Value aggregation of pine (*Araucaria angustifolia*) nuts agro-industrial waste by cellulose extraction

Agregação de valor de resíduos agroindustriais do pinhão (*Araucaria angustifolia*) por extração de celulose

Valor agregado de residuos agroindustriales de jatropha (*Araucaria angustifolia*) por extracción de celulosa

Abstract

*Araucaria* (*Araucaria angustifolia*) is a tree species found in the Southeast and South of Brazil. It is also known as Brazilian pine, presenting fruits of high acceptance. However, its processing generates by-products that are little used. Thus, this work aimed to extract and characterize the cellulose obtained from the pinion husk, as well as to evaluate the contents of ash, lignin, cellulose and α-cellulose in its composition. The raw material and the extracted cellulose were characterized by X-ray fluorescence analysis (XRF), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). As for the contents of chemical composition detected, the husks showed 1.6% ash, 7% extractives, 34% lignin and 55% cellulose, being 46% α-cellulose and 9% hemicellulose. It was observed by XRD that the removal of amorphous materials resulted in a gain of crystallinity (from 19 to 33%). Proving the efficiency of the extraction, the characterization of the cellulose obtained was shown to be of high purity, since the main band of the lignin (FTIR) and the amorphous materials of the cellulosic sample (TGA) disappeared. Finally, this work shows that the pinion bark is a rich source of cellulose, making it possible to obtain nanocrystals.

Keywords: Pine nut husks; Cellulose extraction; Value aggregation.

Resumo

*Araucária* (*Araucaria angustifolia*) é uma espécie arbórea encontrada nas regiões Sudeste e Sul do Brasil. É também conhecido como pinho brasileiro, apresentando frutos de alta aceitação. Porém, seu processamento gera subprodutos que...
1. Introduction

Araucaria (Araucaria angustifolia) is a species of tree found in Southeast and South Brazil, known as Brazilian pine, of the Araucariaceae family, it is a long-lived species, native to the Atlantic forest of Brazil, the species has 20 to 50 m in height (E. da Silva, de Lima, de Andrade, & Brown, 2019; Montagna et al., 2019; Peralta et al., 2016). This species has a fruit called pinecone, which is a set of pine nuts ripening between the months of April to June. This fruit is one of the main sources of food for some native animals, also widely used in the field of medicine and drugs (Peralta et al., 2016; Santos et al., 2018).

Pine nuts are made up of 91.75% carbohydrates, 58.8% cellulose, 19.38% lignin, also have values of 1.89% fats, 1.27% proteins, and vitamin C (Babich et al., 2019; Daudt et al., 2017). This fruit is widely used for the production of bread, soups, and even alcoholic beverages typical of the indigenous peoples of the southern region of South America (Henríquez et al., 2008). After processing the fruit for use in the aforementioned areas, the peels are generated as a by-product. This agro-industrial waste is normally discarded in the environment, and its application is a major problem to be solved due to the large amount generated during processing (De Freitas et al., 2018; Peralta et al., 2016; Zortéa-Guidolin et al., 2017).

According to IBGE, 2018, the production of pine nuts was 9.3 thousand tons, where most of this production is concentrated in the southern region of Brazil. The production of this fruit becomes even more interesting because keeps Araucaria angustifolia alive, threatened with extinction since 1992 (Mantovani, Costa, & Freitas, 2018). The use of agro-industrial by-products as a raw material or substitute ingredient in human and/or animal diets, or as a source of compounds of interest, becomes an extremely interesting alternative, since the number of nutrients present in these by-products may be similar or higher than those found in the main raw material (E. P. da Silva et al., 2020), even presenting high levels of vitamins, minerals, dietary fiber, in addition to wall compounds (lignin, cellulose, hemicellulose, among others) (Lan, Liu, & Sun, 2011).

The use of by-products generated during the processing of pine nuts to obtain cellulose presents several advantages, such as the reduction of environmental impacts, as well as the obtaining of a product with high added value, which can be used...
as a raw material in the manufacture of paper, composites, drug, and food manufacturing. According to Oprea; Voicu, 2020 and Vanitha; Kavitha, 2020, the application of cellulose can be carried out in different areas such as drugs, food packaging, polymeric reinforcements, among others with high added value.

Cellulose is considered an important natural polymer, formed by β-1,4 glycosidic bonds, constituting about 35 to 50% of plant walls (Kale, Bansal, & Gorade, 2018). Its production in the paper and cellulose industry occurs mainly from planted forests, where 85.57% comes from eucalyptus and 14.19% from pine woods (ABRAF, 2013). Therefore, the use of agro-industrial by-products as a raw material in obtaining cellulose, becomes an extremely viable alternative, adding value and developing manufactured products that directly impact socioeconomic indices. Thus, this research has the objective of extracting and characterizing the cellulose from the pine nut husks.

2. Methodology

2.1 Lignocellulosic material

Pine nuts were collected in the city of Lages, State of Santa Catarina, Brazil, Latitude: -27.816 7′ South, Longitude: 50°19′35″ West. The husks were washed and dried in an oven at a temperature of 70°C. Afterwards, the husks were ground in the mill (ACD LAB TE-650/1) for 4 h and passed through a 45 mesh sieve.

2.2 Materials

Reagents used: ethanol (> 95% vol, Vetec); sulfuric acid (> 97%, Nuclear); sodium chlorite (> 80%, Sigma-Aldrich); glacial acetic acid (> 99.85%, Nuclear) and sodium hydroxide P.A (Dinâmica).

2.3 Assessments of cellulose content and extraction

Ash percentage

To identify the ash percentage we used the method of TAPPI, 2007, where the crucibles were weighed before adding the ground pine nut husks to get to know the mass of the crucibles. 3g of the ground sample was added and dried in crucibles, later inserted in the muffle at 600 °C for 4h. At the end, the crucibles were weighed to constant weight to calculate their percentage.

Extractive percentage

In order to find out the percentage of extractive that the sample presents, the methodology of (TAPPI, 1997) was used, where, in a paper cartridge, 4g of the dry sample was added, in a 500mL flask, 150mL of ethanol was added. the material in soxhlet, remaining for 4h, later the alcohol from the balloon was recovered in a rotavaporator and the material from the cartridge was dried to constant weight.

Lignin percentage

In order to find out the percentage of lignin that the sample presents, the methodology (TAPPI, 2011), was as The evaluation of lignin follows: first 1g of the sample without extractive was used, the sample was added to a porcelain mortar with 8.5 mL of sulfuric acid (72%) (w/w) and macerated for 15 minutes and kept in digestion for 24 hours, then the digested material was placed in a glass flask together with 153 mL of distilled water. Then, the flask with the contents was placed in a thermal blanket, remaining for 4h, at a temperature of 70 °C. After cooking the sample, the sample was washed and filtered with distilled water and dried in an oven until constant weight, the methodology described in (TAPPI, 2011).

Cellulose percentage and extraction
In order to extract and quantify the percentage of cellulose, the methodology was used Kumode et al., 2017 and Pinheiro et al., 2017, 5g of the sample in an Erlenmeyer with 1mL of acetic acid, 5g of sodium chlorite, a magnetic stirrer and 150mL of distilled water, and added to a hot plate at a temperature of 70°C for 1h. After that, he placed again the same amount of CH₃COOH and chlorite, remaining for another 1h, at the end of that hour, he added the same amount of CH₃COOH and chlorite, remaining for another 2h. Subsequently, the Erlenmeyer flask was cooled in an ice bath. Thereafter, the contents were washed, filtered and dried to constant weight.

α-cellulose percentage

The percentage of α-cellulose was performed by inserting 1g of the cellulose 8 mL of 17.5% sodium hydroxide in a porcelain mortar, where the mixture was macerated for 2min, then the content was washed, filtered with distilled water and dried to constant weight.

2.4 Characterization of samples

The samples of the fresh husks and extracted cellulose were characterized by the techniques of X-ray fluorescence (XRF), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and infrared spectroscopy with Fourier Transform (FTIR).

X-ray fluorescence

The ground and dried ff husks were analyzed by X-ray fluorescence technique (Panalytical brand equipment, model Epsilon 3-XL), using a maximum voltage of 50 kV, current of 3 mA and helium gas (pressure of 10 atm / 10 kgf / cm²).

X-ray diffraction

X-ray diffraction measurements were performed on a diffractometer (Bruker D2 Phase), using a copper anode and nickel filter (CuKα), where fresh and cellulose samples (powder form) were inserted into a sample holder of acrylic, using scanning range 20 = 10 to 60°, step 0.02°, and 5s/step 20, operating with a power of 40 kV, and current of 30 mA. Rietveld method (Rietveld, 1969) was applied using the program package GSAS (Von Dreele, 1994). The starting parameters were obtained on the ICSD database (Karlsruhe, 1995). Peak shapes were modeled using a modified Thompson-Cox-Hasting pseudo-Voigt function that takes into account line broadening due to instrumental effects, small crystallite size, and microstrain (Stephens, 1999). Thermal parameters were assumed to be isotropic. Background, scale factors, and sample position shift parameters were refined before the structural parameters’ refinement.

Knowing the crystallinity of cellulose is of paramount importance. Thus, to calculate the Crystallinity Index (CI), equation 1 was used (Segal, Creely, Martin, & Conrad, 1959), where the crystalline part of the material is represented by the height of the highest peak in the diffractogram and the amorphous part of the material that refers to the amorphous halo. The Crystallinity Index (CI) is the difference between these two intensities, divided by the intensity of the most intense peak.

\[ CI(\%) = \frac{I_{011}}{I_{am}} \times 100 \]  

(eq.1)

where \( I_{011} \) is the maximum intensity of the peak located in \( 2\theta = 22.3^\circ \) (plane 011) and \( I_{am} \) is the intensity of the amorphous halo. Fourier Transform Infrared Spectroscopy (FTIR)

For the FTIR analysis an attenuated reflectance spectrophotometer (FTIR-ATR Cary 630 - Agilent) was used. The analyzed spectra were in the range from 4,000 to 650 cm⁻¹, with a resolution of 8 cm⁻¹ with 128 scans per sample. Thermogravimetric analysis (TGA)
To perform the thermal analysis, a thermal analyzer (Shimadzu, model TGA-50) was used. The analysis was carried out with a heating rate of 10°C/min, starting from room temperature up to 700°C in a nitrogen atmosphere, using 3g of each sample.

3. Results and Discussions

Lignocellulosic material content

From the chemical characterization, it was found that the pine nut husk showed 1.6% ash, 7% extracts, 34% lignin, and 55% cellulose, of which 46% is α-cellulose and 9% de hemicellulose. These percentages demonstrated that this by-product is a potential source for the extraction of cellulose, adding value to the waste from the culture of pine nuts in southern Brazil. The husks also present significant values of lignin (34%), that has several applications, from the generation of energy in the industrial sector to the production of cosmetics as sunscreens (Lobosco, Silva, Pereira, Carneiro, & Andrade, 2020; Yang, Yan, Chen, Lee, & Zheng, 2007). It is extremely important to note that the percentage of cellulose obtained (55%) is associated to the cellulose yield that the extraction method used was able to achieve.

When comparing the values obtained with those of the study by JACINTO et al., 2017 that used pine husks in the production of wood pellets, it is possible to observe contents with close values (Table 1). It is also observed that the cellulose content in the pine nut husks is much higher than that found in other agro-industrial residues such as soybean husks, banana pseudostem, passion fruit peels and açai.

| Raw materials       | Content (% m/m) | Reference                  |
|---------------------|-----------------|----------------------------|
|                     | Ash  Extractive| Lignin Cellulose α-cellulose|
| Pine nut husk       | 1.6  7          | 34  55                      | 46 | This work |
| Pine nut husk       | 2.5  7.56       | 41  58.8                   | -  | Jacinto et al., 2017 |
| Soybean husk        | -   7.78        | 40.64                      | -  | Robles Barros et al., 2020 |
| Banana pseudostem   | -   4.25        | 23.82                      | -  | Meng et al., 2019 |
| Passion fruit peels | -   36.18       | 28.58                      | -  | Wijaya et al., 2017 |
| Açaí seeds          | 1.01 4.48       | 24.36 45.49                | -  | Barros et al., 2021 |

Source: Authors.

In Table 1, we can pay attention to the percentages of extracted cellulose in relation to other agro-industrial residues, as it is evident that the percentage of extracted cellulose is higher than other residues, being higher than passion fruit, banana and açai peels, because the more cellulose, better for the purpose of the research and its applications.
X-ray fluorescence (XRF)

With the results of the XRF analysis of the raw material (ground pine nut husks) it was observed that the residue is rich in Potassium (K; 89.89%), followed by chlorine (Cl), which may be related to soil and water present where the plant is located, and small percentages of phosphorus (P), iron (Fe), silicon (Si) and others (Table 2).

| Elements | K    | Cl   | P    | Ag  | Fe  | Si  | Rb  | Others |
|----------|------|------|------|-----|-----|-----|-----|--------|
| % (m/m)  | 89.89| 5.77 | 2.65 | 0.81| 0.22| 0.21| 0.15| 0.29   |

Table 2: Elemental analysis of pine nut husks (fresh sample).

Source: Authors.

It is noteworthy that this analysis highlights the chemical components of the material studied, which can interfere with the results of ash content when oxides are formed, for example, resulting in CO₂ adsorption. The percentages of these elements can vary depending on the climate, temperature, soil, and region where it is inserted.

In Table 2, it is worth highlighting the percentage of potassium present in the fiber, knowledge about these levels can also help to guide the waste application. For example, residues with high potassium (K) content, as presented by pine nut husk, have been applied to obtain heterogeneous catalysts for biodiesel production (de S. Barros et al., 2020; Mendonça, Machado, et al., 2019; Mendonça, Paes, et al., 2019).

X-ray diffraction (XRD)

Fig. 1 shows the XRD patterns for the ground pine nut husk in natura (black curve) and extracted cellulose (blue curve) samples. The red curve shown the simulated pattern by using the FindIt program (Woo, Lee, Kim, & Lee, 2004) with the crystallographic data obtained from the Crystallographic Information File (CIF) - code 4114382.

Figure 1: XRD patterns for the husk (black curve), extracted cellulose (blue curve) samples, and simulated pattern (red curve) using CIF code file 4114382.

Source: Authors.
In Figure 1 we can make a comparison of the fresh sample with cellulose in relation to the input Cif, we can observe the intensity of the peaks between 20° and 30°, showing more intensity for the cellulose sample, which is related to the increase in crystallinity.

Both patterns have shown two peaks broaden halos between 20\( \approx 10^\circ \) – 30°. In addition, a low-intensity diffraction peak located at 20 \( \approx 34^\circ \) is observed. Furthermore, a main amorphous halo centered at 20 \( \approx 15.7^\circ \) can be identified in both pattern samples. Using the Ehrenfest equation (2Rsinθ=1.23λ) (Manzato, Trichês, De Souza, & De Oliveira, 2014) an interatomic distance of R\approx 6.9 Å was calculated for a second neighbor husk. It is important to note that the peak located at 20 \( \approx 34^\circ \) and both amorphous halos have their intensity increasing when compared with the XRD pattern of in natura sample. This suggests that both samples have a natural crystalline cellulose phase dispersed in an amorphous matrix. For the cellulose sample, the crystallinity is increased, showing the partial success of the cellulose extraction adopted method.

The patterns shown in Fig. 1 were compared with the CIF file n° 4114382 of triclinic symmetry (S.G. P 1, n° 1) give in the Crystallography Open Database for \( \alpha \) cellulose (red curve), where a good agreement can be observed. This CIF was used as a structural model for the Rietveld Refinement with the following initial parameters: a=10.400(10) Å, b= 6.717(6) Å, c=5.962(7) Å, \( \alpha=80.37(5)^\circ \), \( \beta=118.08(5)^\circ \) and \( \gamma=114.80(5)^\circ \). Fig. 2 shows the Rietveld refinement for the extracted cellulose sample.

**Figure 2:** Experimental (open circles) and simulated (red curve) XRD pattern of the extracted cellulose sample. The background (green curve) as well the residual line (blue curve) are also shown.

In Figure 2 we can see a good agreement between the experimental and simulated patterns can be observed for the extracted cellulose sample. The refinement was done using Chebyshev function twelve order for background fit. Table 3 summarizes the data obtained from refinements.
Table 3: Structural parameters obtained from refinements of in pine nut husks and extracted cellulose.

| Parameters | Pine nut husks | Cellulose |
|------------|----------------|-----------|
| a (Å)      | 10.16(8)       | 10.24(3)  |
| b (Å)      | 6.73(3)        | 6.73(3)   |
| c (Å)      | 6.04(1)        | 6.02(3)   |
| α (°)      | 81.92(7)       | 81.08(3)  |
| β (°)      | 116.99(5)      | 117.14(5) |
| γ (°)      | 112.71(6)      | 113.56(7) |
| Vol (Å³)   | 339.62(0)      | 338.61(0) |
| $R_{wp}$ (%) | 4.27          | 3.84     |
| $R_p$ (%)  | 3.33           | 2.94     |

Source: Authors.

The Table 3 shows cell sizes after refinements, it is noteworthy that the results are like those found in the literature.

The average crystallite size was calculated using the Scherrer equation (Phys., Chem., 2018) by the most intense peak located at about 20 ~ 22.3º of XRD patterns. For the extracted cellulose sample, we obtained an average crystallite size of 11 nm for Iα cellulose. The apparent crystallinity percentage (C) was estimated using the eq. (1). We observed 19% and 33% of crystallinity for the husks and extracted cellulose, respectively. For the cellulose sample, the crystallinity obtained is lower when compared to other studies (Naduparambath et al., 2018). This can be explained by the small nanocrystals obtained, resulting in low crystallinity.

**Fourier Transform Infrared Spectroscopy (FTIR)**

Fig. 3 shows the FTIR spectra for samples ground pine nut husk and extracted cellulose. The band found at 3310 cm⁻¹ for the two samples corresponds to the OH stretching vibrations of the cellulose molecules and inter and intramolecular hydrogen bonds (Tanpichai, Biswas, Witayakran, & Yano, 2019). Similar bands were observed in the passion fruit peels (Wijaya et al., 2017). At 2880 and 2335 cm⁻¹, asymmetric and symmetrical C-H elongation vibrations were observed for aliphatic portions in polysaccharides attributed to cellulose components (Cheng et al., 2017; Singh, Ranawat, & Meena, 2019). At 1630 cm⁻¹, for the sample of the ground pine nut husk sample, a marked band was noticed and is attributed to the acetyl and uronic ester groups of the hemicelluloses or ester bonds of the lignin carboxylic groups present in the sample (Kale et al., 2018; Tanpichai et al., 2019). It was also observed that this band is not perceived in the cellulose spectra, showing a good removal of amorphous materials from the sample. The band located at 1240 cm⁻¹ is attributed to compounds of ester, ether, or phenol that are corresponding elements present in lignin in the spectrum of the raw material. And, at 1110 cm⁻¹, a band attributed to the anti-symmetric elongation of the bridge of the COC groups of the cellulose structure - β (1,4) glycosidic bonds (Singh et al., 2019; Tanpichai et al., 2019). Therefore, these changes and disappearances of the bands confirm the complete removal of lignin from the raw material, showing the efficiency of the method applied for this purpose and generating cellulose.
In Figure 3 of the spectra, we can turn our attention to the disappearance of some of the bands for the cellulose sample in relation to the fresh sample, mainly at 1630 and 1240 cm\(^{-1}\), showing removal of lignin after treatment.

**Thermogravimetric analysis**

Analyzing the TG and DTG curves (Fig. 4) of the cellulose obtained from the pine nuts, can be observed there was a loss of mass in three stages for the raw material and two stages of degradation for the cellulose. Up to 100 °C, a loss of mass is observed due to the volatilization of water and low molecular weight compounds present on the material surface (Cheng et al., 2017). The second degradation stage started at around 240 °C for both samples, which may be related to the beginning of depolymerization, and decomposition of the cellulose glycosidic binding units (Cheng et al., 2017). Between 280 – 300 °C, a slight shoulder is noticed referring to the beginning of hemicellulose shedding. The dominant thermogravimetric peak was observed at 350 °C for both samples, a step related to the total decomposition of glycosidic chains by depolymerization, dehydration, and decomposition of glycosidic bonds, followed by the formation of a residue after burning (Mokhena & John, 2020). The third stage of degradation occurred at around 460 °C, where the degradation of lignin from the fresh sample occurred. This event was not observed for the cellulose sample, confirming that no lignin was found in the cellulose sample. This event was not observed for the cellulose sample, confirming that no lignin was found in the cellulose sample. This stage shows that cellulose has less thermal stability than lignin, because the lignin contains different types of bonds, making it difficult to decompose and, therefore, starting its degradation at around 420 °C. Studies show that depending on the origin of the material, lignin can degrade up to 900 °C (Fauzan et al., 2018). When comparing the thermogravimetric curves of the cellulose sample with those observed by, it is possible to notice a similarity in all stages of degradation. For the fresh sample, the lower thermal instability of the material is attributed to the presence of amorphous materials in the sample, which degrade at high temperatures. Based on these results, it was noted the effectiveness of removing amorphous materials from the sample after treatment, corroborating with FTIR and XRD results that showed absence of the characteristic peak of hemicelluloses.
Figure 4: Thermogravimetric analysis graphs: a) TG and b) DTG of pine nut husks and extracted cellulose.

In this Figure 4 of DTG we can highlight the disappearance of some peaks, for example at a temperature of 450 °C, which was not seen in the cellulose sample, showing success in the removal of amorphous materials.

4. Conclusions

This article highlights the great potential of this waste for cellulose extraction. The fiber yielded 55% cellulose, a much higher value when compared to other agro-industrial residues. The husks were characterized in terms of lignocellulosic content, with 7% of extracts, 34% of lignin, 1.6% of ash and 46% of α-cellulose and 9% hemicellulose. The characterization of cellulose by XRD, FTIR and TGA techniques showed that high purity cellulose was obtained, confirming that the methodology used removed amorphous materials, mainly lignin, from the sample, resulting in cellulose with excellent qualities, which enhances the use of this waste for this purpose. These results open the way for research based on this culture, as well as the application of other agro-industrial waste as an alternative source of cellulose. From the extracted cellulose and
its lignocellulosic fractions evaluated, as future works we can mention the application of the fiber for composites in a polymer matrix, applying the cellulose as drug enablers, the lignin can be applied in the cosmetics sectors for sunscreens, from the cellulose can also be extracted from nanocellulose, which have a range of applicability, from the treatment of burns, applied to materials for implants, production of thin films, etc.

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References

ABRAF. (2013). Anuário Estatístico da ABRAF. Brasília.

Babich, O., Dyshlyuk, L., Noskova, S., Sukhikh, S., Prosekov, A., Ivanova, S., & Pavsky, V. (2019). In vivo study of the potential of the carbohydrate-mineral complex from pine nut shells as an ingredient of functional food products. Bioactive Carbohydrates and Dietary Fibre. https://doi.org/10.1016/j.bcdif.2019.100185

Barros, S. de S., Oliveira, E. da S., Pessoa Jr, W. A. G., Rosas, A. L. G., Freitas, A. E. M. de, Lira, M. S. de F., … Freitas, F. A. de. (2021). Waste açai (Euterpe precatoria Mart.) seeds as a new alternative source of cellulose: Extraction and characterization. Research, Society and Development, 10(7), e31110716661. https://doi.org/10.33448/rsd-v10i7.16661

Silva, E., de Lima, O. G., de Andrade, D. P., & Brown, G. G. (2019). Earthworm populations in forestry plantations (Araucaria angustifolia, Pinus elliottii) and Native Atlantic forest in Southern Brazil compared using two sampling methods. Pedobiologia. https://doi.org/10.1016/j_pedobi.2018.10.002

Daudt, R. M., Sinrod, A. J. G., Avena-Bustillos, R. J., Kükamp-Guerreiro, I. C., Marczak, L. D. F., & McHugh, T. H. (2017). Development of edible films based on Brazilian pine seed (Araucaria angustifolia) flour reinforced with husk powder. Food Hydrocolloids. https://doi.org/10.1016/j.foodhydro.2017.04.033

De Freitas, T. B., Santos, C. H. K., da Silva, M. V., Shirai, M. A., Dias, M. I., Barros, L., … Leimann, F. V. (2018). Antioxidants extraction from Pinhão (Araucaria angustifolia (Bertol.) Kuntze) coats and application to zein films. Food Packaging and Shelf Life. https://doi.org/10.1016/j.fpsl.2017.10.006

de S. Barros, S., Pessoa Junior, W. A. G., Sá, I. S. C., Takeno, M. L., Nobre, F. X., Pinheiro, W., … de Freitas, F. A. (2020). Pineapple (Ananás comosus) leaves ash as a solid base catalyst for biodiesel synthesis. Bioresouce Technology. https://doi.org/10.1016/j.biortech.2020.123569

Henríquez, C., Escobar, B., Figuerola, F., Chiffelle, I., Speisky, H., & Estévez, A. M. (2008). Characterization of pífon seed (Araucaria araucana (Mol) K. Koch) and the isolated starch from the seed. Food Chemistry. https://doi.org/10.1016/j.foodchem.2007.08.040

Instituto brasileiro de geografia e estatística. (2018). Produção da Extração Vegetal e da Silvicultura 2017. Rio de Janeiro: IBGE.

Jacinto, R. C., Brand, M. A., da Cunha, A. B., Souza, D. L., & da Silva, M. V. (2017). Utilização de resíduos da cadeia produtiva do pinhão para a produção de pellets para geração de energia. Floresta. https://doi.org/10.5380/rf.v47i1.52080

Kale, R. D., Bansal, P. S., & Gorade, V. G. (2018). Extraction of Microcrystalline Cellulose from Cotton Sliver and Its Comparison with Commercial Microcrystalline Cellulose. Journal of Polymers and the Environment. https://doi.org/10.1007/s10994-017-0936-2

Karlsruhe. (1995). ICSD – Inorganic Crystal Structure Database. Gmchin-Intitut fur Anorganische Chemie und Fachinformationszentrum FIZ.

Kumode, M. M. N., Bolzon, G. I. M., Magalhães, W. L. E., & Kestur, S. G. (2017). Microfibrillated nanocellulose from balsa tree as potential reinforcement in the preparation of ‘green’ composites with castor seed cake. Journal of Cleaner Production. https://doi.org/10.1016/j.jclepro.2017.02.083

Lan, W., Liu, C. F., & Sun, R. C. (2011). Fractionation of bagasse into cellulose, hemicelluloses, and lignin with ionic liquid treatment followed by alkaline extraction. Journal of Agricultural and Food Chemistry. https://doi.org/10.1021/jf201508g

Lobosco, M. P. J., Silva, R. M. C. R. A., Pereira, E. R., Carneiro, E. C. da S. P., & Andrade, A. C. dos S. (2020). The relationship between environmental education and natural sunscreens: an integrative review. Research, Society and Development, 9(6), e15896555. https://doi.org/10.33448/rsd-v9i6.355

MANTOVANI, A., COSTA, N., & Freitas, C. (2018). Situação Atual e Conservação das Florestas com Araucária. SEMINÁRIO SUL-BRASILEIRO SOBRE A SUSTENTABILIDADE DA ARAUCÁRIA. Passo Fundo, RS.

Manzato, L., Trичè, D. M., De Souza, S. M., & De Oliveira, M. F. (2014). Synthesis of nanostructured SnO and SnO2 by high-energy milling of Sn powder with stearic acid. Journal of Materials Research. https://doi.org/10.1557/jmr.2013.220

Mendonça, I. M., Machado, F. L., Silva, C. C., Duvoisin Junior, S., Takeno, M. L., de Sousa Maia, P. J., … de Freitas, F. A. (2019). Application of calcined waste cupuçaçu (Theobroma grandiflorum) seeds as a low-cost solid catalyst in soybean oil ethanolysis: Statistical optimization. Energy Conversion and Management, 200(September), 112095. https://doi.org/10.1016/j.enconman.2019.112095

Mendonça, I. M., Paes, O. A. R. L., Maia, P. J. S., Souza, M. P., Almeida, R. A., Silva, C. C., … de Freitas, F. A. (2019). New heterogeneous catalyst for...
