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Cassava Flour Enriched with Açaí (*Euterpe oleracea* Mart.) by Coating and Agglomeration

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This study presents the technique of coating and agglomeration, using a fluidized bed equipment, to incorporate nutrients and to make cassava flour (*Manihot esculenta Crantz*) a functional food. The flour was enriched using aqueous solution of fresh açaí (*Euterpe oleracea* Mart.) pulp atomized on the cassava particles at different operating conditions. The tests were carried out following a factorial 2^2 experimental design with 3 repetitions at the center point. Satisfactory results were obtained with the particles of flour coated or agglomerated by the aqueous solution 1:1 by weight of water and açaí pulp. The determination of total anthocyanins was performed using the method of single pH. Results of anthocyanins incorporation in the coated/agglomerated cassava flour were verified by spectrophotometry UV-VIS analysis. The anthocyaninins' content found in the pure pulp was 32.35 mg of anthocyanins in 100 g of sample, while for the enriched flour it reached up to 5.48 mg of anthocyanins in100 g of sample, depending on the operating conditions of the fluidized bed. Total anthocyanins' content obtained for coated/agglomerated cassava flour was considered significant, as raw cassava flour does not have anthocyanins in its composition. In addition, the final product also incorporated up to 54.53 g of açaí for each 500 g of cassava flour bringing together other nutrients of açaí not quantified in this work.

1. Introduction

The incessant demand for nutrient-rich foods to complement the basic needs of good nutrition, with balanced and healthy diet, has resulted in the development of several researches aiming at obtaining new food products. Nowadays the researches points in the direction of the called functional foods. Functional foods benefit the metabolism by improving the energy supply for a smooth functioning of the body.
Usually people do not feed properly and modern life contributes to fast food consumption, decreasing the amount and quality of nutrients necessary for metabolism in the human body. Junk food consumption in excess contributes to the onset of cardiovascular diseases, anemia and malnutrition (Monteiro, 2003). The incorporation of proteins, minerals, vitamins, and flavonoids in solid foods can help to correct this deficiency.
The idea of incorporating minerals, proteins and/or vitamins to solid foods (powder) brings some advantages and benefits, especially in the administration and replacement of these nutrients ensuring the consumption of healthy and low cost food. In addition, a good nutrition can prevent diseases and improve quality of life of the population.
One possible technique for incorporating nutrients in solid foods is the fluidized bed coating, by atomization of the solution or suspension to be incorporated. The fluidized bed coating process must be rigorously controlled, because any modification in the operating variables such as: solution or suspension flow rate, temperature and relative humidity of fluidizing air and atomizing air pressure can lead to wetting of the bed, with the formation of undesirable huge agglomerates or even the fluidization collapse (Silva and Rocha, 2002).
The fluidized bed is widely adopted in several physical and chemical processes, as described in Kunii and Levenspiel (1991). The main advantages of using the fluidized bed as coating equipment is the great amount of material that can be processed in less time of process and high rates of heat and mass transfer.

This technique has already proved its efficiency in granulation (da Cunha et al., 2009) and coating of particles (Silva and Rocha, 2002). Due to their advantages, fluidized bed coaters and granulators are available in laboratory and industrial scales (Glatt Company Profile, 2013).
The objective of this work was the enrichment of cassava flour with açaí pulp by means of fluidized bed coating and agglomeration, resulting in a functional food incorporating nutrients from the açaí fruit.
Açaí pulp is rich in nutrients and has important antioxidant properties due to the presence of anthocyanins in its constitution (Rogez, 2000). It is a natural source of energy, which brings together a rich complex of amino acids, proteins, carbohydrates, lipids and minerals such as sodium, potassium, calcium and iron, besides the anthocyanins and vitamins B1, C and E (Meneses et al., 2008; Cohen; et al., 2006). Other information about açaí composition can also be found in Embrapa (2005). The flour particles coated with the incorporated nutrients of açaí can be mixed with other foods, with the goal of preventing nutritional deficiency.
Anthocyanins stand out as the main nutrient incorporated into the coated and/or agglomerated flour analyzed in this work. They are phenolic pigments found in many red and purple fruits with potential to replace dyes. In addition, these natural antioxidants (flavonoids belonging to the group of phenolic compounds) have significant nutraceutic potential. Recent researches have also reported anti-inflammatory and analgesic properties for anthocyanins (Volp et al., 2008).

2. Materials and Methods

2.1 Solid Particles

The material to be coated with açaí pulp solution was the cassava flour (*Manihot esculenta Crantz*) acquired in the local market. The flour was characterized by particle size in a set of standard Tyler sieves and its average diameter was calculated using the definition of Sauter (371 μm). This particle size is in the same size range of microcrystalline cellulose analyzed in coating (Silva and Rocha, 2002) and granulation (da Cunha et al., 2009) in fluidized-bed and resulted in good quality of fluidization regime.
The particles of flour were coated/agglomerated by spraying an aqueous solution obtained from the pulp of fresh açaí (*Euterpe oleracea* Mart.).

2.2 Coating/Agglomerating Solution

The solution used for the coating/agglomeration processes was prepared from the pure pulp of açaí purchased at the local market. The pulp was mixed with water at a rate 1:1 by weight and homogenized in a mechanical shaker. The tests were carried out aiming at obtaining good process efficiency, minimization of formation of lumps and fluidization regime maintenance, in addition to uniformity of coating.

2.3 Experimental equipment

The experiments were performed in a fluidized bed system with a transparent column of 60 cm of height and 14 cm of diameter. Figure 1 shows the schematic of the experimental system. Details of the experimental setup can be found in da Cunha et al. (2009).

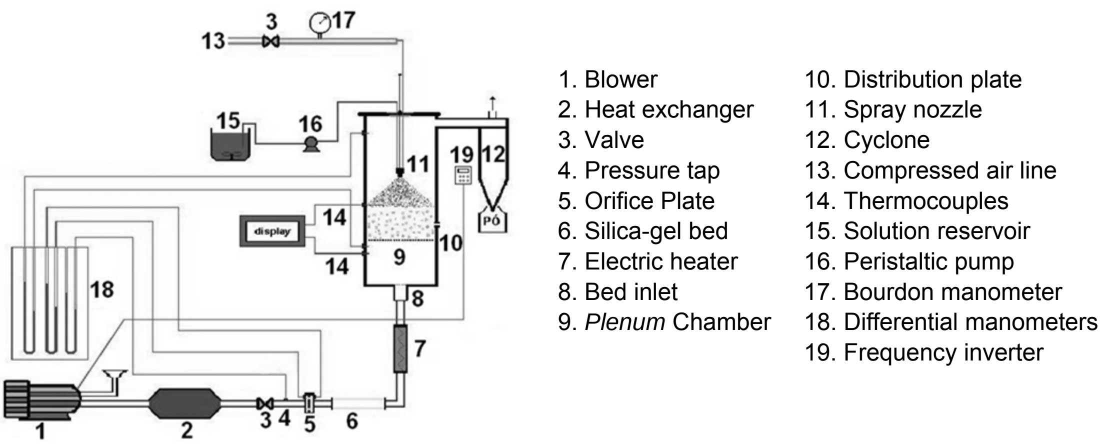

Figure 1 – Schematic of the experimental system

2.4 Fluid dynamic Tests

Before starting the experiments of granulation and coating, fluid dynamic tests were made to analyze the behavior of the particles of cassava flour inside the bed.

The fluid dynamic tests were based in previous works on granulation (da Cunha et al., 2009) and coating of particles in a similar equipment (Silva and Rocha, 2002), using loads of 500 g. The results of bed pressure drop and air flow rate were plotted in typical fluid dynamic graphics, which allowed determination of the minimum fluidization velocity (U_{mf}) and the operating velocity for coating/agglomeration operations, set in $2xU_{mf}$.

2.5 Coating/Agglomeration of cassava flour

The tests were conducted following an experimental design, factorial type 2^2 with 3 repetitions at the center point. The independent factors analyzed were air atomizing pressure (P_{at}) and fluidizing air temperature (T_{ar}). The factors and their established levels are listed in Table 1. The content of anthocyanins incorporated to the flour was the response of the experimental design.

Table 1: Operating conditions.

Variables	Conditions		
	-1	0	+1
P_{at} (kPa)	68.95	103.42	137.89
T_{ar} (°C)	60	70	80

The bed was loaded with cassava flour (500 g). After, the equipment was turned on and the particles were fluidized at a low air flow rate, close to U_{mf}. The fluidizing air was heated by means of an electrical heater until it reached the preset temperature of the test. After temperature stabilization, the air flow was increased gradually until it reached the operating velocity, and then starting atomization of the coating solution.

The coating solution was stored in a container with capacity of 600 mL. The atomization of the solution was made using a double-fluid nozzle attached to the top of the fluidized bed (Figure 1). The spraying was stopped every time the bed presented fluid dynamic instability (preferential channeling and formation of dead zones) and restarted with the re-establishment of stable fluidization regime. During each stop of the solution atomization, air flow was increased to maintain and ensure the fluidization regime. For each essay 500 mL of the coating solution and 500 g of cassava flour were processed.

3. Methods for extraction and determination of anthocyanins

3.1 Extraction of anthocyanins

Extraction of anthocyanins was carried out according to the method described in Texeira et al. (2008), adapted to the coated/agglomerated flour. Samples containing coated/agglomerated cassava flour were previously weighted (60 g) and put into a beaker. After, 80 mL of the extractor solvent ethanol: water (70:30), and HCl sufficient to adjust the pH of the medium to 2.0 were added to the sample. These samples were stored in the dark (protected from light for extraction) for 24 h at 5 °C.

3.2 Determination of the total anthocyanins' content

The determination of anthocyanins' content of the coated/agglomerated particles was performed through the method of single pH, which has already been used by several authors (Giusti and Wrolstad, 2001; Kuskoski et al., 2006; Lee; Durst; Wrolstad, 2005; Teixeira et al., 2008). Before the determination of anthocyanins' content, the sample was filtrated using quantitative black belt filter paper (fast 28 μm filtration) to remove suspended solids. The absorbance was measured in UV-VIS spectrophotometer Varian brand, model: Gary 1 G (Sugar Land, U.S.A). The wavelength used was 535 nm, based on the work of Fuleki and Francis (1968). The total content of anthocyanins is expressed in this work in milligrams of anthocyanins per 100 grams of sample, in wet basis (mg AT/100 g).

3.3 Single pH method

The single pH method consisted in the quantitative transfer of a portion of the concentrated extract to a volumetric flask of 10 mL and completing its volume with ethanol-1.5 N and HCl (85:15). The absorbance values were contrasted with the blank test (ethanol:1.5 N: HCl).

Total anthocyanins were quantified by spectrophotometry according to the method of Fuleki and Francis (1968), Equation 1, and the result expressed on wet basis.

The value of absorptivity (ε) was the same used by Fuleki and Francis (1968) for cranberry extract, equal to 98.2. This value corresponds to the mixture of purified anthocyanins obtained from cranberry juice. The calculation of concentration was carried out using Equation 1.

$$AT = \frac{A.FD.100}{\varepsilon^{1\%}} \tag{1}$$

where AT – total anthocyanins, mg; A – absorbance; FD – dilution factor; $\varepsilon^{1\%}$ – molar absorptivity coefficient; 100 – conversion factor.

4. Results and discussion

The results of the fluid dynamic test of fluidization carried out with cassava flour for the determination of operating velocity is represented on the fluidization curves (Figure 2). The curves obtained follow the same typical behavior of fluidized regime found in the literature (Saxena and Vogel, 1977).

It was observed a decline in the pressure drop for decreasing velocities in the region of complete fluidization, as shown in Figure 2. The most likely hypothesis for this behavior is the morphology of the flour particles and their size distribution that directly affects the fluid dynamics, with occurrence of preferential channels and/or drag between particles. This kind of fluid dynamic behavior is described in the literature as being typical of non-spherical particles having wide size distribution (Kunii and Levenspiel, 1991). Hysteresis is also observed in the graphics for increasing and decreasing velocities, which is typical of the fluidization regime.

The minimum fluidization velocity (U_{mf}), shown in Figure 2 was obtained from the descending curve and corresponds to the intersection of the line fitting the pressure drop data for fixed bed with the line fitting the points for the totally fluidized bed. The minimum fluidization velocity obtained is equal to 6.25 cm/s. For the tests of particle coating/agglomeration it was defined the point of operation with an air velocity of twice the minimum fluidization velocity ($U_{op} = 2 \times U_{mf} = 12.5$ cm/s).

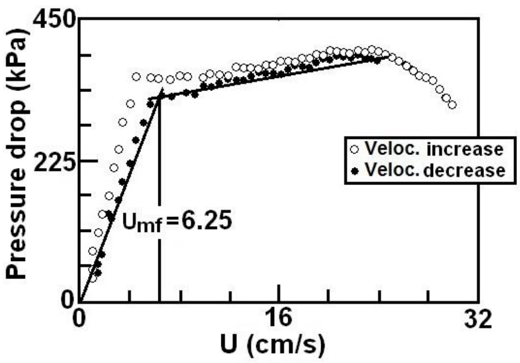

Figure 2- Fluid dynamic curves. Cassava flour, 500 g, dp = 371 µm.

4.1 Coating/agglomeration of cassava flour

During the tests, it was noted the influence of the moisture of the flour particles inside the bed on the bed dynamics. Aiming at avoiding the fluidized regime collapse, atomization of the solution was made intermittent. It was visually observed that cassava flour particles were coated and agglomerated with success by the pulp solution in the proposed equipment, well-denoted by its change from light beige to purple color. To confirm the visual observations, optical micrographs were obtained, as the example shown in Figure 3. The results shown in Figure 3 were obtained for experimental condition at the center point (solution flow rate of 10 mL/min; atomizing pressure of 103.42 kPa and fluidizing air temperature of 60 °C).

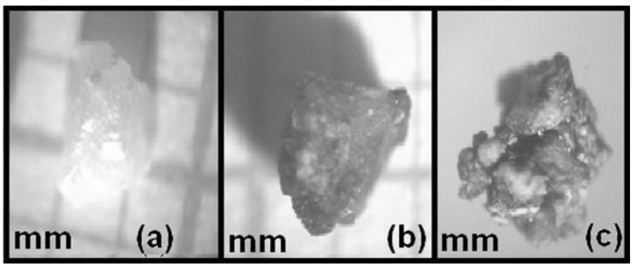

Figure 3: Cassava flour particles (a) without coating (b) coated and (c) agglomerated.

The coated/agglomerated particles had an increase of about 22% over their initial diameter, depending on the operating conditions used. Final diameters ranged from 434 µm to 473 µm and agglomerates up to 1400 µm were observed in some cases.

With the results of the tests, it was concluded that the açaí pulp can be used in the process of agglomeration and coating of cassava flour as a natural colorant due to the observable presence of anthocyanins in the product (purple color). Besides natural coloring, the açaí berry also contributes as a natural source of nutrients and micronutrients such as: iron, calcium, potassium, vitamins and lipids, among others, as cited in the works by Rogez (2000) and Embrapa (2005).

4.2 Content of anthocyanins

Açaí pulp and processed cassava flour were analyzed in relation to the content of total anthocyanins. Analyses were made using the Spectrophotometric method of single pH, as described previously.

The results of total anthocyanins found in açaí pulp and in the processed flour are shown in Table 2. Replications were made only at the central point. The content of anthocyanins in the açaí pulp is in accordance with values found in the literature. Texeira et al. (2008) reported 23.21±4.75 mg AT/ 100 g, while Cohen (2006) found values in the range of 33.7±0.34 mg AT/ 100 g to 39.74 ±0.77 mg AT/ 100 g. The anthocyanins contents found for the samples of processed flour were considered satisfactory and promising, even though they are about 6 times less than that found in natural pulp. Degradation of anthocyanins is due to exposure of the pulp to temperatures above room temperature during processing and exposure to light.

Table 2: Results of the contents of total anthocyanins in the acaí pulp and coated/agglomerated cassava flour.

Samples	Anthocyanins' content (mg AT/100 g)
Açaí Pulp	32.35
(-1, -1)	5.20
(+1, +1)	1.54
(-1, +1)	5.48
(+1, -1)	4.27
(0, 0)	2.60
(0, 0)	3.45
(0, 0)	4.94

Analyzing the results shown in Table 2, it can be observed that the contents of anthocyanins varied from 1.54 to 5.48 mg AT/100 g in the processed flour.

The low value obtained for the condition (+1, +1) can be related to the air temperature used in this condition associated with high pressure of atomization, as the increase in temperature decreases the content of anthocyanins. For higher atomizing pressures, smaller droplets of the coating solution are sprayed on the bed, which are more susceptible to high temperatures. As stated in the literature (Hillmann et al., 2011; Stringheta 1991), the temperature significantly interferes with the stability of anthocyanins; when submitted to temperatures higher than the room temperature (25 °C) its degradation increases.

As the results at the central point fail with respect to good reproducibility, it was not possible to statistically analyze the results. We attribute the differences to the process complexity resulting in coated and agglomerated granules in a unique test, which interferes in the bed dynamics, as well as the process intermittence that may have caused the differences on the results at the same conditions (center points).

It is worth mentioning that in addition to the content of anthocyanins added to the product for the condition (-1, +1), the process also added 54.53 g of coating material for each 500 g of cassava flour, bringing together other nutrients not quantified in this work.

5. Conclusions

- The fluid dynamic curve obtained experimentally for fluidization of cassava flour followed the typical behavior found in the literature for fluidization of non-spherical particles with wide size distribution;
- In preliminary tests of cassava coating it was identified the need of intermittent feeding of the coating solution to prevent the fluidizing regime collapse;
- The coating/agglomeration of cassava flour with açaí pulp was carried out successfully demonstrated by optical microscopic analysis;
- The total anthocyanins' content of coated/agglomerated flour reached up to 5.48 mg AT/100 g, which was considered satisfactory, even though it is 6 times smaller than the value found in the pure açaí pulp (32.35 mg AT/100 g), due to the absence of anthocyanins in the composition of raw cassava flour. In

addition, the product also incorporated 54.53 g of for each 500 g of cassava flour bringing together other nutrients of the açaí.

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