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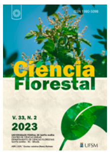

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Artigos

Extraction and characterization of two residual lignins from eucalyptus wood

Extração e caracterização de duas ligninas residuais da madeira de eucalipto

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ABSTRACT

Lignin, the second most abundant biopolymer on the planet, has properties that can be widely explored, moving from waste to products with high added value. Therefore, this work aimed to extract and characterize Klason and Kraft lignins from sawdust and black liquor, considered industrial waste. The raw material used was *Eucalyptus grandis* chips. To obtain Klason lignin according to TAPPI 222 om-02 (2002), part of the chips were transformed into sawdust. To obtain Kraft lignin, another part of the chips passed through a digester to obtain black liquor, which was subsequently subjected to acid precipitation. The characterization of lignins was performed by granulometry analysis, scanning electron microscopy with elemental chemical analysis (EDS), transmission electron microscopy, medium infrared spectroscopy, thermogravimetric analysis and differential calorimetry. Microscopy analyzes showed irregular structures of various shapes, including spherical structures, most evident and frequent in Kraft lignin. The elementary chemical analysis showed that the lignin washing process was satisfactory, due to the small percentage of sulfur detected in the samples. The results of the granulometry confirmed that the lignins had micrometric dimensions. The medium infrared spectra showed the characteristic peaks of the chemical composition of lignin. The thermal analysis showed three ranges of degradation, attributed to the drying of the samples, degradation of the hemicelluloses and the lignin itself. All results confirmed the obtaining of Klason and Kraft lignins. Therefore, the techniques were satisfactory in transforming waste into lignin with the potential for a variety of commercial applications, mainly in the chemical and pharmaceutical industries.

Keywords: Industrial waste; Lignin; Morphological and thermal analysis

RESUMO

A lignina, o segundo biopolímero mais abundante do planeta, possui propriedades que podem ser amplamente exploradas, passando de resíduos a produtos de alto valor agregado. Portanto, este trabalho teve como objetivo extrair e caracterizar as ligninas Klason e Kraft de serragem e licor negro, considerados resíduos industriais. A matéria-prima utilizada foram cavacos de *Eucalyptus grandis*. Para a obtenção da lignina Klason conforme TAPPI 222 om-02 (2002), parte dos cavacos foi transformada em serragem. Para a obtenção da lignina Kraft, outra parte dos cavacos passou por um digestor para a obtenção do licor negro, que posteriormente foi submetido à precipitação ácida. A caracterização das ligninas foi realizada por análise de granulometria, microscopia eletrônica de varredura com análise química elementar (EDS), microscopia eletrônica de transmissão, espectroscopia de infravermelho médio, análise termogravimétrica e calorimetria diferencial. As análises microscópicas mostraram estruturas irregulares de vários formatos, incluindo estruturas esféricas, mais evidentes e frequentes na lignina Kraft. A análise química elementar mostrou que o processo de lavagem da lignina foi satisfatório, devido ao pequeno percentual de enxofre detectado nas amostras. Os resultados da granulometria confirmaram que as ligninas apresentaram dimensões micrométricas. Os espectros de infravermelho médio mostraram os picos característicos da composição química da lignina. A análise térmica mostrou três faixas de degradação, atribuídas à secagem das amostras, degradação das hemiceluloses e da própria lignina. Todos os resultados confirmaram a obtenção das ligninas Klason e Kraft. Portanto, as técnicas foram satisfatórias na transformação de resíduos em lignina com potencial para diversas aplicações comerciais, principalmente nas indústrias química e farmacêutica.

Palavras-chave: Resíduo industrial; Lignina; Análise morfológica e térmica

1 INTRODUCTION

Lignocellulosic biomass is an interesting alternative to develop chemicals and bioproducts to replace fossil feedstocks in terms of biorefinery and bioeconomy. Forest-based industries - especially pulp mills and sawmills - are two main examples of large producers of residues. This scenario is steadily observed in the Brazilian forestry sector, since, for example, Brazil has the second-largest pulp worldwide production. Around 10.3 million metric tons of residues – mainly chips, sawdust, and black liquor – are generated yearly in Brazil (IBA, 2022), with a special focus for *Eucalyptus spp*. biomass contribution. Thus, research efforts have been steadily required to optimize their reuse at an industrial scale, especially due to their environmental-friendly and biodegradable nature.

Among these residues, wood sawdust and black Kraft liquor demand attention because of their large amount and potential as a renewable source of cellulose, hemicelluloses, and lignin for the production of biofuels and various high-added value chemicals. In the case of black Kraft liquor – around 1.6 billion tonnes of weak Kraft black liquor are produced every year - for example, around 74% of this waste is usually allocated by the pulping industries for combustion for heat recovery since they aim energy self-sufficiency (IBA, 2022). Many kraft pulp mills have a desire to increase their production capacity. Often in such cases the recovery boiler isone of the bottlenecks. Recently lignin recovery from black liquor (LignoBoost) technology has become availablethat promises increased pulp mill capacity and can help to achieve a completely fossil-fuel free mill.The separation of lignin is an option that is considered by the pulp mills for several reasons. Firstly, the heat transfercapacity of the recovery boiler is often a bottleneck that limits pulp production. Removing part of the lignin from theblack liquor decreases the heat load on the recovery boiler and more pulp can be produced (VAKKILAINEN; VÄLIMÄKI, 2009).

However, black Kraft liquor is rich in lignin due to the cooking process procedure, in which 90-95% of the lignin is dissolved into the liquor (CHEN; CHEN; ZHOU; LIU; HU; FAN, 2015). The industrial and technical lignins presented in both wastes, sawdust, and black Kraft liquor, are an abundant, renewable, and biodegradable material with interesting characteristics, such as antimicrobial activity (GORDOBIL; HERRERA; YAHYAOUI; İLK; KAYA; LABIDI, 2018) and amphiphilicity (ÖSTERBERG; SIPPONEN; MATTOS; ROJAS, 2020). These lignins are a source for different industrial applications, such as precursor for carbon fibers (SADEGHIFAR; SEN; PATIL; ARGYROPOULOS, 2016), phenol substituent in phenol-formaldehyde adhesives, dispersants and binders in printing inks (BAJPAI, 2018), adsorbents, composites, surfactants and polymers (MATSAKES; KARNAOURI; CWIRZEN; ROVA; CHRISTAKOPOULOS, 2018).

The success of this wide range of applications is driven by the valorization of lignin as an industrial stream and the interest as an alternative to replace synthetic particles (ÖSTERBERG; SIPPONEN; MATTOS; ROJAS, 2020). Also, broader use of lignin can be promoted by applying biorefinery concepts in the forest-based industry (VISHTAL; KRASLAWSKI, 2011).

However, large-scale applications of lignin depend on the sources and processes of extraction (MISHRA; EKIELSKI, 2019). Depending on the technology used to extract the lignin can increase its chemical complexity, which demands additional challenges to target for new applications (BEISL; MILTNER; FRIEDL, 2017). One of the most problems of lignin application is its large heterogeneity because different pulping processes result in molecules ranging from virtually monomeric phenols to high-molecular-weight polymers, which can affect its structure and chemical characteristics (GILCA; GHITESCU; PUITEL; POPA, 2014), such as thermal stability (MARTÍN-SAMPEDRO; SANTOS; FILLAT; WICKLEIN; EUGENIO; IBARRA, 2019) and reactivity with aldehydes due to higher amount of activated free aromatic ring positions (FARIS; RAHIM; IBRAHIM; HUSSIN; ALKURDI; SALEHABADI, 2017).

In the knowledge of wide applications of lignin and its well-known heterogeneity, a fundamental understanding of technical and industrial lignins is an interesting way to propose reliable applications of this low-cost material. In our study, we report a comparison between technical lignin obtained from acid hydrolysis and industrial lignin extracted from black Kraft liquor. Both lignins came from the processing of *Eucalyptus grandis* biomass, one of the main and attractive feedstocks for pulp and paper production in the world. They were compared by thermal kinetics, morphology, particle size distribution, and chemical aspects.

2 MATERIAL AND METHODS

Eucalyptus grandis wood chips have been kindly donated by the institute of technology Embrapa Florestas (Colombo, Parana State, Brazil). The wood chips were ground into small particles using a Willey mill and then they were classified according to TAPPI T-257 (2012) standard. The wood eucalypt wood chips presents the following chemical composition: NaOH solubility of 12.91±0.87%, hot-water extractives of 2.22±0.13%, ethanol:toluene extractives of 2.60± 0.05%, holocellulose content of 69.09±0.23% and ash content of 0.39±0.01. The chemicals used in the treatments of biomass for isolation of the lignins were analytical grade.

2.1 Isolation of Klason lignin

The chemical treatment for the isolation of acid insoluble lignin from *Eucalyptus grandis* wood chips was carried out by acid hydrolysis procedure as described in the TAPPI 222 om-02 (2002) standard. The wood chips were kept in contact with 72% H_2SO_4 (3% in aqueous media v/v) for 2 h at room temperature. The mixture of wood chips and acid was diluted with distilled water and the suspension was heated in a boiling water bath for 4 h at 94ºC. The treated biomass was filtered for isolation of the lignin, followed by washing with distilled water and oven-drying at 103 ºC for 24 h.

2.2 Isolation of Kraft lignin

The conventional Kraft process of wood chips was carried out in a digester with computerized control of time and temperature. The digester was filled with wood chips, distilled water and white liquor (NaOH and Na_2S) with a 18% chemical charge. The Kraft cooking process was performed for 59 minutes at 170ºC. The obtained pulp was sieved and washed abundantly with water at room temperature to collect the black Kraft liquor. The back Kraft liquor presents pH 12.19, residual effective alkali of 7.37 g/L, density of 1.062 g/cm³ and solids content of 0.1478 g/mL.

The recovery of Kraft lignin was performed by slow acidification of the black Kraft liquor using 20% H_2SO_4 (v/v). The sulfuric acid solution was dipped under constant magnetic stirring and control of the pH with a pHmeter. The pH 2.0 was chosen as the optimal condition for Kraft lignin recovery based on the highest yield obtained in the process. Also, the degree of purity of Kraft lignin is higher at pH 2.0 due to its lower content of inorganics and carbohydrates in the structure, since the substantial amount of acid employed to set this pH. The dissolved lignin was precipitated in the liquid media and then collected by vacuum filtration, followed by washing steps with hot distilled water. The solid phase corresponding to Kraft lignin was oven-dried at 103°C overnight. The average yield of Kraft lignin isolated from the black liquor was 30.25%.

2.3 Characterization of the lignins

2.3.1 The particle size of lignin

The particle size distribution of both acid insoluble and Kraft lignin powders was determined by a laser diffraction analyzer Microtrac S3500 (Microtrac Retsch GmbH, Montgomeryville, PA).

2.3.2 Morphology

The morphology of dried-lignin particles was analyzed by Scanning Electron Microscopy (SEM). High-resolution images were acquired in an FEI Quanta 450 FEG equipment with a resolution of 1 nm in magnifications of 800 – 80,000x. Chemical mapping was performed simultaneously by Energy-dispersive X-ray spectroscopy (EDS) coupled to SEM. The morphology of the lignin particles was also investigated by Transmission electron microscopy (TEM) in a JEOL JEM 1200EX-II equipment with a resolution of 0.5 nm. A small amount of lignin was diluted in a high volume of distilled water. A single drop of each aqueous media was deposited onto the grids and subsequently dried at room temperature for 24 h.

2.3.3 Chemical composition

Chemical functional groups of the lignins were characterized by Fourier-transform infrared spectroscopy (FTIR). Five spectra of each lignin were collected on a Vertex 70 spectrometer (Bruker Corporation, Billerica, Massachusetts, USA). The equipment was set to operates at resolution of 2 cm^{-1} and 64 scans in a spectral range of 1,000 – 4,000 cm^{-1}.

2.3.4 Thermal stability

The thermal stability and degradation of the lignins were investigated by thermogravimetry (TGA-DTA) in a Setaram Setsys Evolution device. Around 5 mg of each lignin was subjected in alumina pans to the following analysis conditions: an inert atmosphere of argon (Ar), the gas flow of 20 mL/min, a heating rate of 20°C/min, and a temperature range from 20 to 700°C.

3 RESULTS AND DISCUSSION

3.1 Particle size distribution

Firstly, practical gradation analysis (Table 1) demonstrate the heterogeneous particle size distribution of the lignins, especially due to its isolation steps. Although both lignins possess a geometric size, it was observed lower retention percentage of Kraft lignin probably because the smaller fragments generated in the acid precipitation since Klason lignin presented common aggregation of the particles.

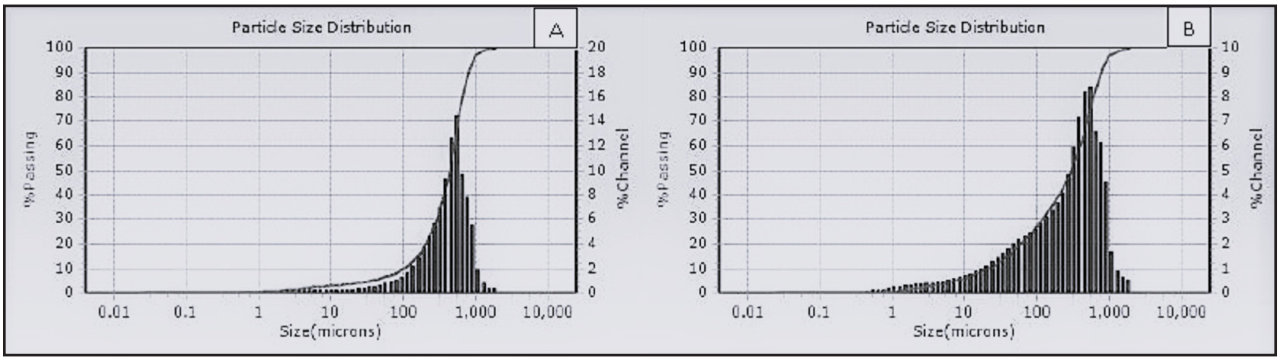
Table 1 – Particle retention percentage of Klason and Kraft lignin

Sample	Sieve: 5 mesh (%)	Sieve: 9 mesh (%)
Lignin Klason	8.29	31.15
Lignin Kraft	0.00	2.79

Source: Authors (2022)

Particle size distribution by laser analysis illustrates this geometric micron size distribution. The average particle size was 439.2 µm for Klason lignin and 300.8 µm, for Kraft lignin (Fig 1). Furthermore, Klason lignin demonstrates a narrower density distribution than Kraft lignin. Abdelaziz and Hulteberg (2017), in their work, attributes this type of aggregation behavior to a greater degree of crosslinking of the molecules.

Figure 1 – Granulometric distribution of lignin: (A) Klason and (B) Kraft



Source: Authors (2022)

3.2 Surface morphology of the lignin's particles

The lignin surface morphology (Fig 2) illustrates and confirms the results observed by analyzing the particle size distribution. Micron-sized lignins showed irregular morphology with aggregates and without a predominant shape. But several spherical particles are observed in the Klason lignin particles with a diameter of less than 1 µm. In addition, some superficial fractures found in the particle morphology indicate intrinsic characteristics of the first stages of chemical degradation, probably due to the action of sulfuric acid during the acid hydrolysis process. These surface characteristics corroborate the findings by Hu, Dekui Shen, Wu, Zhang and Xiao (2014) who observe an irregular and smooth polygonal surface in the lignin particles. Thus, mechanical treatments can be a useful alternative to individualize these smaller particles of lignin for application in new areas and also in those areas that already use lignin, such as in panel additives or even for preservative treatment.

The transmission electron microscopic images of Klason lignin samples (Fig 3) revealed particles on the micrometer scale. Figure 3B also possible shows smaller spherical structures, similar to the compacted particles visualized within fractures of the Klason lignin structures.

Figure 2 – SEM image of Klason lignin at magnification of 800x (A), 10000x (B), 20000x (C) and 80000x (D)

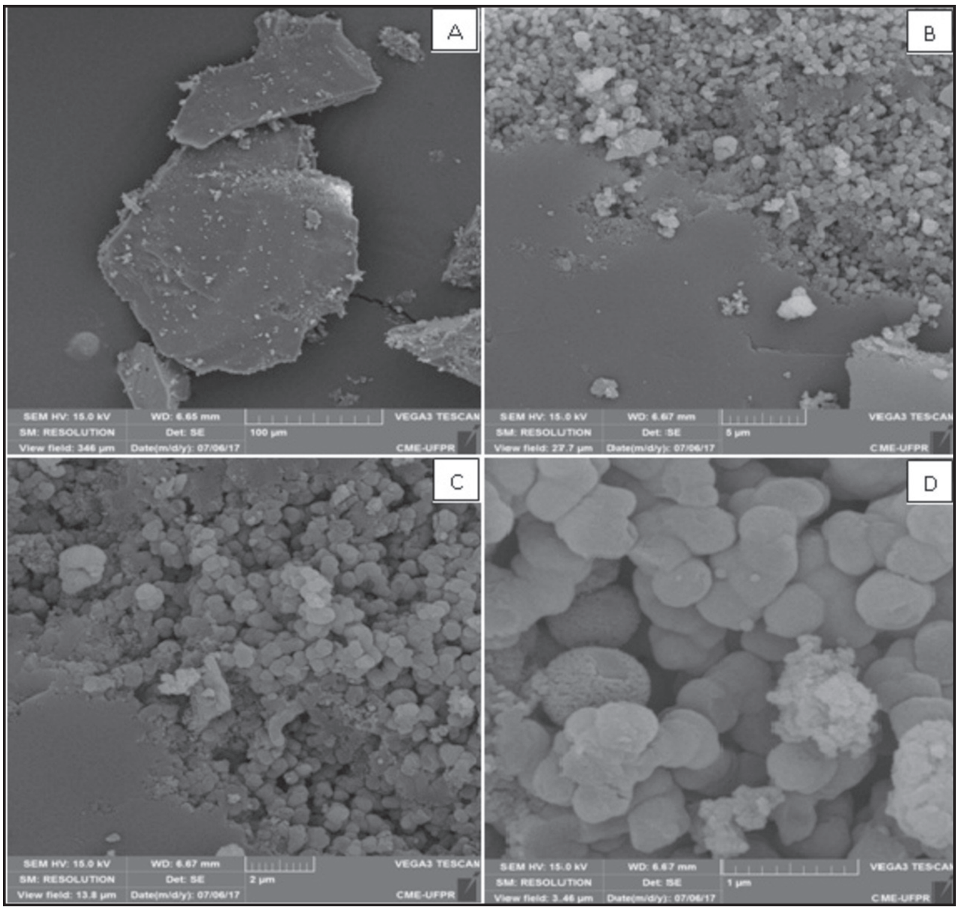


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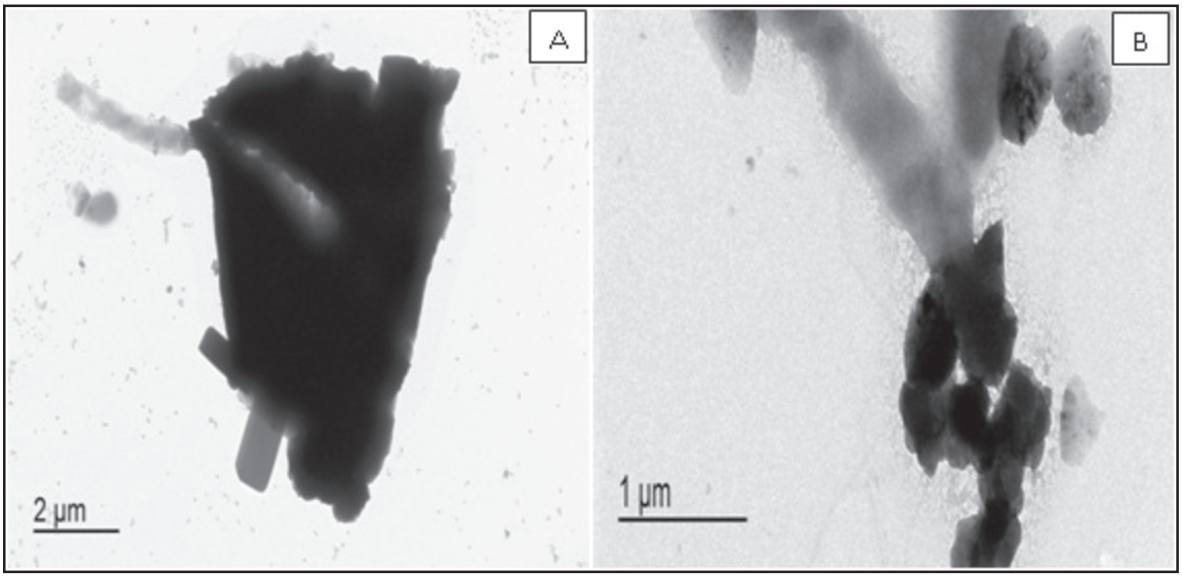
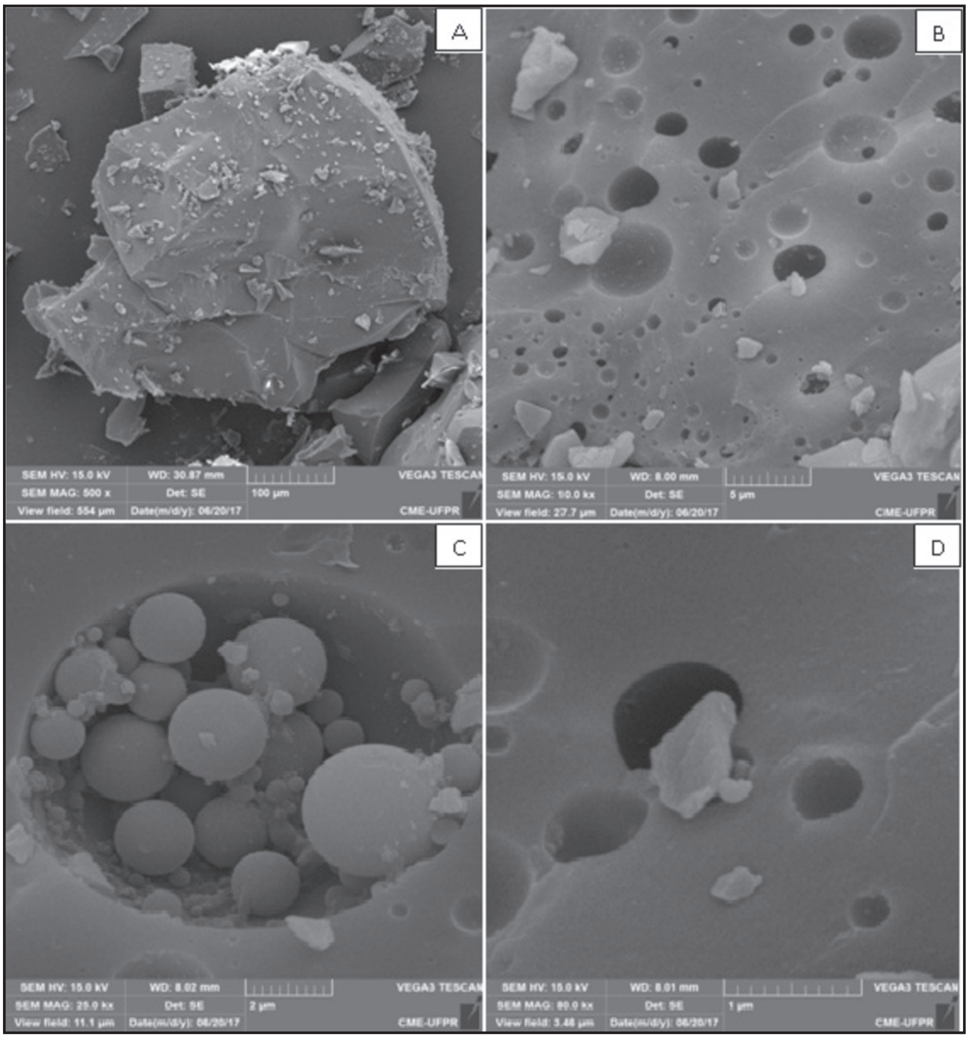
Figure 3 – TEM images of Klason lignin with magnification of 2000x (A) and 6000x (B)



Source: Authors (2022)

The Kraft lignin particles also presented micrometer size, irregular morphology and varied shapes (Fig 4A). These structures presented smooth surfaces with many rounded cavities (Fig 4B), which corroborates with the findings of Gan, Pan, Zhang, Dai, Yin, Qu and Yan (2014). These rounded cavities probably indicate chemical degradation by the sulfuric acid used in the isolation of the Kraft lignin particles. In several of these holes, we observe round microspheres (Fig 4C), as also previously found by Lee, Yoo, Lee and Won (2020). Likewise, Podkościelna, Sobiesiak, Zhao, Gawdzik and Sevastyanova (2015) observed irregular structures with heterogenous sizes which agglomerates together with other smaller irregular particles.

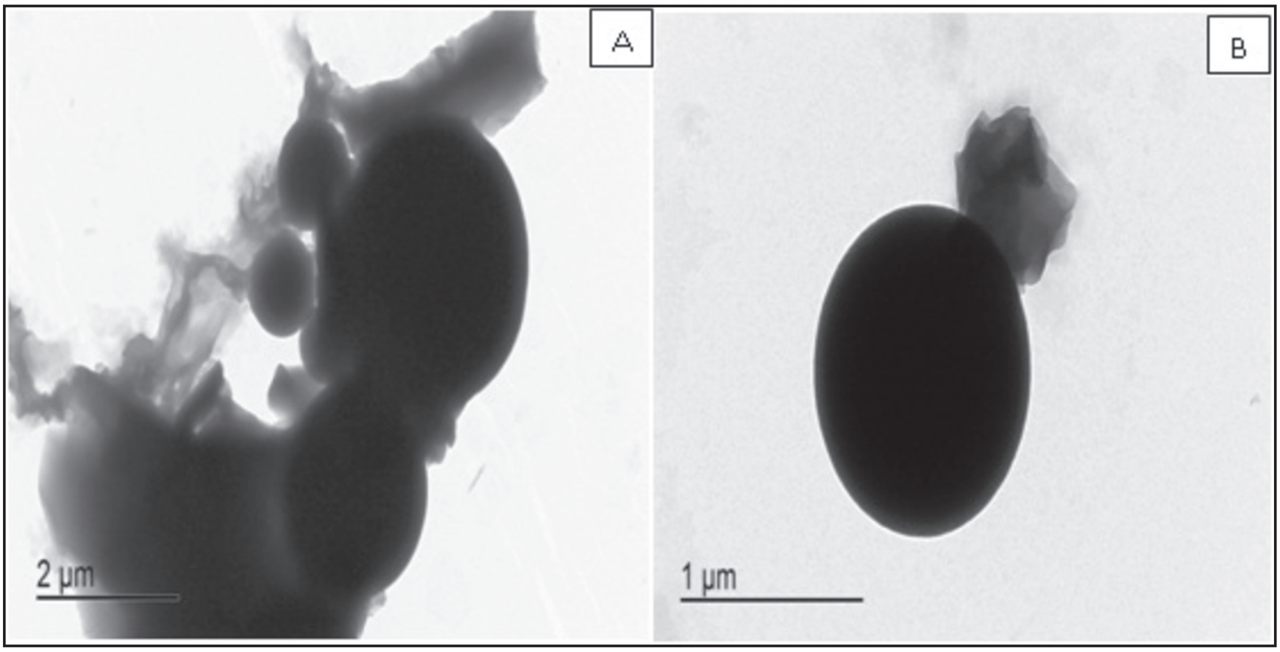
Figure 4 – SEM images of Kraft lignin with magnification of 600x (A), 10000x (B), 25000x (C) and 80000x (D)



Source: Authors (2022)

TEM analysis for Kraft lignin confirmed the presence of irregularly shaped structures and spheres (Fig 5). As in SEM analysis, these structures had micrometer scale. Therefore, transmission electron microscopy analysis reaffirmed both irregular and spherical structures, both micrometric, as already evidenced by SEM.

Figure 5 – TEM images of Kraft lignin with magnification of 3000x (A) and 8000x (B)



Source: Authors (2022)

Österberg, Sipponen, Mattos and Rojas (2020) declareted that spherical lignin particles with well-defined surface chemistry and morphology have a great potential in many applications. They can improve the properties of renewable and biodegradable composites, be part of greener adhesives and decrease the need for synthetic emulsifiers.

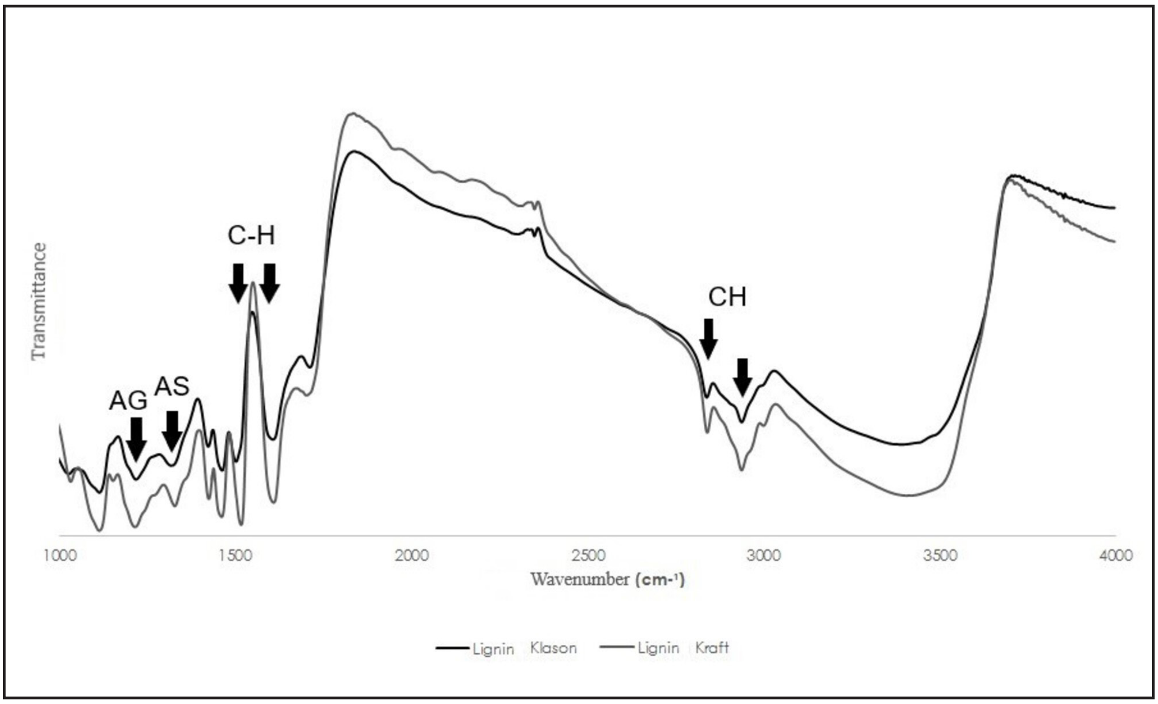
3.3 Chemical features of the lignins

The elemental chemical mapping determined by EDS illustrated no qualitative differences between the lignins' composition. Klason lignin presented 87.04% carbon (C), 12.94% oxygen (O) and 0.01% sulfur (S), and Kraft lignin presented 84.90% carbon

(C), 14.90% oxygen (O) and 0.2% sulfur (S). These results indicated smaller amounts – lower than 0.2% - of residual sulfur content, which is beneficial for specific applications.

The obtained infrared spectra for both Klason and Kraft lignins exhibit identical characteristics (Fig 6). For both lignins, a peak at 3400 cm^{-1} is observed for hydroxyl groups (OH). Weake signals at 2930 cm^{-1} and 2830 cm^{-1} for both lignins denoted a characteristic band of aliphatic C-H. The band at 1710 cm^{-1} is assigned to carboxylic group stretching (C=O). These same bands were also described by Beisl, Loidolt, Miltner, Harasek and Friedl (2018) for organosolv micro and nano lignins of wheat straw extracted in different acid precipitation conditions.

Figure 6 – FTIR spectra of Klason and Kraft lignins



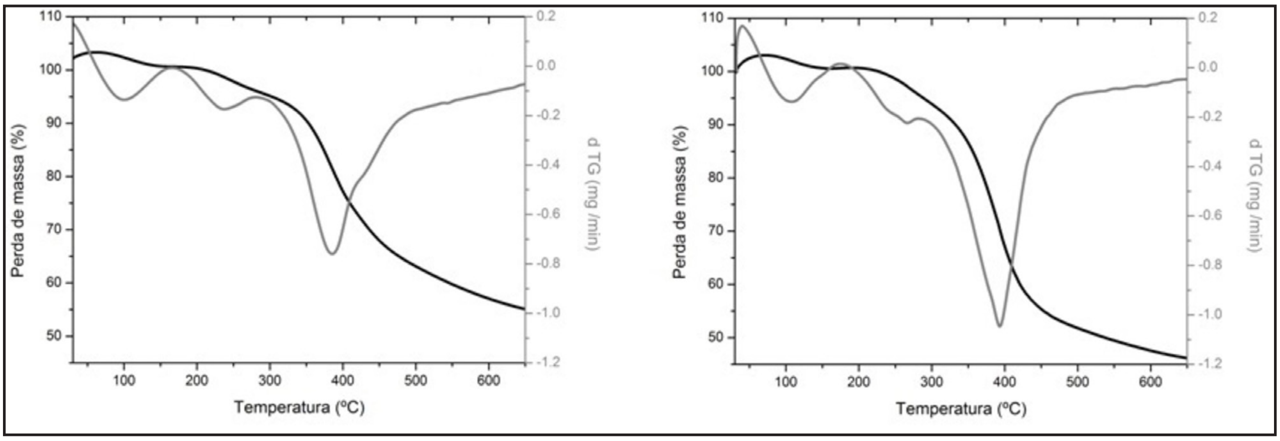
Source: Authors (2022)

Both lignins presented bands at 1600 cm^{-1} and 1510 cm^{-1} referred to aromatic C-H bonds, as also described by Zhou, Taylor and Polle (2011). Two other bands at 1420 cm^{-1} and 1460 cm^{-1} are assigned to C-C bonding of aromatic rings and the C-H bonding of methyl groups, respectively. The band at 1310 cm^{-1} refers to the syringyl rings, corroborating with the findings of Oliveira, Pimenta, Silva, Ramos, Siqueira and Fonseca (2017) in Kraft lignin extracted from the black liquor. Also, the band at 1230 cm^{-1} is assigned to guaiacyl rings, as also described by Liu, Hu, Zhang and Xiao (2016). The C-H bonds of secondary alcohols were illustrated at 1105 cm^{-1} and the deformation of the C-O bond of primary alcohol is related to the band at 1030 cm^{-1} found in both Klason and Kraft lignins.

3.4 Thermostability of the lignins

The thermal degradation profiles of the lignins (Fig 7) were similar, with small differences in the temperatures corresponding to the maximum degradation peaks.

Figure 7 – TG and DTG curves of Klason (A) and Kraft (B) lignins



Source: Authors (2022)

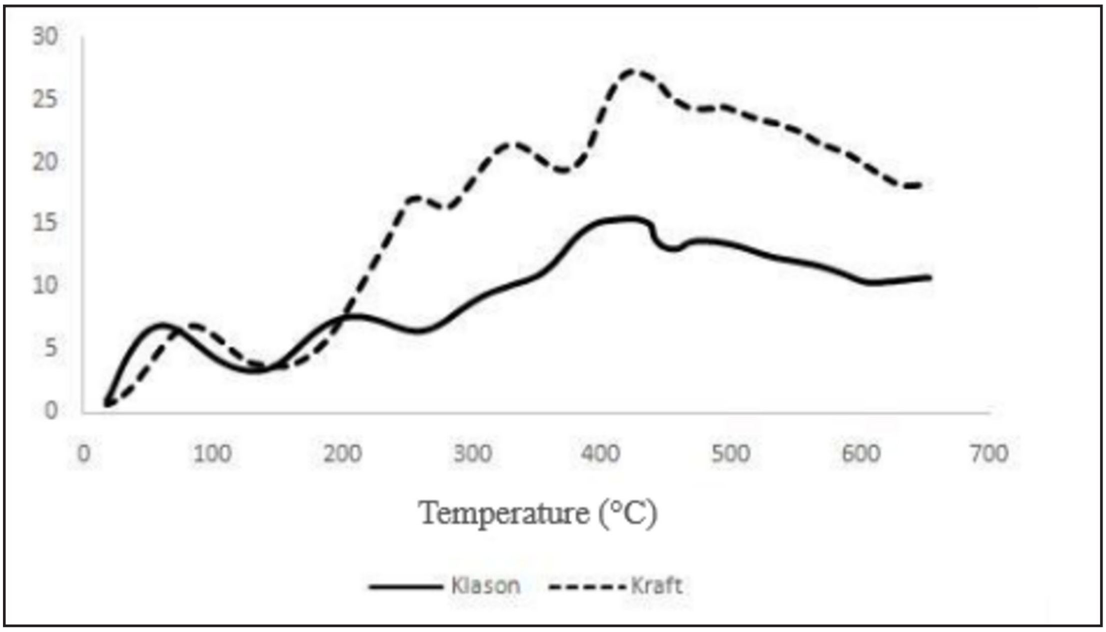
The TGA/DTG curves indicated three stages of thermal degradation. First, it was verified adsorbed water evaporation around 100°C. Although the lignins were previously dried, residual adsorbed water molecules remained on the lignin particles. This was also reported by Azimvand, Didehban and Mirshokrai (2018). In the second stage, thermal degradation of both Klason and Kraft lignins occur in smaller proportions at 200-300°C. This weight loss is assigned to residual hemicelluloses presented in the lignins after the isolation processes. The range from 300 to 400°C was the most intense thermal degradation stage of the lignins. The maximum degradation was around 385°C for both Klason and Kraft lignins. Jiang, He, Jiang, Ma and Jia (2013) observed that the average maximum lignin degradation temperature in their work was 380°C, which is consistent with the results found in this study. This weight loss is assigned to the fragmentation of the weak inter-units linkages (β-O-4) of the lignin (GUO; ZHOU; WEN; SUN; SUN, 2015).

The maximum weight loss rates were reached at temperatures around 425°C for both Klason and Kraft lignins. Then, both lignins presented slower weight losses. Usually, lignin degradation tends to be constant or weakly decrease above 500°C (GUO; ZHOU; WEN; SUN; SUN, 2015; MOUSTAQIM; KAIHAL; MAROUANI; YAKHAF; TAIBI; SEBBAHI; HAJJAJI; SAHBAN, 2018). This corroborates with the findings of Liu, Hu, Zhang and Xiao (2016), who reported a wide range of lignin degradation temperatures (400 to 550°C) related to the degradation of aromatic rings and different oxygenated functional groups in their structure.

Differential thermal analysis of the lignins (Fig 8) illustrated the presence of a first endothermic peak between 56 and 98°C attributed to water loss, as previously observed in the TGA analysis; followed by an exothermic peak at 225°C assigned mainly to the breakdown of lignin's syringyl and guaiacyl polymer units. Adversely, Azimvand, Didehban and Mirshokrai (2018) observed this degradation at around 150°C. The third exothermic peak occurred in the temperature of 450°C. From approximately 410°C, the DSC curves became linear and increasing due to the thermal degradation of lignin, in which heat release became more intense. Azimvand, Didehban and Mirshokrai (2018) reported that the maximum degradation peaks were reached at temperatures from 361 to 390°C.

It is also important to note that this last released heat flux was higher in relation to the previous one, since the greater the formation of gaseous products, the greater the released energy will be, and the peak related to Kraft lignin presented larger amplitude, due to probably to the source material, black liquor, which has a high chemical charge and can generate more gaseous products.

Figure 8 – DTA curves of Klason and Kraft lignins



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4 CONCLUSIONS

In this work, technical lignin obtained from acid hydrolysis and industrial lignin extracted from black Kraft liquor from eucalypt wood waste were examined in terms of thermal and physicochemical properties. The isolation processes of both lignins was satisfactory resulting in micrometric particles with irregular and spherical morphology, the last one being more common in Kraft lignin. Both Klason and Kraft lignins presented lower residual sulfur amount, probably due to the intense washing step, and similar profile of thermal degradation with intense exothermic reactions. Thus, our findings illustrated simple procedures to obtain lignins with excellent characteristics as alternatives in the production of higher added value products in fine chemistry and for pharmaceutical applications, for instance. In addition, reuse of wood waste for isolation of lignin could be an interesting alternative to improve the bioeconomy and circular economy trends.

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