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PREPARATION AND CHARACTERIZATION OF NANOPARTICLES OF KLASON AND KRAFT LIGNIN FROM *Eucalyptus grandis* WOOD

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Resumo

Preparação e Caracterização de nanopartículas de lignina Klason e Kraft da madeira de Eucalyptus grandis. Este trabalho teve como objetivo preparar e caracterizar nanopartículas de lignina produzidas a partir de serragem (lignina Klason) e licor negro (lignina Kraft), materiais considerados resíduos industriais. A matéria-prima deste estudo foram cavacos de Eucalyptus grandis. Para a lignina Klason, os procedimentos foram realizados de acordo com a norma TAPPI 222 e para a lignina Kraft os cavacos foram cozidos para coletar o licor negro, seguido de precipitação ácida. As nanoligninas foram obtidas pelo processo mecânico através de um moinho utilizando de 2, 8 e 13 passes. A caracterização das nanoligninas foi realizada por microscopia eletrônica de varredura com análise química elementar e microscopia eletrônica de transmissão, análise de granulometria, análise termogravimétrica e calorimetria de varredura diferencial. A microscopia eletrônica de varredura e a microscopia eletrônica de transmissão mostraram nanoestruturas irregulares de vários formatos e estruturas esféricas, sendo estas últimas mais evidentes e frequentes na nanolignina Kraft. A análise química elementar mostrou que o processo de lavagem das nanoligninas foi satisfatório, pois apenas uma pequena porcentagem de enxofre foi detectada nas amostras. A análise granulométrica confirmou que as nanoligninas tinham dimensões nanométricas. A análise térmica mostrou que as nanoligninas apresentam três bandas de degradação, atribuídas à secagem das amostras e também à degradação das hemiceluloses e da própria lignina. Portanto, foi possível confirmar a obtenção de nanoligninas Klason e Kraft através do uso do moinho, e que um número crescente de passes produziu uma maior porção de partículas com tamanho nanométrico.
Palavras-chave: madeira de eucalipto, resíduo industrial, nanolignina, nanotecnologia.

Abstract

This work aimed to prepare and characterize nanoparticles of lignin produced from sawdust (Klason lignin) and black liquor (Kraft lignin), materials considered to be industrial waste. The raw material of this study was *Eucalyptus grandis* chips. For Klason lignin, the procedures were carried out according to the TAPPI 222 and, for Kraft lignin, the chips were cooked to collect the black liquor, followed by acid precipitation. The nanolignins were obtained by the mechanical process through a mill using passes from 2, 8 and 13. The characterization of nanolignins was performed by scanning electron microscopy with elemental chemical analysis and transmission electron microscopy, granulometry analysis, thermogravimetric analysis and differential scanning calorimetry. Scanning electron microscopy and transmission electron microscopy showed irregular nanostructures of various shapes and spherical structures, the latter of which were more evident and frequent in Kraft nanolignin. The elemental chemical analysis showed that the washing process of the nanolignins was satisfactory, as only a small percentage of sulfur was detected in the samples. The granulometric measurement confirmed that the nanolignins had nanometric dimensions. Thermal analysis showed the nanolignins had three degradation bands, attributed to the drying of the samples and also to the degradation of hemicelluloses and lignin itself. Therefore, it was possible to confirm the obtainment of Klason and Kraft nanolignins through the use of the mill, and that an increasing number of passes produced a greater portion of particles with nanometric size.
Keywords: eucalyptus wood, industrial residue, nanolignin, nanotechnology.

INTRODUCTION

Lignin is the second most abundant biopolymer (CHAUHAN, 2020) and has potential to produce various chemicals of interest. Its value is influenced by color, polymeric nature, and the presence of high bond dissociation enthalpies in its functional groups, among other factors. The leading applications of industrial lignin are energy production and recycling of inorganic compounds involved in the pulping process. In recent years, new studies

have indicated other important applications, such as production of lignin-based hydrogels, surfactants, three-dimensional printing materials, electrodes and fine chemicals (SETHUPATHY *et al*., 2022).

The use of lignin with nanoparticle morphology resolves some problems of heterogeneity and low solubility of lignin, and nanodispersions in different formulations can be applied to prepare nanobiomaterials (HENN; MATTINEN, 2019). In recent years, production of nanoparticles from lignin has been gaining interest and involves a wide range of synthesis techniques, which can influence their properties and potential applications, such as antibacterials, UV adsorbents, antioxidants, hybrid nanocomposites, drug delivery vehicles, bioremediation substances and carbon precursors (CHAUHAN, 2020).

In addition to the complex chemical structure, in many cases the different technologies applied to obtain lignin nanoparticles can further increase the complexity, with reduced homogeneity, thus adding additional challenges for the production of nanolignins (BEISL *et al*., 2017).

A review by Hussin *et al*. (2022) described the differences in dimensions and shape of lignin nanoparticles in function of production/isolation methods. For example, material from mechanical processes can have dimensions from 20-100nm and will be in a solid state. The shape of lignin nanoparticles can be spherical or irregular (non-spherical), and they can form clusters or aggregates (CHAUHAN, 2020; ZHANG *et al*., 2021).

Possible applications of lignin nanoparticles include drug delivery systems, UV barriers, antibacterials, antioxidants, anticarcinogens, antibiotics and polymer reinforcements (QIAN *et al*., 2014; GILCA; POPA, 2013; LU *et al*., 2012; YANG *et al*., 2015). Also, according to Nair *et al*. (2014), lignin nanoparticles can also be used as an alternative to phenols in resins to produce thermoplastic polyesters and carbon fibers.

Some other potential applications with added value include fiber modification for textiles to improve the adhesion, hydrophobicity, antimicrobial and anti-oxidative properties of the material. Also, they can be used as carriers for enzymes, emulsifiers for colloids, adsorbents for water purification and controlled-release vectors for drugs and pesticides, as described in the review carried out by Henn & Mattinen (2019).

Therefore, the study of new nanolignins aims to meet new industrial and consumer demands for economically and environmentally sustainable products. Thus, this work aimed to prepare and characterize lignin nanoparticles based on lignin from pulp and paper industry waste.

MATERIAL AND METHODS

Material

The initial raw material was *Eucalyptus grandis* chips from five-year-old trees from the interior of the state of São Paulo, Brazil. The material was provided by the forestry research unit of the Brazilian Agricultural Research Corporation in Paraná (Embrapa Florestas-PR). Two different processes were used to produce lignin:

1) Klason lignin*:* The isolation of acid insoluble lignin occurred by acid hydrolysis, as described in the TAPPI 222 om-02 (2002) standard. The material was kept in contact with 72% H_2SO_4 (3% in aqueous media v/v) for 2 h at room temperature. The mixture was diluted with distilled water and the suspension was heated in a boiling water bath for 4 h at 94 ºC. Then the material was filtered for isolation of the lignin, followed by washing with distilled water and oven-drying at 103 ºC for 24 h;
2) Kraft lignin: The kraft cooking process was performed with maximum temperature of 170 ºC and 18% chemicals (NaOH and Na_2S). The black kraft liquor obtained had pH of 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 Kraft lignin was isolated according to procedure described by Souto *et al*. (2015) in your review article, based on slow acidification using 20% H_2SO_4 (v/v). The optimal condition for Kraft lignin recovery was set at pH 2.0, after which the lignin was precipitated and washed with distilled water. The solid phase was oven-dried at 103 °C for 24 h.

Nanolignin production

Klason and Kraft lignin samples were mechanically processed in a Masuko Sangyo Super Masscolloider mill, with rotation of 1500 rpm, distance between discs of 0.1 mm, number of passes equal to 2, 8 or 13, and consistency of 1%.

The different number of passes (2, 8 or 13) was performed in order to verify possible structural, chemical or thermal differences between the lignin nanoparticles produced.

Nanolignin characterization

a) Scanning electron microscopy and elemental analysis (SEM/EDS): A FEI Quanta 450 FEG scanning microscope was used, with a resolution of 1 nm. This equipment also performed the elemental chemical analysis by EDS. The material was prepared by depositing a small amount of the dried nanolignin on double-sided copper tape adhered to the sample holder. Different scales were used for

the Klason (50.000 X) and Kraft (100.000 X) nanolignin samples to obtains better visualizations of the structures.

b) Transmission electron microscopy: A JEOL JEM 1200EX-II transmission electron microscope was used, with resolution of 0.5 nm. The materials used in the analysis were prepared by the dilution of a small amount of the nanolignin in distilled water. A single drop of each suspended sample was placed on the sample holder and then dried at room temperature.

c) Granulometric analysis: A Microtrac S3500 particle size analyzer was used for the integrated granulometric characterization, by sieving and laser application. This analysis makes it possible to observe the particle size distribution over a wide range of the material produced with 13 passes.

d) Thermogravimetry and differential scanning calorimetry: One curve was obtained per sample, in which the nanolignin was heated from 20 to 700°C at a heating rate of 20°C/min, in an argon flow of 20 mL/min. The equipment used was a Setaram Setsys Evolution TGA-DTA/DSC system, which performs both analyses at the same time. An alumina melting pot was used.

RESULTS

Morphology

The scanning and transmission electron microscopic images (Figures 1 and 2, respectively) of the Klason and Kraft lignin nanoparticles confirmed that the material obtained had nanometric dimensions. In general, the structures were composed of agglomerates with micrometer scale after three passes. However, when analyzing these agglomerates, it can be observed they were formed by particles with nanometer scale.

These nanoparticles had irregular morphology, with undefined shapes. It is also possible to observe spherical nanoscale structures for both lignins, but mainly for Kraft nanolignin (1F). The size decreased as the number of passes increased, going from 1 µm particles to particles less than or equal to 500 nm.

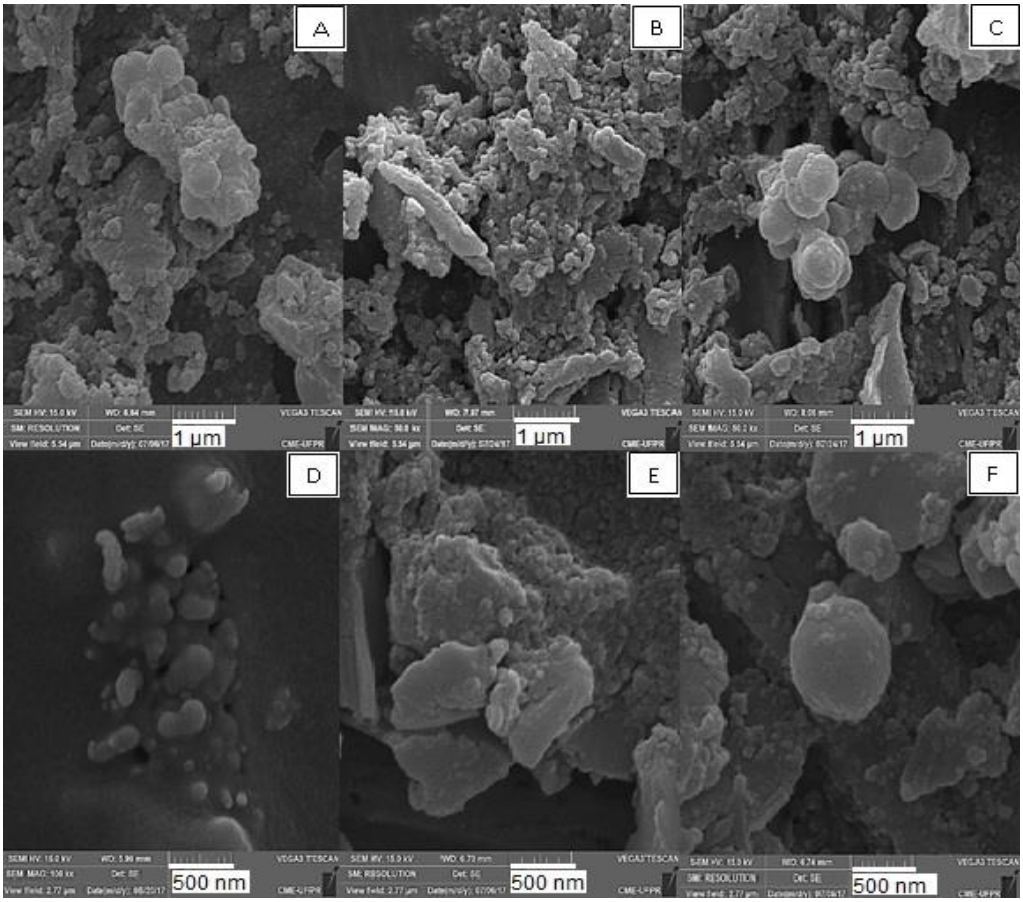

Figure 1. Scanning Electron Microscopy images from Klason (A, B, C) with scale of 50K and Kraft (D, E, F) nanolignin with scale of 100K 2 passes (A, D); 8 passes (B, E); 13 passes (C, F).

Figura 1. Imagens de Microscopia Eletrônica de Varredura de nanolignina Klason (A, B, C) com escala de 50X e Kraft (D, E, F) com escala de 100X 2 passes (A, D); 8 passes (B, E); 13 passes (C, F).

The SEM images (Figure 1) demonstrated that lignin nanoparticles were obtained using the mechanical process as particles on this scale can be observed. Thus, the use of the Super Masscolloider proved to be efficient in producing nanoscale materials with different numbers of passes, from two different lignins.

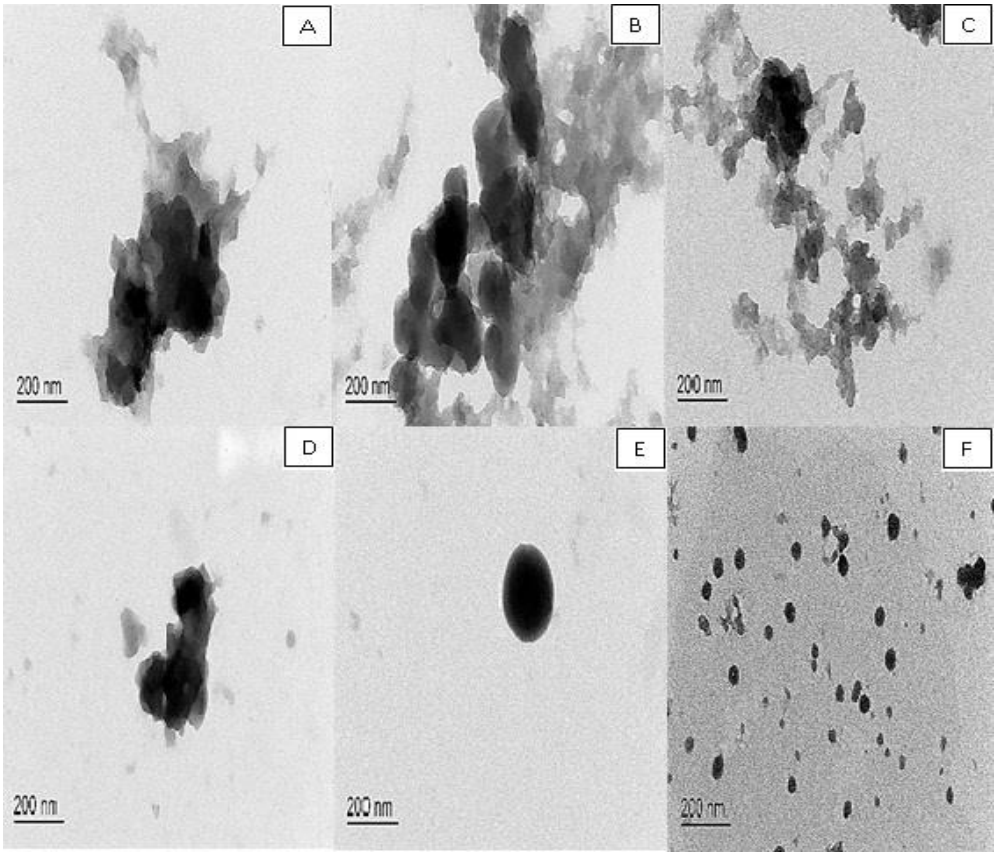

Figure 2. Transmission Electronic Microscopy images of Klason (A, B, C) and Kraft (D, E, F) nanolignin. 2 passes (A, D); 8 passes (B, E); 13 passes (C, F).
Figura 2. Imagens de Microscopia Eletrônica de Transmissão de nanolignina Klason (A, B, C) e Kraft (D, E, F). 2 passes (A, D); 8 passes (B, E); 13 passes (C, F).

The transmission electron microscopic analysis (Figure 2) confirmed that the Klason and Kraft lignin nanoparticles had undefined and spherical shapes and that more passes produced particles with smaller dimensions, also reaffirming the irregular, slightly spherical shape and micrometric scale already evidenced by SEM.

Granulometry

After SEM and TEM analysis, granulometry was evaluated (Figure 3).

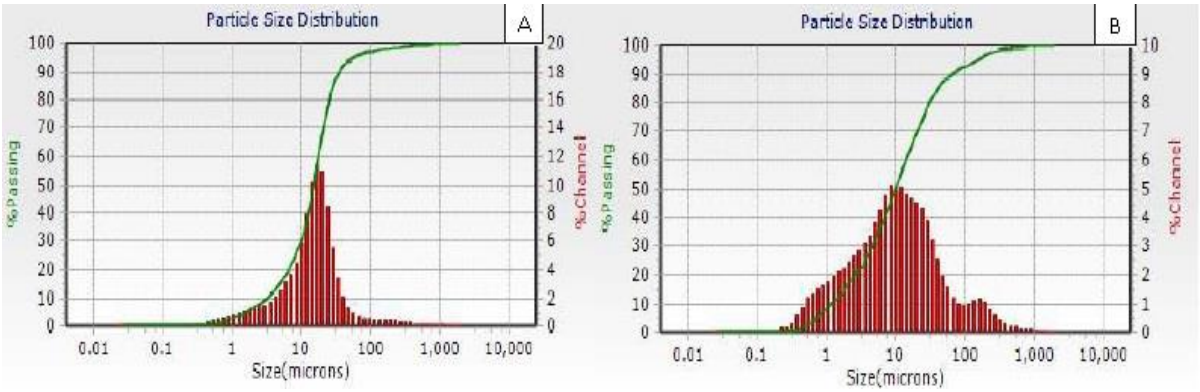

Figure 3. Granulometry of Klason (A) and Kraft (B) nanolignin produced with 13 passes.
Figura 3. Granulometria de nanolignina Klason (A) e Kraft (B) produzidas com 13 passes.

The software showed that for Klason and Kraft nanolignin, there were average particle sizes of 15.14 µm and 9.88 µm respectively. Furthermore, 10.27% of the Klason sample consisted of nanometric particles, while for the Kraft sample, 18.90% of the particles had nanometric scale.

Chemical composition based on EDS

Regarding the elemental chemical analysis, the EDS result of Klason lignin nanoparticles showed average values of 82% carbon (C), 17% oxygen (O) and 0.1% sulfur (S). For Kraft lignin nanoparticles, the EDS analysis showed values of 78% carbon (C), 21% oxygen (O) and 0.16% sulfur (S). This analysis was particularly important for the samples of lignin nanoparticles, as it demonstrated there was no contamination during the mechanical processing when using the Super Masscolloider.

Thermogravimetric analysis and differential exploratory calorimetry

The Thermogravimetric Analysis (TGA/DTG) curves of the Klason and Kraft nanolignins (Figure 4) revealed similar thermal degradation profiles, with small differences in the temperatures corresponding to the maximum degradation peaks.

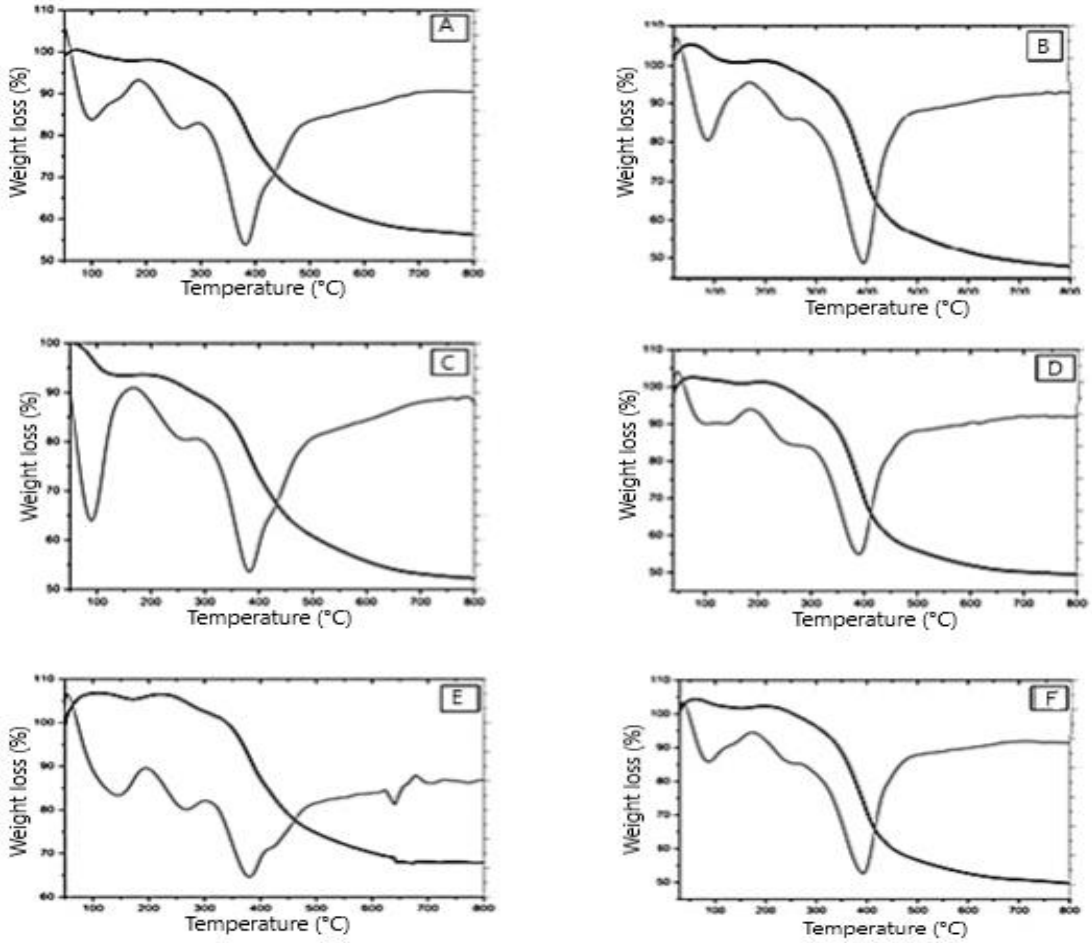

Figure 4. TGA/DTG curves of Klason (A, C, E) and Kraft (B, D, F) nanolignin. 2 passes (A, B); 8 passes (C, D); 13 passes (E, F).

Figura 4. Curvas TGA/DTG de nanolignina Klason (A, C, E) e Kraft (B, D, F). 2 passes (A, B); 8 passes (C, D); 13 passes (E, F).

The TGA/DTG curves indicated three thermal degradation ranges, the first (100°C) being attributed to the drying of the materials. The second temperature range (230 °C) corresponded mainly to the thermal degradation of hemicelluloses, and of lignin to a lesser extent. The third range (400°C) of thermal degradation corresponded mainly to the degradation of lignin.

Maximum mass loss rates were achieved at temperatures close to 425 °C for both samples and independent of the number of passes. After that, the nanolignin continued to be degraded, but more gradually.

In this study, after 400-500 °C, Klason nanolignin had a residual mass varying from 43.74% (2 passes) to 32.10% (13 passes), while Kraft nanolignin varied from 52.26% (2 passes) to 50.30% (13 passes).

Differential scanning calorimetry (DSC) analysis provides information about the reaction, characterized as heat release (exothermic) or heat absorption (endothermic), in addition to measuring the level of heat involved in the reaction (Figure 5).

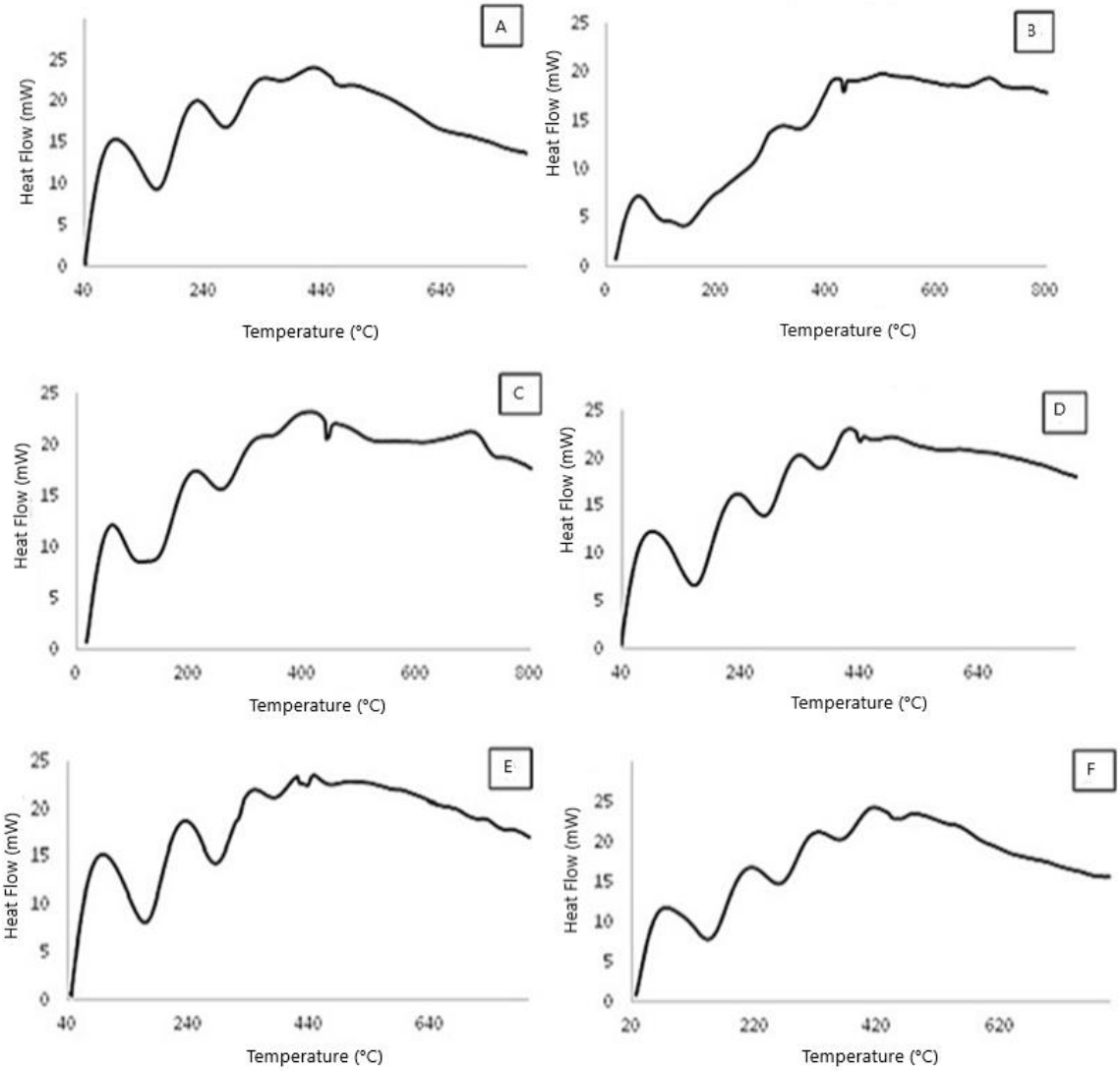

Figure 5. Differential Scanning Calorimetry curves of Klason (A, C, E) and Kraft (B, D, F) nanolignin. 2 passes (A, B); 8 passes (C, D); 13 passes (E, F).

Figura 5. Curvas de Calorimetria de Varrimento Diferencial de nanolignina Klason (A, C, E) e Kraft (B, D, F). 2 passes (A, B); 8 passes (C, D); 13 passes (E, F).

The DSC curves indicated a first peak between 56°C and 98°C, attributed to water loss. Although the material was dry at the time of analysis, the total elimination of water did not occur. The next peak was found at approximately 235°C. This exothermic peak can be attributed mainly to the thermal degradation of hemicelluloses.

The third exothermic peak occurred at an average temperature of 455°C. Therefore, from approximately 412°C, the DSC curves became linear and increasing due to the thermal degradation of lignin, in which the heat release became more intense.

We also observed that this last heat flux release was greater in relation to the previous one, since the greater the formation of gaseous products, the greater the energy released, and the peak referring to Kraft nanolignin had greater amplitude, probably due to the source material, black liquor, which has a high chemical load and can generate a greater amount of gaseous products. Therefore, the thermal analyses showed similar patterns of degradation between the Klason and Kraft nanolignin samples.

DISCUSSION

Morphology

Particles with irregular shapes and agglomerates were obtained. The irregular shape of the particles and the presence of agglomerates has also been observed in other studies involving the mechanical production of this characteristic nano lignin (CHAUHAN, 2020; ZHANG *et al*., 2021).

The transmission electron microscopy analysis showed that the Klason e Kraft lignin nanoparticles had spherical shapes and that more passes produced particles with smaller dimensions. A similar result was described by Lievonen *et al*. (2016) in a study with hardwood lignin, who obtained spherical lignin nanoparticles with an average diameter between 200 and 500 nm, similar this study. Nair *et al*. (2014) used the mechanical homogenization method to produce lignin nanoparticles. The size of these particles was determined by SEM analysis. The results showed that initially 50% of the lignin particles were larger than 500 nm. After 2 hours of mechanical treatment (shearing), 75% of the particles reached diameters below 100 nm. After 4 hours, SEM analysis revealed that 100% of the particles had diameters lower than 100 nm, i.e., lignin nanoparticles were obtained by the method used, and the longer the time used, the greater the percentage of nanoparticles obtained.

Granulometry

This analysis demonstrated a higher proportion of nanometric particles percentage of nanoparticles of Kraft lignin that Klason lignin.

Gupta *et al*. (2014) in your study observed a variation in the size of the particles, with average diameter of 181 nm. Therefore, it is possible to conclude that the use of the Masuko Sangyo Super Masscolloider enabled obtaining of Klason and Kraft lignin nanoparticles.

Chemical composition based on EDS

The EDS analysis demonstrated there was no contamination during the mechanical processing. Gupta *et al.* (2014) obtained lignin nanoparticles by acid precipitation process with HCl and observed, also by EDS, the presence of 81.69% C and 18.31% O in nanolignin obtained by precipitation with HCl, values similar to those obtained in this work.

Thermogravimetric analysis and differential exploratory calorimetry

The first curve of TGA/DTG was attributed to the drying of the materials. Trugilho *et al*. (2001) observed the occurrence of this event and attributed it to loss of moisture.

The second temperature range corresponded to the thermal degradation of hemicelluloses and lignin, while the third range corresponded only to the degradation of lignin. These results are in agreement with those of Santos *et al*. (2013), who observed that the thermal degradation of lignin started at approximately 150 °C and occurred up to 500 °C.

In a comparative work on the degradation of lignin and nanolignin produced by of acid hydrolysis, Gupta *et al.* (2014) observed similar stages of degradation at 100°C; at 235–260°C; and peak in the range of 351–399°C.

Maximum mass loss rates were achieved at temperatures close to 425 °C for both samples and after that, the nanolignin continued to be degraded, but more gradually, in agreement with Brebu and Vasile (2010), who reported that the wide range of lignin degradation is related to the different oxygenated functional groups in its structure, which provides different thermal stabilities. After 400-500°C, Klason and Kraft nanolignins had a residual mass that variety conform the passes.

The DSC curves indicated a peak attributed to water loss between 56 °C and 98 °C. Santos *et al*. (2011) indicated the occurrence of this event in their work, also relating it to the evaporation of water. On the other hand, Gupta *et al.* (2014), evaluating nanolignin produced by acid hydrolysis, reported that peaks attributed to the dehydration of lignin were in the temperature region of 122–200°C, because lignin nanoparticles contain some ethylene glycol, furfuryl alcohol and hexamethylenetetramine, which might have contributed to the dehydration as well as to the degradation of lignin through C–H, C–N and C–O bond cleavage of the compound.

The exothermic peak, at approximately 235°C, can be attributed mainly to the thermal degradation of hemicelluloses. Pereira *et al*. (2013) observed peaks around 200 °C, attributing them hemicellulose degradation.

The third exothermic peak occurred at 455°C. From approximately 412 °C, the DSC curves became linear and increasing due to the thermal degradation of lignin. Pereira *et al*. (2013) reported in that the maximum degradation peak of their lignin samples was reached at a temperature of 400°C. Santos *et al*. (2011) observed this peak in the DSC curve at 371°C, referring to the maximum degradation of lignin.

The mechanical method proved to be efficient in producing nanolignins in a simple way, a material that can be used in products with higher added value, thus reducing the environmental impact.

CONCLUSIONS

- The EDS analysis showed that the nanolignin washing process was efficient because it eliminated residual sulfur used in the process of obtaining nanolignin and confirmed that the mechanical process used in the production of lignin nanoparticles was satisfactory, since there was no indication of contamination in the analyzed samples.
- The results of the granulometry analysis showed that Klason and Kraft lignin nanoparticles were obtained, but the best results were obtained with Kraft lignin, which presented a higher percentage of nanometric particles. This analysis also demonstrated that the mechanical treatment using the Masuko Sangyo Super Masscolloider, even with a small number of passes, enabled obtaining nanoparticles, whose parameters could be modified to obtain a greater amount of nanometric particles.
- The TGA/DTG curves showed three ranges of thermal degradation, attributed to the drying of the samples, the degradation of hemicelluloses and the degradation of lignin, respectively.
- The DSC curves also showed three peaks related to the TGA analysis. The thermal analyses did not show significant variations between the types of lignin and lignin nanoparticles.
- The results of the analyses showed that the methods used to obtain Klason and Kraft lignin nanoparticles were efficient, since all the characterization analyses revealed chemical, thermal, morphological and structural characteristics of nanolignin in line with previous reports in the literature.

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