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Use of Recycled Acid for *Kraft* Lignin Production

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SUMMARY

The present study aimed to obtain and characterize *Kraft* lignin from black liquor from a cellulose industry. The black liquor was collected and subjected to physical-chemical analysis. Then, acid precipitation was carried out using recycled acid from car batteries (ARA) to obtain *Kraft* lignin. The characterization of lignin involved techniques such as Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), dynamic light scattering (DLS) and Zeta potential. Morphological analyzes revealed irregular structures, including plates and spherical structures. The XRD results allowed the identification of the phases present in the structure of the samples. DLS indicated variation in average sizes throughout the filtration and centrifugation process, attributed to clumping during phase separation. Zeta potential values were consistent with previous studies. The FTIR analysis highlighted characteristics of the chemical bonds of *Kraft* lignin, indicating the viability of the obtaining process, especially when using recycled acid, contributing to the removal of two environmentally harmful wastes: black liquor and battery acid. The lignin yield was as expected, with an average of 30.74 ± 0.0004% for PA sulfuric acid and 29.76 ± 0.0059% for recovered sulfuric acid. These results are in accordance with literature standards, especially considering the use of *Eucalyptus grandis.*

KEYWORDS: Black Liquor, Lignin, Industrial Waste

1 INTRODUCTION

Over the years, due to industrial development, natural resources are being increasingly consumed and the concern for their renewal grows every year. The increase in this consumption rate can be seen from the observation of a simple residence, markets or bakeries to large industries, such as the paper and cellulose industry due to the high level of paper consumption by the population (SOUZA, 2008).

Products such as paper and cellulose are obtained through the process called *Kraft*. In this process, initially the wood for use is obtained from replanted forests, both eucalyptus and pine. Thus, it is cut and taken by trucks to the industry. In industry, after the wood is received at an appropriate location, it is sawn, washed, peeled and chopped into small pieces, called chips, to facilitate cooking in the digester (CARVALHO, 2014).

In the digester, the wood is operated in a continuous or batch process, promoting a stage of delignification of the wood and generating cellulosic pulp, which is then washed and purified to remove impurities, thus removing excess black liquor from processing, and sending it to evaporation (SOUZA, 2014). The cellulosic pulp goes to the bleaching process, a stage in which the aim is to add process chemicals and remove the black liquor present in the pulp. After this, the pulp is sent to storage towers, waiting to be transformed into market cellulose or paper (ALBERTI, 2014)

In the digester, the wood is cooked in a continuous or batch process, promoting the wood delignification stage and generating cellulose pulp, which is then washed and purified to remove impurities, thus removing excess black cooking liquor, and sending it to evaporation (SOUZA, 2014). The cellulosic pulp goes to the bleaching process, a stage in which the aim is to add process chemicals and remove the black liquor present in the pulp. After this, the pulp is sent to storage towers, waiting to be transformed into market cellulose or paper (ALBERTI, 2014)

Due to the *Kraft* process, whether due to the products or by-products generated throughout it, there is a need to carry out research and develop technologies that seek, in turn, to optimize the processes for obtaining the by-products present in this industrial process. This advance highlights the improvement of the destination of these products, allowing the production of new products, adding value to the waste produced. Furthermore, there is a need to take better care of resources, without causing a decrease in industrial consumption, with one of the alternatives for this process being the treatment of *Kraft* black liquor (SOUZA, 2019).

There is therefore a great opportunity and a great challenge, which consists of exploring the potential of this renewable resource. However, within this process it can be highlighted that the use of lignin for energy generation is no longer an alternative, due to the high functionality that this macromolecule presents. As a result, with the high demand for increased energy consumption in the coming years, as well as the need to promote alternative applications for waste and co-products, greater awareness is needed in obtaining biodegradable products and inputs. Thus, we must focus on materials of plant origin, such as lignin, and use it in the production of new products with high technology and adding value (LAURICHESSE and AVÉROUS, 2014).

In the present study, we sought to analyze the main advantages that could occur through process black liquor, as well as the use of lignin for various uses. To this end, the use of *Kraft* lignin for commercial use could provide greater savings and better efficiency in the parameters characteristic of industrial equipment, resulting in greater cellulose production in the *Kraft* process.

During this research, we sought to analyze and investigate the acid precipitation process, using recycled battery acids (ARA) to obtain *Kraft* lignin from black liquor in the process of obtaining cellulose and paper, with the purpose of characterizing the lignin samples obtained in powder form. In this way, the use of *Kraft* lignin for commercial use can provide a more economical process with better efficiency in the parameters characteristic of industrial equipment, resulting in greater cellulose production in the *Kraft* process.

2 OBJECTIVE

The objective of this work is to characterize the black liquor *Kraft* de Eucalyptus grandis aiming to obtain *Kraft* lignin. To this end, one must: evaluate the black liquor generated in the *Kraft* cellulose manufacturing process ; identify its chemical composition; carry out the acidification of black liquor with recycled acid to obtain *Kraft* lignin ; quantify the lignin yield after the acidification process, verifying the effect of pH variation on the *Kraft* black liquor acidification process and, finally, with the material obtained, analyze the elementary structure and characterization of *Kraft* lignin after the acidification processes.

3 LITERATURE REVIEW

Over the past few years, the National Environmental Council (CONAMA) has defined numerous resolutions for waste management, which is related to the disposal and sustainable management of solid waste in accordance with Resolution 313/2002. Solid waste can be defined as: all substances harmful to the environment that cannot be discarded without prior adequate treatment, which can be in solid, liquid or gaseous state (CONAMA, 2002). There are several examples of solid waste that are generated by the most diverse companies, in this case we will deal with sulfuric acid, present in lead-acid batteries, which have a high level of contamination, but which can be inserted into other processes, with a perspective of circular economy and use of waste as raw material. In this case, the waste will be used in the pulp and paper process.

The management of waste from pulp and paper production is an important issue both for the environment and for the sustainability of the company itself. Day after day, this issue is being discussed with great relevance in the management of companies in the sector. The paper and cellulose industry can generate high potential impacts on fauna and flora in regions close to manufacturing plants, this causes companies and environmental bodies to adopt measures to conserve the use of raw materials, energy generation, and thus, use increasingly sophisticated technologies for controlling water and atmospheric emissions, aiming to avoid incidents and accidents, which could have severe consequences for the environment and people (SOUZA, 2008).

The structure of wood, which is considered a chemically heterogeneous material, is composed of a polymeric matrix of different chemical compounds (KOLLMANN, 1959). According to Sarto and Sansigolo (2010), the main components of wood are: cellulose, lignin, hemicellulose, extractives and inorganic compounds or (ash), which are classified into macromolecular and low molecular mass components. One of the functions of lignin in plants is to keep them standing, providing structural support, thus providing greater mechanical resistance and elasticity in the wood, as lignin is a very large molecule, with a three-dimensional structure and polymeric in nature. (DIAS, 2014).

According to Fengel and Wegener (1989), lignin has a complex carbon chain, is composed of units: phenyl, propane, C, O and H, it has a branched chain, lignin is amorphous. According to Llevot (2015), the *Kraft* lignin degradation process generates a wide range of chemical products such as phenols, cresol, catechols, as well as products such as vanillin, syringaldehyde, coniferaldehyde, vanillic acid, ferulic acid through oxidation steps.

For Watkings (2014), because lignin is considered a natural and renewable raw material, as well as low cost of obtaining, it can be applied to any product currently originating from substances. According to Wang (2009), lignin consists of an organic material that can be widely applicable in different types of polymer compound industries due to its physical and chemical properties.

The cellulose and paper manufacturing process consists of removing the cellulose present in the wood structure, separating it from other components such as lignin, through alkaline pulping processes (SOUZA, 2019). Lignins are processed in large quantities throughout the world by paper and cellulose industries in the form of by-products (MONTEBELLO; BACHA, 2011). Because cellulose is the desired product in processing, this residue therefore has a high quantitative value in relation to the amount of Brazilian cellulose and paper production (BES, 2015).

When lignin is obtained through the *Kraft* manufacturing process, it is present in the black liquor and can be used as a source of energy through burning in chemical recovery boilers. However, the paper and cellulose industry in general is unable to consume all black liquor, one of the options would be to use it in other applications (DIAS, 2014).

Over the years, researchers have been carrying out experiments on the lignin present in black liquor with the aim of promoting various applications. In this way, we begin to gain knowledge of the physical-chemical properties of lignin, being a complex liquid with abundance on the planet. This research aims to dispose of excess industrial production and thus mitigate environmental impacts (POTRICH, 2014).

In contemporary times, companies have a great interest in valuing *Kraft lignin* from eucalyptus and pine, as there are many researches and studies of great importance for the application of *Kraft lignin* in different sectors of the industry, as shown by studies by Dias (2014).

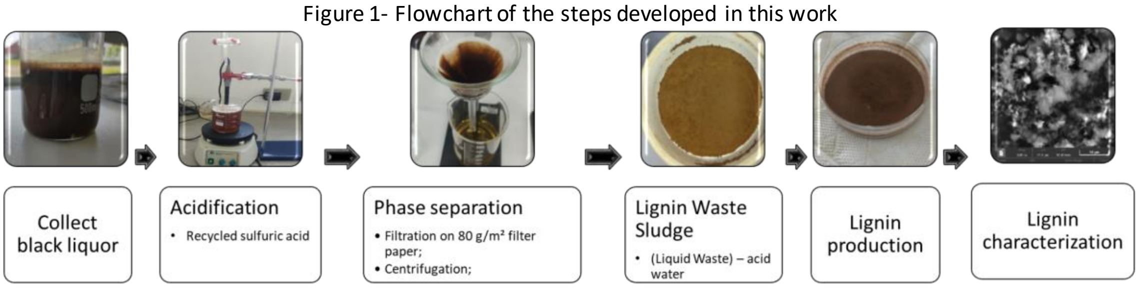
According to Al- Kaabi *et al*. (2018), black liquor consists of approximately 10% to 50% lignin by mass in the suspension. Around 50 million tons of lignin are produced per year by the paper and cellulose industry (ADDEPALY *et al*., 2019). And of the entire amount of lignin generated, only around 5% is being used in the manufacture of high-value-added products, such as additives for adsorption of metallic ions, metallic composites, surfactants, dispersants and binders (OLIVEIRA *et al*., 2017). The remainder, 95% of this co-product is burned in boilers to produce energy to feed the industry that generated it (SANTOS, RODRIGUES and MENDONÇA, 2018).

As mentioned by Jorge (2018), lignin is a very advantageous alternative to combine compounds that have properties that can further improve materials made from cellulose and other polymers and bio-polymers. The responsibility of biorefineries present in the pulp industry is to discover new and creative ways to use the valuable raw material, wood, while managing existing pulp and by-product businesses as efficiently as possible.

4 METHODOLOGY

Figure 1 presents a flowchart with the main steps developed in this study. Initially, approximately 20 liters of black liquor were collected at a cellulose and paper company in the Campos Gerais region of Paraná, where it came from the alkaline pulping process of *Eucalyptus grandis*, aiming to obtain bleached eucalyptus cellulose.

Figure 1- Flowchart of the steps developed in this work



Source: The authors, 2023

For the precipitation process, the methodology carried out by Silva (2014) and Lopes (2018) was used, with a process of recovering the lignin present in the black liquor of the *Kraft* process through acidification in an aqueous medium, as shown in Figure *2.*

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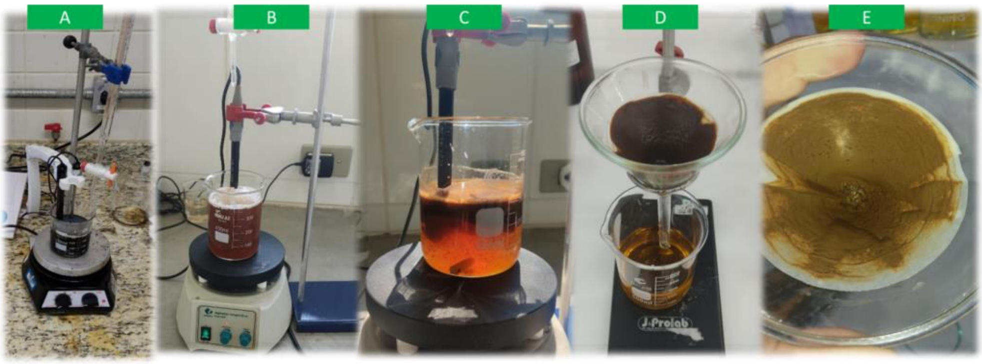
Figure 2 - Steps for obtaining *Kraft* lignin (A) *Kraft* black liquor, (B) Lignin during acidification, (C) Lignin obtained after precipitation, (D) Filtering and washing the lignin, (E) Removal of the lignin.



Source: The authors, 2023.

Aiming for greater efficiency in the process, the pH of the samples was adjusted to obtain the ideal amount of precipitation. For this study, we chose the pH range of 2.0, taking into account the studies carried out by Andrade (2010), which demonstrated efficient recovery of lignin in this same pH range, originating large and complex fragments, which are retained in a more efficient in the filtration system, in addition to obtaining lignin samples with a higher degree of purity without large formation of inorganic materials and carbohydrates.

Subsequently, the black liquor was heated to an average temperature of approximately 60°C before the precipitation stage, thus facilitating coagulation and filtration. After heating, recycled acid was used to precipitate lignin.

A certain sample of black liquor was placed in a 1000 mL beaker, and it was kept under constant stirring and heating and with the aid of a pH electrode, pH variations were verified throughout the process. Recycled sulfuric acid was added to every 1 mL and the values of the pH variation suffered by the sample were noted. The procedure was performed in triplicate. The lignin sample after the addition of recycled sulfuric acid was called ARA.

Precipitation was carried out using approximately 300 mL of black liquor with 106 mL of recycled acid in a pH 2 range, as described by Lopes (2018), 44.6 mL of H_2SO_4 were used. As the adjustment of the pH of the samples became favorable, the emergence of neutralization and condensation reactions of the charges, and compounds such as chromophores (quinones, carboxylic acids, etc.) were removed, after this step and the liquor solution presented a appearance of brown color and formation of colloids, thus indicating the precipitation of intermediate lignin.

The lignin sample obtained in each precipitation process was transported from the beaker to a Büchner funnel with the aid of filter paper to carry out filtration and washing steps. By using lignin washing steps with one liter of hot distilled water, the main pollutants of organic origin and inorganic salts contained in the black liquor are then removed.

After the vacuum filtration step and washing, the solid phase (lignin) was separated from the liquid phase (process residues). The *Kraft lignin* was then stored in glass bottles and part of the material was subjected to the characterization proposed for the present study.

The samples that underwent the washing process were called L and the samples that did not undergo the washing step were called SL, while those that went through a centrifugation process were called C

A chemical analysis of the black liquor sample was carried out and then the lignin powders were analyzed. These were characterized using the following analyses: scanning electron microscopy, X-ray diffraction, with Energy Dispersive Spectroscopy and particle size was performed by Dynamic Light Scattering, Zeta potential, and spectroscopy in the infrared region with Fourier transform.

The black liquor sample had a pH range of approximately 13.12±0.0200 and a conductivity value of approximately 66.02±0.0400 milliSiemens /cm. The average density of the black liquor sample obtained was 1.064±0.0040 g/cm³ for 10 mL of the sample. It can be seen that in the liquor sample collected for every 10 mL of black liquor there is around 9.0174±0.0030 g of water and 1.6226±0.0030 g of solids (inorganic and organic). In the study carried out by Lopes (2018), for every 10 mL of liquor, the solids content was approximately 1.4791 g.

Thus, in the present study, the following information can be considered, that for every 300 mL of liquor used, approximately 319.20±0.0022 g of black liquor was obtained at the end of the process, considering therefore a content of solids of 15.25±0.0016% present in the black liquor obtained around 48.6870±0.0051 g of (inorganic and organic).

Kraft lignin recovery process in the collected black liquor can be seen in Table 1. According to Andrade (2010), the values obtained in the present study are in accordance with the values practiced in industrial units.

Table 1- Final values of lignin mass as a function of liquor volume

Sample name	Average in (g)	Standard Deviation σ (±)	Performance Average (%)	Standard Deviation σ (±)	Mass x Acid volume (%)	Standard Deviation σ (±)	Acid volume in (ml)
ARA pH2 P80 SL	14.39	0.2354	29.57	0.0048	13.58	0.0022	106
ARA pH2 P80 L	14.47	0.2223	29.73	0.0046	13.65	0.0021	106
ARA pH2 C	14.48	0.2850	29.76	0.0059	13.66	0.0027	106

Source: The authors, 2023

The best average yield was observed for ARA pH 2 C samples, with the average value obtained of 29.76 ±0.0059%, or 14.48±0.2850 g. These were the values obtained when calculating the ratio of organic and inorganic substances in relation to the total solids fraction of the black liquor.

The pH values were recorded for each 1 mL dosed using the constant stirring step, after the addition of 106 mL of recycled sulfuric acid to the ARA sample, both for a final pH of 2±0.0500.

The yields obtained during this study are favorable and similar to those proposed by Lopes (2018), who obtained approximately 30.25% of lignin precipitation using eucalyptus black liquor at pH 2 together with H_2SO_4 at 60ºC, as well as the results obtained by Andrade (2010), where the lignin content precipitated from pine black liquor varied between 30% and 50%, for different pH ranges analyzed.

Regarding particle diameter, the results were based on the sizes of lignin particles obtained through DLS, where the largest average size observed was around 2,747.67±562.88 nm for the ARA pH 2 C sample. The lowest was approximately 852.73 ±100.74 nm for the ARA pH 2 P80 SL sample. They are similar to those obtained by Pavaneli (2020)

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The measured values of Zeta potential and particle diameter for lignins produced in the pH 2 range are demonstrated in Table 2.

Table 2– Lignin Zeta Potential

Sample name	Average Zeta Potential [mV]	Standard Deviation σ (±)	Average Hydrodynamic diameter [nm]	Standard Deviation σ (±)
ARA pH2 P80 SL	- 22.50	0.2646	852.73	100.74
ARA pH2 P80 L	- 23.53	0.2309	1,282.03	157.50
ARA pH2 C	- 23.17	1.2741	2,747.67	562.88

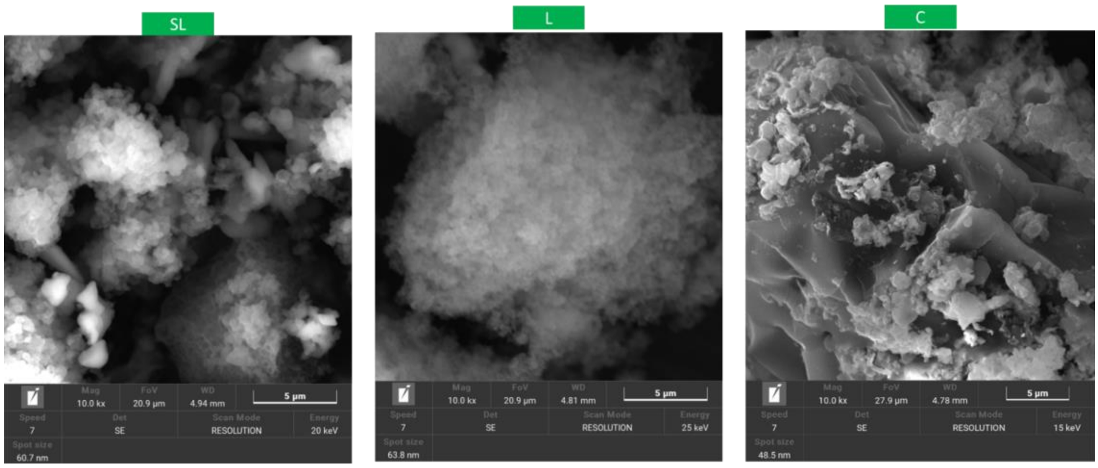
Source: The authors, 2023

The values present in Table 2 verify that the system has moderate colloidal stability. While the values observed in the literature for lignin powders ranged from -25 to -60 mV, for pH greater than 4 (FRANGVILLE *et al.*, 2012 and LIEVONEN *et al.*, 2016).

Kraft lignin samples with the addition of analytical standard sulfuric acid increased and it can be seen that the electrophoretic mobility of the lignin is related to the greater negative charge on its surface, as described by Frangville *et al.*, (2012).

After the filtration stage, physical characterization tests were carried out, using scanning electron microscopy analysis, for the lignin samples, acidified to pH 2, making it possible to observe that the samples represented in Figure 3 (L) were more dispersed. And deagglomerated into small spherical formats, the sample in Figure 3 (SL) demonstrated a morphology of agglutinated spherical lignin particles. In both cases, the formation of spherical structures is observed. However, for the centrifuged samples, in Figure 3 (C), the formation of structures in the form of plates can be observed. These results are similar to those presented in the work of Lopes (2018), in which the presence of spherical particles and compacted aggregates on its surface was observed.

Figure 3- Scanning electron micrograph of lignin powders



Source: The authors, 2023

In Table 3, it is observed that the highest percentage found is the element Carbon (C) with 65.98% in (m/m), there is Oxygen (O) which presented 31.41% in (m/m). The presence of these compounds is related to the hydroxyl groups and ethers present in the chemical structure of lignin, since it has a high quantity of these.

Table 3- Elementary chemical analysis for lignin powders – EDS % in (m/m)

Element	ARA pH 2
W	65.98
O	31.41
At	0.21
Al	0.34
s	2.06

Source: The authors, 2023

Kraft manufacturing process, and these results are similar to those found by Vaz Junior *et al*. (2020).

The analysis of the X-ray diffractograms, which consists of verifying the crystalline structures present in the lignin powders obtained, Table 3, with the purpose of determining the phases present in these materials using the X'Pert High Score Plus database (X'Pert High Score, 2001).

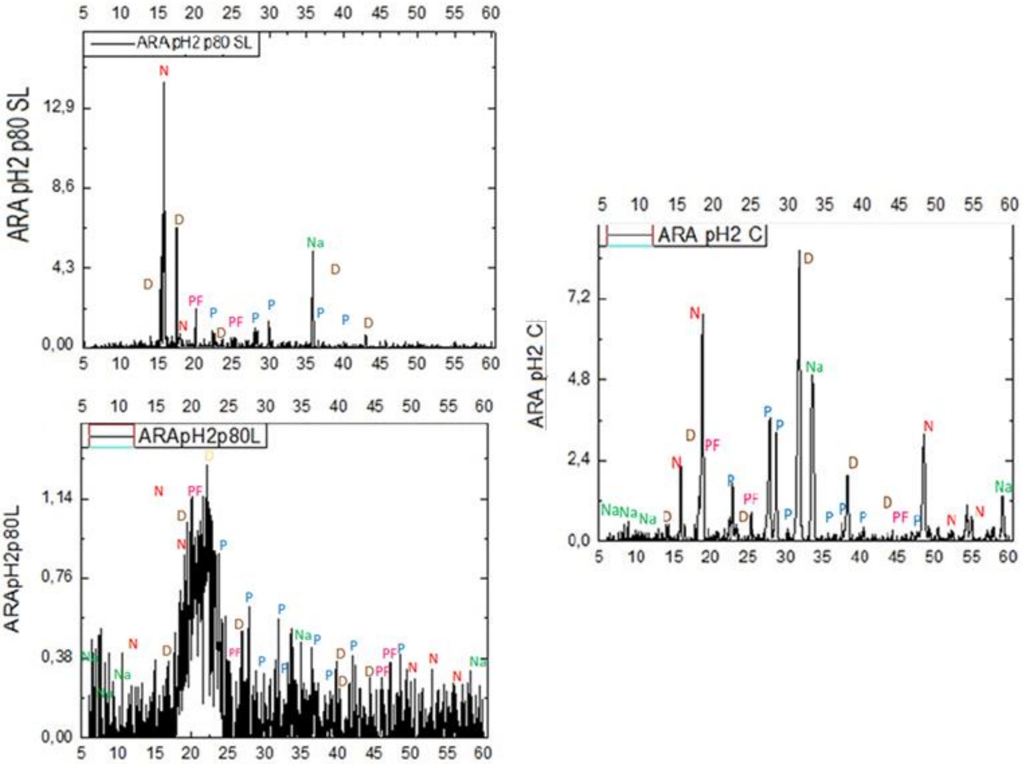
Table 4*Kraft* lignin samples.

Identification	Compound name	Chemical composition	Catalog sheet
D	Dibenzene-anthracene	$C_{22}H_{14}$	00-041-1649
N	Naphthacene-Pentacene	$C_{40}H_{26}$	00-048-2327
At	Sodium methylacetanilide	C_3H_3Na	00-021-1914
P	Pentacene	$C_{22}H_{14}$	00-048-2326
PF	Polyphenylacetylene	$(C_8H_6)n$	00-020-1862

Source: The authors, 2023

For the ARA pH 2 (SL, L) samples, more intense peaks appeared at different values of 2θ, as can be seen in Figure 4. The existence of two peaks stands out, one with greater amplitude at 33 ° for the ARA pH 2 (C) samples, and another with lower intensity at 19°, attributed to amorphous lignin. Such values are similar to those demonstrated in the literature, as exposed by Lopes, Carneiro, Andrade and Potulski (2017), Goudarzi *et al* (2014), Kubo *et al*. (2003) and Ansari and Gaikar (2013).

Figure 4- X-ray diffraction diagram of lignin powders with the addition of recycled acid (ARA)

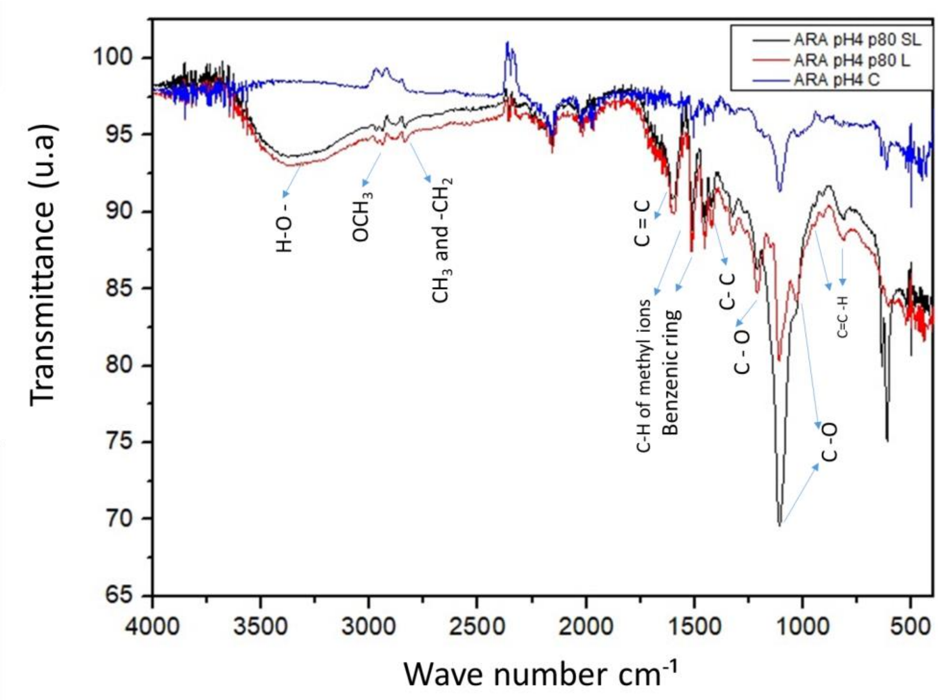


Source: The authors, 2023

For the ARA pH 2 C and L samples, Figure 4, 2θ values were found, in the ranges of 32° and 19°, these being the most intense peaks for the samples analyzed. These results are in collaboration with those obtained by Pompeu (2017) and Talabi (2020).

Figure 5 presents the infrared spectra of the ARA pH 2 SL, L and C samples.

Figure 5– Spectra in the infrared region with Fourier transform for *Kraft* lignin samples



Source: The authors, 2023

The signals of the connections referring to the bands observed in Figures 5 are presented in Table 4.

Table 5- Assignment of absorption bands in the infrared region of *Kraft lignin samples.*

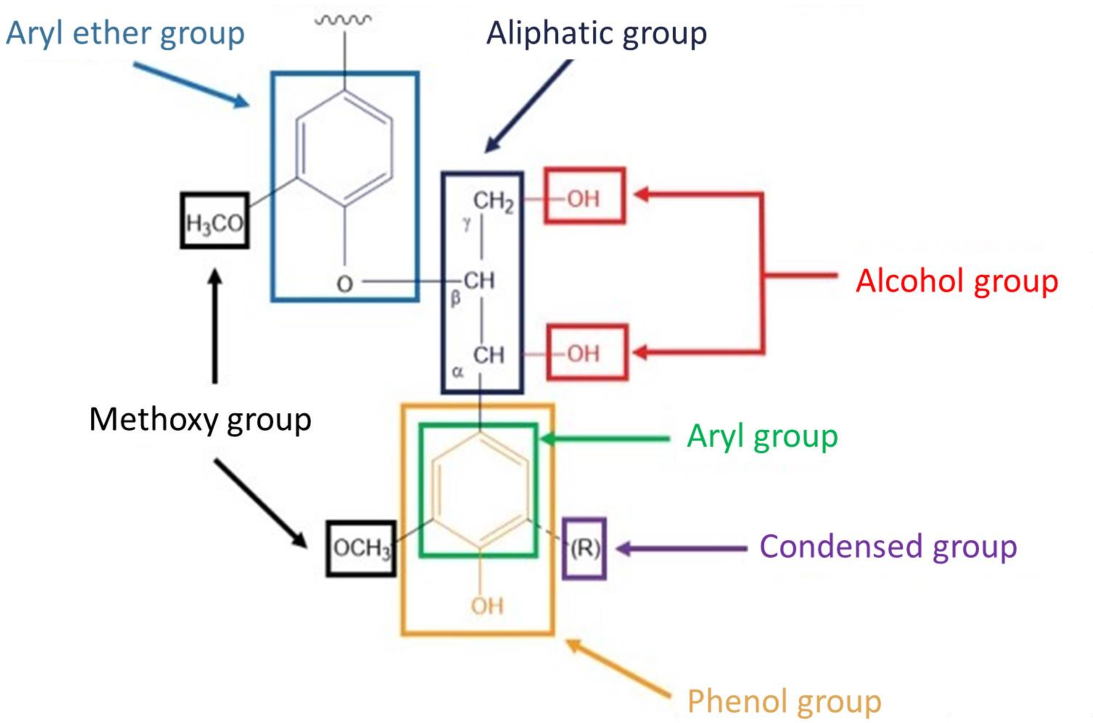
Wavenumber (cm^{-1})	Chemical bond
3410	HO-
2940	$-OCH_3$
2835	CH_3- and $-CH_2$-
1605	C=C
1465	CH of methyl groups
1415	aromatic ring CC
1210	C=O
1120	C=O
1022	CH and C=O
907	CH and C=O
850	C=C -H

Source: The authors, 2023

The results obtained observed in Table 4 are in turn collaborated with approximate values found for FTIR analyzes obtained by Silva (2013), Silva (2014), Damaceno (2016), Lopes (2018), Souza (2019) and Vaz Junior *et al.* (2020).

These results prove the presence of chemical bonds between carbon, hydrogen and oxygen elements, as expected in the lignin structure, as can be seen in Figure 6.

Figure 6- Possible functional groups of *Kraft* lignin



Source: Adapted from (HEITNER *et al.*, 2010 and WASTOWSKI, 2018)

Thus, it can be seen that the results obtained in this study prove the presence of chemical bonds between carbon, hydrogen and oxygen elements, for the ARA samples, in the pH 2 range expected for the *Kraft* lignin *structure.*

5 CONCLUSION

In the present work it can be seen that the *Kraft black liquor acidification process* can use recycled sulfuric acid, which is considered a cleaner alternative to this process.

Lignin can be obtained using recycled acid from the battery process, thus achieving the originally proposed objectives. The process of obtaining *Kraft* lignin with recycled acid must be studied in more depth, in order to obtain more references that can assist in recycling the battery electrolyte to its final destination in the cellulose manufacturing process.

The lignin yields were within expectations, as the average yield was 29.76 ± 0.0059%, for the ARA sample, meeting literature standards for *E. grandis,* thus the recycled acid proved to be effective for the process.

Kraft lignin showed that the parameters are consistent with those in the literature. This shows that the product obtained can be used and reinserted during the process without causing damage. These parameters are important because they can directly influence the product obtained.

The values obtained in this work demonstrate the effectiveness of the method for obtaining *Kraft* lignin using the black liquor remaining in the *Kraft* process. Most importantly, the characterization techniques described here are consistent with the literature exemplified here.

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