



## Improvement in spray-drying technology for preparation of pregelatinized cassava starch

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### Abstract

Native cassava starch was gelatinized under different pretreatment conditions (preheating temperature, starch concentration and heating time) and spray-dried. A rotational compound central design was used to test the three independent variables: the preheating temperature, starch concentration, and heating time, and the behavior of the system was assessed by response surface methodology. The results showed a significant effect of both the preheating temperature and heating time on the cold viscosity. The combination of the preheating temperature and starch concentration affected the crystallinity, enthalpy change, solubility, and final viscosity. Modification by spray-drying resulted in a decrease in the crystalline regions, and enthalpy change, as well as an increase in the cold viscosity. The optimal conditions for obtaining partially gelatinized cassava starch with high cold viscosity and lower breakdown, desirable characteristics for commercial pregelatinized starch, are as follows: starch concentration of 25%, preheating temperature of 52 °C, and processing heating time of 10 min.

**Keywords:** morphology; X-ray diffraction; thermal properties; pasting properties; pregelatinization.

**Practical Application:** Spray-dried starch can be used in products that require high viscosity during production, and it is also favorable for application in products of convenience that require rapid preparation of pastes and gels.

### 1 Introduction

Starch is biodegradable, derived from renewable sources, and is relatively cheap. Therefore, it can be used in foods, chemicals, textiles, papermaking, and medicine, among other industries (Hoover et al., 2010). Native starch granules are insoluble at room temperature and their application in industrial processes is limited due to their quick loss of viscosity, and therefore, their tendency to produce thin, elastic, and cohesive pastes. To overcome such drawbacks, physical, chemical, and enzymatic processes can be used to modify the properties of starch (Chiu & Solarek, 2009). Modification can confer functional properties not found in native starches, thereby facilitating applications in various industries (Zavareze & Dias, 2011). Physical modifications of starch have gained wide acceptance because no by-products of chemical reagents are present in this modified starch.

Pregelatinization is a physical modification that can be carried out by spray-drying. This modification has been used for decades in the production of pregelatinized starch and does not lead to loss of the granular integrity (Fu et al., 2012; Pitchon et al., 1981; Rubens, 1992). Spray-drying is a very common technique for preparing starch-based materials because of its low cost and available equipment (Gharsallaoui et al., 2007). Spray-drying is a rapid drying process that converts a dispersion in amorphous particles or a suspension into semi-amorphous particles. Pregelatinized starches can be divided in two groups: fully gelatinized and

partially gelatinized starches. Fully gelatinized starches can be used in pharmaceutical formulations and as main ingredients, bulking agents, or thickening agents for many food products. Partially gelatinized starches present a mixture of properties inherent to both native and fully gelatinized starches (Lai, 2001; Adedokun & Itiola, 2010; Liu et al., 2010; Zhang et al., 2013). In many cases, the use of pregelatinized starch instead of native starch allows for simplified and shortened production processes.

Cassava (*Manihot esculenta*) is globally one of the main sources of starch and has low production costs. The world production of cassava reached 268 million tons in 2014 (Food and Agriculture Organization of the United Nations, 2014). Cassava starch exhibits a high peak viscosity and low setback, forms a clear and high transparent paste, and has a light flavor (Rolland-Sabate et al., 2013).

This study was conducted in order to investigate the effect of spray-drying under different pretreatment conditions on the characteristics of cassava starch, such as the crystallinity, pasting, and thermal properties. This study is of significance, because there is a growing industrial interest in processed starches (partially or fully gelatinized starches) for application in food and non-food products, and it presents a method of improving the functional properties of cassava starch.

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## 2 Materials and methods

### 2.1 Materials

The plants of cassava (*Manihot esculenta*), cultivar IAC 90, were cultivated in accordance to the technical recommendations for the crop and harvested after 22 months of planting. Cassava starch was extracted in the Flor de Lotus industry, located in Cândido Mota, SP, Brazil. All reagents were of ACS grade. The physicochemical analysis was performed according to the methods of the Instituto Adolfo Lutz (2008), and the amylose content was determined according to the methodology described by Takeda et al. (1987).

### 2.2 Experimental design

Response Surface Methodology (RSM) is the most widely used statistical technique for industrial process optimization and is suited for the study of responses to several factors and interactions. A Central Composite Rotatable Design (CCRD) was used to predict the responses based on a few sets of experimental data, in which all factors were varied within a chosen range. For this process, a three-factor and five-level experimental design was adopted. The experimental design included eight factorial points, six axial points, and six replicates of the central point. The starch concentration was varied between 5.0 and 25.0%, the preheating temperature was varied between 40 and 52 °C, and the heating time was varied between 10 and 30 min. (Table 1).

### 2.3 Spray drying

The spray-drying process was carried out by following the methodology described by Fu et al. (2012), with some changes. Suspensions of starch were prepared with distilled water at  $40 \pm 1$  °C, according to the experimental design (w/w). The suspensions were stirred in a thermostatic water bath; the preheating temperature and heating time used were according to the experimental design. The preheating temperature and heating time were considered after reaching the desired temperature. Evaporation of water was minimized by using a plastic film to cover the beaker. The hot starch suspensions were then spray-dried (Spray-dryer, MSD 0.5 model, LABMAQ, São Paulo, Brazil) with a double-atomizer nozzle having a 0.7 mm diameter nozzle hole. The inlet and outlet temperature were 130 and 105 °C, respectively, and the feed rate was  $0.5 \text{ L h}^{-1}$ . The flow rates of the compressed air and hot air were  $0.40 \text{ L min}^{-1}$  and  $3.8 \text{ m}^3 \text{ min}^{-1}$ , respectively, and the pressure of the compressed air was set at 6 bar.

**Table 1.** Independent variables and levels of variation of parameters during the spray-drying process.

Independent variables	Levels of variation*				
	<math>-\langle\alpha\rangle</math>	-1	0	1	<math>+\langle\alpha\rangle</math>
Starch concentration (% dry starch basis)	5.0	9.0	15.0	21.0	25.0
Preheating temperature (°C)	40.0	42.0	46.0	50.0	52.0
Heating time (min.)	10	14	20	26	30

\*<math>\langle\alpha\rangle = 1.682</math>.

### 2.4 X-ray diffraction and relative crystallinity

The starch samples were incubated in a desiccator for 10 days with a saturated solution of  $\text{BaCl}_2$  (25 °C,  $a_w = 0.9$ ) in order to reach equilibrium humidity (90%) and improve the quality of the diffraction diagram. X-ray patterns were examined using a goniometer unit (RINT2000, Rigaku MiniFlex 300, Rotaflex, Tokyo, Japan), with copper  $K_\alpha$  radiation ( $\lambda = 0.1542 \text{ nm}$ ). The scanning speed was  $1^\circ \text{ min}^{-1}$  and irradiation was performed 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 & Komiya, 1983).

### 2.5 Thermal properties

Spray-dried and native starch samples (2.5 mg, dry basis) were studied using a differential scanning calorimeter (DSC, Pyris 1, Perkin Elmer, Norwalk, Connecticut, USA) with distilled water (7.5  $\mu\text{L}$ ). The sealed pans were kept at room temperature for 2-3 h for equilibration. The scanning temperature range and the heating rate were 25-100 °C and  $10^\circ \text{ C min}^{-1}$ , respectively (Santos et al., 2016).

The degree of gelatinization (DG) of the spray-dried starch samples was calculated according to the procedure described by Di Paola et al. (2003) following Equation 1.

$$\text{DG (\%)} = [1 - (\Delta\text{H of spray-dried starch} / \Delta\text{H of native starch})] \times 100 \quad (1)$$

### 2.6 Swelling Power (SP) and Solubility (S)

The starch samples (0.2 g, wet basis) were placed in centrifuge tubes and their weight was subsequently adjusted to 20 g with distilled water, considering the initial moisture of the 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, before 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 applying the following Equations 2 and 3:

$$\text{S (\%)} = [\text{supernatant weight} / \text{sample weight (dry basis)}] \times 100 \quad (2)$$

$$\text{SP (g g}^{-1}\text{)} = \text{decanted weight} \times 100 / \text{sample weight (dry basis)} \times (100 - \% \text{ solubility}) \quad (3)$$

### 2.7 Pasting properties

The samples were analyzed using a Rapid Visco Analyzer (RVA Super 4, Newport Scientific, Warriewood, New South Wales, AU). The starch samples (2.5 g, 14% w/w) were weighed, and 25 g of distilled water was added. The 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  $6^\circ \text{ C min}^{-1}$ , held at 95 °C for 5 min, and then cooled to 25 °C at rate of  $6^\circ \text{ C min}^{-1}$ ; stirring at 160 rpm was applied throughout the experiment.

## 2.8 Statistical analysis

The significant terms in the model were determined by analysis of variance (ANOVA) for each response. The model was fitted by the stepwise selection of the SAS (Statistical Analysis Software) program, and the model obtained was validated by the *F* test using the pure error mean square as the denominator. The second-order polynomial response surface models were generated from adjusted models using the Statistica® 7.0 (StatSoft Inc.) program, and then fitted to each of the response variables (Y). All measurements were carried out in triplicate.

## 3 Results and discussion

### 3.1 Centesimal composition 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. The results obtained in the analysis of centesimal composition and amylose content of unmodified cassava starch used in this study were: 13.20% of moisture, 0.47% of ash, 0.88% of lipids, 0.14% of protein, 94.36% of starch, pH 6.23, and 21.66% of amylose.

### 3.2 Starch crystallinity and thermal properties

Regression analysis of the percentage crystallinity and thermal properties are presented in Table 2 and the response surface drawn from the adjusted model is shown in Figure 1.

Native cassava starch displayed an A-type diffraction pattern, with the most intense peaks at  $2\theta$  values of 15, 17, 18 and 23°. The percentage crystallinity ranged from 27.99 to 32.54% and the spray-dried cassava starch did not show any change in the polymorphic structure (A-type), however the percentage crystallinity of the spray-dried starch was lower than that of native starch (35.6%). The spray-drying gelatinization process of starch, at high temperatures and excess water can become semi-crystalline structure of the starch more mobile resulting in full or partial interruption of the intermolecular interactions, inducing disintegration the ordered structures (Fu et al., 2012). Regression analysis showed a quadratic positive effect of the preheating temperature. The response surface drawn from the adjusted model showed lower crystallinity at intermediate preheating temperatures. Due to low temperatures, temperatures immediately below the onset gelatinization temperature, spray-drying process it resembled with annealing. Molecules in the amorphous regions

of the granule hydrate and increase the mobility of amorphous area and cause a limited but reversible swelling of the granule, resulting in a more perfectly ordered structure and in an increase in the granule stability by improving the arrangement of double helices, as well as the perfection of starch crystallites (Tester & Debon, 2000; Jayakody & Hoover, 2008). Thus, contributing to the increase in crystallinity of the starch.

The onset and peak gelatinization temperature varied between 60.17 and 63.13 °C and between 66.12 and 67.61 °C, respectively, and the regression analysis showed a linear and quadratic positive effect of the preheating temperature on both parameters. The onset and peak gelatinization temperatures of the spray-dried starches were higher than that of native starch (59.40 and 65.60 °C, respectively). Regression analysis did not show any effect on the conclusion gelatinization temperature and the values varied between 73.30 and 74.69 °C, however the conclusion temperature increased after spray-drying, that can be result of reorganization of crystalline structure (Fu et al., 2012).

The temperature range indicates the degree of heterogeneity of the crystals within the starch granules, whereas the enthalpy change reflects the number of double helices that were broken during gelatinization (Cooke & Gidley, 1992). The temperature range varied between 7.9 and 10.5 °C, and the regression analysis showed a linear and quadratic negative effect of the preheating temperature.

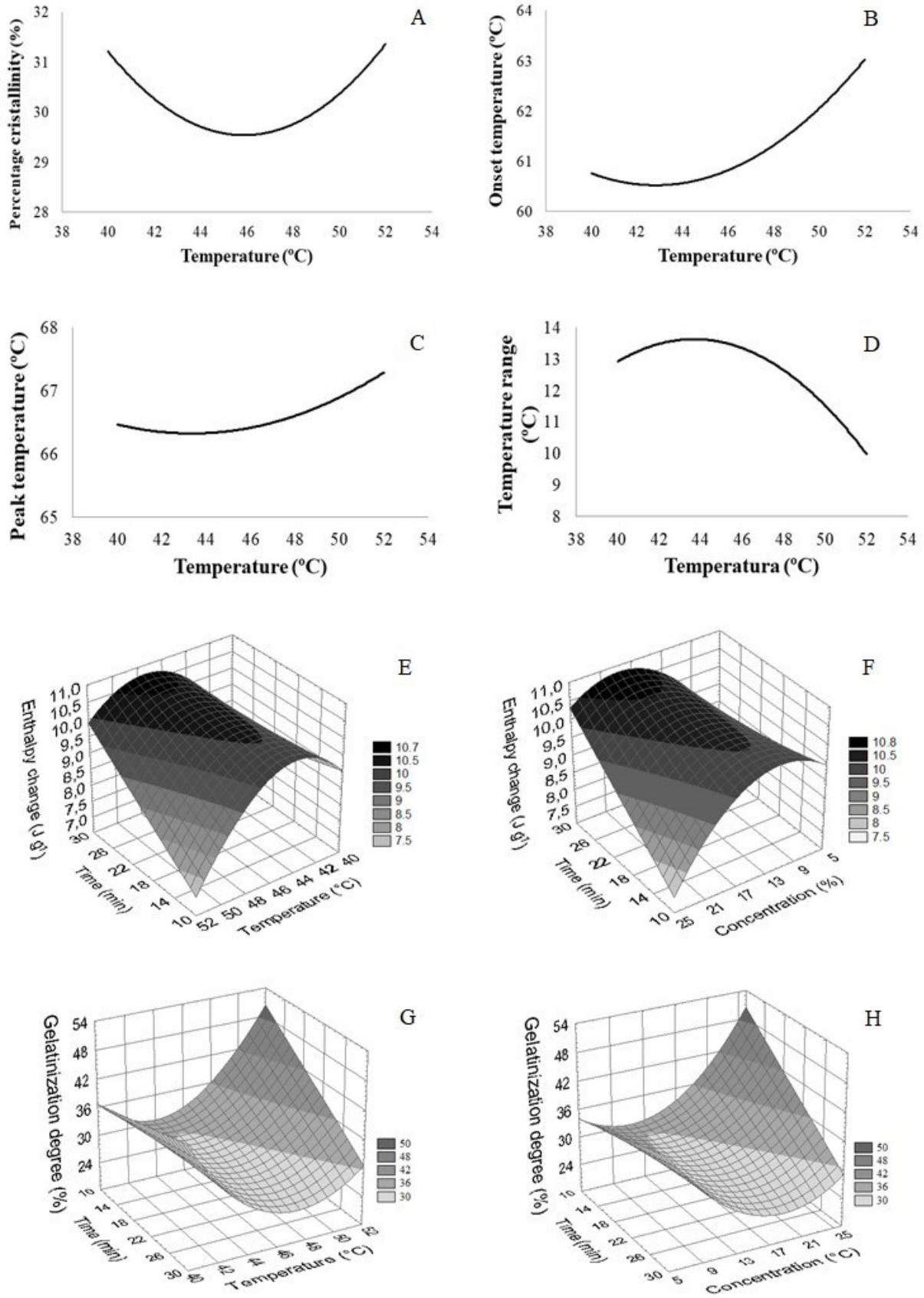
The enthalpy changes and gelatinization degree of spray-dried starch ranged from 7.9 to 10.5 J g<sup>-1</sup> and 23.60 to 44.43%, respectively. Regression analysis showed, for these both parameters, a linear negative effect of the heating time, as did the interaction between the heating time and preheating temperature and between the heating time and starch concentration whereas the preheating temperature and starch concentration had quadratic positive effects. The spray-dried starches showed a lower temperature range and enthalpy change compared to native cassava starch (14.4 °C and 14.2 J g<sup>-1</sup>).

These results indicate that the treatments performed with shorter heating time, higher preheating temperature, and lower starch concentration yielded partially gelatinized starches with a high gelatinization degree. Thus, this pretreatment condition produced starch with less homogeneous crystallites (Cooke & Gidley, 1992; Gunaratne & Hoover, 2002).

**Table 2.** Regression equation of crystallinity and thermal parameters of spray-dried cassava starch (codified model).

Parameters	Predicted regression equation	Pr>f	R <sup>2</sup>	F value
Crystallinity	$Y = 29.51 + 0.63X_1X_1$	0.0009	0.9870	27.06
T <sub>onset</sub>	$Y = 60.74 + 0.64X_1 + 0.40X_1X_1 + 0.30X_1X_2 - 0.35X_2X_3$	0.0001	0.9310	14.99
T <sub>peak</sub>	$Y = 66.38 + 0.23X_1 + 0.17X_1X_1$	0.0005	0.7172	2.82
T <sub>conclusion</sub>	$Y = 74.23$	0.5520	0.4501	0.91
ΔT	$Y = 13.44 - 0.82X_1 - 0.71X_1X_1$	0.0059	0.8368	5.70
ΔH	$Y = 10.20 + 0.26X_3 - 0.60X_1X_1 - 0.47X_2X_2 + 0.34X_1X_3 + 0.35X_2X_3$	0.0083	0.8242	5.21
GD	$Y = 28.43 - 1.85X_3 + 4.22X_1X_1 + 3.29X_2X_2 - 2.37X_1X_3 - 2.45X_2X_3$	0.0082	0.8243	5.21

T = temperature; ΔT = (T<sub>conclusion</sub> - T<sub>onset</sub>); ΔH = enthalpy change; GD = gelatinization degree; X<sub>1</sub> = preheating temperature; X<sub>2</sub> = starch concentration; X<sub>3</sub> = heating time; R<sup>2</sup> = determinant coefficient; Pr>f = probability; F<sub>calculated</sub> > F<sub>tabulated</sub>.



**Figure 1.** Effect of temperature on crystallinity and thermal parameters of spray-dried cassava starches. (A) Percentage crystallinity; (B) Onset temperature; (C) peak temperature; (D) Temperature range; (E) Enthalpy change (heating time × temperature); (F) Enthalpy change (heating time × concentration); (G) Gelatinization degree (heating time × temperature); (H) Gelatinization degree (heating time × concentration).

### 3.3 Swelling Powder (SP), Solubility index (S), and pasting properties

The regression coefficients estimated with the adjusted model using the results, their significance, and their corresponding determination coefficients, swelling power, solubility, and parameters relative to the pasting properties are presented in Table 3, and the response surface data for each variable are presented in Figure 2.

The swelling power varied between 32.15 and 42.61 g g<sup>-1</sup>, and the regression analysis showed a quadratic positive effect of the starch concentration. During the spray-drying process, heat could induce partial gelatinization at the surface of starch granules, resulting in the formation of solid bridges when water in a spraying droplet was evaporated. These solid bridges assisted starch particles in adhering together to form granular particles that can be absorb more water increasing the swelling power (Tukomane et al., 2007). The solubility ranged from 10.89 to 22.77%, and regression analysis showed quadratic negative effects of the preheating temperature and a quadratic positive effect of the starch concentration. (Figure 2A and 2B). This behavior may be the result of internal rearrangement that may have occurred inside the starch granules, causing interaction between the functional groups of the starches, forming groups of more ordered amylopectin double helices chains, and less hydroxyl groups to linkage to more water, thus contributing to the decrease of solubility.

The cold viscosity, which corresponds to the viscosity at room temperature, was higher (2.70 RVU), than that of native starch. Spray-drying led to an increase in the cold viscosity relative to that of native starch (1.24 RVU). Regression analysis showed a linear positive effect of the preheating temperature and heating time. The response surface drawn from the adjusted model showed a higher cold viscosity at high preheating temperatures and with extended heating time (Figure 2C and 2D).

The peak viscosity is generally achieved after the beginning of the heating process and prior to cooling the suspension; during the heating cycle, swelling and gelatinization of the starch granules occur. The peak viscosity also indicates the hot water swelling capacity of the starch granules, which reflects the ability of the ordered starch to hydrate and its swelling power. The peak viscosity varied between 204.15 and 251.77 RVU (Figure 2E). Regression analysis showed linear and quadratic negative effects of the preheating temperature, showing that

increasing the temperature resulted in a decrease in the peak viscosity, evidencing the intensity of the treatment.

The viscosity of breaking, or breakdown, allows for evaluating of the stability of the product at high temperatures under mechanical agitation, and is directly related to the peak viscosity (Leonel & Cereda, 2002). The breakdown varied between 152.54 and 221.71 RVU. Regression analysis showed linear and quadratic negative effects of the preheating temperature, showing that the increasing of the preheating temperature results in a decrease in the breakdown. Thus, the spray-dried starch processed with high preheating temperature showed low breakdown viscosity, which results in a high stability of this starch during industrial processes such as high temperatures under mechanical agitation. The spray-dried starches showed a lower peak viscosity than that of native starch (323.1 RVU), whereas the breakdown remained unchanged (186.8 RVU).

The final viscosity in the RVA curves is a measure of the dispersion of the macromolecules and is related to their hydrodynamic volume and hence their molecular weight (Moisio et al., 2015). The decrease in the final viscosity of the starches after processing indicates degradation of the macromolecules. The final viscosity varied between 314.33 and 371.67 RVU (332.8 RVU), and regression analysis showed linear positive and quadratic negative effects of the preheating temperature, as well as a quadratic negative effect of the starch concentration. The response surface drawn from the adjusted model showed a higher final viscosity at high preheating temperatures and low starch concentration (Figure 2G).

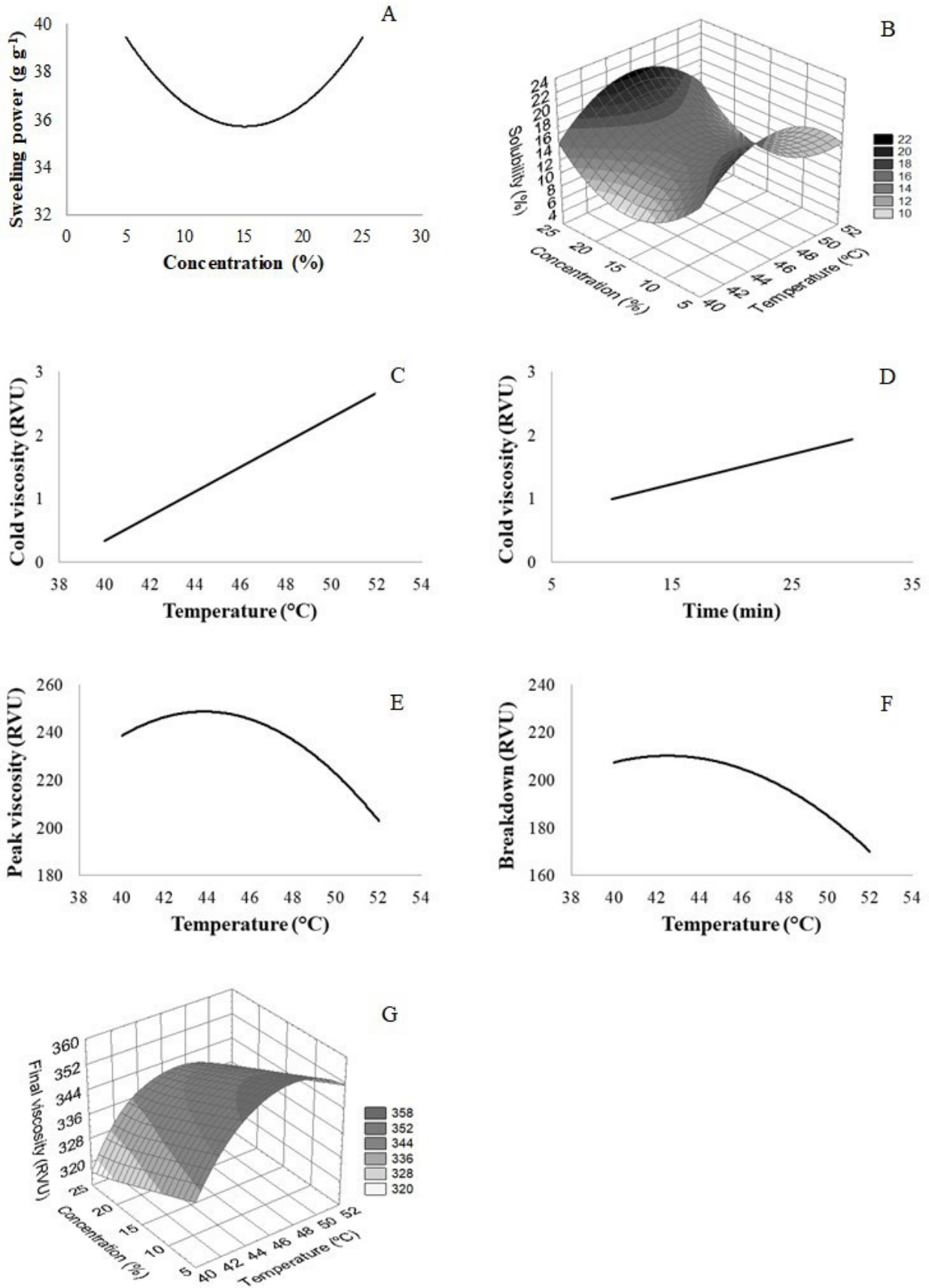
The changes in the starch granules during gelatinization and retrogradation are the main determinants of the pasting properties, which are mainly evaluated through changes in the viscosity during heating and cooling of starch suspensions (Lustosa et al., 2009). This characteristic is paramount from an industrial point view, due to the multiple applications of these starches in foods. The setback is a measure of starch retrogradation and depends on the changes occurring within the granules structures. The setback varied between 195.42 and 230.75 RVU, and this parameter increase after spray-drying process when compared by that of native starch (196.40 RVU).

In the spray-drying process, the starch is partially converted to an amorphous mass (Fu et al., 2012), with reduced crystallinity, increased gelatinization, and viscosity development at room temperature. These factors facilitate the use of the spray-dried starch in products that require high viscosity during production,

**Table 3.** Regression equation of swelling power, solubility, and pasting properties crystallinity of spray-dried cassava starch (codified model).

Parameters	Predicted regression equation	Pr>f	R <sup>2</sup>	F value
Swelling Power	$Y = 35.71 + 1.30X_2X_2 - 2.42X_1X_2$	0.0332	0.9296	4.72
Solubility	$Y = 14.63 - 2.18X_1X_1 + 2.31X_2X_2$	0.0027	0.9831	20.89
Cold viscosity	$Y = 1.46 + 0.69X_1 + 0.28X_3$	0.0040	0.8509	6.34
Peak viscosity	$Y = 346.79 - 9.92X_1 - 9.18X_1X_1$	0.0396	0.6483	2.05
Breakdown	$Y = 205.99 - 10.63X_1 - 6.05X_1X_1$	0.0002	0.7005	2.60
Final viscosity	$Y = 348.45 + 5.50X_1 - 5.33X_1X_1 - 5.17X_2X_2$	0.0343	0.6943	2.52
Setback	$Y = 208.21 + 8.08X_2X_3$	0.1128	0.6682	2.24

X<sub>1</sub> = preheating temperature; X<sub>2</sub> = starch concentration; X<sub>3</sub> = heating time; R<sup>2</sup> = determinant coefficient; Pr>f = probability; F<sub>calculated</sub> > F<sub>tabulated</sub>.



**Figure 2.** Effect of temperature on the swelling power, solubility, and pasting properties of spray-dried cassava starches. (A) Swelling power; (B) Solubility; (C) Cold viscosity (temperature); (D) Cold viscosity (heating time); (E) Peak viscosity; (F) Breakdown; (G) Final viscosity.

and in the final product. These changes are very important because they will provide the starchy materials with new and relevant properties either for food or non-food applications.

#### 4 Conclusion

This study provides an extension of the knowledge-base regarding the changes in cassava starch granules after spray-drying, using different pretreatment conditions and presents a method of obtaining partially pregelatinized starch. The formation of partially pregelatinized starch was evidenced by a reduction of the gelatinization temperature, and peak viscosity, as well as an increase in the viscosity at room temperature (cold viscosity), gelatinization degree, swelling power, and solubility. The combination of the preheating temperature and starch concentration had a significant impact on the structural characteristics and thermal and pasting properties of cassava starch in this process. Understanding the effects of these variables during this process, as well as their influence on the starch applicability parameters, is of outmost importance. The results obtained in this study indicate that a higher preheating temperature and starch concentration, and less heating time (52 °C, 25%, and 10 min) yield cassava starches with a low temperature range, enthalpy change of gelatinization, and higher gelatinization temperature and gelatinization degree, making it suitable for industrial use as partially gelatinized starch, and is favorable for application in products of convenience that require rapid preparation of pastes and gels.

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