Research, Society and Development, v. 9, n. 8, e935986621, 2020
(CC BY 4.0) | ISSN 2525-3409 | DOI: http://dx.doi.org/10.33448/rsd-v9i8.6621

Comportamento da secagem, propriedades da farinha e amido de sementes de *Araucaria angustifólia*

Araucaria angustifolia seeds drying behaviour, flour and starch properties

Comportamiento de secado, propiedades de la harina y el almidón de semillas de *Araucaria angustifolia*

Recebido: 11/07/2020 | Revisado: 19/07/2020 | Aceito: 21/07/2020 | Publicado: 02/08/2020

Laisa Pellizzaro Pereira
ORCID: https://orcid.org/ 0000-0002-9555-5150
Universidade Federal de Santa Catarina
E-mail: laisa.pellizzaro@gmail.com
Edna Regina Amante
ORCID: https://orcid.org/0000-0001-9593-5674
Universidade Federal de Santa Catarina
E-mail: e.amante@ufsc.br
Deise Helena Baggio Ribeiro
ORCID: https://orcid.org/ 0000-0001-6023-9812
Universidade Federal de Santa Catarina
E-mail: deise.baggio@ufsc.br

Resumo

O processamento de sementes de *A. angustifolia* permite estender seu período de oferta. Esta pesquisa objetivou o estudo das características de secagem de sementes cruas frescas e congeladas, estabeleceu as propriedades microbiológicas da farinha, as propriedades morfológicas e de pasta do grânulo de amido. A metodologia empregada foi a pesquisa laboratorial, na qual o amido foi extraído e determinado o teor de amilose, os grânulos foram examinados por MEV, as propriedades de pasta por RVA e o comportamento térmico por DSC. As sementes congeladas apresentaram maior taxa de secagem, porém, a partir da umidade crítica, apresentaram resistência interna semelhante. O rendimento de amido foi de 19,5% e o seu teor de amilose foi de 12,9%. Através do MEV foram identificados grânulos lisos, sem erosão, forma oval e arredondada. O padrão de viscosidade corresponde a uma matriz com tendência à retrogradação. A temperatura de pasta inicial do amido, a temperatura de pico

endotérmica, a temperatura de gelatinização completa e a entalpia de gelatinização encontradas foram 53,34, 60,32, 67,25 e 2,58 J / g.

Palavras-chave: Pinhão; Secagem; Amilose; Propriedades de pasta.

Abstract

A. *angustifolia* seeds processing allows to extend its offer period. This research had the aim to study differences between fresh and frozen raw seeds drying characteristics, establish the flour microbiological, the starch granule morphologic and pasting properties. The methodology used was laboratory research. The starch was extracted and determined the amylose content, the granules were examined by SEM, the pasting properties by RVA and the thermal behaviour by DSC. The frozen seeds presented higher drying rate, however from the critical moisture, they had similar intern resistance. The starch yield was 19.5% and its amylose content was 12.9%. Through SEM was identified smooth granules without erosion, thus oval and rounded shape. The viscosity pattern corresponds to a matrix with tendency to retrogradation. The starch initial pasting temperature, endothermic peak temperature, complete gelatinization temperature and enthalpy of gelatinization found were, 53.34, 60.32, 67.25 and 2.58 J/g.

Keywords: Pinhão; Drying; Amylose; Pasting properties.

Resumen

El procesamiento de semillas de *A. angustifolia* permite extender su período de oferta. Esta investigación tuve como objectivo el studio de las características de secado de semillas crudas frescas y congeladas, estableció las propiedades microbiológicas de la harina, las propiedades morfológicas y de pasta del gránulo de almidón. La metodología empleada fué la investigación laboratorial, desde la qual se extrajo el almidón y se determinó el contenido de amilosa, se examinaron los gránulos mediante SEM, las propiedades de la pulpa mediante RVA y el comportamiento térmico mediante DSC. Las semillas congeladas mostraron una mayor tasa de secado, sin embargo, debido a la humedad crítica, presentaron una resistencia interna similar. El rendimiento de almidón fue del 19,5% y su contenido de amilosa fue del 12,9%. A través de SEM, se identificaron gránulos lisos, sin erosión, ovales y redondeados. El patrón de viscosidad corresponde a una matriz con tendencia a retrógrarse. La temperatura de la suspensión de almidón, la temperatura pico endotérmica, la temperatura de gelatinización completa y la entalpía de gelatinización encontradas fueron 53,34, 60,32, 67,25 y 2,58 J / g.

Palabras clave: Piñón; Secado; Amilosa; Propiedades de pasta.

1. Introduction

The *Araucaria angustifolia* (Bertol.) Kuntze can be found in South America, inserted in the area of Atlantic Forest (BRDE, 2005). Araucaria it is a plentiful gender, diverse, thus with large geographic range, thereby nineteen of its species are located in the south hemisphere, of which only two are native from South America: *A. angustifolia* Bertol. O. Kuntze, reached out in Brazil, Argentina and Paraguai, and *A. araucana* (Molina) K. Koch, situated in Chile and Argentina (Dutra & Stranz, 2003).

The *A. angustufolia* seeds (*pinhão*) are found in greater quantity during winter-fall season, it is important as food and has a role to generate income to stakeholders, small farmers and collectors (BRDE, 2005). Due to cultural aspects, restrictions of seasonality and amount of production, the seeds commercialization flow has a low degree of industrialization (Santos *et al*., 2002).

Regarding the nutritional characteristics, *pinhão* is considered source of starch, dietary fiber, lipids, proteins, calcium, phosphorus, iron, zinc, magnesium, copper, and antioxidants compounds (Cordenunsi *et al*., 2004; Freitas *et al*., 2018; Santos *et al*., 2018). It is still necessary to develop conservation and industrialisation techniques to enhance its consumption and production. The critical variables to extend the food shelf life, preserving its sensory, physical and chemical properties are: moisture and temperature (Capella *et al*., 2009; Osorio *et al*., 2011).

Dehydration process could be an efficient alternative product conservation, stability of the aromatic components at room temperature, protection against enzymatic and oxidative degradation, reduction of the weight and volume, reduction of the transport and storage costs, shelf-life increase and product availability at any season of the year. The flour processing is suitable to aggregate value to seeds, enables the income increment of the rural communities, and could reinforce the importance of these species, contributing to the conservation of forest remnants (Silva *et al.*, 2009).

The flour enables the production of several *pinhão* based products, allowing a varied way of consumption of a nutritive and energetic product, instead of just cooked. Furthermore, the seeds flour due to the fact of not contain gluten proteins may be used to develop products to celiac consumers (Olivera, 2008). Hence, the studies regarding its processing could contribute to establish a scientific base necessary to the industrialization of this raw material.

2. Methodology

This study is based on a laboratory research (Pereira et al. 2018). The samples were collected on a natural spot and the data were reported with a quantitative criteria and reflected the study design on the described conditions.

2.1 *Araucaria angustifolia* seeds (*pinhão*)

Samples were originated from the São José do Cerrito (SC – Brazil - 27° 39' 45" S, 50° 34' 48" W). The sample was collected between March and April, selected in order to exclude the mechanically damaged seeds or attached by insects or fungi, visually deteriorated.

2.2 Preparation of *Araucaria angustifolia* seed sample

Pinhão were divided in two batches: fresh raw and frozen raw, which were manually peeled and packaged in PVC films. The fresh raw *pinhão* were maintained under refrigeration for 7 days and the frozen raw were preserved under –18 °C.

Preparation and flour processing For drying, the *pinhão* were chopped in small slices of 0.5 cm, spread on a tray and placed in oven at 65 °C, with constant circulation and renewal of forced air (TECNAL brand, model TE – 394/2, Brazil.) The water mass loss determination was done during regular intervals of 30 minutes in an 8-hour period to each sample, using analytical weighing (Katashi, model ATX/ATY, Brazil). In addition, the water activity was measured every one hour (Decagon, Alab 4TE). The measures were done in triplicate. The dehydrated material was ground in mill (Ika, model AKA 11 basic, Brazil) and sifted in 60 mesh sieves.

2.3 Mathematical modelling of the drying curves

The drying process modelling was performed by adjusting the experimental data to the models of Lewis, Page, Henderson e Pabis, Logarithmic, Midili, Diffusion Approximation, Two-Terms, Two-Terms Exponential, Wang and Singh. In order to adjust the mathematical models to the experimental data of the drying, regression non-linear analysis was performed, using the method Quasi-Newton, through the software STATISTICA 12®. The

adjustment quality was evaluated by the coefficient of determination (R^2), root mean square error (RMSE) and chi-square (χ^2).

2.4 Microbiological Analysis

The raw fresh, raw froozen and dry pinhão, were analysed regarding to *Salmonella* sp. (ISO 6579:2002), *E. coli* (ISO 7251: 2005) and *Bacillus cereus* (ISO 7932:2004).

2.5 Pinhão starch extraction

Starch was extracted according to Wang and Wang (2004) with modifications. P*inhão* seeds were washed to remove dirt and then manually peeled. The seeds were crushed in an industrial blender for five minutes at a 1:10 *pinhão*-water ratio (w / w), forming a mass that was sieved (200 mesh). Successive washes were performed in order to obtain colorless filtrate. The obtained starch milk was centrifuged (3000 rpm, 20 min), and then, resuspended in 0.10% NaOH, with subsequent successive washes with water until pH 6.0. Then, the supernatant was removed and the starch was dried in an oven with air circulation, at a temperature of 45ºC. After drying, the starch was placed in a glass bottle. The yield of *pinhão* starch after extraction was calculated according to Equation 1, from 500g of pine nut seeds.

$$Yield\ (\%) = \frac{Weight\ of\ starch\ obtained\ after\ extraction\ (g)}{Total\ weight\ of\ raw\ material\ (g)} \times 100 \qquad (1)$$

2.6 Amylose content (Iodometric Method)

The amylose content was determined according to Williams *et al*. (1970). The absorbance was read at 625 ηm on spectrophotometer UV-visible (Gold spectrumlab 53 UV-*Vis* spectrophotometer, BEL photonics, Brazil), the amylose and amylopectin contents were assessed using an external standard-curve with amylose and amylopectin solutions in the proportions of, 0:20; 2:18; 4:16; 6:14, 8:12, 10:10 and 12:08, extracted from the *pinhão* starch according to the method proposed by McCready and Hassid (1943).

2.7 Scanning eletronic microscopy

Approximately 10 mg of each sample were placed on double sided carbon tape fixed on the aluminium stubs and covered with a thin layer of gold using polarina E5000. The micrographs were recorded in scanning electronic microscope model (JEOL, model JSM-6390LV, USA), in magnifications of 300, 600, 1000, 1500 and 2000 times, operating in the range of 10 kV.

2.8 Starch pasting properties

Rapid Visco Analyser (RVA- Newport Scientific, Narabee, NSW, Australia) was utilized to assess the variations of samples viscosity during the paste formation, under temperature and stirring effects (160 rpm). The analysis started at 50 ºC for 2 minutes; heated at a rate of 14 ºC per minute until reach 95 ºC and remain in this temperature for 5 minutes; cool down until 50 ºC at the same rate of 14 ºC per minute and remain at this temperature for more 2 minutes, totalizing 13 minutes of analysis. The data provide information about paste temperature (ºC), maximum peak viscosity (cP), temperature of the maximum peak viscosity (ºC), time to reach the maximum peak viscosity, minimum viscosity (cP), final viscosity of the cooling cycle (cP) and downgrading (cP). The tendency to retrogradation was obtained through the difference between the final and the minimum viscosity.

2.9 Differential scanning calorimetry (DSC)

Suspensions of starch in distilled water were weighted and placed in aluminium recipients. These were immediately hermetic sealed and balanced for 3 hours at room temperature before heating in the DSC. The equipment utilized was a calorimeter (TA Instruments, model 2010, USA) and the samples were heated from 30 to 120 ºC, under a heating rate of 5 ºC per minute. An empty recipient was used as reference. The gelatinization enthalpy (ΔHg) and the endothermic peak temperature (T_p) were obtained through thermogram. The initial temperature (T_i) and the final or conclusion (T_c) were determined through endotherm.

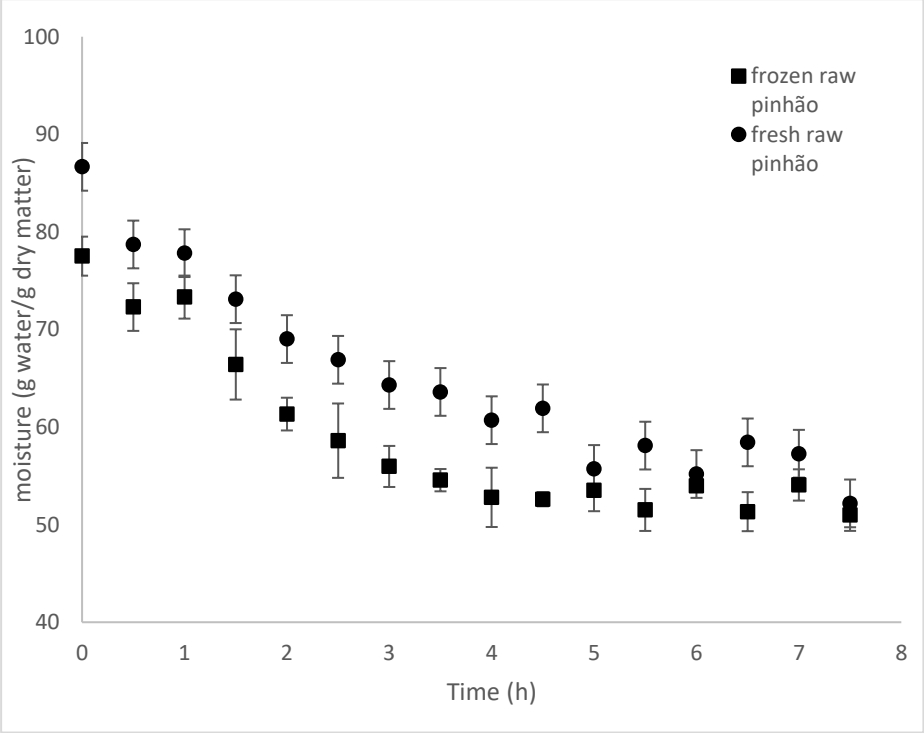
2.10 Statistical analysis

All results were achieved from three replicates and are presented as mean and standard deviation. The significance between the means was provided by analysis of variance one-way (ANOVA), followed by the complementary Turkey test ($p \leq 0.05$), when applicable. The statistical analyses were performed using the Excel software (Microsoft Office, 2008, USA) and Statistica 12 (Stasoft, Tulsa, USA).

3. Results and Discussion

The drying curves of the moisture on a dry basis (d.b.) versus time are shown in Figure 1.

Figure 1 - Variation of the moisture of frozen raw *pinhão* and fresh raw as function of time, under temperature of 65 ◦C.



Source: The authors.

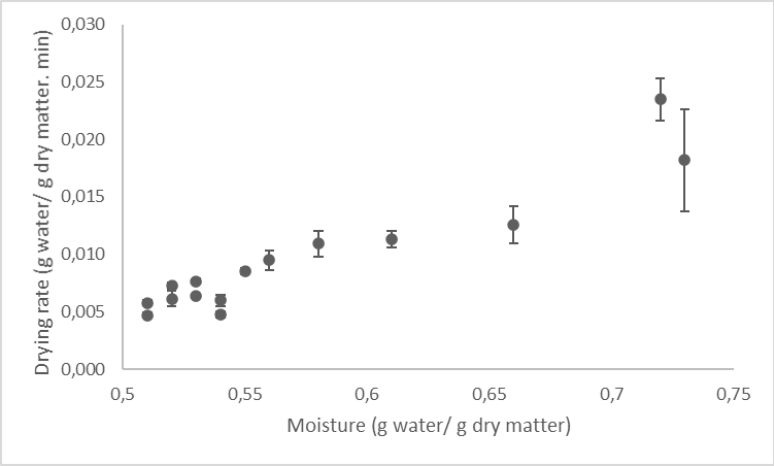
It was observed a significant drop in the moisture of the frozen raw *pinhão* comparatively to the fresh raw *pinhão*. This occurs because, the cellular structure of *pinhão* when submitted to the freezing process suffers damage generated by the development of water crystals, which grown in the intra and inter cellular spaces, thus deforming and burst

the cell wall (Provesi *et al*., 2016). Such damage conduces to a greater water lost through exudation during defrosting, which occurs simultaneously to dehydration of the seeds.

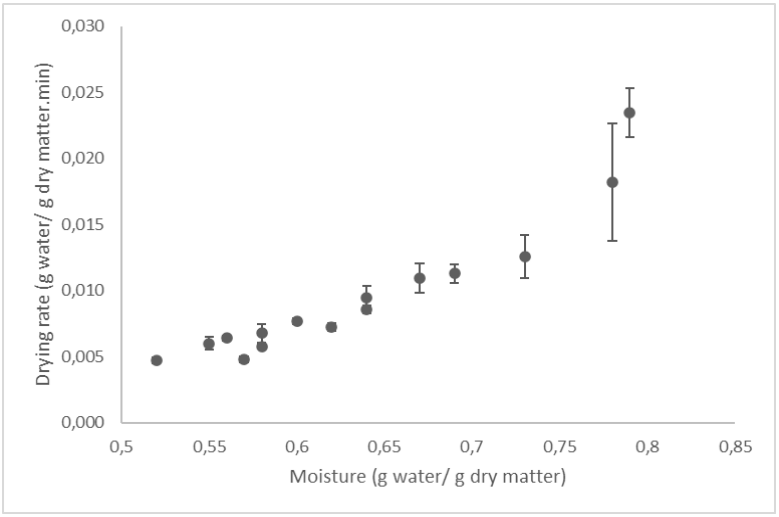
Similar behaviour was obtained by Capella *et al*. (2009), the moisture of frozen *pinhão* was relatively lower than the fresh *pinhão*. The final moisture achieved for both frozen raw and fresh raw *pinhão*, on a dry basis, was approximately 0.45 g of water/ g dry matter. Therefore, during the drying process, until the critical moisture be reached, the frozen raw *pinhão* showed a drying rate higher than the fresh raw, however from the critical moisture both presented similar internal resistance, hindering the liquid movement from interior to the surface.

The curves expressing the drying rate in function of moisture for both frozen raw *pinhão* and fresh raw are shown in the Figure 2. The moisture being decreasing continuously over drying time, thus there is no phase of constant rate of drying. During the decreasing phase the drying is controlled only by diffusion of water in the solid. These results indicate that the diffusion is probably the physical mechanism which conducts the movement of water into the *pinhão*.

Figure 2 - Drying rate of frozen raw *pinhão* (a) and fresh raw (b) as function of moisture, under temperature of 65 ˚C.



a



b

Source: The authors.

Regarding the coefficient of determination (R^2) of the mathematical models adjusted, these varied between 0.97 and 0.99 to the frozen raw *pinhão* drying and between 0.95 and 0.99 to the fresh raw *pinhão*. Therefore, it could be observed that both Diffusion Approximation and Two Terms models had the best match to drying model of frozen raw *pinhão*, and Page, Diffusion Approximation, Two Terms and Two Terms Exponential to fresh raw *pinhão* (Tables 1a and b).

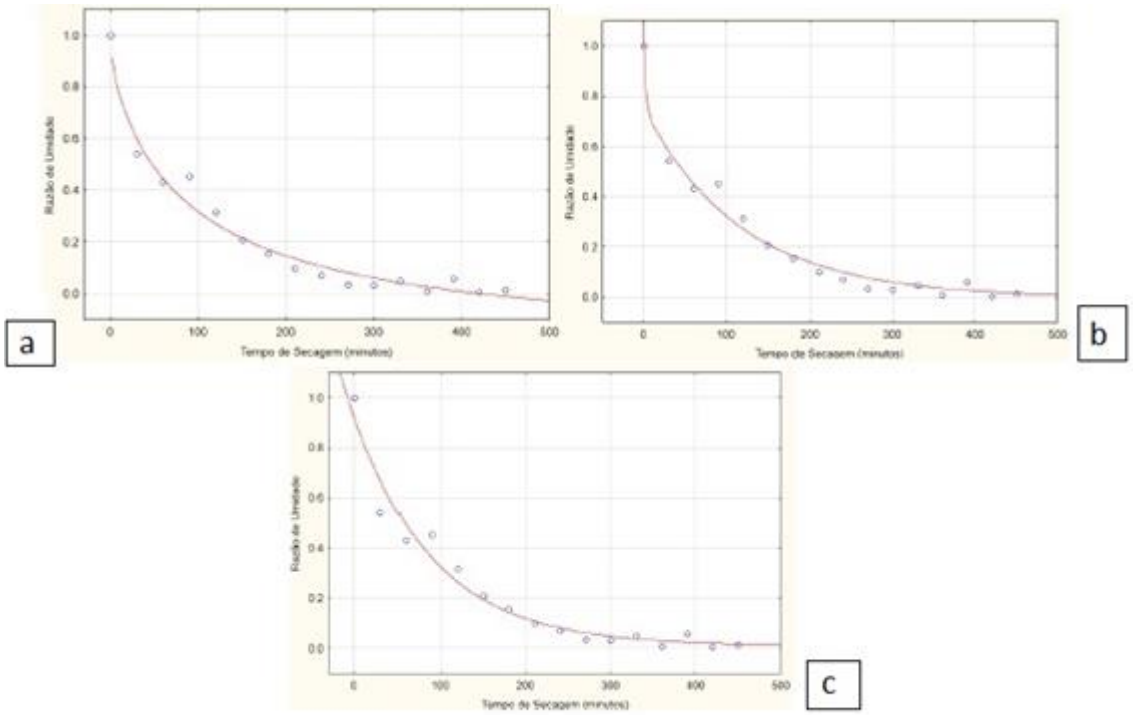
Table 1 - R^2, χ^2, DMQ data from drying models used in frozen (a) and fresh raw *pinhão* (b).

Models (a)	Parameters							R^2	X^2	RMSE
	a	k	K_1	K_0	n	b	C			
Lewis	-	0.0111	-	-	-	-	-	0.9769	3.714E-06	0.0019
Henderson and Pabis	0.9181	0.0102	-	-	-	-	-	0.9810	1.041E-04	0.0095
Page	-	0.0340	-	-	0.7686	-	-	0.9858	7.273E-04	0.0252
Midili	0.9901	0.0500	-	-	0.6699	-0.0001	-	0.9878	4.448E-06	0.0018
Logarithimic	0.9133	0.0106	-	-	-	-	0.0101	0.9812	4.891E-11	6.304E-06
Wang and Shing	-0.0064	-	-	-	-	0.00001	-	0.9244	1.341E-02	0.1083
Diffusion approximation	0.2180	0.3701	-	-	-	0.0227	-	0.9907	3.776E-04	0.0175
Two term	0.2480	-	0.0084	0.6778	-	0.7519	-	0.9907	4.068E-04	0.0175
Two term exponential	0.1609	0.0592	-	-	-	-	-	0.9860	1.313E-04	0.0107
Models (b)	Parameters							R^2	X^2	RMSE
	a	k	K_1	K_0	n	b	C			
Lewis	-	0.0067	-	-	-	-	-	0.9800	6.404-06	0.0024
Henderson and Pabis	0.9187	0.0061	-	-	-	-	-	0.9857	4.607E-04	0.0200
Page	-	0.0219	-	-	0.7729	-	-	0.9920	2.89E-05	0.0050
Midili	0.9901	0.5998	-	-	0.00001	-0.0013	-	0.9581	6.519E-03	0.0699
Logarithimic	0.8808	0.0077	-	-	-	-	0.0684	0.9889	1.7661E-16	1.197E-08
Wang and Shing	-0.0052	-	-	-	-	0.00007	-	0.9652	5.154E-03	0.0671
Diffusion approximation	0.1938	0.0669	-	-	-	0.0798	-	0.9929	5.883E-06	0.0022
Two term	0.1942	-	0.0053	0.0671	-	0.8063	-	0.9929	8.621E-07	0.0008
Two term exponential	0.1736	0.0322	-	-	-	-	-	0.9908	7.289E-07	0.0008

Source: The authors.

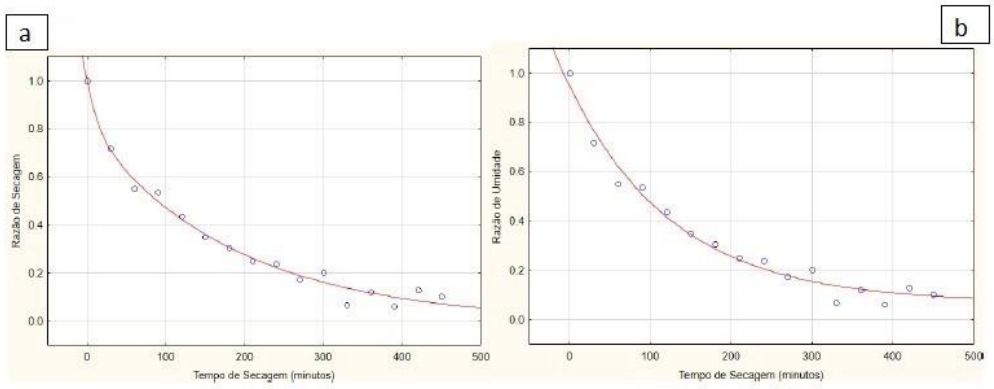
Furthermore, it can be affirmed that, according to Madamba *et al*. (1996), these models indicate a satisfactory representation of the phenomenon under study. Nevertheless, only the coefficient of determination is not a good criterion to the selection of non-linear models, thus, the assessment of other parameters become necessary, for instance, qui-square (χ^2) and the root mean square error (RMSE). The lower the χ^2 and RMSE, better the model is adjusted (Akpinar *et al*., 2003; Midilli and Kucuk, 2003; Günhan *et al*., 2005). Figures 3 and 4 illustrate the adjustments of the mathematical models to the experimental data of frozen raw and fresh raw *pinhão* drying, respectively.

Figure 3 - Mathematical models adjustments to the experimental data of frozen raw *pinhão* drying. Where (a) Approximation of Diffusion Model; (b) Logarithmic Model and (c) Midili Model.



Source: The authors

Figure 4 - Mathematical models adjustments to the experimental data of fresh raw *pinhão* drying. Where (a) Two-Terms Model; (b) Logarithmic Model.



Source: The authors

Several researchers observed that Page model was recommended and applied to predict the drying phenomenon to many agricultural products, such as, red beans (Corrêa *et al*., 2007), seed of black beans (Afonso Júnior & Corrêa, 1999), tomato (Doymaz, 2007), amaranth seed (Abalone *et al*., 2006), apple pulp (Wang *et al*., 2007) and castor bean (Goneli *et al*., 2007).

According to Madamba *et al*. (1996) and Babalis and Belessiotis (2004), the drying constant (k), can be utilized as an approximation to characterize the effect of temperature and it is related to the effective diffusivity in the drying process during the decreasing period and to the liquid diffusion which controls the process.

As a result of the seeds dehydration to reach moisture content below 15%, the water activity values obtained during the drying process, both for fresh and frozen *pinhão*, were very similar by the end of the eight hours of drying was of 0.30±0.06.

After 3 hours of drying, samples were microbiologically stable, once its water activity was lower than 0.6. However, the moisture was 0.31g water/g sample for fresh raw *pinhão* and 0.25g water/g sample for frozen raw *pinhão*, which could result in risk of chemical and enzymatic deterioration.

Countless works refer to the proximate composition of the *pinhão*, always justifying the performance of works so that the product is made available to the consumer for a longer time. Considering the high seed moisture, with many variations between publications from 38.1 to 87.6% (Wosiacki & Cereda, 1985; Cordenunsi *et al*., 2004; Olivera, 2008; Capella *et al*., 2009; Corrêa and Helm, 2010; Peralta et al., 2016).

There is a wide variation between data on the centesimal composition of *pinhão* in the literature. The contents of ash, crude protein, total lipids and total fibers can vary between: 1.50-1.63, 3.42-5.92, 1.67-7.38, 1.29-4.89, respectively and other carbohydrates can achieve 48.42%, (Cordenunsi *et al*., 2004; Olivera, 2008; Capella *et al*., 2009; Corrêa & Helm, 2010; da Silva et al., 2016). However, functional compounds are being studied in pine nuts such as phenolic compounds and complex carbohydrates of nutritional interest (Peralta *et al*., 2016).

Other authors assessed the water activity after the drying process, Olivera (2008) presented similar values of raw *pinhão* drying, at 70 °C for 8 hours, obtaining final value around 0.25. Capella *et al.* (2009) found water activity higher than that presented in this study, of 0.50, after drying at 65°C, for 5 hours.

Frozen raw *pinhão* flour and fresh raw *pinhão* flour showed absence of *Salmonella* spp. in 25g, $< 10^2$ UFC.g^{-1} of *Bacillus cereus* and also < 3 NMP.g^{-1} of *E. coli*, they are suitable for consumption and may be used to manufacture of new products. The fresh sample of *pinhão* had 21 NMP.g^{-1} of *E. coli*, absence of *Salmonella* and $< 10^2$ UFC.g^{-1} of *Bacillus cereus.*

The starch extraction yield was of 19.3%, similar value was also presented by Wosiacki and Cereda (1985), however differ from Daudt *et al.* (2014), which obtained yield of 41.3%. This difference could be attributed to different methodologies utilized, which diverge basically regarding the amount of water used in the beginning of the starch extraction process. Furthermore, in the current study the "starch milk" was centrifuged instead of only allowed to decant as in the cited references.

Although it is recognized that the calibration curve creation with standards commercially available, which certified concentration, is the best way to quantify the sample components. As there is no certified *pinhão* starch standard available, in the current experiment, the amylose and amylopectin levels were quantified by means of a calibration curve made with the *pinhão* starch itself. The curve was measured by analysing the amylose in a standard sample of corn amylose (MEGAZYME®), which had a known percentage of amylose of 63%, according to the manufacturer. The result indicated a variation of 10% between the expected and the experimentally obtained. This factor was considered in the correction of the sample's values. The amylose content determined in the fresh *pinhão* was 12.9 %.

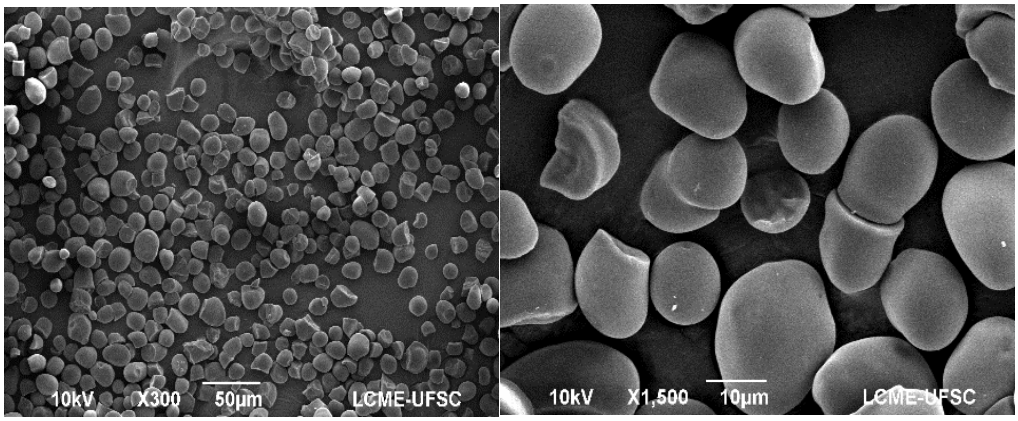
The results found differ from those reported by Thys *et al*. (2010), Bello-Pérez *et al*. (2006) and Costa *et al*. (2013), which reported values of 26.3, 25.0 and 23.7%, respectively. These variations result in starch granules with different psychochemical and functional properties, defining their use in food or industrial applications. The use of different methods

by such authors for the extraction and starch determination, together with the use of potato standard to build the calibration curve are factors that could be generating such discrepancy between the values obtained and those from the literature. Besides the variations in the starch properties according to the place of cultivation, as well as the sampling that differs between the works.

Regarding the *pinhão* starch granule morphology, oval and rounded shapes are predominant, as observed also by Daudt *et al*. (2014) and Stahl *et al*. (2007). The medium diameter is between 15 and 25 µm. The size and shape of the starch granule were similar to others found in previous studies (Bello-Pérez *et al*., 2006; Conto *et al*., 2011; Henríquez *et al*., 2008). The surface of the granules is smooth, without irregularities or erosion. The presence of pores on the starch granules surface may affect its reactivity when it is chemically modified, as well as its functional and physicochemical properties (Bello-Pérez, *et al*., 2006; Fannon *et al*., 1992).

Figure 5 illustrates the micrographs obtained through scanning electronic microscopy of the extracted *pinhão* starch.

Figure 5 - Micrographs obtained by scanning electronic microscopy of *pinhão* starch (300x and 1,500x)



Source: The authors

The viscosity profile is extremely useful in determining the behaviour of the starch under several conditions. One of the most important aspects of viscosity profiles is the measurement of the effects of reagents or processes that modify the starches upon their paste properties (Peroni, 2003). Data show that the increasing of the temperature leads to starch gelatinization, causing the increasing of the viscosity due to the granule swelling. At this point, polymers with lower molecular weight, particularly amylose, begin to be leached from the

granules (Thomas & Atwell, 1999). The temperature when the granules begin to swell is called paste temperature, which for the *pinhão* starch was of 68°C. Similar value was obtained by Costa *et al*. (2013), which was of 68.1°C, also by Klein *et al.* (2013), of 64.4°C and by Stahl *et al*. (2007), which found 59.6°C. Bello-Pérez *et al*. (2006) explained that the low paste temperature of *pinhão* indicates that its starch presents less resistance to the dissociation of intramolecular hydrogen bounds and greater ease of swelling comparing to corn starch.

The viscosity peak is obtained during the pasting, when the granules are totally swollen, but there is also the presence of some intact granules (Thomas & Atwell, 1999). The maximum viscosity reached by the *pinhão* starch (viscosity peak) was of 3095.5 cP, similarly was obtained by Costa *et al*. (2013), which was of 3011 cP. The value found by Stahl *et al.* (2007) and by Klein *et al.* (2013) were higher, respectively, of 4512 cP and 4279 cP. This parameter is important to evaluate the starch quality, once the fluidity can interfere in the equipment and its dimension in a production line and even on the product to be manufactured (Bello-Pérez *et al*., 2006). In this context, *pinhão* starch is an important alternative to the development of products that require high viscosity, under process temperatures not too high.

After the viscosity peak is reached, the viscosity decreases gradually, during the constant temperature phase (95 °C) due to molecular dissociation. The difference between the maximum and minimum viscosity is called “Breakdown”, which represents the resistance of the starch to mechanic stir, when it is possible to assess the starch stability at high temperatures, whose granules break under mechanical agitation (Thomas & Atwell, 1999). The breakdown value obtained in this experiment was lower than that found by Costa *et al*. (2013), of 1840 cP, by Stahl *et al*. (2007), of 2427 cP and by Klein *et al.* (2013), of 2186cP.

Immediately after the cooling period the re-association between the molecules occurs, thus the viscosity increases, due to the reorganization of the linear chains (mainly amylose) of the starch which were solubilized during the heating period and the constant temperature at 95 °C. This process produces a higher number of cross-links between the chains of molecules, producing a network which retains large amounts of water molecules, representing the retrogradation phenomena.

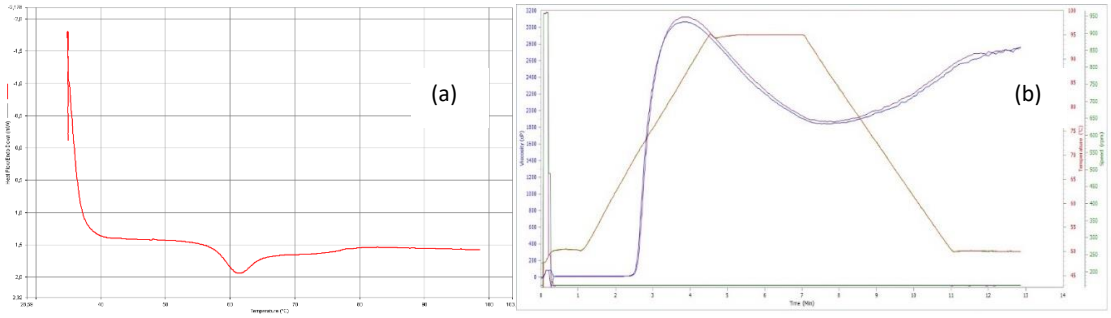
The biass to retrogradation (setback) was 894 cP, similar value was found by Klein et al. (2013), of 996 cP, nevertheless lower than that obtained by Stahl et al. (2006), of 1524 cP and by Costa *et al*. (2013), of 1354cP, which indicates a higher stability to retrogradation of the *pinhão* starch studied in this work. In accordance with Peroni (2003), the high tendency of retrogradation is representative of starches with high amylose content because

it is easier for this molecule to reassociate after cooling. This fact is in agreement with what was obtained in this experiment, in which the low tendency to retrogradation. Although amylopectin is retrogradable, linear molecules are more likely to reassociate and build hydrogen bonds than larger amylopectin molecules (Thomas & Atwell, 1999).

It was possible to establish through thermograms the initial gelatinization temperature (T_o), endothermic peak temperature (T_p), gelatinization completion temperature (T_c) and gelatinization temperature (ΔH_{gel}), which were, respectively, 53.48 (±1.6)◦C, 61.48 (±1.2), 69.28 (±2.21) ◦C e 4.31 J/g (±0.32). Similar values were found by Daudt et al. (2014), who reported values of 51.38◦C (T_o), 55.55◦C (T_p), 61.02 (T_c) e 14.03 J/g (ΔH_{gel}). Bello-Pérez *et al.* (2006) also analysing the *pinhão* starch observed peak temperature of 63.4 °C, close value to that found in this study.

The paste temperature obtained by RVA (68.8 °C) was bigger than the initial gelling temperature (T_o) of DSC (53.5 °C), as shown in the Figure 6. According to Peroni (2003) this happened because DSC can detect when the first granules begin to disorganize, bringing more accurate values. The RVA has sensitivity to detect the first additions to the general viscosity of the paste.

Figure 6 - Termogram (a) and viscoamilogram (b) obtained through DSC and RVA of *pinhão* starch.



Source: The authors.

In the starch retrogradation, the enthalpy value provides a quantitative measure of the energy transformation that occurs during the amylose fusion and recrystallization, resulting in a precise measurement of the transition temperature (T_o, T_p and T_c) of this endothermic event (Peroni, 2003). This fact could also be explained due to the experimental differences, such as the use of distinct equipment and different calibration conditions, which can justify the enthalpy differences.

Still, there are the diversity of growth and genetics which can affect the gelatinization properties of starch. According to Whistler & Paschal (1965), the thermal parameters are influenced by granule composition (amylose/amylopectin rate, phosphorous content, lipids, enzymes and proteins present), molecular structure of amylopectin (crystalline and amorphous regions rate), granule morphology and size distribution of the starch granules.

4. Conclusion and Suggestions

The mathematical models that best described the *pinhão* drying behaviour is Logarithimic. The pinhão starch extraction yield was 19.5%, and the amylose content was 12.9%, which contributed to the low tendency to retrogradation found in the paste properties analysis through RVA and also for the low value for enthalpy obtained in the DSC.

It was evidenced through the MEV images that the predominant geometric shapes were oval and rounded. Furthermore, that the granule surface is smooth, without irregularities and erosion.

The authors suggest that future studies could include comparison among different sampling years of the seeds.

Acknowledgment

Authors are grateful to the Brazilian governmental agencies CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) (grant number 304741/2014-0), support, and Central Laboratory of Microscopy of the Santa Catarina Federal University.

References

Abalone, R., Gastón, A., Cassinera, A., & Lara, M.A. (2006). Thin layer drying of amaranth seeds. *Bios. Eng*., 93, 179-188.

Afonso Júnior, P. C. & Corrêa, P. C. (1999). Comparison of mathematical models for the description of kinetics of thin layer drying of bean seeds. *Braz. J. Agric. Environ. Eng*., 3, 349-353.

Akpinar, E. K., Bicer, Y. & Midilli, A. (2003). Modeling and experimental study on drying of apple slices in a convective cyclone dryer. *J. Food Proc. Eng*., 26, 515-541.

Babalis, S. J. & Belessiotis, V. G. (2004). Influence of the drying conditions on the drying constants and moisture diffusivity during the thin-layer drying of figs. *J. Food Eng*., 65, 449-458.

BRDE (2005). Banco Regional de Desenvolvimento do Extremo Sul. Cultivo da *Araucaria angustifolia*: análise de viabilidade econômico-financeira. Florianópolis: BRDE, 53 p.

Bello-Pérez, L. A., García-Suárez, F. J., Méndez-Montealvo, G.; Nascimento, J. R. O., Lajolo, F. M. & Cordenunsi, B. R. (2006). Isolation and characterization of starch from seeds of *Araucaria brasiliensis*: a novel starch for application in food industry. *Starch/ Stärke*, 58, 283–291.

Capella, A. C. V., Penteado, P. T. P. S., & Balbi, M. E. (2009). *Araucaria Angustifolia* seed: morphologic aspects and flour chemical composition. *CEPPA*, 27, 135-142.

Conto, L. C., Plata-Oviedo, M. S. V., Steel, C. J. and Chang, Y. K. (2011). Physico-chemical, morphological, and pasting properties of Pine nut (*Araucaria angustifolia*) starch oxidized with different levels of sodium hypochlorite. *Starch – Stärke*, 63, 198–208.

Cordenunsi, B. R., Menezes, E. W., Genovese, M. I., Dolli, C., Souza, A. G., & Lajolo, F. M. (2004). Chemical composition and glycemic index of Brazilian pine (*Araucaria angustifolia*) seeds. *J. Agric. Food Chem*. 52, 3412-3416.

Corrêa, M. F. & Helm, C. V. (2010). Characterization of the nutritional composition of raw and cooked pinhão (*Araucaria angustifolia*). In: IX EVINCI, Colombo, Paraná, Brazil.

Corrêa, P. C., Resende, O., Martinazzo, A. P., Goneli, A. L. D., & Botelho, F. M. (2007). Mathematical modelling for description of the drying process of beans (*Phaseolus vulgaris* L.). *Engenharia Agrícola*, 27, 501- 507.

Costa, F. J. O. G., Leivas, C. L., Waszczynskyj, N., Godoi, R. C. B., Helm, C. V., Colman, T. A. D. & Schnitzler, E. (2013). Characterization of native starches of seeds of *Araucaria angustifolia* from four germplasm collections. *Thermochimica Acta*, 565, 172-177.

Daudt, R. M., Kulkamp-Guerreiro, I. C., Cladera-Oliveira, F., Thys, R. C. S., & Marczak, L. D. F. (2014). Determination of properties of pinhão starch: analysis of its applicability as pharmaceutical excipient. *Ind. Crops Prod*., 52, 420-429.

Doymaz, I. (2007). Air drying characteristics of tomatoes. *J. Food Eng*. 78, 1291-1297.

Dutra, T. L. & Stranz, A. (2003). The history of Araucariaceae: The contribution of fossils to the understanding of m aodern family adaptations in the Southern Hemisphere, with a view to their management and conservation. In: Ronchi, L.H. and Coelho, O.G.W. (org.) Technology, diagnosis and environmental planning. UNISINOS, São Leopoldo, Rio Grande do Sul, Brazil. 293-351.

Fannon, J. E., Hauber, R. J., & Bemiller, J. N. (1992). Surface pores of starch granules. *Cereal Chem*., 69, 284–288.

Freitas, T. B. de, Santos, C. H. K., Silva, M. V. da, Shirai, M. A., Dias, M. I., Barros, L., Barreiro, M. V., Ferreira, I. C. F. R., Gonçalves, O. H., and Leimann, F. V. (2018). Antioxidants extraction from Pinhão (*Araucaria angustifolia* (Bertol.) Kuntze) coats and application to zein films. *Food Pack. Shelf Life*, 15, 28-34.

Goneli, A. L. D., Corrêa, P. C., Resende, O., & Reis Neto, S. A. (2007). Study of the diffusion of moisture in wheat grains during drying. *Food Sci. Tech*., 27, 135-140.

Günhan, T., Demir, V., Hancioglu, E. & Hepbasli, A. (2005). Mathematical modelling of drying of bay leaves. *Energy Conv. Man*., 46, 1667-1679.

Henríquez, C., Escobar, B., Figuerola, F., Chiffelle, I., Speisky, H., & Estévez, A. M. (2008). Characterization of piñon seed (*Araucaria araucana* (Mol) K. Koch) and the isolated starch from the seed. *Food Chem*. 107, 592–601.

ISO 6579. (2002). Microbiology of food and food stuff – Horizontal method for the detection of *Salmonella* spp. (4th ed.), The international Organization for Standardization, Amendment 1: 15/07/2007.

ISO 7251. (2005). Microbiology of food and food stuff – Horizontal method for the detection and enumeration of presuntive *Escherichia coli* – Most probable number technique. (3th ed.), The international Organization for Standardization.

ISO 7932. (2004). Microbiology of food and food stuff – Horizontal method for the enumeration of presuntive *Bacillus cereus* – Colony count technique at 30ºC. (3th ed.), The international Organization for Standardization.

Klein, B., Pinto, V. Z., Vanier, N. L., Zavarese, E. R., Colussi, R., Evangelho, J. A., Gutkoski, L. C., & Dias, A. R. G. (2013). Effect of single and dual heat–moisture treatments on properties of rice, cassava, and pinhão starches. *Carb. Polym*., 98, 1578- 1584.

Madamba, P. S., Driscoll, R. H., & Buckle, K. A. (1996). Thin-layer drying characteristics of garlic slices. *J. Food Eng*., 29, 75-97.

McCready, R. M. & Hassid, W.F. (1943). The separation and quantitative estimation of amilose and amilopectina in potato starch. *J. Am. Chem. Soc.*, 65, 1154 -1157.

Midilli, A. & Kucuk, H. (2003). Mathematical modelling of thin layer drying of pistachio by using solar energy. *Energy Conv. Man*., 44, 1111-1122.

Olivera, F. C. (2008). Technological studies and of engineering for storage and processing of pinhão. 200 f. Thesis (PhD in Engineering) – Engineering College, Federal University of Rio Grande do Sul, Porto Alegre, Brazil.

Osorio, C., Carriazo, J. G, & Barbosa, H. (2011). Thermal and structural study of Guava (*Psidium guajava* L) powders obtained by two dehydration methods. *Química Nova*, 34, 636-640.

Peralta, R. M., Koehnlein, E. A., Oliveira, R. F., Correa, V. G., & Ferreira, I. C. F. R. Biological activities and chemical constituents of Araucaria angustifolia: An effort to recover a species threatened by extinction. Trends in Food Science & Technology 54 ,85-93, 2016.

Pereira AS et al (2018). Methodology of cientific research. [e-Book]. Santa Maria City. UAB / NTE / UFSM Editors. Retrived from https://repositorio.ufsm.br/bitstream/handle/ 1/15824/Lic_Computacao_Metodologia-Pesquisa-Cientifica.pdf?sequence=1.

Peroni, F. H. G. (2003). Structural and physical-chemical characteristics of starches obtained from different botanical sources. 135 f. Dissertation (Maters in Engineering and Food Science) - Food Science Postgraduate Studies, Paulista State University "Júlio de Mesquita Filho", São José do Rio Preto, São Paulo, Brazil.

Provesi, J. G., Valentim Neto, P. A., Arisi, A. C. M., and Amante, E. R. (2016). Antifreeze proteins in naturally cold acclimated leaves of *Drimys angustifolia*, *Senecio icoglossus* and *Eucalyptus* ssp. *Braz. J. Food Techn*. 19, e2016110.

Santos, A. J. dos, Corso, N. M., Martins, G., and Bittencourt, E. (2002). Productive and commercial aspects of pinhão in Parana State. *Floresta*, 32, 163-169.

Santos, C. H. K., Baqueta, M. R., Barros, L., Barreiro, M. F., Ferreira, I. C. F. R., Gonçalves, O. H., Bona, E., da Silva, M. V., and Leimann, F. V. (2018). Systematic study on the extraction of antioxidants from *pinhão* (*Araucaria angustifolia* (bertol.) kuntze) coat. *Food Chem.*, 261, 216-223.

Silva, C. V., Miguel, L. de A., & Reis, M. S. (2009). Comercialization of *Araucaria angustifolia* (pinhão) in Taquara Verde district, city of Caçador – SC. In: Brazilian Conference of Agroecology ,6; Latin-American Conference of Agroecology, 2., 2009, Curitiba. Resumos... *Rev. Bras. de Agroecologia*, 4, 841-844.

Stahl, J. A., Lobato, L. P., Bochi, V. C., Kubota, E. H., Gutkoski, L. C., and Emanuelli, T. (2007). Physicochemical properties of pinhão (*Araucaria angustifolia*, Bert, O. Ktze) starch phosphates. *LWT – Food Sci. Technol*., 40, 1206–1214.

Thomas, D. J. and Atwell, W. (1999) Starches: Practical Guides for the Food Industry. Minessota: Eagan Press, 94p.

Thys, R. C. S., Noreña, C. P. Z., Marczak, L. D. F., Aires, A. G., and Cladera-Olivera, F. (2010). Adsorption isotherms of pinhão (*Araucaria angustifolia* seeds) starch and thermodynamic analysis. *J. Food Eng.*, 100, 468-473.

Wang, Z., Sun, J., Chen, F., Liao, X. and Hu, X. (2007). Mathematical modelling on thin layer microwave drying of apple pomace with and without hot air pre-drying. *J. Food Eng*., 80, 536-544.

Wang, L. and Wang Y.J. (2004) Rice starch isolation by neutral protease and high-intensity ultrasound. *J. Cereal Sci*., 39, 291-296.

Whistler, R. L. E. and Paschal, E. F. (1965). Starch: Chemistry and Technology. Fundamental Aspects. Academic Press, N. Y. and London. 1, 579.

Williams, P. C., Kuzina, F. D., and Hlynka, I. (1970). A rapid colorimetric procedure for estimating the amylose content of starches and flours. *Cereal Chem*., 7, 412-420.

Wosiacki, G and Cereda, M. P. (1985). Characterization of pinhão starch. Part I. Extraction, physical and chemical properties of the starch fraction. *Starch/Stärke*, 37, 224–227.

Percentage of contribution of each author in the manuscript

Laisa Pelizzarro Pereira 70%

Edna Regina Amante 15%

Deise Helena Baggio Ribeiro 15%