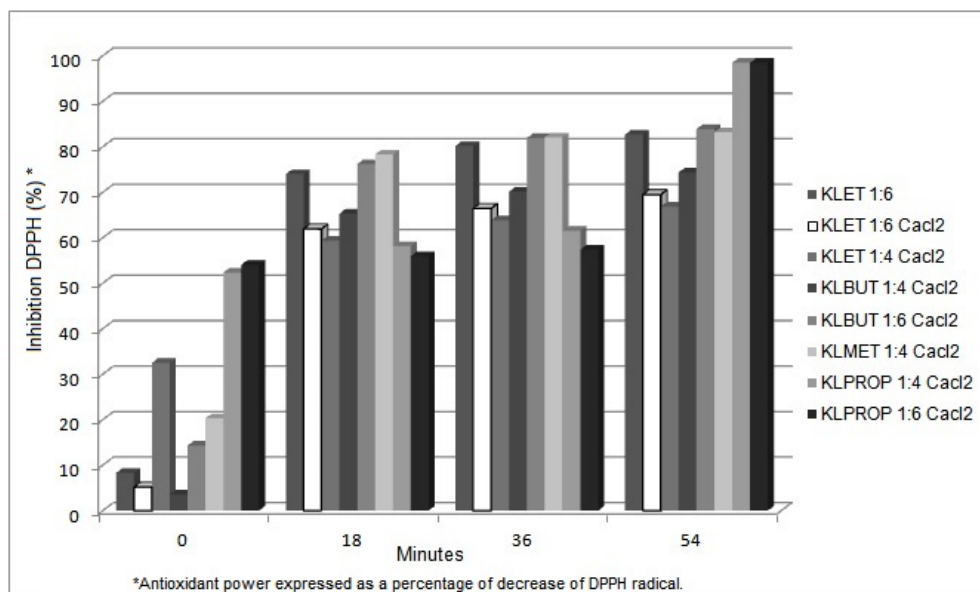


Figure 2. Average values of % DPPH inhibition of Kraft Lignin Precipitated with Different Alcohols.

- **ABTS radical**

Figure 3 shows the results for antioxidant properties analysis of Kraft lignin precipitated with different alcohols, where it can be seen that the antioxidant properties of all studied lignin revealed a low antiradical (ABTS) scavenging activity (<15%) with the exception of lignin which showed a value of KLET 1:4 CaCl<sub>2</sub>.

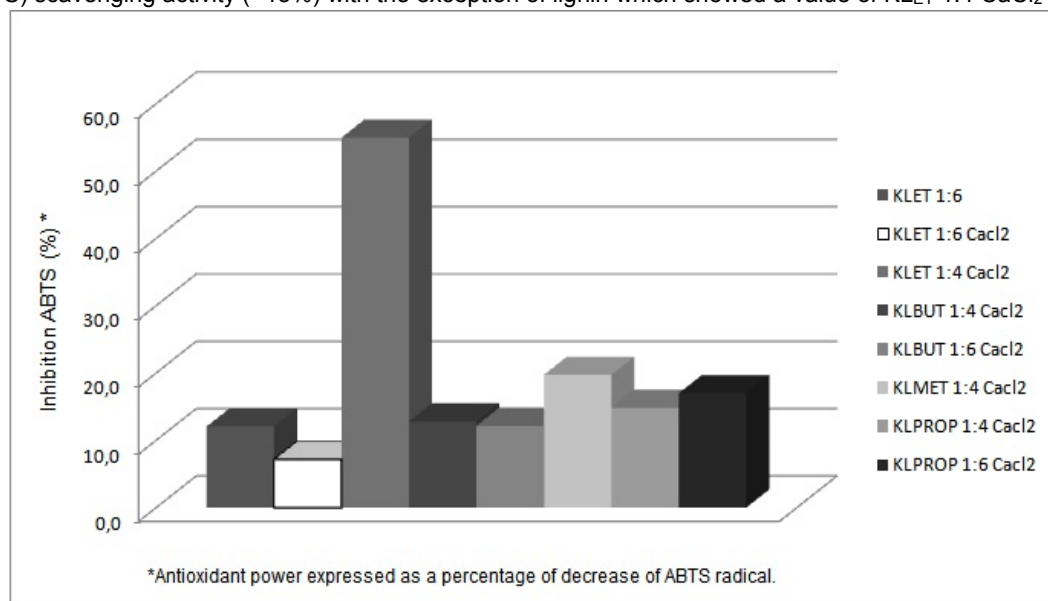


Figure 3. Average values of % ABTS inhibition of Kraft Lignin Precipitated with Different Alcohols.

### 3.4 FTIR spectroscopy

In general, all the spectra from 4,000 to 650 cm<sup>-1</sup> (Figure 4) showed the same typical peaks of the Kraft lignins.

However, some differences in relative intensity of the peaks were observed. In the region of at cm<sup>-1</sup> referred to OH stretching according to Liu (2005), which was larger in KLET 1:6 CaCl<sub>2</sub>. According to Coates (2000), at 2,970 – 2,800 cm<sup>-1</sup> referred to C-H extending in methylene groups presented in different quantities nonexistent in KLMET 1:4 CaCl<sub>2</sub>.

Moreover, according to Dos Santos et al. (2014), the vibration in (1,515 and 1,438 cm<sup>-1</sup>) refers to aromatic structures, with the highest intensity in the sample KLBUT 1:4 CaCl<sub>2</sub>, in 1592 cm<sup>-1</sup> which is related to aromatic skeletal vibrations (C=O) stretching. At 1,330 cm<sup>-1</sup> a vibration refers to syringyl.

Prado et al. (2014) reported that C-H in plane deformation in guaiacyl ring and syringyl ring, occurs a vibration in  $1,110\text{ cm}^{-1}$ .

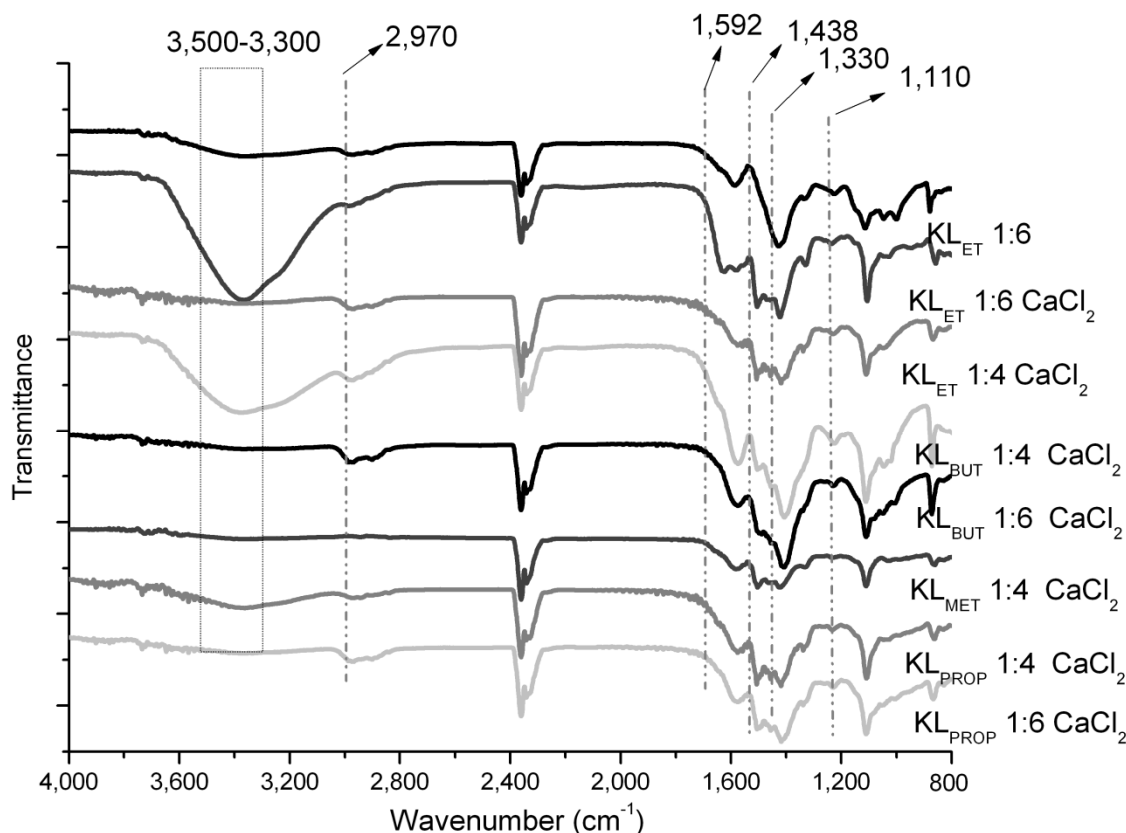


Figure 4: FTIR spectra (from  $4,000$  to  $800\text{ cm}^{-1}$ ) of Kraft lignin with different Alcohols.

#### 4. Conclusions

To determine the best precipitation method with different alcohols is necessary to consider several factors, including the yield of lignin and quality of product produced by different methods of precipitation.

Taking into account these two factors it can be concluded that the sample that had the best quality ( $\text{KL}_{\text{ET}} 1:6$ ) which was precipitated with ethanol, which also presented the lowest yield of lignin precipitation.

It is possible to conclude that the total phenol content in the samples was not influenced by the addition of  $\text{CaCl}_2$ .

The samples that showed the highest percentage of inhibition of DPPH about (98 %), was the lignin ( $\text{KL}_{\text{PROP}}$ ) with 1: 4 and 1:6, after 54 min of exposure.

The antioxidant properties of all studied lignin revealed a low antiradical (ABTS) scavenging activity (<15 %) with the exception of lignin sample  $\text{KL}_{\text{ET}} 1:4\text{ CaCl}_2$  which showed a value of 36.5 % Inhibition of ABTS radical.

Further studies for the precipitation of lignin with alcohol are needed to determine if this method could be an alternative to acidic precipitation of Kraft lignin.

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