POTENTIAL USES FOR *Araucaria angustifolia* UNDEVELOPED SEEDS

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Undeveloped *pinhão* seeds (*Falhas de Pinhão*, FP) are potential by-products on the exploitation of pine cones of *Araucaria angustifolia*, and this material has no use and little academical research available. In this work, its chemical characterization was conducted, and new uses for this material were proposed, with focus on the potential for the food, cosmetics, energy, and nano-technological areas. The results indicate FP as potential dietary fibers supplement for the application in the food industry. FP can be utilized on the obtention of extracts for the application as source of phenolic compounds and sugars. The high calorific value and low ash content on FP indicates its potential on the energy generation. Yet, other applications were tested, such as the obtention of briquettes, and cellulose-based nanosuspensions and films.

KEYWORDS: NUTRITIONAL COMPOSITION; *PINHÃO*; PHENOLIC COMPOUND; ENERGETIC POTENTIAL; NANOTECHNOLOGY.

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1. INTRODUCTION

Araucaria angustifolia is a native conifer from South America, mainly found in Southern Brazil (FISCHER et al., 2022), and presents a great importance both on economic, cultural, and social spheres in Brazil (CASTRILLON et al., 2023). The pines products consist of seeds – known in Portuguese as *Sementes de Pinhão* (SP) – and sterile bracts – known in Portuguese as *Falhas de Pinhão* (FP).

Pinhão seeds are materials rich in carbohydrates, especially starch, dietary fibers, phenolic compounds, and macro and micronutrients, such as K, P, Cu, and Mn (BARBOSA et al., 2019), and are consumed in Brazilian culinary either cooked or roasted (CASTRILLON et al., 2023). FP, on the other hand, has no consolidated uses and represent a considerable mass fraction on the *A. angustifolia* pines (FISCHER et al., 2022). There are, however, little studies on the use of FP, specifically focused on the obtention of aqueous extracts with antioxidant activity (SOUZA et al., 2014; MICHELON et al., 2012).

The circular economy concept, promoted by the United Nations (2015), has presented a crescent tendency on both academical and industrial fields. It is associated to the conscient consumption and sustainable development, and it proposes minimizing the residue generation and environmental damage and optimizing the use of raw materials. The management of agroforestry wastes, for instance, is a major objective on the circular economy proposal, but the selection of the best application and optimum conditions of use for a biomass based on the economic, social, and environmental dimensions is a challenge.

Hence, once studying potential applications for a different matrix, whether it is a by-product or a residue, it’s necessary to indicate all the possibilities of use and, then, determine the best application. Thus, the objective of the present work is to characterize the *A. angustifolia* undeveloped seeds and to present different potential uses for this material.

2. MATERIALS AND METHODS

2.1 Materials

Twenty-five pine cones were collected in 2023 in *Embrapa Florestas* in Colombo, Paraná (-25.3217023, -49.1698741). Pine cones were integrally weighted and separated in seeds (SP) and undeveloped or sterile seeds (FP), which were weighted separately.

FP was dried (105 °C, 72 h), grinded in knife mill, sieved to 100 mesh granulometry, and stored in plastic bags for further analysis and applications.

For the chemical analysis, analytical grade reagents were utilized.

2.2 Chemical composition

FP was characterized on its nutritional composition according to Adolfo Lutz Institute (IAL, 2008) analyses: moisture and ash contents were determined by gravimetric methods after heating until constant mass (105 °C, 16 h and 550 °C, 4 h, respectively); lipid content was determined on a Soxhlet extraction with diethyl ether; protein level was determined according to the micro-Kjeldahl method; total dietary fibers were determined using Megazyme's Total Dietary Fiber Assay Kit; and the carbohydrate content was calculated according to the difference between 100 % and the sum of the previously determined contents.

Total calorific value on FP was calculated by considering a calorific value of 4 kcal g^{-1} for proteins and carbohydrates, and 9 kcal g^{-1} for lipids.

An aqueous extract was obtained (10 g FP, 100 mL H_2O) on an incubator (60 °C, 2 h, 100 rpm) and its phenolic compounds content was determined according to methodology adapted from Singleton and Rossi (1965): reactions were carried in the dark at 22 °C for 2 h, and the absorbance was determined on a spectrophotometer (UV-1800, SHIMADZU) at 760 nm. A standard curve was built using gallic acid for quantification.

An ion chromatographer was utilized on the semi-quantification of arabinose, galactose, glucose, mannose, sucrose, fructose, and sugar alcohols, using fucose as an external standard, with injection parameters according to Soares et al. (2023).

Elemental composition on FP was determined in an elemental analyzer (Elementar Vaio Macro Cube) in triplicate, and the carbon-nitrogen ratio was calculated.

2.3 Energetic potential

Higher Calorific Value of FP was determined, in triplicate, in a calorimeter (C-5000, IKA), using a pan with 0.5000 ± 0.0010 g samples, and briquettes were produced in a briquette machine (LB 32, LIPPEL), at 90 °C and under 90 bar for 5 minutes.

2.4 Nano-technological potential

Cellulose nanosuspensions were produced using a colloidal mill (Super Masscoloider, MASUKO) using FP with a solid content of 5 %. Nanocellulose films were prepared with FP nanosuspension, according to Claro et al. (2020) with a grammage of 20 g m^{-2}.

3. RESULTS AND DISCUSSION

3.1 Matrix availability and chemical characterization

The average weight of *A. angustifolia* pines is 1.53 ± 0.10 kg (n = 25), and FP represents 55.1 % (w/w) of the pines. When considering the seeds production of 12,485 t during the year of 2021 (IBGE), a generation of 15,321 t of FP was achieved, which emphasizes the importance on proposing uses for this material.

The results on the nutritional composition of FP and chemical composition of the extract are presented in Tables 1 and 2, respectively. Besides presenting low levels of lipids (3.27 %) and non-fiber carbohydrates (3.49 %), and considerable levels of total phenolic compounds, FP can be considered a source of dietary fibers (81.42 %) according to the Resolution

RDC 54/2012 (ANVISA, 2012), which justifies its use in the development of functional food products with high levels of fibers and bioactive compounds.

TABLE 1 – NUTRITIONAL COMPOSITION ON FP

Compost	Content
Moisture (g 100 g^{-1})	7.56 ± 0.37
Ash (g 100 g^{-1})	2.26 ± 0.08
Protein (g 100 g^{-1})	2.01 ± 0.31
Lipid (g 100 g^{-1})	3.27 ± 0.06
Total Dietary Fiber (g 100 g^{-1})	81.42 ± 1.41
Non-Fiber Carbohydrate (g 100 g^{-1})	3.49 ± 2.23
Total Caloric Value (kcal 100 g^{-1})	51.4 ± 10.7

Note: FP stands for *Falhas de Pinhão*. Data presented with media ± standard deviation (n = 3). Levels of moisture, ash, protein, lipid, and total dietary fibers were determined experimentally, and levels of non-fiber carbohydrate and total caloric value were calculated from experimental data.

The high level of phenolic compounds of FP also justifies its use on extraction processes for the obtention of natural extracts with high content of nutraceuticals compounds, which can be utilized on food, pharmaceutical, or cosmetics industries. Yet, FP can be utilized on the obtention of sugar alcohols (e.g., mannitol, xylitol).

TABLE 2 – CHEMICAL COMPOSITION ON FP EXTRACT

Compost	Content
Phenolic Compounds (mg GAE L^{-1})	655.3 ± 17.7
Arabinose (mg L^{-1})	59.97 ± 4.49
Galactose (mg L^{-1})	9.09 ± 0.47
Glucose (mg L^{-1})	40.89 ± 4.37
Mannose (mg L^{-1})	3.91 ± 0.71
Sucrose (mg L^{-1})	1.14 ± 0.29
Fructose (mg L^{-1})	2.64 ± 0.54
Sugar alcohols (mg L^{-1})	1,050 ± 145

Note: FP stands for *Falhas de Pinhão*. Data presented with media ± standard deviation (n = 3).

Based on the elemental composition (Table 3), FP presents a high content of carbon (47.45 %) and can be considered a potential material for the obtention of coal, which might be considered a high-quality charcoal due to the low ash content on FP (GOTTI et al., 2013). A high carbon-nitrogen was observed (C/N, 187), level similar to the C/N of several matrices utilized as substrates for the cultivation of edible mushrooms, such as corncob (C/N, 120) and sawdust (C/N, 325) (OSUNDE et al., 2019), suggesting the potential use of FP as additive on the formulation of new substrates.

TABLE 3 – ELEMENTAL COMPOSITION ON FP

Element	Content
Carbon (C) (%)	47.39 ± 0.13
Hydrogen (H) (%)	10.18 ± 0.21
Nitrogen (N) (%)	0.25 ± 0.03
Sulfur (S) (%)	0.071 ± 0.003
C/N	187 ± 20

Note: FP stands for *Falhas de Pinhão*. Data presented with media ± standard deviation (n = 3). Content of C, H, N, and S were determined experimentally, and C/N ratio was calculated from experimental data.

3.2 Energetic potential

FP presents a high Higher Calorific Value (18.55 ± 0.05 MJ kg^{-1}, n = 3), similar to the calorific value of several biomasses utilized on the generation of energy, such as sorghum panicle (19.09 MJ kg^{-1}), pearl millet (14.37 MJ kg^{-1}), corn stalk (16.80 MJ kg^{-1}) (HU et al., 2014; VELUSAMY et al., 2021). The low level of ashes (2.26 %, Table 1) on FP is also a positive factor when proposing its use on the generation of energy, once its use on kettles generates low levels of solid wastes.

The development of briquettes from FP also presents a positive attribute when comparing to other matrices: materials such as charcoal need the addition of binding materials, which play a key-role on holding the briquette together during transportation and storage (ZHANG et al., 2018), while FP, due to its chemical composition, especially the high amount of lignin, allows the material to be pressed into briquettes without the use of binding agents (DIAS et al., 2012).

3.3 Nano-technological potential

Due to its high levels on dietary fibers, which are majorly cellulose and lignin, FP can be considered a potential matrix for the development of cellulose nanosuspensions.

Due to the high content of antioxidant compounds, nanosuspension of whole-FP can be utilized on the development of food products (TIMM et al., 2020) and cosmetics, or on the production of bioactive films with antioxidant activity, which can be employed as coating on food products or as wound healing material (ZANONI et al., 2021).

3.4 Overview

FP is a material with no consolidated use, with interesting chemical composition for different segments (e.g., food, pharmaceutical, and cosmetics industries), and it is widely available in South and Southern Brazil during winter.

This work presented some potential uses on this material, which are briefly summarized in Figure 1.

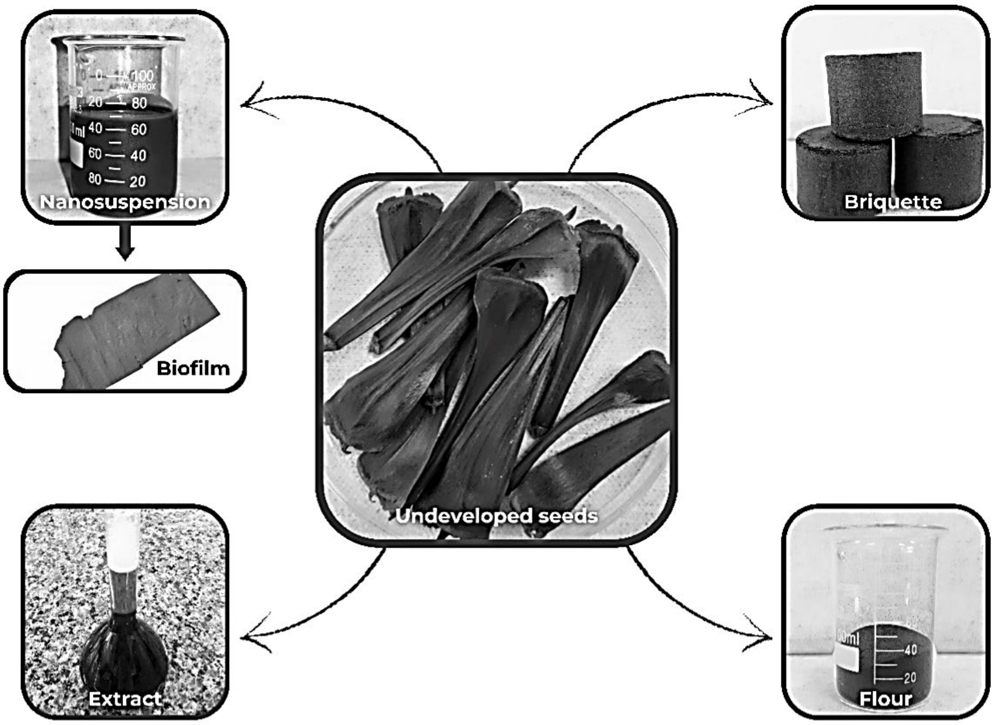

FIGURE 1 – POTENTIAL USES ON UNDEVELOPED OR STERILE SEEDS (FP).

Note: FP stands for *Falhas de Pinhão*. Authors. (2023).

The utilization of FP promotes several Sustainable Development Goals (SDG) proposed by the United Nations (2015), such as the development of products to promote "Zero hunger", "Affordable and Clean Energy", or "Responsible Consumption and Production" (SDG 2, 7, and 12, respectively).

4. CONCLUSION

PF represents 55.1 % (w/w) of the *Araucaria angustifolia* pines. The material is a potential source of total dietary fibers (81.42 %) on the formulation of special food products, and can be utilized on several other applications, such as additive on the formulation of substrates for mushrooms (C/N ratio of 187), energy generation (HCV of 18.55 MJ kg^{-1}), and development of nanocellulose suspensions and films.

POTENCIAIS USOS DE SEMENTES NÃO DESENVOLVIDAS DA *Araucaria angustifolia*

Sementes não desenvolvidas de pinhão (Falhas de Pinhão, FP) são sub-produtos potenciais da exploração de pinhas de *Araucaria angustifolia*, e esse material não tem uso e tem pouca pesquisa acadêmica disponível. Neste trabalho, foi realizada sua caracterização química, e foram propostos novos usos para esse material, com foco

no potencial para as áreas de alimentos, cosméticos, energia e nanotecnologia. Os resultados indicam o PF como um potencial suplemento de fibras dietéticas para aplicação no setor de alimentos. O PF pode ser utilizado na obtenção de extratos para aplicação como fonte de compostos fenólicos e açúcares. O alto valor calorífico e o baixo teor de cinzas do PF indicam seu potencial na geração de energia. No entanto, outras aplicações foram testadas, como a obtenção de briquetes, nanosuspensões e filmes à base de celulose.

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