

Production of partially gelatinized cassava starch: effects of preheating temperature and starch concentration on physicochemical characteristics during the spray-drying process

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Abstract

Starch has application in several industrial sectors, such as food, textile, paper, pharmaceutical, among other industries. To meet this demand, native starches have been modified by chemical, physical and enzymatic methods. Cassava is the second source of starch. Furthermore, understanding the effects of spray-drying modification on the structural and physicochemical characteristics of its starch is important. Therefore, this study aimed to evaluate the effects of the main interfering factors in the process of spray-drying on the characteristics of cassava starch, aiming at increasing the industrial applicability of this starch. A Central Composite Rotational Design (CCRD) was employed to assess the experimental data. Experimental design included four factorial points, four axial points and three replicates of the central point. The starch concentration ranges from 5 to 11 % and preheating temperature ranges from 54 to 60 °C. Results showed influence of the variable factors on the characteristics of cassava starch. The processing conditions that allowed obtaining pregelatinized starches with higher viscosity at room temperature, higher resistance to hot and agitation, lower retrogradation tendency, and with partial solubility, desired quality parameters for this product were: 6 % of starch concentration (wet basis) and 60 °C of preheating temperature.

Keywords: pregelatinization starch; structure; viscosity.

Abbreviation: DSC_differential scanning calorimeter; T_temperature; ΔT _temperature range; ΔH _enthalpy change; DG_gelatinization degree; Retro_retrogradation; SSA_specific surface area; RVA_Rapid Visco Analyzer; RVU_Rapid Visco Unit.

Introduction

The starch is biodegradable, comes from renewable sources and is relatively cheap. Therefore, it can be used in food, chemical, textile, papermaking, and medicine, among other industries (Hoover et al., 2010).

Different fractions of polysaccharides, amylose and amylopectin, form the starch. These polysaccharides are composed of chains of glucose molecules differing from each other in size and shape. Amylose consists essentially of $\alpha(1,4)$ glycosidic bonds forming a linear helical structure. Amylopectin displays a semi-crystalline structure, highly branched, with $\alpha(1,4)$ glycosidic bonds and 4-5 % of $\alpha(1,6)$ glycosidic bonds, responsible for the formation of branches. Amylopectin and amylose are arranged as a semi-crystalline complex, involving the formation of hydrogen bonds between double helices composed primarily of branched chains of amylopectin (Warren et al., 2016).

Starches applications are dependent on their physical and chemical properties, environmental and agronomic factors, as well as the variations in properties across diverse

cultivars. Native starches are structurally too weak and functionally too restricted for application in today's advanced technologies; processing is necessary to engender a range of functionality (Beninca et al., 2008; Lacerda et al., 2008). To overcome such drawback, physical, chemical and enzymatic processes can be used to modify starch properties (Chiu and Solarek, 2009). These modification methods could improve the functional properties of native starches and thereby, contribute to increasing their use in various industrial sectors. Physical modifications of starch have gained wide acceptance as they do not require the use of chemical reagents.

Pregelatinized starches can be divided in two categories: fully gelatinized and partially gelatinized starches. Partially gelatinized starches present a mixture of properties inherent to both native and fully gelatinized starches (Adedokun and Itiola, 2010; Lai, 2001; Liu et al., 2010; Zhang et al., 2013). Fully gelatinized starches can be used as binders in pharmaceutical formulations and as main ingredients, bulk

agents, or thickeners for many food products. In many cases, the use of pregelatinized starch instead of native starch allows for simplified and shortened production process. Pregelatinized starch can be produced by heating a starch suspension at a certain temperature for a specific time, before applying spray-drying.

The spray-drying process can produce uniformly cooked or gelatinized starch granules with minimal shear and heat damage (Haghayegh and Schoenlechner, 2011); however, this process also can disrupt the ordered starch granular structure, thereby yielding amorphous starch (Fu et al., 2012). The different conditions during the process will be responsible to intensity in the characteristics of the pregelatinized starch.

Cassava (*Manihot esculenta*) is mainly produced in tropical regions, at a low cost, and represents the main source of starch in these regions. The world production of cassava reached 268 million of tons in 2014 (FAO, 2017). According to the International Starch Institute (International Starch Institute, 2016), the world production of starch has grown at an average rate of 4 % per year and cassava starch is increasing its market share, representing about 7.5 % of the world starch market. Cassava starch presents high peak viscosity, low retrogradation, clearness, and high transparency paste, with light flavor (Rolland-Sabate et al., 2013), and these characteristics can be changed by physical methods.

The spray-drying process is a method aimed at improving native starches properties, thereby increasing their market values. The effects of spray-drying processes on starches from different sources have been investigated (Fu et al., 2012; Gharsallaoui et al., 2007; Haghayegh and Schoenlechner, 2011; Izidoro et al., 2011; Zhu, 2015). However, the effects of spray-drying on starches obtained from tubers are still unknown. From the industrial point of view, understanding the property changes undergone by tuberous starches during this process is of importance toward improving their functional properties, as well as increasing their production.

Considering the importance of process parameters during the production of pregelatinized starches and the increased number of cassava starch applications, this study aimed at investigating the effect of starch concentration and temperature during the spray-drying process on the morphological characteristics and physical properties of cassava starch.

Results and discussion

Characteristics of unmodified cassava starch

The unmodified cassava starch presents variable characteristics, which change mainly among genotypes, and with the conditions and stage of plant growth. Table 1 shows the results obtained in the analysis of unmodified cassava starch used in this study and shows that this starch showed typical characteristics already reported by several authors as described in the review of Zhu (2015) i.e. circular granules, A-type of X-ray pattern, low temperature of gelatinization, high apparent viscosity and low retrogradation tendency.

Starch crystallinity and thermal properties

Regression analysis of crystallinity and thermal properties are shown in Table 2 and the response surface drawn from the adjusted model are shown in Figure 1. Native cassava starch displayed an A-type diffraction pattern, with the most intense peaks found at 15, 17, 18 and 23° 2 θ . Spray-dried cassava starch did not show any change in diffraction pattern (A-type).

Crystallinity varied between 21.66 and 30.10 %. The results showed that the crystallinity decreases with increasing preheating temperatures (Fig. 1A). The intensity of the process influenced in the structure disintegration of the starch, showing a decrease in percentage crystallinity and a loss of crystalline pattern with the linear increase in gelatinization temperature. This disintegration occurred due to semi-crystalline structure of the native starch, because when starch is heated in excess water, can occur the disorder on structure of starch, with an increase in absorption of water. With heating at higher temperature, starch polymers become more mobile, reduce or lose their intermolecular interactions, which induce the disintegration of ordered structure (Fu et al., 2012). Thus, results showed that the spray-drying process resulted in a progressive decrease in starch crystallinity (Table 1).

The gelatinization process is mainly dependent on the dissociation of the helical structure present in the starch chains, and the energy required to dissociate this structure varies across different sources of starch. The onset and peak temperatures of gelatinization varied between 58.99 and 63.25 °C and between 64.49 and 67.35 °C, respectively. The response surface drawn from the adjusted model showed higher onset and peak temperatures of gelatinization with increased in preheating temperatures (Fig. 1B and 1C). Conclusion temperature and temperature range varied from 71.93 to 73.69 °C and from 9.78 to 14.70 °C, respectively. The regression analysis did not show any effect on the conclusion temperature; however, the temperature range showed a negative linear effect of temperature (Fig. 1D). The decrease in temperature range with increasing preheating temperatures could be caused by higher homogeneity among the crystallites.

The enthalpy changes and gelatinization degrees ranged from 5.51 to 11.88 J g⁻¹ and from 16.66 to 61.29 %, respectively. The enthalpy change of the starch is attributed to amylopectin crystallite disorder. As observed in crystallinity results, the extent of crystallinity decreased with intensity of modification of the starches, and as a result, the enthalpy change values of spray-dried starches showed similar behavior, due to the disintegrated of starch structure, as thickness of crystals, polymorphic structure and free energy of surface of face side, which affect the gelatinization temperature of starch granules (Błaszczak et al., 2007; Fu et al., 2012; Santos et al., 2018). Regression analysis of the enthalpy change showed a linear negative effect of preheating temperature, while for the gelatinization degree a linear positive effect was shown (Fig. 1E and 1F).

Spray-dried starches with higher preheating temperatures showed higher gelatinization degrees. The increase in the onset and peak temperatures of gelatinization, combined with the decrease in temperature range and crystallinity,

resulted in a reduction of the energy required for the gelatinization of the starch granules. This fact can be explained by the higher degree of modification of the starch granules at higher temperatures, weakening their structure. Onset temperature of retrograded starches ranged from 36.11 to 38.88 °C, and the regression analysis did not show any significant effect. Regression analysis showed linear and quadratic negative effects of preheating temperature on peak temperature, which varied between 45.66 and 48.56 °C (Fig. 1G). The conclusion temperature of retrograded starches ranged from 55.05 to 57.02 °C, and the regression analysis showed a negative quadratic effect of preheating temperature (Fig. 1H). Range temperature after retrogradation varied between 16.74 and 19.52 °C, and the regression analysis did not show any significant effect.

The enthalpy change of retrograded starches ranged from 4.82 to 6.67 J g⁻¹, however, effect of the variable parameters of the process on this property was not observed. After spray-drying process, starch samples showed lower enthalpy change than that native cassava starch, due to the fragility and instability of the structure formed during storage at low temperatures, which decreases the energy required for starch gelatinization (Lawal, 2005).

The results of thermal properties of retrograded starch to the peak and conclusion temperatures were already expected, due to the strong tendency of formation of hydrogen bonds between the hydroxyl groups of the adjacent molecules of the starch. This reorganization happens to a lower extent after gelatinization, therefore, gelatinization of crystals requires less energy (Karim et al., 2000), and consequently, lower gelatinization temperatures. The percentages of retrograded starches varied between 33.83 and 46.85 %, and the regression coefficient analysis did not show any significant effect on the parameters under study. Starch retrogradation is undesirable for some food products, such as bread and pudding, because it causes staling and syneresis and, thus, shortens the shelf life of the products (Karim et al., 2000; Jane, 2004).

Starches morphology

Starch granules range in size (from 1 to 100 µm diameter) and shape (polygonal, spherical, lenticular), and can vary greatly with regard to content, structure and organization of the amylose and amylopectin molecules, the branching architecture of amylopectin, and the degree of crystallinity (Lindeboom et al., 2004). Native cassava starch granules showed predominantly circular shape, and some concave-convex, with an average granule size (D[4.3]) of 15.7 µm, with a unimodal distribution (Fig. 1B and 1b), in agreement with the cited in the literature (Leonel, 2007; Zhu, 2015).

In treatment at 54 °C with starch concentration of 8 %, the polarized light images show the Maltese cross in most of the granules, revealing slight modification of the starch under the effects of the variables applied in this treatment (Fig. 2B and 2b). Comparing the treatments with same temperature (57 °C) and different concentrations, the treatment with median concentration (8 %) presented a higher number of granules at the beginning of gelatinization (Fig. 2C, 2D, and 2E). The images obtained after treatment at 57 °C with starch concentration of 8 % illustrate the characteristic change occurring at the beginning of gelatinization, a small

opening of the hilum within the expansion of the Maltese cross (Fig. 2E and 2e). However, a different result was observed after treatment at 60 °C with 8 % of starch concentration, which generated the most intense effect, yielding a few intact granules and several pieces of granules, as well as fully gelatinized granules (Fig. 2F and 2f).

The specific surface area (SSA) is defined as the total area of the particles divided by the total weight, based on the assumption that particles are both spherical and non-porous (Molenda et al., 2006). The SSA of spray-dried starch varied between 0.395 and 0.498 µm. Regression analysis showed a linear negative effect of preheating temperature (Table 3, Fig. 3A).

Average granule sizes of spray-dried starch varied between 12.12 and 15.21 µm. Regression analysis showed a linear positive effect of preheating temperature (Table 3, Fig. 3B). These results confirm that granule size increases with increasing of preheating temperatures.

The granules of spray-dried starch decrease in diameter, but also presented a wrinkled appearance, which can be evidenced by the decrease in the surface area than that of native starch, that showed 26.71 and 0.31 µm for granule size (D[4.3]) and SSA, respectively (Table 1).

The parameter D(0.5) is the size in microns at which 50 % of the sample is smaller and 50 % is larger, D(0.9) gives the size of particle below which 90 % of the sample lies. The median diameter (D(0.5)) and largest diameter (D(0.9)) of spray-dried starch varied between 12.87 and 16.24 µm and 19.24 and 21.77 µm, respectively. An increase in the median diameter and larger particles was observed with the increase in temperature (Fig. 3C and 3D), due to the higher water absorption and partial gelatinization, until the structure was ruptured, and the number of smaller particles consequently increased. The median diameter (D(0.5)) and largest diameter (D(0.9)) decreased comparing than that native cassava starch, that showed 21.93 and 43.70 µm, respectively.

Pasting properties, swelling powder (SP) and solubility (S)

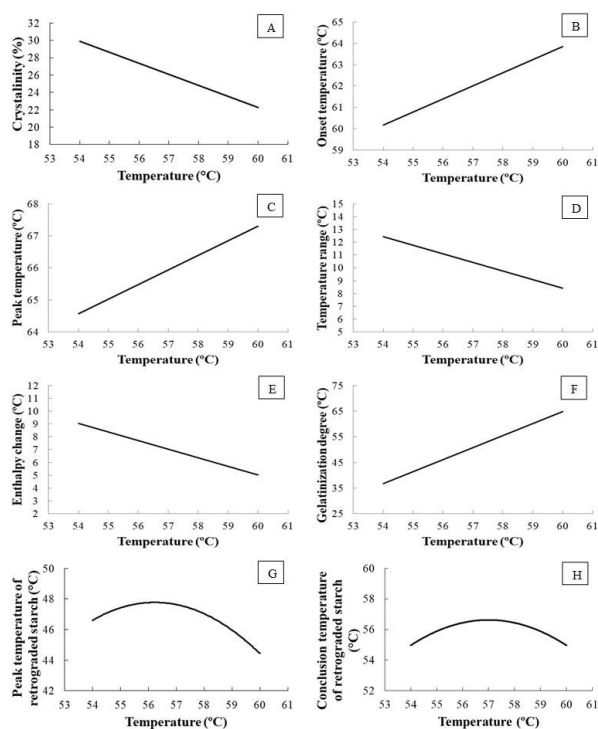
The regression coefficients estimated by the adjusted model from the results and their significance, as well as their corresponding determination coefficients, regarding the parameters relative to pasting properties, swelling power, and solubility, are presented in Table 4, while the response surface data for each variable are shown in Fig. 4.

Cold viscosity varied between 0.46 and 12.04 RVU. Regression analysis showed a linear positive effect of preheating temperatures, while for starch concentration, it showed linear negative and quadratic positive effects, as well as an interaction between both parameters (preheating temperature and starch concentration). The response surface drawn from the adjusted model showed higher cold viscosity at high preheating temperatures and lower starch concentrations (Fig. 4A).

When the starch is heated to higher temperatures, the structure of the granules becomes frangible and large granules can disintegrate (Fu et al., 2012). According to the existing literature, the treatments carried out at higher temperatures exhibit starch granules at breaking point, as well as broken granules, resulting in an increased average

Table 1. Characteristics of unmodified cassava starch (native starch).

Parameters (Unit)	Value	Parameters (Unit)	Value
Crystallinity	35.57±1.70 (A-type pattern)	SSA	0.31±0.02
Gelatinization		D[3.2]	19.61±0.95
T _{onset} (°C)	59.41±0.34	Granule size D[4.3]	26.71±0.54
T _{peak} (°C)	65.63±0.32	D(0.1)	11.46±0.62
T _{conclusion} (°C)	73.72±0.81	D(0.5)	21.93±1.08
ΔT (°C)	14.44±0.62	D(0.9)	43.70±1.21
ΔH (J g ⁻¹)	14.22±0.31	RVA (RVU)	
Retrogradation		Cold Peak	1.24±0.02
T _{onset_retro}	37.32±0.33	Peak	323.17±9.63
T _{peak_retro}	48.23±0.24	Breakdown	186.82±9.54
T _{conclusion_retro}	56.16±0.32	Final viscosity	332.83±7.41
ΔT _{retro} (°C)	18.84±0.19	Seatback	196.43±4.24
ΔH _{retro} (J g ⁻¹)	5.40±0.08	Swelling power	20.01±0.64
Retrogradation (%)	37.68±0.73	Solubility	16.43±0.29

**Fig 1.** Effect of temperature on crystallinity and thermal parameters of spray-dried cassava starches. A, Crystallinity; B, Onset temperature; C, peak temperature; D, Temperature range; E, Enthalpy change; F, Gelatinization degree; G, Peak temperature of retrograded starch; H, Conclusion temperature of retrograded starch.**Table 2.** Regression equation of crystallinity and thermal parameters of spray-dried cassava starch (codified model).

Parameters	Pr>f	R ²	F value	
Crystallinity	Y = 26.08 - 2.34X ₁	0.0008	0.6373	9.13
Gelatinization				
T _{onset}	Y = 62.01 + 1.13X ₁	0.0006	0.8792	7.28
T _{peak}	Y = 65.93 + 0.84X ₁	0.0001	0.9392	15.44
ΔT	Y = 10.42 - 1.23X ₁	0.0049	0.7566	3.11
ΔH	Y = 7.02 - 1.23X ₁	0.0233	0.6817	2.14
GD	Y = 50.77 + 8.66X ₁	0.0233	0.6818	2.14
Retrogradation				
T _{peak}	Y = 47.52 - 0.66X ₁ - 0.72 X ₁ X ₁	0.0111	0.7230	2.61
T _{conclusion}	Y = 56.53 - 0.57X ₁ X ₁	0.0048	0.8022	4.06

T, temperature; ΔT, (T_{conclusion}-T_{onset}); ΔH, enthalpy change; GD, gelatinization degree; X₁, preheating temperature; X₂, starch concentration; R², determinant coefficient.

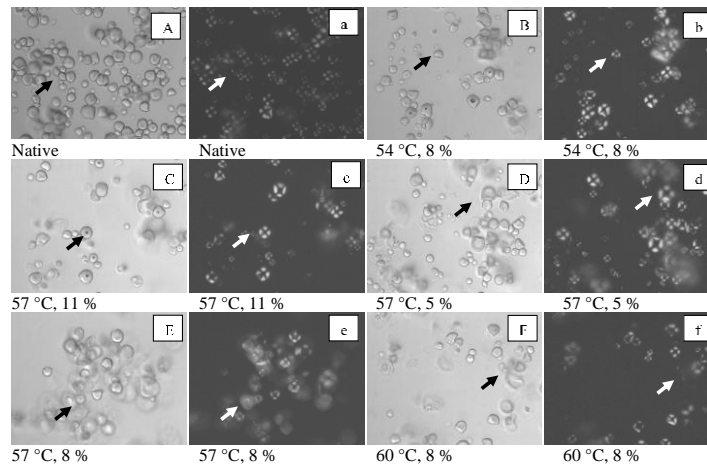


Fig 2. Bright-field light microscopy images and the corresponding polarized light microscopy images for native and spray-dried cassava starches. Axial and central treatments of experimental design. Uppercase letters are images under bright-field and lowercase letters under polarized light. A, native starch; B, Treatment 54 °C, 8 %; C, Treatment 57 °C, 11 %; D, Treatment 57 °C, 5 %; E, Treatment 57 °C, 8 %; F, Treatment 60 °C, 8 %.

Table 3. Regression coefficients of spray-dried starch granule sizes (codified model).

Parameters		Pr>f	R ²	F value
SSA	$Y = 0.47 - 0.02X_1$	0.0153	0.6406	1.78
Granule size D[4.3]	$Y = 14.30 + 0.79X_1$	0.0161	0.6438	1.81
D(0.5)	$Y = 13.61 - 0.75X_1$	0.0168	0.6396	1.77
D(0.9)	$Y = 20.81 - 1.23X_1$	0.0150	0.6525	1.88

X₁, preheating temperature; R², determinant coefficient.

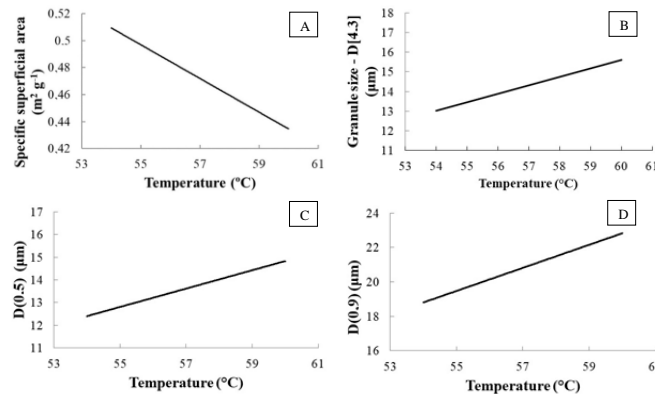


Fig 3. Effect of temperature on the parameters analyzed using the Mastersizer on spray-dried cassava starches. A, Specific superficial area (SSA); B, Granule size D[4,3]; C, D, D(0.5); E, D(0.9).

Table 4. Regression coefficients of parameters analyzed by RVA, swelling power, and solubility of spray-dried cassava starch (codified model).

Parameters		Pr>f	R ²	F value
Cold viscosity	$Y = 2.37 + 3.20X_1 - 2.46X_2 + 1.74X_2X_2 - 1.85X_1X_2$	<0.001	0.9875	79.02
Peak viscosity	$Y = 323.11 - 82.64X_1 - 45.02X_1X_1$	0.0012	0.9646	27.27
Breakdown	$Y = 186.78 - 58.20X_1 - 33.31X_1X_1$	0.0017	0.9600	24.05
Final viscosity	$Y = 332.76 - 37.66X_1 - 16.35X_1X_1 + 12.78X_1X_2$	0.0007	0.9726	35.50
Setback	$Y = 194.55 - 13.22 X_1 + 8.63X_2$	0.0067	0.9294	13.16
Swelling Power	$Y = 50.10$	0.4588	0.5243	1.10
Solubility	$Y = 46.03 + 9.10X_1X_1 + 5.54X_2X_2$	0.0238	0.7532	3.05

X₁, preheating temperature; X₂, starch concentration; R², determinant coefficient.

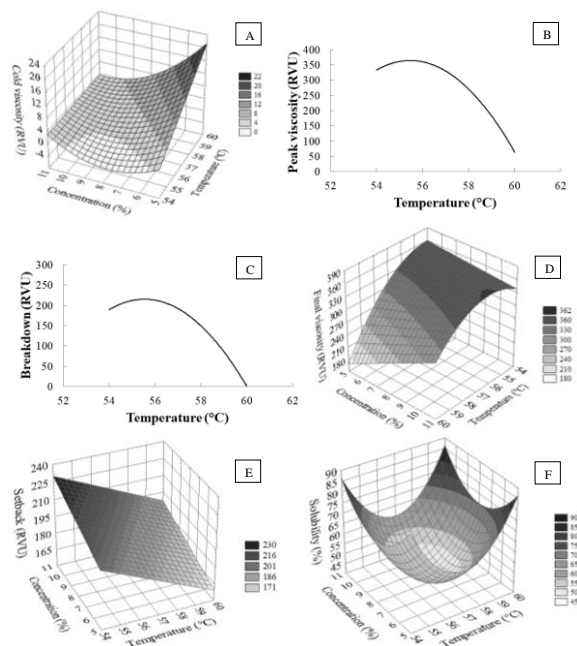


Fig 4. Effect of temperature and starch concentration on the parameters analyzed by RVA, on spray-dried cassava starches. A, cold viscosity; B, Peak viscosity; C, Breakdown; D, Final viscosity; E, Setback; F, Solubility.

Table 5 Independent variables and levels of variation of parameters during the spray-drying process.

Independent variables	Levels of variation				
	-α	-1	0	1	+α
Preheating temperature (°C)	54.0	55.0	57.0	59.0	60.0
Starch concentration (% wet basis)	5.0	6.0	8.0	10.0	11.0

$\alpha = 1.414$.

granule size and in cold viscosity, accompanied by a decrease in crystallinity. Peak viscosity ranged from 100.99 to 352.73 RVU. The regression analysis showed linear and quadratic negative effects of the temperature, showing that the increase in temperature at the central point led to an increase in viscosity; however, further maintaining the increase in temperature result in a reduction in the peak viscosity, evidencing a higher treatment intensity (Fig. 4B). Peak viscosity indicates a hot water swelling capacity of the starch granules, which reflects the ability of the ordered starch to hydrate and swell. Results showed that starches lost their ordered structure during spray-drying process and displayed reduced swelling abilities. Breakdown ranged from 69.41 to 205.53 RVU. Regression analysis showed linear and quadratic negative effects of the preheating temperature, and the same impact was observed on peak viscosity (Fig. 4C). The final viscosity of the spray-dried starch ranged from 240.41 to 363.48 RVU. Regression analysis showed a linear positive effect of starch concentration and linear and quadratic negative effects of preheating temperature, as well as the interaction between these two parameters (Fig. 4D). The response surface drawn from the adjusted model showed higher final viscosity at high preheating temperatures and low starch concentrations. Treatments at high temperatures and low to medium concentrations yielded the highest cold viscosities, as well as the lowest peak and breakdown viscosities. These results showed an increased degradation of the starch granules,

which could be correlated with both the reduction in crystallinity and the increase in average granule size. The changes occurring in starch granules during gelatinization and retrogradation are the main determinants of pasting properties, which are mainly evaluated through changes in viscosity during heating and cooling of starch suspensions (Lustosa et al., 2009). This characteristic is paramount from an industrial point view, due to the multiple applications of these starches in foods. Setback is a measure of starch retrogradation and depends on changes occurring within the granule structures. Setback ranged from 162.91 to 209.66 RVU, and regression analysis have showed a linear negative effect of preheating temperature and a linear positive effect of starch concentration (Fig. 4E). Therefore, higher preheating temperatures and lower starch concentrations result in lower setback. Swelling power of spray-dried starches ranged from 46.48 to 83.52 g g^{-1} , it was higher than that of native starch (20.01 g g^{-1} , Table 1), and regression analysis did not show any significant effect. However, the solubility varied between 45.18 and 71.88 %, showing higher values than that of native starch (16.40 %, Table 1), and regression analysis showed negative quadratic effects of both preheating temperature and starch concentration (Fig. 4F). These results show that both lower and higher values of temperature and concentration yield in higher solubilities. In spray-drying process, the starch is partially converted to an amorphous mass (Fu et al., 2012; Sing and Van den Mooter,

2016), showing reduced crystallinity, increased granule size and gelatinization, and viscosity development at room temperature. These factors make the spray-dried starch able to be used in products that require high viscosity during production, and also in the final product. Spray-drying process has seen increasing application as a tool for the incorporation of bioactive ingredients into foods, as flavorings and functional ingredients, especially since it protects them from moisture, heat, oxygen, and other adverse conditions (Gosh, 2006; Tontul and Topuz, 2013; Anal and Singh, 2007).

Materials and methods

Plant materials

The plants of cassava (*Manihot esculenta*), cv IAC 14, were cultivated in according to the technical recommendations for the crop and harvested after 22 months of planting. The unmodified cassava starch was extracted in industrial processing by Flor de Lotus industry, located in Cândido Mota city, São Paulo state, Brazil
All reagents were of ACS grade.

Experimental design

A Central Composite Rotational Design (CCRD) was employed to predict responses based on few sets of experimental data, in which all factors varied within a chosen range. For this process, a two-factor and five-level experimental design was adopted (Table 5). Experimental design included four factorial points, four axial points, and three replicates of the central point, with total of 11 treatments. The preheating temperatures ranged from 54 to 60 °C, and starch concentrations varied between 5.0 and 11.0 %.

Spray drying process

The spray-drying process was carried out following the methodology described by Fu et al. (2012). Starch dispersions were prepared according to the experimental design, as starch concentration (w/w, dry starch basis) and preheating temperatures. Starch dispersion was prepared with add starch in distilled water at 40±1 °C. Starch dispersion was kept under stirring in a water bath for 10 minutes (after reaching the desired temperature) and beakers containing the starch dispersions were covered with plastic film to minimize water evaporation. After this time, the hot dispersions of starch were then spray-dried (Spray-dryer, MSD 0.5 model, LABMAQ, São Paulo, Brazil) fitted with a double-atomizer nozzle, with 0.7 mm diameter of the nozzle hole. The inlet and outlet temperature were 130 and 105 °C, respectively, and the feed rate was 0.5 L h⁻¹. The flow of compressed air and hot air were 0.40 L min⁻¹ and 3.8 m³ min⁻¹, respectively, and air pressure was set at 6 bars.

Starch crystallinity

To analyze X-ray diffraction patterns and percentage crystallinity, starch samples were incubated in a desiccator for 10 days with a saturated solution of BaCl₂ (Barium

chloride, 25 °C, a_w = 0.9) in order to reach humidity equilibrium (90 %) and improve diffraction diagram quality. X-ray patterns were examined using a goniometer unit (RINT2000, Rigaku MiniFlex 300, Rotaflex, Tokyo, Japan), with copper K_α radiation (λ = 0.1542 nm). The scanning speed was 1° min⁻¹ at 50 kV and 100 mA (Santos et al., 2016). The percentage crystallinity was calculated based on the relationship between the peak and total areas, using Origin v.7.5 software (Microcal Inc., Northampton, Massachusetts, USA) (Nara and Komiya, 1983).

Thermal properties

Spray-dried starch samples (2.5 mg, dry basis) were studied using a differential scanning calorimeter (DSC, Pyris 1, Perkin Elmer, Norwalk, CT, USA), used with distilled water (7.5 µL). The sealed pans were kept at room temperature for 2-3 h to equilibrate. The scanning temperature range was 25 to 100 °C and the heating rate was 10 °C min⁻¹ (Santos et al., 2016). The degrees of gelatinization of spray-dried starch samples were calculated according to the procedure described by Di Paola et al. (2003) as following equation:
DG (%) = [1 – (ΔH of processed starch / ΔH of native starch)] x 100

Retrogradation properties were assessed following the same procedure as those used for the determination of the thermal properties of gelatinization. After thermal scanning, aluminum pans were kept 14 days at 4-6 °C, and then analyzed. Retrogradation percentage was obtained by applying the following equation:

$$R = (\Delta H \text{ of processed retrograded starch} / \Delta H \text{ native retrograded starch}) \times 100$$

Morphology

To evaluate the birefringence of the starch granules samples, these were dispersed in a 50 % aqueous solution of glycerol, applied on a slide, and examined under a binocular optical microscope (Nikon, Melville, NY, USA), under bright-field and polarized light. The software used to capture images was the Infinity Capture Application version 6.2.0. The average granule sizes of starch samples were determined using the laser light diffraction technique with a He-Ne laser (Mastersizer 2000, Malvern Instruments Ltd., Worcestershire, UK). Anhydrous ethanol was used as the solvent. The refractive indexes of the starch samples and the solvent were 1.500 and 1.360, respectively. Average granule sizes of the particles were obtained using the software provided by the manufacturer. The specific surface area (SSA) is defined as the total area (m² g⁻¹), and D[4,3] is the average granule size (µm). The largest (10 %) particle size (D(0,9), µm), and the median diameter (D(0,5), µm) were also determined (Mesquita et al., 2016).

Pasting properties

Samples were analyzed using a Rapid Visco Analyzer (RVA Super 4, Newport Scientific, Warriewood, New South Wales, AU), by *Extrusion 1* program. Starch samples (2.5 g, 14 % w/w) were weighted, and 25 g of distilled water was added. Samples were analyzed using the *Extrusion 1* program. The

samples were equilibrated at 25 °C for 1 min, heated to 95 °C at a rate of 6 °C min⁻¹, held at 95 °C for 5 min and then cooled down to 25 °C at rate of 6 °C min⁻¹, while stirring at 160 rpm was applied throughout the whole experiment. Cold viscosity, peak viscosity, final viscosity, breakdown, and setback properties were measured.

Swelling power (SP) and solubility (S)

The starch samples (0.2 g, wet basis) were placed in centrifuged tubes and was added 20 g with the distilled water, considering the moisture of starch. The suspension was immersed in a 95 °C water bath for 30 minutes, with constant agitation. The samples were centrifuged at 2,000 g for 15 minutes, then collecting 5 mL of the supernatant, which was subsequently left to dry in an oven at 105 °C until constant weight was reached (Schoch, 1964). The decanted samples were then weighed. The parameters were determined by the following equations:
Solubility (%) = dried supernatant weight x 400 / sample weight

Swelling power (g g⁻¹) = decanted sample weight x 100 / sample weight x (100 - Solubility)

Statistical analysis

The significant terms in the model were determined by analysis of variance (ANOVA) for each response. Response surface methodology describes the behavior of a system in which the independent variables (X_k) and the dependent variable or response (Y_i) are combined. The response is a function of the levels at which these factors are combined and defined. The model was fitted by the stepwise selection of the SAS program, and the model obtained was validated by the *F* test using the pure error mean square as denominator. The second-order polynomial response surface models were generated from adjusted models using the Statistica® 7.0 (StatSoft Inc.), and then fitted to each of the response variables (Y). All measurements were carried out in triplicate.

Conclusion

This study allowed extending the knowledge on the changes undergone by cassava starch granules produced by preheating followed by spray-drying, in term of morphological and physical characteristics. This process allows the production of partially gelatinized starch; nevertheless, the preheating temperature is the main variable to monitor. This variable has effects on granule size, crystallinity, and thermal properties of the spray-dried starches. Higher temperatures lead to a decrease in crystallinity and thermal properties, as well as an increase in granule size. However, the combination of preheating temperature and starch concentration affects both the pasting properties and solubility. Understanding the effects of these variables during the pregelatinized starch production process, as well as their influence on starch applicability parameters, is of the outmost importance. The results obtained in this study indicate that lower starch concentrations (6 %) and higher temperatures (60 °C) yield pregelatinized cassava starches with high cold viscosity,

higher heat resistance and agitation (lower breakdown), low tendency to retrograde, and intermediate solubility, make them suitable toward industrial uses as partially gelatinized starches.

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