Microencapsulation of blackberry pulp with arrowroot starch and gum arabic mixture by spray drying

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Abstract: This research work aimed to obtain blackberry pulp powder by spray drying and, by an experimental design, evaluated the effect of inlet air temperature (100–150°C) and blackberry pulp solids:arrowroot starch/gum Arabic solids ratio of 1:0.5–1:2 on the physicochemical properties of the powders. Arrowroot starch and gum Arabic present Tg values above 100°C; hence it was possible to employ them as carriers in blackberry pulp spray drying in order to increase Tg of the system. Powder yield and solubility increased with increasing blackberry pulp solids:arrowroot starch/gum Arabic solids ratio of 1:0.5-1:2, whereas hygroscopicity decreased. Yield, solubility and hygroscopicity of the powders increased and water activity decreased, with increasing inlet air temperature. The powders presented low moisture content and water activity. Temperature of 143°C and blackberry pulp solids:arrowroot starch/gum Arabic solids ratio of 1:1.78 were the optimal conditions to obtain high yield and blackberry powders that are soluble in water and less hygroscopic.

Keywords: glass transition temperature; process yield; moisture content; average size; hygroscopicity; solubility.

Introduction

Rubus fruticosus or blackberry, belonging to the Rosaceae family, grows abundantly in regions of cold weather, in the north of Europe, Australia, part of Asia, North America and South America (Ferrari et al., 2012; Gomar et al., 2014).

The fruits are highly appreciated by consumers, not only for the combination of their appealing color and desirable flavor and taste, but also for their high nutritional value (D’Agostino et al., 2015). In addition to high contents of fibers, vitamins, and essential minerals, blackberry is an important source of phenolic compounds, such as phenolic acids, tannins and anthocyanins, which have high antioxidant capacity (Elisia et al., 2007; Hager et al., 2008; Machado et al., 2015). Its consumption has been associated with benefits for human physical and mental health (antioxidant, anticancer, anti-inflammatory and anti-neurodegenerative activities) (Dai et al., 2007; Tavares et al., 2012; Zia-Ul-Haq et al., 2014).

However, blackberry is one of the most perishable berries because of its thin and fragile skin and high respiration and transpiration rates, which limit its consumption in the fresh form (Ferrari et al., 2012; Joo et al., 2011). During postharvest period, there are fast changes in the blackberry's physicochemical and nutritional properties, such as mass loss, texture alteration and microbiological deterioration. Most blackberries destined for fresh markets became unmarketable after 2 or 3 days when held at 0°C due to decay (Hardenburg et al., 1986; Joo et al., 2011). About 60% of its production is lost if processed improperly (Romero and Yépez, 2015).

For this reason, spray drying is an alternative for the processing of blackberry, since the powder obtained is easier to handle, package and transport than the fruit itself, and also provides a high-quality product with prolonged shelf life (Santana et al., 2016).

More specifically, spray drying is a technological process in which a fluid product is transformed into a powder by atomizing it into a hot gas stream (Gharsallaoui et al., 2007). The feed flow rate, the inlet and outlet air temperatures, atomizer speed, feed concentration, feed temperature and inlet air flow rate are process parameters of spray drying that influence physicochemical properties of the powders produced (Ré, 1998; Chegini and Ghobadian, 2005). Different parameters can be controlled during spray drying process in order to obtain desired characteristics in the final product (Daza et al., 2016).

However, some intrinsic drawbacks, such as stickiness, hygroscopicity and low solubility may occur. In addition, the adhesion of droplets to the drying chamber walls decreases the process yield (Santana et al., 2016). The sticky behavior of juices or fruit pulp powders is attributed to the presence of low molecular weight sugars and organic acids in their composition, which have low glass transition temperatures (Bhandari and Datta, 1997; Saavedra-Leos et al., 2012; Araujo-Díaz et al., 2017).

Alternatively, high molecular weight encapsulating agents are added to pulps or fruit juices prior to the drying process in order to increase the glass transition temperature of the system and to reduce such problems (Araujo-Díaz et al., 2017). Gum arabic, maltodextrins, starches, gelatin, methyl cellulose, gum tragacanth, alginates, pectin, silicon dioxide, tricalciumphosphate, glycerol monostearate and mixtures of some of them are some examples of encapsulating and coating agents used in spray drying (Igual et al., 2014). Among polysaccharides, starches are being widely studied as potential encapsulating agents due to their low cost, abundance and renewability, besides the advantage of existing in various forms, depending on the source of the raw material (Sartori and Menegalli, 2016), which can generate exceptional functional properties when compared to conventional encapsulating agents. Arrowroot starch has not been used as an encapsulating agent. However it, presents a great potential for application for being multifunctional, non-toxic, biodegradable, blood-compatible, bioactive, besides having a high digestibility (Hoover, 2001; Winarti et al., 2015; Wu and Liao, 2017). Due to its high digestibility, gelling and thickener ability, arrowroot starch (Hoover, 2001; Villas-Boas and Franco, 2016) has been widely used in preparation of bakery products, as in confection of biscuits, cakes, creams and sweets (Leonel et al., 2002).

However, arrowroot starch cannot be easily thermal processed, which limits its application in industries. Thus, to increase the functionality of arrowroot starch, it is blended with other polymers to make biocomposites, creating a biomaterial with more functional applications (Wu and Liao, 2017). The mixture of arrowroot starch with gum Arabic has a great potential for use as encapsulating agent, since gum Arabic presents many desirable characteristics of a good wall material for drying encapsulating techniques, such as increasing glass transition temperature, imparting high solubility, low viscosity and good emulsifying properties to feed dispersions (Ramírez et al., 2015).

This study aimed to produce powdered pulp from blackberry by spray drying using mixture of gum Arabic and arrowroot starch as encapsulating agent, in order to evaluate the impact of drying conditions on the physical properties of spray-dried pulp.

Materials and methods

Materials

Blackberry fruits

Frozen fruits of blackberry (*Rubus fruticosus*), cv Tupy, were acquired from "Agro Monte Verde Eirelli", company of Cambuí – MG, Brazil, and used in this research work. Pulp was obtained by grinding blackberry fruits in a blender, previously thawed in refrigerator (8°C) for 24 h. Then, the pulp was sieved to remove seeds, homogenized and packed in polypropylene bottles and coated with aluminium foil to protect against photodegradation. The samples were stored in freezer at -40 ± 3°C until drying. Pulp soluble solids content was 9°Brix, determined with a manual refractometer with a 0–90°Brix range and 0.2°Brix resolution (Reichert, Model AR200, USA). The pulp presented total solids content of 10.3 g/100g of pulp.

Carrier agent

The encapsulating agents used were gum Arabic Instantgum® (colloids Naturels, São Paulo, Brazil) containing 14.00±0.10% of moisture content, 1.38±0.16% of proteins, 0.37±0.02% of lipids, 3.70±0.10% of ash and 80.46±0.00% of carbohydrates (A.O.A.C., 2006), and arrowroot starch containing 15.24±0.19% of water, 0.40±0.03% of protein, 0.12±0.01% of fat, 0.33±0.01% of ash and 83.91±0.00% of carbohydrates (A.O.A.C., 2006). The arrowroot starch was extracted according to the methodology developed by Cruz and El Dash (1984). Arrowroot rhizomes used in the extraction of the starch were obtained in the Faculty of Agronomy, Federal University of Grande Dourados, Mato Grosso do Sul, Brazil, in 2014. All other reagents used for the analyses presented analytical grade.

Methods

Differential Scanning Calorimetry (DSC) of carrier agents

The thermal properties of arrowroot starch and gum Arabic (powder) were studied using a Differential Scanning Calorimeter (DSC1, Mettler Toledo, Schwerzenbach, Switzerland). Aliquots of 10 mg of the samples were weighed in a microanalytical scale (MX5-Mettler Toledo, Schwerzenbach, Switzerland), in an aluminum pan (40 μl). For reference, an empty aluminum pan was used. The samples were submitted to heating program between 25 and 100°C at a rate of 10°C/min, in an inert atmosphere (50 mL/min of N_2). When temperature reached 100 °C, samples were held for 10 minutes at this temperature. After this first scan, the measurement cells were cooled with liquid nitrogen to 25°C, followed by a second heating sweep between 25 and 270°C at rate of 10°C/min in an inert atmosphere (50 mL/min of N_2). The glass transition temperature (Tg) was calculated as the baseline inflection point, caused by the discontinuity of specific heat of the sample.

Experimental Design

Drying experimental runs were conducted following an experimental design using mixture of arrowroot starch/gum Arabic (1:1, weight/weight) as encapsulating agent. A central composite design – including 4 factorial runs, 4 experimental runs in axial conditions and 3 repetitions of central point, totalling 11 runs – was developed (**Table 1**) to study the effects of dryer inlet air temperature (100–150°C) and blackberry pulp solids:arrowroot starch/gum Arabic solids ratio of 1:0.5–1:2 (weight/weight) on the powder properties. The response variables considered were drying process yield, moisture content, water activity, hygroscopicity, solubility and particle size.

Microcapsule production

The solution of encapsulating agents and blackberry pulp was prepared in mixer type homogenizer at room temperature for 5 minutes. The solutions obtained were diluted in water in a ratio of 1:2 (weight/weight) to facilitate spraying, due to its high viscosity. The total solids contents of the spray feed solutions are presented in Table 1 and were determined from the determination of the dry weight obtained by drying in a vacuum oven at 60 °C until obtaining constant weight (A.O.A.C., 2006).

The resulting homogenized solutions were immediately fed into laboratory spray dryer (Model B191, Büchi, Flawil, Switzerland) equipped with a drying chamber (diameter of 110 mm and height of 435 mm) and dual fluid atomizer nozzle with an orifice of 0.5 mm in diameter, using the following process conditions: airflow of 19 m^3/h; pressurized air flow of 0.6 m^3/h; feed mass flow of 0.2 kg/h. Three drying repetitions were performed for each test. The resultant powder was stored in polyethylene packages in desiccators until its characterization.

Powder characterization

Drying process yield. Drying process yield was determined by the ratio between powder solids mass and feeding solids mass of blackberry pulp.

Moisture content and water activity. The powder's moisture content was gravimetrically obtained by vacuum oven at 60°C until constant weight, in triplicate (A.O.A.C., 2006). Water activity (Aw) was determined by direct reading at 25°C, using a water activity meter (Aqualab, Decagon Devices, USA). All determinations of AW were carried out from three independent preparations, in triplicate.

Microstructure. Electronic Scanning Electron Microscope with X-ray Dispersive Energy Detector (SEM) bench (model of MEV: Leo 440i, model of EDS: 6070, Leo 440i - LEO Electron Microscopy/Oxford- Cambridge, England) was used to observe the morphological characteristics of the powder samples. Powder sample was placed on double-sided carbon adhesive tape adhered to stub, submitted to application of a gold layer (model K450, Sputter Coater EMITECH, Kent, United Kingdom) and observed in scanning electron microscope operated at 20 kV.

Hygroscopicity of blackberry powders. Hygroscopicity was determined according to methodology proposed by Cai and Corke (2000), with some modifications. Approximately 1 g of each powder sample was placed in a hermetic container at 25°C, with a saturated NaCl solution, to create a 75.7% relative humidity atmosphere. The samples were weighed, in triplicate, after seven days and the hygroscopicity was determined and expressed in g of adsorbed water per 100 g of dry solid (100 g g^{-1}).

Solubility of the blackberry powders. Solubility was determined according to the method described by Eastman and Moore (1984), cited by Cano-Chauca et al. (2005). The method consists in adding 1 g of sample to a vessel containing 100 mL of distilled water, operating with high-speed magnetic stirring – level 4 of magnetic stirrer for 5 minutes, followed by centrifugation at 3000 g for 5 minutes. Aliquot of 25 mL of supernatant was removed and kept in the oven at 105°C until constant weight. The solubility was calculated by weight difference.

Particle size distribution. The particle size distribution (d 0.1, d 0.5, d 0.9, µm) was determined by a particle size analyzer based on laser diffraction (Mastersizer 2000, Malvern Instruments, UK). The mean diameter was determined based on the diameter of a sphere with equivalent volume (De Brouckere Mean Diameter, D[4.3]). The surface mean was determined based in volume/surface mean (also called the Sauter mean, D[3.2]). Samples were analyzed in triplicate with dispersion in 99.5% ethanol.

Statistical analysis

The results of variable response of the experimental design were evaluated using Statistica 9.0 software. Significant differences between mean results were evaluated by analysis of variance (ANOVA) and Tukey test at 5% level of significance, using SAS software (Cary, NC, USA).

Results and discussion

Differential Scanning Calorimetry (DSC) of the carrier agents

One of the difficulties of spray drying of sugar-rich food products, such as pulps or fruit juices, is the high chemical affinity between water molecules and the low molecular weight sugars contained in the pulp or juice (Araújo-Díaz et al., 2017). As a consequence, the overall glass transition temperature (Tg) of the system decreases, observing processing problems of fruit pulp powders obtained by spray drying, such as stickiness, hygroscopicity and low solubility. In addition, the adhesion of droplets to the drying chamber walls decreases the process yield (Santana et al., 2016).

Encapsulating agents may be employed as improver in the spray drying process of pulps or fruit juices, with the main function of increasing Tg of the system, since these agents are characterized by high molecular weight, low viscosity and Tg in the range of 100–188°C (Araújo-Díaz et al., 2017; Saavedra -Leos et al., 2015). The quality of the powder is closely linked with the choice of encapsulating agent. Thus, knowledge of the glass transition temperature behavior of the polymeric materials supports its choice as an encapsulating agent and helps to understand its performance in processes such as dehydration, evaporation, and conservation.

Glass transition temperature (Tg) is a value referring to a temperature range that, during the heating of a polymeric material, allows the amorphous chains to acquire mobility (Schlemmer et al., 2010). Tg is an important information obtained from DSC curves. Differential scanning calorimetry (DSC) is a commonly employed analytical technique for analysis and characterization of amorphous solid dispersions. This technique has proven to be a highly versatile technique for understanding the glass transition temperature (Tg), relaxation, and crystallization behavior of polymeric material (Bechgaard et al, 2018). Phase transitions in foods are often a result of changes in composition or temperature during processing or storage. The DSC curves of arrowroot starch and gum arabic are shown in Figure 1. According to Araújo-Díaz et al. (2017), for any substance or compound to be used as an encapsulating agent, it must present a Tg value above boiling temperature of water (approximately 100°C). Considering that carbohydrate polymers, arrowroot starch and gum Arabic present Tg values above 100°C, hence, they can be employed as encapsulating agents in spray drying blackberry pulp.

The thermogram of arrowroot starch, with moisture content of 15.24% (dry base), presented in Figure 1A, showed Tg of 118.19°C, with the beginning of this transition at about 116.52°C and the end at about 118.20°C. The endothermic peak around 140°C observed in thermogram (**Figure 1A**) of arrowroot starch was attributed mainly to evaporation of water present in starch.

The thermogram of potato starch with moisture content of 3.7% w/w (RH 11%) showed Tg of 161.72°C, while for the same sample with moisture content of 18.8% w/w (RH 75%) Tg of 141.91°C (Chuang et al., 2016). The Tg presented by starch depends heavily on moisture content of amylose and amylopectin, molecular interactions between starch and low molecular weight co-solutes and the inherent characteristics of the used measurement protocol (Perdomo et al., 2009).

For gum Arabic with moisture content of 14% (dry base), the thermogram showed Tg of 125.8°C, with the beginning of this transition at around 124.16°C and the end at around 125.97°C (**Figure 1B**). A similar endothermic peak for gum Arabic was reported by Mothé and Rao (2000) at about 90°C. According to the authors, this peak appeared due to the melting of crystallites during heating of gum Arabic with lower moisture content (0–40%).

Insert Figure 1 here

Experimental design

The experimental data for process yield (Y), moisture content (M), water activity (Aw), hygroscopicity (H) and solubility (S) were determined using 11 combinations of the independent variables, as shown in **Table 1**.

The results were fitted using a second-order regression model. The codified regression coefficients, F-values, p-values and coefficients of determination (R^2) are presented in **Table 2**. Nonsignificant terms, at confidence level of 95%, were eliminated and the predictive models were tested for adequacy and accuracy of fit by ANOVA. When calculated F-value (Fc) was greater than the tabulated F-value (Ft), the variation was explained by the regression and not by residues. Thus, the regression was significant, and the model could be considered predictive. **Figure 2** shows the response surfaces generated by the proposed models.

Inserts Table 1 and 2 here

Insert Figure 2 here

Process yield

According to **Table 1**, the experimental process yield values for blackberry pulp spray drying using arrowroot starch and gum Arabic mixture as encapsulating agent ranged between 28.77 and 56.95%. These values were similar to those obtained for spray drying of açai of 34.3–55.7% (Tonon et al., 2008), for jussara pulp of 33.88 to 76.55% (Santana et al., 2016), for beetroot juice ranged between 41.31% and 54.63% (Bazaria and Kumar, 2016). Eldridge et al. (2014) demonstrated a recovery of 61.3% of blackberry powder contained at 6.3:1 (w/w) mannitol:blackberry extract.

Blackberry is a fruit rich in sugars of low molecular weight such as glucose, fructose and sucrose (Kafkas et al., 2006), which have low Tg value: 32°C, 14.5°C, and 45°C, respectively (Saavedra-Leos et al., 2012). The Tg of the pulp was influenced by the present sugars, which makes difficult the drying process. In this work, it was not possible to obtain powdered blackberry pulp without addition of encapsulating agent, because the pulp behaved as syrup, sticking to the walls of dryer and obtaining a caked product instead of a dry powder. Without carrier, pomegranate juice formed a hard glass film on spray dryer chamber walls in dehydration process (Yousefi et al., 2011).

With incorporation of encapsulating agent in blackberry pulp before drying process, it was possible to obtain powder, but at smaller ratios of arrowroot starch/gum Arabic solids in relation to the total blackberry pulp solids, a large powder deposit was still observed in the walls of drying chamber and cyclone. This same behavior was reported by Igual et al. (2014) and Santana et al. (2016) during drying of lulo pulp and jussara pulp, respectively. Retention of product on the chamber wall is undesirable

(Santana et al., 2016). Process yield corresponds to product recovery and is mainly determined by the powder collection efficiency (Wang and Langrish, 2009).

The blackberry pulp drying process yield was significantly ($p<0.05$) influenced by inlet air temperature of the dryer and blackberry pulp solids:arrowroot starch/gum Arabic solids ratio, which presented quadratic negative effect and positive linear effect, respectively (**Table 2**).

The highest yields were obtained when higher blackberry pulp solids:arrowroot starch/gum Arabic solids ratio and inlet air temperature were used, as shown in **Figure 2A**. The experimental run 8 and the central point runs presented the highest drying process yield values (53.17–56.95%), which were significantly different ($p<0.05$) from results of other experimental runs. This behavior indicates that addition of encapsulating agent to blackberry pulp before spray drying was sufficient for a possible increase of glass transition temperature of system. Increased blackberry pulp solids:arrowroot starch/gum Arabic solids ratio favored blackberry pulp drying, reducing stickiness of powders encapsulation by encapsulating agents, consequently decreasing adherence of solids in drying chamber, which resulted in increased yield values. One way of confirming this hypothesis of reducing the viscosity of the powders is to determine the tg of the powders and relate to the temperature of the dryer's outlet air.

As for temperature, the increase in dryer’s inlet air temperature caused increase in process yield, which could be attributed to the greater efficiency of heat and mass transfer processes (Bazaria and Kumar, 2016). However, at temperatures above 143°C, there was decrease in yield, probably due to the caramelization of encapsulating agents, as well as of sugars present in blackberry pulp (Souza et al., 2015), which resulted in more adhesion to wall, so the amount of powder production and yield was reduced.

All the produced powders showed marked reddish color and flavor characteristics of blackberry fruit (**Figure 3**).

Moisture content

The results of statistical analysis applied to experimental data of the powders moisture content showed that the effects of linear, quadratic and interaction factors were not significant at 95% confidence interval ($p>0.05$). Due to these nonsignificant factors, it was not possible to construct a predictive mathematical model for behavior of moisture content of blackberry powders in function of independent variables.

However, **Table 1** shows that all powders produced presented moisture content values lower than 6%. Ferrari et al. (2012) obtained approximately 3% moisture content for blackberry juice powder produced by spray drying using inlet air temperature of 160°C and 5% of maltodextrin as encapsulating agent (w/w). The moisture content of sumac extract powders ranged between 2.94 and 4.22% (wet basis) (Caliskan and Dirim, 2016) and 0.9 to 7% for lulo powders (Igual et al., 2014).

For powder products, moisture content had great impact on flowability, stickiness and storage stability because of its plasticizing effects and crystallization behavior (Islam et al., 2016). Since water acts as plasticizer, only a small amount is required to change glass transition temperature, which increases the food matrix mobility during storage and causes alterations in powder (Goula and Adamopoulos, 2010). Thus, low water contents are desirable for powders. Any experimental run within the studied range for inlet air temperature and blackberry pulp solids:arrowroot starch/gum Arabic solids ratio will result in formation of powder with mean moisture content below 6% that is desirable to keep it microbiologically stable.

Water activity

Water activity values of powders ranged from 0.18±0.03 to 0.36±0.04 (**Table 1**). Cagaita (*Eugenia dysenterica* DC.) fruit extract powders presented water activity values lower than 0.3 (Daza et al., 2016). In the present study, except for run 5, that showed water activity of 0.36±0.04, results of all other runs were below the limit of 0.30, indicating that they are microbiologically stable, as there is no microbial growth below this value, as well as that there is delay in non-enzymatic browning, one of the main reactions of deterioration (Reid and Fennema, 2010).

The powders water activity was not significantly influenced ($p>0.05$) by the blackberry pulp solids:arrowroot starch/gum Arabic solids ratio. This means that powders produced with any blackberry pulp solids:arrowroot starch/gum Arabic solids ratio within the range studied will present low values for water activity. On the other hand, the dryer's inlet air temperature significantly influenced ($p<0.05$) the water activity (**Table 2**).

Figure 2B shows that the lowest water activity values are found at inlet air temperatures above 100°C, regardless of the blackberry pulp solids:arrowroot starch/gum Arabic solids ratio. This may be due to higher heat transfer to the particle, resulting in greater driving force for water evaporation, thus producing powders with lower moisture content and water activity (Daza et al., 2016).

Average Size

Powder particles of all the experimental runs presented varied and large sizes, with diameters ranging from 50.94±0.61 to 119.79±3.54 μm (**Table3 and Figure 3 A and B**). Mango powders produced with maltodextrin by spray drying ranged from 0.47 to

549 μm, while, without maltodextrin they ranged from 1.9 to 955 μm (Zotarelli et al., 2017).

Drying temperatures and blackberry pulp solids:arrowroot starch/gum Arabic solids ratio are parameters that may affect the particle size of powders obtained by spray drying. When drying is performed at higher temperatures, the process is faster than drying at lower temperatures, leading to immediate formation of particles and avoiding particle shrinkage. Similarly, encapsulating agent concentration increases feed viscosity and results in particles with larger diameters (Calomeni et al., 2017). Higher liquid viscosities result in larger particles in atomizers and larger particles in spray drying chamber (Jafari et al., 2017).

Besides the encapsulating agent, high content of sugars and acids in the fruit also increases viscosity of feed mixture during spraying in drying chamber. This introduces agglomeration and, consequently, produces larger particles (Shrestha et al., 2007). Solutions of blackberry pulp and encapsulating agent used in feeding were visually very viscous, which may have led to particles with larger diameters.

Araujo-Díaz et al. (2017) observed a general contraction of the volume of blueberry powder without encapsulating agent, indicating collapse of microstructure of the sample and suggesting crystallization of low melting sugars present in fruit juice. Islam et al. (2017) observed with scanning electron microscopy that orange juice/maltodextrin 60:40 powders were fused and clumped together and that orange juice/maltodextrin 50:50 powders were agglomerated. Agglomerations were not found in the powders produced with higher maltodextrin ratio (orange juice/maltodextrin 40:60 and orange juice/maltodextrin 30:70).

In this study, inlet air temperature and blackberry pulp solids:arrowroot starch/gum Arabic solids ratio did not significantly affect particle size. The results of statistical analysis applied to the experimental data of the powders average size showed that the effects of linear, quadratic and interaction factors were not significant at 95% confidence level (p>0.05). Due to these nonsignificant factors, it was not possible to construct a predictive mathematical model for the behavior of average size of blackberry powders in function of independent variables.

It is believed that, in this work, the presence of larger particles was due to a possible agglomeration process (Figure 3 A and B). The particle size distributions of the samples are shown in **Table 3**. Similar behavior was observed by Zotarelli et al. (2017) for mango powder obtained by spray drying. This can be attributed to the formation of bridges between the smallest particles, resulting in agglomeration that formed larger particles (Zotarelli et al., 2017).

Insert Table 3 here

Hygroscopicity

Hygroscopicity is a material's capacity to absorb moisture from the surrounding environment, and it is an important property to be considered, due to its influence on food stability (Daza et al., 2016). The blackberry powders were stored for 7 days in desiccators with saturated NaCl solution and 75.7% relative humidity at 25°C. As shown in **Figure 3 C**, after 3 days in this condition, the powders of all tests absorbed water from environment, causing caking of the particles and darkening of the powders. After 7 days, powders had a very sticky appearance, indicating that blackberry powders are unstable and hygroscopic, which may hinder their handling.

Insert Figure 3 here

Hygroscopicity values of powders obtained by blackberry pulp drying using an arrowroot starch and gum arabic mixture as encapsulating agent ranged from 10.93±0.17 to 15.31±0.17 g of adsorbed water/100 g of solids (**Table 1**). These results were lower than those found by Daza et al. (2016) for cagaita powders obtained by using gum arabic (14.8–18.8 g of absorbed water per 100 g of sample) and inulin (13.8 and 19.4 g of absorbed water per 100 g of sample) as carrier. Dried beetroot juice particles presented hygroscopicity values of 14.46–20.68 g of water/100 g of dry matter (Bazaria and Kumar, 2016).

Inlet air temperature and blackberry pulp solids:arrowroot starch/gum Arabic solids ratio significantly influenced ($p<0.05$) the hygroscopicity of blackberry powders, which presented positive and negative linear effect, respectively (**Table 2**). Inlet air temperature was the variable that most influenced the final product's hygroscopicity.

According to **Figure 2C**, the lowest values of hygroscopicity were obtained when lower inlet air temperature and higher blackberry pulp solids:arrowroot starch/gum arabic solids ratio were used. This same behavior was observed by Bazaria and Kumar (2016) for dried beetroot juice particles. According to the authors, this could be well explained by the increasing moisture content with lower inlet air temperature. Powders with very low moisture content tend to be more hygroscopic. The capacity to adsorb ambient moisture is related to the water concentration gradient between the product and the surrounding air (Tonon et al., 2008).

As for the blackberry pulp solids:arrowroot starch/gum Arabic solids ratio, both arrowroot starch and gum arabic are materials with low hygroscopicity; consequently, blackberry pulp microencapsulation tends to reduce the resulting powder's hygroscopicity. This fact demonstrated the capacity of arrowroot starch and gum arabic mixture as encapsulating agent to improve the hygroscopicity values of the blackberry powders obtained and make them more stable. These results are in agreement with those observed for orange juice, cactus pear juice, cagaita fruit extracts and beetroot juice powders obtained by spray drying, which showed decreased hygroscopicity due to increased carrier agent concentration (Rodriguez-Hernandez et al., 2005; Bazaria and Kumar, 2016; Daza et al., 2016; Islam et al., 2016).

Hygroscopicity of orange juice powder decreased from 0.195±0.02 to 0.143±0.01 g H_2O/g with increasing maltodextrin concentration (Islam et al., 2016). In this study, the blackberry powder of run 3 produced with inlet air temperature of 143 °C and ratio of blackberry pulp solids:arrowroot starch/gum Arabic solids of 1:0.72 was the most hygroscopic (15.31 g of adsorbed water/100 g of solids), whereas the powder of run 2, produced with inlet air temperature of 107 °C and ratio of blackberry pulp solids:arrowroot starch/gum Arabic solids of 1:1.78, was the least hygroscopic (10.93 g of adsorbed water/100 g of solids).

Solubility

Solubility is another important parameter that may be evaluated after powder production, because it can potentially affect some of their properties, such as the reconstitution of dry extract or the availability of encapsulated compounds in a food system (Daza et al., 2016). Solubility of blackberry powder particles ranged from 58.39±0.99 to 79.37±5.25% (**Table 1)**, lower than those reported by Daza et al. (2016) and Santana et al. (2016) in their studies on spray dried cagaita (*Eugenia dysenterica* DC.) fruit extracts obtained by using gum arabic (94.4–97.8%) and inulin (87.7–95.9%) and spray dried jussara pulp produced by using ternary mixture of gum arabic/maltodextrin/whey protein concentrate (78.81–93.46%) and gum arabic/modified starch/soy protein isolate (81.23–92.75%), respectively.

The differences in solubility can be explained by chemical structure of each carrier agent. The occurrence of water adsorption by a carbohydrate is attributed to the links between hydrogen present in water molecules and hydroxyl groups available in amorphous regions of substrate as well as in regions that have a crystalline surface (Negrão-Murakami et al., 2017).

The solubility of blackberry powders was significantly ($p<0.05$) influenced by variable inlet air temperature, presenting a positive linear and quadratic effect. The interaction between inlet air temperature and blackberry pulp solids:arrowroot starch/gum Arabic solids ratio also showed a significant positive effect on the solubility of blackberry powders (**Table 2**).

Less soluble powders were obtained at lower inlet air temperatures and higher blackberry pulp solids:arrowroot starch/gum Arabic solids ratio (**Figure 2D)**, similar to the behavior observed for hygroscopicity. Although gum arabic is highly soluble (Daza et al., 2016), arrowroot starch in its natural form is highly insoluble in water at room temperature, which probably contributed to the decrease of blackberry powders solubility.

On the other hand, more soluble powders were produced when extreme inlet air temperatures were used, as shown in **Figure 2D**. Higher temperatures result in faster drying rates, avoiding the particle encountering during drying, maintaining the initial structure formed. Consequently, more porous or fragmented particles are produced at higher temperatures, increasing the surface of particles exposed to water, facilitating the access of water into its structure, hence favoring solubilization (Souza et al., 2015).

Optimization of process parameters and analysis of the model

The optimum spray drying conditions for blackberry pulp were determined by surface response methodology, in order to obtain higher process yield and soluble powders in water with low hygroscopic. Due to variation in particle size causing agglomeration it was not possible to generate a predictive mathematical model for the behavior of average size of blackberry powders as a function of independent variables, this response variable was not considered for choosing optimal drying conditions.

Moisture content and water activity were low for all runs (moisture content < 6% and water activity < 0.36). Therefore, powders produced with any inlet air temperature and blackberry pulp solids:arrowroot starch/gum Arabic solids ratio within the studied range would present good microbiological stability, hence these response variables were not considered to choose optimal drying conditions.

Analyzing the model for process yield (**Figure 2A**), the highest values were observed using intermediate inlet air temperature and high blackberry pulp solids:arrowroot starch/gum Arabic solids ratio. According to **Figure 2C**, the lowest values for hygroscopicity were obtained when lower inlet air temperature and higher blackberry pulp solids:arrowroot starch/gum Arabic solids ratio were used. On the other hand, more soluble powders were produced at extreme inlet air temperatures and high blackberry pulp solids:arrowroot starch/gum Arabic solids ratio, as shown in **Figure 2D.**

Thus, the temperature of 143 °C was recommended as optimized condition, since at higher temperatures, powder solubility increased and process yield were reduced at temperatures above 143 °C. As process yield and powder solubility increased with increasing blackberry pulp solids:arrowroot starch/gum Arabic solids ratio and hygroscopicity decreased, the ratio of blackberry pulp solids to arrowroot starch/gum

Arabic solids of 1:1.78 was used as optimum condition. Run 4, with inlet air temperature of 143 °C and blackberry pulp solids:arrowroot starch/gum Arabic solids ratio of 1:1.78 was capable of producing powders with low hygroscopicity (12.99 g of adsorbed water/100 g of solids), good solubility in water (74.47%), and satisfactory process yield (50.06%), as shown in **Table 1**.

The optimized conditions for blackberry pulp spray drying were experimentally reproduced and process yield, hygroscopicity and solubility were determined in triplicate, as shown in **Table 4**, with predicted mean and experimental values according to the quadratic model.

Insert Table 4 here

As expected, the powder produced in optimized condition had low moisture content and water activity, 1.45±0.51% and 0.13±0.04, respectively, indicating microbiological stability. The values observed for process yield, hygroscopicity, and solubility were relatively close to those observed previously for run 4, as shown in **Table 1**. Based on the values for relative deviation (% DR) obtained for each response variable, the optimization methodology used was considered satisfactory.

Conclusions

This study indicated that the arrowroot starch and gum arabic mixture used as encapsulating agent and the increase in the higher drying inlet air temperatures were capable of making blackberry pulp more stable by encapsulation, increasing the efficiency of the drying process and producing powders microbiologically stable, with lower values for hygroscopicity and higher solubility in water. Temperature of 143 °C and blackberry pulp solids:arrowroot starch/gum arabic solids ratio of 1:1.78 were the ideal conditions to obtain high yield and blackberry powders that are soluble in water and less hygroscopic. In future work, the stability of the powders during long periods of storage should be evaluated.

Disclosure statement

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the article.

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