Protein content maximization of vegetable paste by incorporation of whey through the linear programming: drying and rehydration evaluation

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Abstract The vegetable paste was optimized by the protein content maximization through incorporation of whey using the linear programming, with linear restrictions functions. The enriched paste was dried in a spouted bed of cone-cylindrical geometry, at different conditions, and the dried powder products were analyzed by the functional, nutritional, bioactive, chemical, thermal and morphological properties and, also its rehydration characteristics were evaluated. The best results were found in the assay performed at inlet drying air temperature of 100 °C and in paste solids concentration of 10% (w/w). In these drying conditions, the values were of protein solubility of $26.5 \pm 0.1\%$ (w/w), water holding capacity $10.8 \pm 0.1 \text{ g g}^{-1}$, protein digestibility of $84.9 \pm 2.2\%$ (w/w), total phenolic compounds $7.72 \pm 0.1 \text{ mg}_{\text{EAG}} \text{ g}_{\text{sample}}^{-1}$, antioxidant activity of $75.7 \pm 0.2\%$ of DPPH inhibition. The glass transition temperature was in range of 97.3 °C, due to the lactose non-caramelization, this fact aided in the functionality of the bed. The powder morphology presented irregular and rough structure, with particles size lower than 100 µm and, with a low crystallinity index (12.8%). The rehydration constant value was found as 16.5 min^{-1} , showing the rapidity with that the water diffused into the powder in the most suitable condition.

Keywords Linear programming · Physicochemical properties · Rehydration · Vegetable drying

List of symbols

A	Protein concentration (mg mL^{-1})
A_1	Parameter of Equation 16 (dimensionless)
C	Index of crystallinity (%)
C_1	Minimum carbohydrate value (% w/w)
C_2	Maximum carbohydrate value (% w/w)
$C_{d.b.}$	Amount of the constituents of the paste on dry basis (dimensionless)
c_i	Amount of carbohydrates of each constituent (g g^{-1})
F_a	Non-crystalline area (2θ)
F_C	Diffraction peak area (2θ)
k_r	Rehydration kinetic constant (min^{-1})
L_1	Minimum lipid value (% w/w)
L_2	Maximum lipid value (% w/w)
l_i	Amount of lipids from each constituent (g g^{-1})
m	Maximum amount of each constituent (g)
m_i	Amount of each constituent (g)
P_1	Minimum protein value (% w/w)
P_2	Maximum protein value (% w/w)
p_i	Amount of proteins of each constituent (g g^{-1})
P_S	Soluble protein (% w/w)
P_T	Total protein (% w/w)
R^2	Coefficient of determination (dimensionless)
S	Concentration of protein in the sample (% w/w)
t	Time (min)
V_{C1}	Minimum value of caloric value (kcal)
V_{C2}	Maximum value of caloric value (kcal)
vc_i	Caloric value of each constituent (kcal g^{-1})
W	Sample mass (g)
W_{er}	Mass of evaporated residue (g)
X	Moisture content ($\text{kg}_{\text{water}} \text{ kg}_{\text{dry matter}}^{-1} \text{ d.b.}$)

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X_0	Initial moisture content ($\text{kg}_{\text{water}} \text{kg}_{\text{dry matter}}^{-1}$ d.b.)
X_S	Saturation moisture content ($\text{kg}_{\text{water}} \text{kg}_{\text{dry matter}}^{-1}$ d.b.)

Introduction

The Food and Agriculture Organization has recommended a diet rich in agricultural products, and this strong call aims to balance production surpluses, with the consumption increase and improves the nutritional quality of the population (FAO 2017). The desirable nutrients in a diet are proteins as desirable macronutrient, fibers, vitamins (A, C, E), calcium, iron, potassium and magnesium, while the nutrients that should be limited are lipids and carbohydrates (sugars) (Drewnowski 2017). The food consumption containing a vegetable variety is considered healthy and, can be associated the disease prevention/reduction at long-time (Heerman et al. 2017). Despite the nutritional benefits, the vegetables are poor in proteins content, thus, the enrichment in proteins is an alternative to obtain a high quality final product.

The proteins enrichment of a formulation may be performed with products of high proteins concentration. The whey is a byproduct of great interest, and their health benefits are recognized due to its versatile functional properties. There is a great evidence on numerous beneficial aspects (physical, chemical, nutritional and biological) of the whey proteins components (Smithers 2015). Together, with demand for healthy foods and the advancement of the processing technologies, the whey proteins show great importance in supplementation of food formulations (Qi et al. 2017). The protein enrichment of vegetal paste can be performed feasible by linear programming, because this tool establishes an optimal mixture of several variables, through mathematical models, respecting the linear function of effectiveness, satisfying the desired set of linear restrictions (Rocha et al. 2014; Larrosa et al. 2015). The basic idea of linear programming is to find the maximum or minimum of a goal under linear restrictions. This modeling is based on equations set design to describe the system with the highest possible precision, respecting the particular characteristics of each constituent (Bettinger 2017).

The vegetable consumption is limited by its high perishability, thus, an alternative to maintain a diversified diet in all seasons, is to obtain the vegetables in its dehydrated forms, for later reconstitution. Drying operation is a widely used method to minimize losses in the agricultural sector, because it reduces the moisture content and increases the shelf life of the products. This technique is suitable for vegetables due to the large processing volume and fast drying rates (Mujumdar and Huang 2007; Delele et al. 2015). The spouted bed technique has been used for the drying of pastes and suspensions of thermosensitive

materials, being important the control of the fluid dynamics and operational parameters, because these are related to process efficiency and product quality (Epstein and Grace 2011).

The reconstitution of the dried powder can be achieved through rehydration and, the powder rehydration in water is an essential property of dried products, because they are normally consumed reconstituted. The rehydration kinetics describes mechanisms and the influence that certain process variables exert on the moisture transfer. In addition, the drying conditions can also influence the water migration during rehydration, affecting the rehydration capacity of the powders. The rehydration operation is dependent of the diffusion mechanisms that occurred in the drying operation, so that a new mass transfer takes place (Krokida and Marinos-Kouris 2003; Gondek and Lewicki 2007).

The aim of this work was to maximize the protein content of a vegetables paste enriched with whey through linear programming, evaluating the drying operation in spouted bed and the rehydration kinetics of the dried powder. The drying operation was evaluated by the dried powder stability, according to functional, nutritional and bioactive properties, as well as, by infrared spectroscopy, scanning electron microscopy, differential scanning calorimetry and X-ray diffraction.

Materials and methods

Feedstock, formulation and obtaining of whey enriched vegetable paste

The paste consisted of white onion (*Allium cepa* L.), tomato (*Lycopersicum esculentum*), carrot (*Daucus carota* L.), kale (*Brassica oleracea*), potato (*Solanum tuberosum*), soybean oil and whey. All the vegetables and the soybean oil were purchased on local market (Rio Grande, RS, Brazil), and the whey powder was donated by the University of Vale do Taquari (Lajeado, RS, Brazil). The constituents were choice based on its phytochemical contents and their availabilities throughout the year, and its centesimal compositions and caloric values were determined in previous work (Rocha et al. 2014).

In the paste formulation was used as a logical tool the linear programming technique, maximizing the protein content, with restrictions only for macro nutrients, using as application Microsoft Solver Excel, because, based on perfectly defined logical procedures, it is possible to solve a problem in a finite number of steps (Charkhgard et al. 2017). The restricted nutrients were carbohydrates, proteins, lipids and caloric value, the minimum and maximum limits established as restrictions were of 0.50–0.70 (g g^{-1}), 0.15–0.20 (g g^{-1}), 0.04 (g g^{-1}), and 2.00–5.00 (kcal g^{-1}),

respectively. The lipid content was set at a concentration of 0.04 g g^{-1} according to previous work (Rocha et al. 2014), which showed a good circulation of the polyethylene inert particles in the bed, then, it was not necessary to vary this restriction. The software allowed to perform the optimization, being that the objective function was of the protein content maximization. This function is a linear equation, which relates the constituents available with its respective proteins contents, according to Eq. (1).

$$P_T = \sum_{n=1}^{i=7} m_i p_i \quad (1)$$

The restrictions functions are equations and inequations, which delimit the function to be optimized. Equation (2) shows the amount of all constituents in dry basis.

$$C_{db} = \sum_{n=1}^{i=7} m_i \quad (2)$$

The inequations that present the limits of constituents (carbohydrates, proteins, lipids, caloric value) and, that restrict the mathematical possibility of negative values for amount of mass and that the amount of mass is higher than the predetermined maximum quantity are shown in the “Appendix”.

After performed the maximization by the linear programming, which estimated the amounts necessary to obtain a proteins-optimized vegetable paste formulation, the vegetables were washed in potable water, peeled, weighed, cut and crushed, using a turbo juicer (Mondial, model CF-01, Brazil). The remaining solid was blended with the juice extracted in a food processor (Cuisinart, model DLC-2A, China). Finally, the vegetable paste was homogenized in a blender with addition of commercial soybean oil and whey and, then, the material was screened in Tyler series (mesh 10), obtaining the whey enriched vegetable paste.

Drying assays

Drying assays of the whey enriched vegetable paste were performed on a spouted bed cell with cone-cylindrical geometry, built on previous work (Rocha et al. 2014), and the inert bed was of polyethylene particles. The total drying time of each assays was of 6 h. The drying fluid was air, heated by an electric system of 2400 W with thermostatic control, supplied by a radial blower (Ibram, model CR0850, Brazil) of 7.5 HP. The air flow measure was by an orifice plate, and the measurements of air temperatures were performed by copper-constantan thermocouples. The air circulation rate used was 100% higher than the minimum spouting velocity, as recommend for the drying of pastes and suspensions by Epstein and Grace (2011). The

paste feed system in the drying cell was performed with two atomizing nozzles with compressed air at 100 kPa manometric pressure, arranged in the center of the column in opposite positions, and the paste feed rate was of 600 mL h^{-1} , being controlled by peristaltic pump. The dry powder was transported pneumatically to the top of the column, which was connected in a cyclone, and collected in a vessel coupled to the cyclone.

The effects of the inlet drying air temperature (90 and 100°C) and the paste solids concentration (7.5 and 10.0%, w/w) in the dried products were evaluated by the proteins functionality and antioxidant properties. The experimental assays were carried out in four treatments, as following: (no. 1) 90°C and 7.5% (w/w); (no. 2) 90°C and 10% (w/w); (no. 3) 100°C and 7.5% (w/w); (no. 4) 100°C and 10% (w/w).

Analytical methodology

The chemical composition analyzes were carried out on the fresh paste and dried powders. The samples were analyzed for moisture content, ash content, protein content, crude fiber content according to AOAC (1995), lipid content was according to Bligh and Dyer (1959), and carbohydrate content was by difference.

The determination of the protein solubility was in aqueous medium. The sample was diluted in water (1:20), stirred, followed by centrifugation, and finally, the proteins were determined from the supernatant. The soluble protein content was determined on the total protein content of the sample as shown in Eq. (3).

$$P_S = \frac{A \times 50}{W \left(\frac{S}{100} \right)} \times 100 \quad (3)$$

The water holding capacity (WHC) was evaluated by a mixture of powder and water (1:12), respectively, was maintained under stirring and, then centrifuged. The WHC values were calculated by Eq. (4).

$$WHC = \frac{W_{er}}{W - W_{er}} \quad (4)$$

The protein digestibility was performed using solutions of the enzymes pepsin and pancreatin, simulating the characteristic conditions of the gastrointestinal tract, according to Khalil et al. (2007) with modifications. The sample under stirring was hydrolyzed with pepsin solution in $0.1 \text{ mol L}^{-1} \text{ HCl}$, at temperature of 37°C . At the end, the pH of the sample was raised to 7.0 using $0.3 \text{ mol L}^{-1} \text{ NaOH}$ solution and, the pancreatin solution was added in phosphate buffer pH 8.0. After hydrolysis, the undigested material was precipitated, then, the sample was centrifuged and filtered. In the supernatant, the content of

released amino acids was determined using as standard the tyrosine curve (0.01–0.1 mg mL⁻¹).

The quantification of the total phenolic compounds was performed by spectrophotometric method (Bioespectro, model SP-22, Brazil) with the Folin–Ciocalteu reagent, using a standard curve of gallic acid (0–20 µg mL⁻¹). The antioxidant activity was determined by the ability to sequester the stable radical DPPH (1,1-diphenyl-2-picrylhydrazyl) according to Miliauskas et al. (2004).

The methanolic extracts of the vegetable paste were analyzed in the infrared spectrum by means of Fourier transformed (FTIR) (Shimadzu, Prestige 21, model The-210045, Japan) to identify the major peaks representing the functional groups. The analysis is based on Fourier transformed spectroscopy with horizontal attenuated total reflectance (HATR). The analyzes were performed at ambient temperature of 20 °C using a scan through the frequency of 4000–750 cm⁻¹ at resolution of 4 cm⁻¹.

Thermal analysis of differential scanning calorimetry (DSC) (Shimadzu, model DSC60, Japan) was performed to determine the thermal stability of the products. The powders samples were placed in hermetically sealed silver capsules subjected to heating from 24 to 215 °C with a linear heating rate of 10 °C min⁻¹, an empty capsule was used as reference. The calorimetric curves were obtained by Universal Analysis Program software, version 2.2 (TA60 instruments) with the aid of a calorimeter coupled in the control computer.

The morphological structures of the samples were determined by scanning electron microscopy (SEM), using a microscope (Jeol, model JSM-6010LV, Japan). The samples were metallized with gold in a vacuum chamber (Denton Vacuum, Sputtering Desk V, USA), and 15 kV voltage accelerations were used to obtain the images, with magnifications in the order of 250×.

X-ray diffraction was carried out to evaluate the structural impact on the dry samples using a X-ray diffractometer (model D8 Advance, Bruker, Germany), with Cu Kα radiations. The instrument was operated at 40 kV and 40 mA, and the diffraction results were obtained in a range from 2θ = 5°–70°, at a rate of 2° min⁻¹ (2θ) and a pitch size of 0.05° (2θ). The crystallinity (C) was calculated by Eq. (5), using the Diffrac.Eva 3.1 software.

$$C = \frac{F_c}{F_c + F_a} 100\% \quad (5)$$

Rehydration kinetics

The powders samples were rehydrated with distilled water at room temperature (24 ± 1 °C). A powder sample of 1.0 g was placed on filter paper in the buchner funnel, which was attached to a silicone hose in a graduated pipette

(10 mL), at the same level as the funnel. The rehydration kinetics was evaluated by the amount of water adsorbed (0.1 mL) by the powder sample at a given time. The results were expressed in curves as a relation of the moisture content (d.b.) and the rehydration time, being the rehydration constant (k_r) estimated according to Eq. (6) (Gondek and Lewicki 2007).

$$\frac{X_s - X}{X_s - X_0} = A_1 \exp(-k_r t) \quad (6)$$

Statistical analysis

The responses in the statistical analysis used in the evaluation of the drying assays of the whey enriched vegetable paste were: protein solubility, water holding capacity, protein digestibility in vitro, total phenolic compounds and antioxidant activity. All the drying assays were performed in duplicate and, the products analyses carried out were in triplicate. The values were compared using Tukey's test to determine the significant differences between the values in the 95% confidence interval ($p < 0.05$) (Box et al. 2005).

Results and discussion

Linear programming for optimization of the whey enriched vegetable paste

The solution of the problem proposed in the study, in terms of amounts of constituents and optimized restrictions, was found with the higher efficiency and the resolution quality. Therefore, the response of interest to the optimization was restarted several times, according to the finite sequence of logical operations and, when that sequence was applied to a finite number of satisfactory data, the problem was solved. The values of the optimized amounts of all constituents by the linear programming technique, based on centesimal composition of each constituent, were: 329.8 g of tomato, 183.7 g of carrot, 157.8 g of kale, 143.7 g of onion, 74.0 g of potato, 9.5 g of whey and 1.4 g of soybean oil. It was observed that the tomato was the constituent that converged to the higher amount by the linear programming in relation to the other constituents. This was because the proteins limits were restricted between 15 and 20% (w/w), and the tomato presents in its chemical composition high protein content (0.22 g_{protein} g_{dry matter}⁻¹). Although, the objective function is to maximize the protein content, not necessarily the constituents that have higher amounts of proteins would be optimized in greater amount. Because, the optimization of a formulation must respect the

established constraints, which are delimited to achieve the proposed objective.

The optimized restrictions for each constituent based on 100 g of whey enriched vegetable paste, by the linear programming technique, were: carbohydrate content of 61 g, protein content of 20 g and lipid content of 4 g, being the caloric value of 320.4 kcal. It was possible to observe that the carbohydrate content was restricted to the mean value of the restriction range. The protein content was restricted to the established maximum limit, since the main aim was to maximize this constituent. The lipid content had its limits set at 4%, and the caloric value had its restriction converged to the minimum limit.

After to perform the maximization by the linear programming, the whey enriched vegetable paste was experimentally formulated, and its real centesimal composition was: protein content of 19.5 ± 0.3 (% w/w), carbohydrate content of 60.1 ± 0.6 (% w/w), lipid content of 3.8 ± 0.2 (% w/w), fiber content of 9.8 ± 0.1 (% w/w) and ash content of 6.6 ± 0.1 (% w/w); being their the caloric value of 383.5 ± 0.5 (kcal 100 g^{-1}). The enriched vegetable paste presented a composition close to the limits established in the nutrient restrictions, as carbohydrate content, protein content and lipid content. The small variations may have occurred because the composition of the vegetables may change due to its maturation stage. Generally, when its maturation approaches, the senescence tends to increase its protein content, because its seeds are preparing to give rise to a new plant, and also, depends on the year season in which it was harvested, leading to the plant to have a greater or lesser disposition of nutrients (Rajasekar et al. 2017).

Functional, nutritional and bioactive properties

In Table 1, the results for protein solubility, water retention capacity (WHC), protein digestibility, total phenolic

compounds and antioxidant activity showed a significant difference ($p > 0.05$), in the drying conditions studied.

The protein solubility is the most important functional property (Fennema et al. 2010), then, should be the first one verified in pulverized food products. Protein solubility presented the highest value in the treatment with higher temperature, 100 °C (Table 1), this shows the tendency of solubility to increase in certain temperature ranges (40–60 °C), because the drying in the spouted bed presented a low residence time (around 13 min), leading to the product not to reach the outlet drying air temperature. The increases in protein solubility observed after heat treatments may be associated with the highly proteolytic activity of the samples during treatment, which can lead to hydrolysis of the stored proteins making them more easily solubilized in water.

Protein digestibility in vitro showed that the treatments with the highest inlet drying air temperature, 100 °C (Table 1), obtained the highest protein digestibility values [around 85% (w/w)] and, in the drying air temperature of 90 °C the values were around 76% (w/w) of bioavailable protein. This can be due to the lower residence time of the material into the drying cell at air temperature of 100 °C, because the degree of damage depends on the amount of heat applied in the operation time. Another factor associated with protein digestibility is the powder morphology, because the dry powders with rougher surfaces are more susceptible to digestion, and the sample become more easily dissolved and digested (Chen et al. 2016).

The water holding capacity presented values from 4.8 to 10.8 g g^{-1} (Table 1), the best results was obtained at the highest solids concentration. In this study, the paste was processed using all inputs (juice and pulp) of the vegetables, leading the dried product to present ruptured of cellular structures, such as vacuoles, cytoplasm and cell wall. These compartments being composed of several cross-linked biopolymers, thus, the water retention can be seen as good crosslinked polymer gel former. Other substances that

Table 1 Results of powders products by drying assays of the whey enriched vegetable paste

Exp. (no.)	Sol.* (%w/w)	WHC* (g g^{-1})	Digest.* (%w/w)	Phen.* (mg _{EAG} g^{-1})	AA* (%inhibition)
(1)	19.8 ± 0.5^d	4.8 ± 0.5^d	78.8 ± 1.0^c	3.09 ± 0.5^d	72.8 ± 0.3^d
(2)	34.2 ± 1.1^b	10.1 ± 0.5^b	75.4 ± 0.6^d	4.22 ± 0.3^b	74.6 ± 0.3^b
(3)	39.4 ± 0.2^a	8.3 ± 0.1^c	82.1 ± 0.3^b	5.25 ± 0.1^c	73.8 ± 0.6^c
(4)	26.5 ± 0.1^c	10.8 ± 0.1^a	84.9 ± 2.2^a	7.72 ± 0.1^a	75.7 ± 0.2^a

Sol protein solubility, WHC water retention capacity, Digest protein digestibility, Phen total phenolic compounds, AA antioxidant activity. Different letters in the same column show significant difference ($p < 0.05$). Legend for the inlet drying air temperature and the paste solids concentration in each experiment—Exp. (no. 1): 90 °C and 7.5% (w/w); Exp. (no. 2): 90 °C and 10% (w/w); Exp. (no. 3): 100 °C and 7.5% (w/w); Exp. (no. 4): 100 °C and 10% (w/w)

*Values are mean $\pm$ SD of three measurements

act on the water retention are whey soluble proteins, which have an excellent amino acids profile, characterizing as proteins of high biological value that are easily binding water. Kruif et al. (2015) found that a higher concentration of protein molecules caused a greater interaction with the water, evidencing an increase in water retention capacity, this fact was also verified in the present study, where the conditions of operation of higher solids concentration found the highest values of WHC.

The antioxidant capacity values (antioxidant activity and total phenolic compounds) of the dried powder samples increased with the increase of the solids concentration and of the drying air temperature (Table 1). During the spouted bed drying, these results were reached because the products stayed little time in contact with the hot air, preserving the thermosensitive substances. The total antioxidant activity showed a small decrease in all treatments in relation to the fresh sample (value of $76.6 \pm 0.6\%$ DPPH inhibition). The total phenolic compounds values increased in high temperature and high concentration when compared to the fresh sample (value of $4.36 \pm 0.3 \text{ mg}_{\text{EAG}} \text{ g}_{\text{sample}}^{-1}$) and, these increases may be associated with a protective effect of the phenolic content, which occurs during the drying. This protective effect against oxidative damage in cells can be influenced by the concentration of the solids paste, because at higher concentration a thicker film of product forms on the bed polyethylene particles, so that the material is not completely exposed to the drying air. During the drying operation, the phenol group can to present different oxidation states, which may influence the antioxidant activity, as the vegetables in the paste contained numerous phenolic compounds, it is possible to appear differences in the profile of bioactive compounds that can result in complex changes in the antioxidant activity.

Chemical, thermal and morphological properties

The infrared spectra of the methanolic extracts of the dried powders samples (presented in Electronic Supplementary Material) show that, their chemical compositions with respect to the organic clusters bands were found in the regions of 3500 and 3150 cm^{-1} , 2850 and 2750, 1650, 1400, 1150, 840 cm^{-1} in all drying conditions. There was also a peak in the region of 1000 cm^{-1} and, this peak was evidenced in the conditions where the solids concentration was of 10% (w/w) and the air temperature of 100 °C.

The peaks of 3500 and 3150 cm^{-1} when appear in duets correspond to the stretching of the grouping (–OH) characteristic of alcohols or phenols, however, when coming from alcohols these peaks are less intense than the phenols. The peaks of 2850 and 2750 cm^{-1} may correspond to stretching (–CHO) consisting of a pair of weak bands, one

in 2860–2800 cm^{-1} and other in 2760–2700 cm^{-1} representing the aldehyde functional group (Silverstein et al. 2005). The region between 1680 and 900 cm^{-1} represent several peaks and is conferred the phenolic compounds bands and, also it is associated the bands in 1600–1520 cm^{-1} regions of the (C=C) vibrations, which are typical of aromatic systems. In the region between 1640 and 1400 cm^{-1} bands, the (C=O) vibrations correspond of the benzopyran aromatic ring, this grouping is associated with the flavonoids, which are substances with high antioxidant power present in natural foods, such as onion in the form of quercetin, flavonoid with therapeutic properties. The organic acids and sugars may present one or more alcohol (–OH) groups, this presence was confirmed by the bands in range of 1150 and 1000 cm^{-1} . In the present study, the peak in 1000 cm^{-1} was formed during the drying assays, and this information is linked to the increase of the antioxidant compounds, evidencing the ability of the drying operation to develop a protective effect against the oxidative damages in samples. The region from 900 to 750 cm^{-1} may be the (C–H) deformation and shows the characteristic absorptions of the aromatic rings that lie outside the plane (Silverstein et al. 2005), frequently present in biomaterials with antioxidant activity.

Figure 1 shows the thermogravimetric curves of the powders analyzed by differential scanning calorimetry (DSC). In this figure, the samples presented endothermic peaks, with the most pronounced peak in the region of 97 °C for the dried powder at air temperature of 100 °C and concentration of 10% (w/w), indicating that the sample was more thermally stable. This behavior is associated with

Fig. 1 Thermogravimetric curves from the powder samples of whey enriched vegetable paste. Legend for the inlet drying air temperature and the paste solids concentration in each experiment—(no. 1): 90 °C and 7.5% (w/w); (no. 2): 90 °C and 10% (w/w); (no. 3): 100 °C and 7.5% (w/w); (no. 4): 100 °C and 10% (w/w)

Table 2 Results of saturation moisture content and rehydration constant for the dried powders of whey enriched vegetable paste

Exp. (no.)	X_{sat} (kg _{water} kg _{dry matter} ⁻¹)	k_r (min ⁻¹)	R^2
(1)	3.63 ± 0.05 ^a	3.09 ± 1.06 ^c	0.928
(2)	3.35 ± 0.09 ^b	6.37 ± 2.02 ^b	0.971
(3)	3.63 ± 0.04 ^a	7.02 ± 2.17 ^b	0.949
(4)	2.97 ± 0.05 ^c	16.5 ± 2.69 ^a	0.975

Different letters in the same column show significant difference ($p < 0.05$). Legend for the inlet drying air temperature and the paste solids concentration in each experiment—Exp. (no. 1): 90 °C and 7.5% (w/w); Exp. (no. 2): 90 °C and 10% (w/w); Exp. (no. 3): 100 °C and 7.5% (w/w); Exp. (no. 4): 100 °C and 10% (w/w)

Values are mean ± standard deviation of three measurements

the higher thermal stability of the compounds present in the powder, such as functional and bioactive compounds, which remained unchanged and/or higher than the initial value after heat treatment. The DSC analysis is also able to provide information on sample fusion, phase transitions, evaporation, dehydration and pyrolysis of the material (Rahman et al. 2017). Thus, the impact of the drying conditions on the powders of the treatments (nos. 1, 2, 3) and (no. 4) were evaluated by the glass transition temperatures, which were of 121.7, 81.8, 88.3 and 97.3 °C, respectively. This behavior showed that there was a strong tendency of the powders with lower moisture content to reach its transition state at lower temperatures, because the

dried powders samples showed the moisture content values of 9.3, 8.1, 8.2 and 8.9% (w/w), respectively, for treatment from no. 1 to no. 4 (Table 2). In the glass transition temperature, the amorphous system changes from high viscosity to low viscosity, thus, this temperature is associated with the powder stability in relation to its mobility. In addition, particles stored above the glass transition temperature lead to tackiness and agglomeration, which can directly affect the functional properties studied and the reconstitution of the material.

Figure 2 shows the scanning electronic microscopies of the dried powders in the different conditions, with magnifications of 250×. The powders presented particles sizes higher than 100 µm for treatments no. 1 and no. 2, and lower than 100 µm for treatments no. 3 and no. 4. It was also possible to observe the tendency of the particles to agglomerate in the higher drying temperature, because the presence of lactose crystals can lead the caramelization reaction during drying operation. This fact was confirmed by the powders adhesion in the bed generating an accumulation of 18 and 22%, respectively, for the experiments no. 3 and no. 4. Thus, in powder formulations containing lactose are susceptible to caramelization, leading the tendency to agglomerate due to the adhesiveness promoted by the sugar. The images also showed that the powders presented irregular, compact and slightly rough structure. The powders samples on treatments no. 3 and no. 4 showed spherical format with agglomerate formation and tend to

Fig. 2 Scanning electron microscopy from the powder samples of whey enriched vegetable paste. Legend for the inlet drying air temperature and the paste solids concentration in each experiment—

(no. 1): 90 °C and 7.5% (w/w); (no. 2): 90 °C and 10% (w/w); (no. 3): 100 °C and 7.5% (w/w); (no. 4): 100 °C and 10% (w/w)

Fig. 3 X-ray diffraction from the powder samples of whey enriched vegetable paste. Legend for the inlet drying air temperature and the paste solids concentration in each experiment—(no. 1): 90 °C and

7.5% (w/w); (no. 2): 90 °C and 10% (w/w); (no. 3): 100 °C and 7.5% (w/w); (no. 4): 100 °C and 10% (w/w)

solubilize more rapidly, facilitating subsequent rehydration.

Figure 3 shows XRD of the powders samples, and the diffractograms were similar and exhibited less intense crystalline arrangements. The degrees of crystallinity of the powders were of 14.4, 13.4, 9.9 and 12.8%, respectively, for the treatments (nos. 1, 2, 3 and 4), thus, the samples can be classified as amorphous particles. The low crystallinity indexes were attributed to the non-occurrence of lactose crystallization present in the whey, because the powder products in the drying assays reached temperatures in range 40–42 °C and, also, by the low residence time of the material in drying cell of the spouted bed (around 13 min). For sugars crystallization during drying operation the materials should reach temperatures above the glass transition temperature. Another factor responsible for similar degrees of crystallinity is the moisture content of the

powders, which were close in the four treatments, not being sufficient to lead product interactions at crystallinity level. The diffractograms are able to provide information about the final product, as its results may indicate gradual degradation of the crystalline structure, however, these changes were not observed in this work because, normally, they are attributed to the use of different drying techniques, as also, the biomaterial structure.

Rehydration kinetics

Figure 4 shows the rehydration curves of the dried powders samples of whey enriched vegetable paste, which were at room temperature. Rehydration curves of the dried powder samples can be able to indicate the physical and chemical changes that occurred during drying operation, due to both,

Fig. 4 Rehydration kinetics curves for the dried powders of whey enriched vegetable paste. Legend for the inlet drying air temperature and the paste solids concentration in each experiment—(no. 1): 90 °C and 7.5% (w/w); (no. 2): 90 °C and 10% (w/w); (no. 3): 100 °C and 7.5% (w/w); (no. 4): 100 °C and 10% (w/w)

by the operating conditions and by the product composition.

The dried powder samples at higher drying temperature presented a shorter time to reach rehydration equilibrium. Initially, a fast adsorption of water occurred until reaching the transition of moisture content. This phenomenon occurs due to the particles capillarity, because the increase of the water effective diffusivity has been associated with the formation of small channels in the plant tissue, which tend to fill with water rapidly (Farhaninejad et al. 2017). Figure 4 shows that, in all treatments, the powders were able to reach a moisture content more than 70% (w/w, wet basis) (equivalent to 80% of the paste initial moisture) in the first 30 min of rehydration. Afterwards, a slower water adsorption occurred, and the curves showed a strong tendency to remain constant until reaching equilibrium moisture, which corresponded to the end of rehydration.

Table 2 shows the values of the saturation moisture content of the powders samples, the rehydration constants and the coefficient of determination, which were determined for each rehydration assays. The water adsorption capacity of the powders was higher in the samples of the drying treatment no. 4, because the particles were smaller (Fig. 2), thus, its surface areas were larger, and this increased the water diffusivity into the particles. The coefficient of determination showed that the best adjustment was in the condition that obtained the highest rehydration constant. According to Chever et al. (2017), the particles reconstitution capacity can be linked directly

the powders size, affecting the properties of wettability and dispersibility, improving subsequent reconstitution for application in food products.

Conclusion

The formulation of the vegetable paste optimized by the linear programming reached its maximization, converging to a protein content of 0.20 g g^{-1} on the enrichment of the vegetable paste with whey. The drying operation of the paste was performed in spouted bed, showing the best results in the inlet drying air temperature of 100 °C and the paste solids concentration of 10% (w/w). In these conditions, the antioxidant capacity reached 75% of DPPH radical inhibition, showing a preservation of the antioxidant compounds. In the chemical properties were verified functional groups compatible with the material studied as aromatic rings, aldehydes and alcohols. The values of the glass transition temperature for the drying conditions were estimated, which varied from 81 to 121 °C. The powders showed irregular, slightly roughened structures, particles size around of 100 μm , with crystallinity indexes from 9 to 14%, showing the trend for amorphous powders. The reconstitution of the powders occurred quickly, as the particles were able to recover around 80% of the paste initial moisture content in the first 30 min and presented rehydration constants ranging from 3 to 16 min^{-1} , showing the influence of the drying conditions on the dried powders

characteristics. The linear programming showed as an essential and feasible tool for maximizing the protein content from a vegetable paste with whey, because, by means of restrictions it was possible to formulate a product of high protein content using only the necessary amounts of the constituents to reach the aim.

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Appendix

The inequations (7) and (8) limit the carbohydrate content (C); inequations (9) and (10) limit the protein content (P); inequations (11) and (12) limit the lipid content (L); inequations (13) and (14) limit the caloric value (V_c); inequations (15) and (16), respectively, restrict the mathematical possibility of negative values for amount of mass and that the amount of mass is higher than the predetermined maximum quantity.

$$\sum_{n=1}^{i=7} m_i c_i \geq C_1 \quad (7)$$

$$\sum_{n=1}^{i=7} m_i c_i \leq C_2 \quad (8)$$

$$\sum_{n=1}^{i=7} m_i p_i \geq P_1 \quad (9)$$

$$\sum_{n=1}^{i=7} m_i p_i \leq P_2 \quad (10)$$

$$\sum_{n=1}^{i=7} m_i l_i \geq L_1 \quad (11)$$

$$\sum_{n=1}^{i=7} m_i l_i \leq L_2 \quad (12)$$

$$\sum_{n=1}^{i=7} m_i v_{c_i} \geq V_{c1} \quad (13)$$

$$\sum_{n=1}^{i=7} m_i v_{c_i} \leq V_{c2} \quad (14)$$

$$m_i \geq 0 \quad (15)$$

$$m_i \leq m \quad (16)$$

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