

The effect of acid hydrolysis on the technological functional properties of *pinhão* (*Araucaria brasiliensis*) starch

Efeito da hidrólise ácida nas propriedades funcionais tecnológicas do amido de pinhão (Araucaria brasiliensis)

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Abstract

Technological functional properties of native and acid-thinned *pinhão* (seeds of *Araucaria angustifolia*, Brazilian pine) starches were evaluated and compared to those of native and acid-thinned corn starches. The starches were hydrolyzed (3.2 mol.L⁻¹ HCl, 44 °C, 6 hours) and evaluated before and after the hydrolysis reaction in terms of formation, melting point and thermo-reversibility of gel starches, retrogradation (in a 30-day period and measurements every three days), paste freezing and thawing stability (after six freezing and thawing cycles), swelling power, and solubility. The results of light transmittance (%) of pastes of native and acid-thinned *pinhão* starches was higher (lower tendency to retrogradation) than that obtained for corn starches after similar storage period. Native *pinhão* starch (NPS) presented lower syneresis than native corn starch (NCS) when submitted to freeze-thaw cycles. The acid hydrolysis increased the syneresis of the two native varieties under storage at 5 °C and after freezing and thawing cycles.

The solubility of NPS was lower than that of native corn starch at 25, 50, and 70 °C. However, for the acid-thinned *pinhão* starch (APS), this property was significantly higher ($p < 0.05$) when compared to that of acid-thinned corn starch (ACS). From the results obtained, it can be said that the acid treatment was efficient in producing a potential fat substitute from *pinhão* starch variety, but this ability must be further investigated.

Keywords: *unconventional starch source; modified starch; fat substitutes.*

Resumo

As propriedades funcionais tecnológicas do amido nativo e modificado (hidrólise ácida) de *pinhão* (*Araucaria angustifolia*) foram comparadas às propriedades do amido nativo e ácido hidrolisado de milho. As espécies de amido foram hidrolisadas (3.2 mol.L⁻¹ HCl, 44 °C, 6 horas) e avaliadas, antes e após a reação de hidrólise, de acordo com as análises de formação, fusão e termorreversão do gel, retrogradação (em um período de 30 dias, com medidas a cada 3 dias), estabilidade ao congelamento e descongelamento (após 6 ciclos de congelamento e descongelamento), poder de inchamento e índice de solubilidade. Os resultados obtidos demonstraram que o amido de *pinhão* apresenta menor tendência à retrogradação quando comparado ao amido de milho, tanto para a forma nativa quanto na modificada, após períodos similares de armazenamento. O amido nativo de *pinhão* (APN), quando submetido a sucessivos ciclos de congelamento e descongelamento, apresentou menor sinérese do que o amido de milho nativo (AMN). Nas temperaturas de 25, 50 e 70 °C, a solubilidade do APN foi menor do que a obtida pelo AMN. Entretanto, para a forma modificada, o amido de *pinhão* apresentou maior solubilidade ($p < 0,05$) do que o amido de milho. Através dos resultados, pode-se afirmar que o tratamento ácido modificado realizado no amido de *pinhão* foi efetivo para a produção de um potencial substituto de gordura, propriedade que deve ser testada e analisada em estudos futuros.

Palavras-chave: *fonte de amido não convencional; amido modificado; substituto de gordura.*

1 Introduction

Brazilian Pine (*Araucaria brasiliensis* syn. *A. angustifolia*) belongs to the Araucariaceae family and is the most economically important native conifer species in Brazil (ZANDAVALLI; DILLENBURG; DE SOUZA, 2004). The seed of this tree, harvested from April to August, is known as *pinhão*, and it is most commonly eaten after being cooked and peeled. *Pinhão* is also used as raw flour as an ingredient for several dishes, and is considered a source of starch (~36%), dietary fiber, magnesium and copper, besides producing a low glycemic index after its consume (CORDENUNSI et al., 2004). Although nutritional and technological aspects of *pinhão* are scarce in the scientific

literature, recent studies suggest that the *Araucaria* seed is a potential alternative source of starch extraction for industrial purposes (CORDENUNSI et al., 2004; BELLO-PEREZ et al., 2006; STAHL et al., 2007).

Starch is the most commonly thickening and gelling agent used by the food industry in the development of a large number of products such as soups, flans, sauces, and ready-to-eat food among others. In recent years, there has been an effort of researchers to find new sources of unconventional native starch with the necessary properties for the food industry, such as absence of syneresis, transparency, stability,

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and solubility in cold water (ZHANG et al., 2005). One of the reasons for such interest is the fact that native starch, despite being a good texture stabilizer and regulator in food systems, has limitations such as low resistance and thermal decomposition and high tendency to retrogradation, which limits its use in some industrial applications (HERMANSSON; SVEGMARK, 1996). Thus, according to Flores-Gorosquera et al. (2004), it is clear that, unlike the standard range of cereal grains (e.g. corn, wheat, rice) and tubers (e.g. potato, cassava), alternative starch sources are needed.

Currently, to overcome function problems of native starches, the modification of the polysaccharide molecule has been a frequent practice in order to better meet market needs.

Modified starches show better paste clarity and stability (by oxidation), increased resistance to retrogradation, and freeze-thaw stability (by acid hydrolysis) (BEMILLER, 1997). Stahl et al. (2007) previously reported the modification of *pinhão* starch by phosphorylation process. However, no reports were found on acid-thinned *pinhão* starch.

Starches used in gum candies and baked goods are generally modified with hydrochloric acid and are termed "acid-thinned" starches; they are obtained by chemical, physical, or enzymatic methods (AGBOOLA; AKIMBALA; OGUNTIMEIN, 1991). In the chemical method, hydrolyzed starches are produced when a concentrated suspension of starch (30-40 g/100 g solids) is treated with acid (hydrochloric acid and sulfuric acid) at temperatures lower than those of gelatinization (30-60 °C) for one or many hours of reaction time (FLECHE, 1985). Acid hydrolysis reduces the molar mass, and consequently it increases the free aldehyde group content. It also decreases viscosity, increases the solubility of the granules, minimizes syneresis, and causes gel thermo-reversibility when subjected to cooling after melting (WHISTLER; DANIEL, 1990) creating a potential fat substitute for the food industry.

In order for starch to be used as fat substitute, an amylose content of ~20% is recommended, as well as low levels of lipids and proteins attached to the surface (VANDERVEEN; GLINSMANN, 1992).

In a previous study, Cordenunsi et al. (2004) showed that the native *pinhão* starch has interesting structural and functional characteristics as a new source of starch; the granules had a low protein (3%) and lipids content (1.3%) and an amylose content of 26%. The objective of this study was to determine the effect of chemical modifications (acid hydrolysis) on the technological functional properties of *pinhão* starch.

2 Materials and methods

2.1 Materials

Seeds of *pinhão* and native corn starch (food grade) were obtained from the local market in Porto Alegre (RS, Brazil) between April and July (2009). All reagents were purchased from Merck.

2.2 *Pinhão* starch extraction

Pinhão starch was extracted from uncoated seeds (without the internal and external coats) by the method of Leonel et al.

(2003). The seeds were handily uncoated; the starch recovery from the coated seeds was 33.09%, and from the uncoated seeds it was 42.97%.

2.3 Preparation of acid-thinned *pinhão* (APS) and corn (ACS) starches

Acid-thinned starches were prepared according to the Mun and Shin (2006) method. A total of 10g/40 mL (w/v) starch slurry was prepared by adding aqueous HCl solution (3.2 mol.L⁻¹) to water bath (44 °C) with constant stirring (150 rpm). The pH of the starch suspension after the HCl addition was 2.8 ± 0.2. After six hours, the pH of the slurry was adjusted to 5.5 ± 0.2 by slow addition of aqueous sodium hydroxide (1 mol.L⁻¹). The slurry was centrifuged (2000 rpm/10 min/25 °C) and washed three times with distilled water (40 mL), followed by a new centrifugation. The supernatant pH was adjusted to 7.5 ± 0.2 by slow addition of aqueous sodium hydroxide (1 mol.L⁻¹) in order to determine the dextrose equivalent (DE). The starch was dried in a convection oven at 45 °C until reaching moisture content of 11-13% and was ground in a hammer mill (Fritsch – Pulverizette). For comparison purposes, corn starch (Maizena®, Brazil) was hydrolyzed in the same conditions.

2.4 Dextrose equivalent measure (DE)

The reducing sugars content was determined by DE analysis, carried out using dinitro-salicylic acid (DNSA) (MILLER, 1959). The concentration of dextrose equivalent was obtained by a standard curve previously prepared with solutions of different concentrations of glucose (glucose mg/mL solution).

2.5 Formation, melting point, and thermo-reversibility of the starch gel

The gel formation was determined following the methodology described by the National Starch and Chemical Corporation (NATIONAL..., 1985). The obtained gel was melted in a water bath at 100 °C under agitation, according to the procedure reported by Richter, Schierbaum and Klaus-Dieter (1973). The change in consistency was visually observed, and the temperature at which the gel completely melted was registered and regarded as the melting point of the gel. For the gel thermo-reversibility, the gel was melted in a water bath with constant stirring (Precision Scientific Reciprocal Shaking Bath) and allowed to cool down to room temperature, followed by refrigeration at 5 °C for 18 hours. The formation of gel was observed and registered (AMAYA-LLANO et al., 2008).

2.6 Light transmittance (%)

Light transmittance of starch paste from native and acid-thinned *pinhão* and corn starches was measured as described by Albrecht, Nelson and Stainberg (1960).

2.7 Paste freeze-thaw stability

Paste freeze-thaw stability was determined as described by White, Abbas and Johnson (1989). Starch gel (5%, w/w dry basis, total weight 28 g) was prepared by heating at 95 °C for

30 minutes. The resulting gel was allowed to cool down to room temperature for 15 minutes, and the gel was stored in a domestic freezer at $-5\text{ }^{\circ}\text{C}$ over night and thawed at ambient temperature ($25\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$) for 2 hours, repeatedly for up to six cycles. After the last freezing and thawing cycle, the gel was centrifuged at 6000 rpm for 30 minutes, and the water separated was measured. Stability was expressed as the percentage of water separated after six cycles of alternate freezing and thawing.

2.8 Swelling power and solubility

Swelling power and solubility patterns were determined according to the method proposed by Sathe and Salunkhe (1981) using the Equations 1 and 2, respectively:

$$\text{Swelling Power (SP)} = \frac{\text{weight of swollen granules (g)}}{\text{Sample weight in dry basis (g)}} \quad (1)$$

$$\% \text{ solubility} = \frac{\text{dry weight at } 120^{\circ}\text{C (g)}}{\text{Sample weight in dry basis (g)} \times 10} \times 100 \quad (2)$$

2.9 Statistical analysis

The data reported in the Tables were subjected to one-way analysis of variance (ANOVA) using Minitab Statistical Software version 7.0 (Minitab, Inc., State College, USA).

3 Results and discussion

3.1 Dextrose equivalent measure

The DE value of APS (acid-thinned *pinhão* starch) was 6.5 ± 0.026 . In the treatments with $\text{DE} > 2.5$ (percentage of hydrolysis > 0.95), the gel thermo-reversibility can be observed, which indicates a potential applicability of the starch as a fat substitute since thermoreversible starch gel, similarly to fat, has the ability to merge and solidify when exposed to high and low temperatures, respectively. According to the National Starch and Chemical Corporation (NATIONAL..., 1985), acid-thinned starches with $5.0 \leq \text{DE} < 8.0$ form thermoreversible gels of different consistencies, which are appropriate to be used as fat replacers. According to Zambrano and Camargo (1999), fat substitutes are obtained by starch hydrolysis when the degree of hydrolysis (DE value) generated by the reaction is not excessive (greater than 10) because when the acid hydrolysis overextends, either by excessive conditions of time, temperature or acid concentration, the gel-forming properties are lost and the starch has no more use as a fat substitute.

3.2 Formation, melting point, and thermo-reversibility of gel starches

The properties of formation, melting point, and thermo-reversibility of native and acid-thinned starches from *pinhão* and corn varieties are shown in Table 1. The thermo-reversibility analysis was performed in gels that melted under the conditions evaluated. The native starches formed gels that did not melt after heating demonstrating that the acid modification had a strong effect on the properties of both starch species analyzed in this study. The acid-thinned *pinhão* (APS) and corn starches (ACS)

formed gels, which proves that the degree of hydrolysis reached by the starch molecules in both species was not very extensive, retaining the required properties, such as gel formation, for starches to be used as fat substitutes (RADLEY, 1976).

NPS and NCS had the lowest gel texture characteristics when compared to those of acid thinned. It is known that acid treatment of starch causes partial hydrolysis of starch chains, resulting in much lower paste viscosity. However, when the paste cools down, acid-thinned starch chains tend to associate with each other more easily, forming a more rigid gel (HOSENEY, 1994).

The ACS melted at $23\text{ }^{\circ}\text{C}$ and APS, at $46\text{ }^{\circ}\text{C}$. Both showed gel thermo-reversibility when subjected to cooling, after melting. The melting point of APS indicates similarity with fats that have high melting point, which are more stable for storage under high temperatures even though its use is not recommended as a fat substitute in melt-in-the-mouth foods, such as ice cream and chocolate. According to Giese (1996), fat replacing starches work better in food systems with high humidity such as those found in mayonnaise, salad dressings, and in meat emulsions. In addition, they can be used in baked goods such as cakes, but not in cookies due to their low moisture content.

3.3 Light transmittance (%)

The influence of refrigerated storage on the paste clarity of the starches is shown in Figure 1. The reduction in percentage of transmittance of native and acid-thinned starches is a result of retrogradation tendency (STAHL et al., 2007). The light

Table 1. Formation, thermo-reversibility and texture characteristics of native and acid-thinned starches from *pinhão* and corn varieties.

Variety	Gel formation	Gel melting	Gel thermo-reversibility	Gel texture characteristics
NPS	Yes	No	-	soft
NCS	Yes	No	-	soft
APS	Yes	Yes	Yes	hard
ACS	Yes	Yes	Yes	hard

NPS: Native *pinhão* starch, NCS: native corn starch, APS: acid-thinned *pinhão* starch, ACS: acid-thinned corn starch

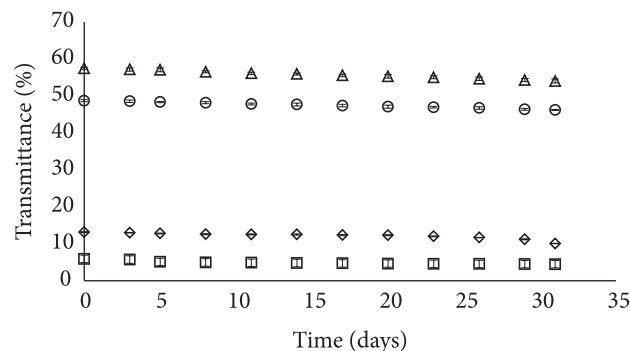


Figure 1. Effect of refrigerated storage on the paste clarity (% transmittance, at 625 nm) of native and acid-thinned starches from *pinhão* and corn. The error bars represent the standard deviation of mean. Native *pinhão* starch, ◇, native corn starch, □, APS, Δ and ACS, ○.

transmittance (%) of pastes of NPS and APS was higher than that obtained for corn starches after similar storage period, which evidenced lower levels of retrogradation in *pinhão* starches if compared to those of corn starches and, according to Bello-Pérez et al. (2006), this is in agreement with the lower content of amylose of *pinhão* starch (23.6%) in comparison to that of corn starch (30%) and suggests the use of *pinhão* starch in products stored for a long time and must have a soft texture, such as some baked products.

APS and ACS pastes showed higher % transmittance in comparison to those of NPS and NCS pastes. According to Lawal (2004), the leaching of amorphous regions during acid thinning enhances interactive bound formation between the amylopectin molecules thus increasing its light transmittance. This result agrees with that obtained by Sandhu, Singh and Lim (2007), who found an effective increase in % transmittance in the acid-thinned corn starch granules, when compared to that of native corn starch.

3.4 Paste freezing and thaw stability

Figure 2 shows that NPS had a greater tolerance (syneresis of 4.91%) than NCS (syneresis of 8.01%) after 6 freeze-thaw cycles. Stahl et al. (2007) reported water exudation value of approximately 77% for native *pinhão* starch and about 82% for native corn starch, both submitted to three cycles of freezing (-18 °C) and thawing (30° C). The difference between these results is probably due to differences in the measurement method and the types of starch used in each experiment.

The lower syneresis of *pinhão* starch, when compared to that of corn starch, makes it more suitable for use in custard, puddings and pie-fillings which are frozen stored (REGE; PAI, 1996; MARCON et al., 2007).

The acid-thinned starches had lower tolerance (extensive syneresis) to the freeze-thaw cycles than the native starches. The freeze-thaw stability of the acid-thinned starches was similar to that found by Takizawa et al. (2004) and Shirai et al. (2007), who attributed the high syneresis to a partial degradation of starch

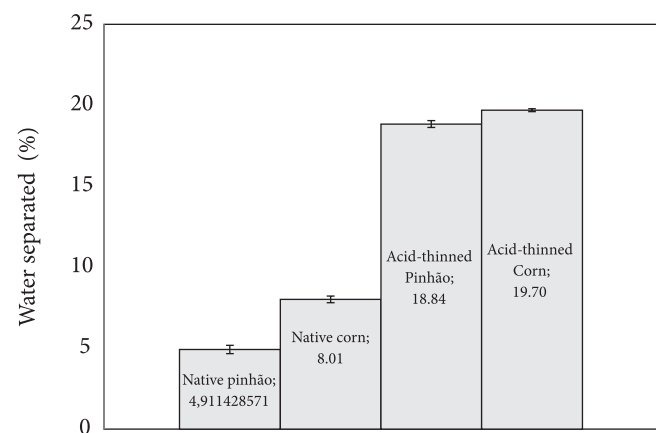


Figure 2. Effect of freeze-thaw cycles on the syneresis (% water separated after 6 cycles) of native and acid-thinned starches from *pinhão* and corn varieties.

macromolecular constituents during acid hydrolysis. According to these authors, the fragmentation of starch chains during the chemical treatment could be associated with the higher water liberation due to intensive molecular re-association.

3.5 Swelling Power (SP) and solubility

Swelling power (SP) of NPS was strongly correlated to the increases in temperature (Table 2). For native starches, the increase in SP is related to the breaking of intermolecular hydrogen bonds in amorphous areas allowing progressive water absorption, as mentioned by Bello-Pérez et al. (2006). However, for the native corn starch, the influence of temperature on SP was observed only above 70 °C, which, according to Li and Yeh (2001), is due to the gelatinization of corn starch, which starts only at 65.7 °C (T_0 , initial temperature of gelatinization), as demonstrated by thermal analysis (DSC).

It can be said that acid-thinned starches differed from native starches since their swelling power decreased with the increase of temperature. This may be related to the fact that during acid hydrolysis the amylose chains are fragmented forming a disorganized structure that cannot retain water during temperature increases (SANDHU; SINGH; LIM, 2007).

For the native species, at 25 and 60 °C, contrary to what was reported by Wosiacki and Cereda (1989), *pinhão* starch showed lower values of swelling power ($p < 0.05$) than those of corn starch, while at 50 °C, no significant difference was found between the species. However, at 70 °C, similarly to a study reported by Stahl et al. (2007) and Bello-Pérez et al. (2006), the value of the swelling power of *pinhão* starch was higher compared to that of corn starch. According to these authors, this finding is expected from the known inverse correlation between swelling power and amylose and lipid levels at temperatures close to 85 °C.

The SP of APS and ACS was higher ($p < 0.005$) than that of similar native starches at temperatures of 25 °C and 50 °C, whereas at 60 °C and 70 °C, the opposite was observed, as similarly reported by Sandhu, Singh and Lim (2007) when assessing acid-thinned corn starch. According to Lawal (2004), this is due to the reduction of the amorphous region of the starch granule, which reduces the number of sites that establish links with the water molecule. Studies have shown that genetic variations, climate and soil conditions, maturation stage, and

Table 2. Swelling power of native and acid-thinned starches (*pinhão* and corn).

Temperature	Swelling power (g water/g starch)			
	NPS	NCS	APS	ACS
25 °C	1.76 ^{aA} ± 0.13	1.93 ^{bA} ± 0.01	2.16 ^{cA} ± 0.01	2.34 ^{dA} ± 0.00
50 °C	1.91 ^{aB} ± 0.01	1.92 ^{aA} ± 0.00	2.25 ^{bB} ± 0.02	2.27 ^{bB} ± 0.02
60 °C	3.84 ^{aC} ± 0.02	4.18 ^{bB} ± 0.01	2.07 ^{cC} ± 0.03	2.18 ^{dC} ± 0.01
70 °C	11.08 ^{aD} ± 0.04	4.82 ^{bB} ± 0.02	1.55 ^{cD} ± 0.00	1.66 ^{dD} ± 0.00

The results are expressed as mean ± standard deviation (n = 3). Means followed by different lowercase letters in the same row indicate significant differences by Tukey test ($p < 0.05$). Means followed by different capital letters in the same column indicate significant differences by Tukey test ($p < 0.05$).

Table 3. Solubility of native and acid-thinned starches from *pinhão* and corn.

Temperature	Variety			
	NPS	NCS	APS	ACS
25 °C	0.31 ^{aA} ± 0.04	0.71 ^{bA} ± 0.01	7.52 ^{cA} ± 0.12	6.87 ^{dA} ± 0.07
50 °C	0.12 ^{aB} ± 0.01	1.48 ^{bB} ± 0.04	7.47 ^{cA} ± 0.12	6.93 ^{dA} ± 0.14
60 °C	4.02 ^{aC} ± 0.20	2.98 ^{bC} ± 0.11	8.65 ^{cB} ± 0.02	8.11 ^{dB} ± 0.04
70 °C	1.45 ^{aD} ± 0.09	2.85 ^{bC} ± 0.06	9.02 ^{cC} ± 0.05	8.19 ^{dB} ± 0.02

The results are expressed as mean ± standard deviation (n = 3). Means followed by different lowercase letters in the same row indicate significant differences by Tukey test (p < 0.05). Means followed by different capital letters in the same column indicate significant differences by Tukey test (p < 0.05).

harvest time also affect the swelling power (FRANCO et al., 2002), which could explain the first situation mentioned above. Man et al. (2012) reported that no significant difference between native and acid-thinned starch was found under 65 °C, but, at temperatures higher than 80 °C, the SP gradually decreased.

The solubility (Table 3) of NPS was lower than that of NCS at 25, 50, and 70 °C, which can be explained by the lower amylose content of *pinhão* starch compared to that of corn starch. Amylose dissociates from the granule, which contributes to solubility increase (MARCON et al., 2007). Wosiacki and Cereda (1989) reported a similar pattern for *pinhão* starch at temperatures higher than 85 °C. Bello-Pérez et al. (2006) reported an inverse behavior, with higher solubility values for *pinhão* starch, which according to these authors is in agreement with the lower temperature and enthalpy of gelatinization of *pinhão* starch assessed by DSC in their study.

APS and ACS showed higher values of solubility than the native starches. This occurs because the acid hydrolyzes preferentially the amorphous region of the starch molecule, where amylose is normally found (ATICHOUDOMCHAI et al., 2000), generating a significant reduction in the amylose chain length in the granule content, and its consequent dissolution resulting in solubility increase; fact that was evidenced with increases in temperature in the corn and *pinhão* species.

In addition, APS had significantly higher (p < 0.05) solubility than ACS showing a higher susceptibility of *pinhão* starch to acid hydrolysis, when compared to that of corn starch.

4 Conclusion

The functional properties of NPS (lower levels of retrogradation and syneresis and highest solubility when compared to native corn starch), which is a non-conventional source of starch, suggest it may have potential use in food systems. The acid hydrolysis (3.2 mol.L⁻¹ HCl and 44 °C) of *pinhão* and corn starches caused gel thermo-reversibility, lower tendency to retrogradation of starch pastes, and higher solubility at an economically viable reaction time (6 hours). Furthermore, the APS showed a melting point (46 °C) close to that of the conventional fats (37-45 °C), which may indicate that the *pinhão* starch could be used as a fat substitute when the gel is prepared (5%, w/w dry basis, total weight 28 g) by heating at 95 °C for 30 minutes. However, this applicability is limited to

frozen or refrigerated food since the acid hydrolysis reduced the tolerance of both starches to refrigerate storage (5 °C) and to the freeze-thaw cycles.

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