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EFFECT OF PROCESS TECHNOLOGY ON THE NUTRITIONAL, FUNCTIONAL AND PHYSICAL QUALITY OF GRAPEFRUIT POWDER

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Abstract

The health properties of fruit are widely known. Powdered fruit may be a practical format to offer the consumer. Nevertheless, the process used to obtain the powder must ensure the maximum retention of the bioactive compounds and the functional value of the fruit while retaining adequate physical properties. The aim of this study was to compare freeze drying and spray drying as drying technologies to obtain grapefruit powder. The obtained results allow freeze-drying to be proposed as a better technology than spray drying in order to obtain a product with a higher content of vitamin C and total carotenoids. Moreover, all of the edible part of the fruit is used in this case, so a greater quantity of healthy compounds is preserved and by-product generation is avoided. Adding about 6 g water, 4 g arabic gum and 0.6 g bamboo fibre / 100 g grapefruit pulp is recommended before freeze-drying.

Keywords: Freeze-drying, spray-drying, vitamin C, phenols, carotenoids, antioxidant capacity

1. Introduction

Grapefruit is a very common variety of citrus fruit and an important source of phytochemicals and micronutrients. Vitamins, carotenoids and phenolic compounds,

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among others, could be independently or jointly responsible for the health protective effects of this fruit (Habauzit et al., 2014). The water soluble fraction of citrus (polyphenols and vitamin C) is mainly responsible for the antioxidant and antiradical activity of fruits while the apolar fraction (such as carotenoids, vitamin E or vitamin A) leads to the protective effects against chronic and degenerative diseases (Sdiri et al., 2012). Within the group of phenols, citrus flavonoids are associated with a reduced risk of coronary heart disease, inflammatory pathologies and tumor progression (Benavente-García and Castillo 2008). Grapefruit is a rich source of flavonoids, especially naringin and narirutin flavanones, with physiological properties that inhibit cell proliferation, promote differentiation, function as antioxidants and are modulators of tyrosine kinases (Vanamala et al., 2006). Grapefruit is also a source of vitamin C, commonly recognized as a major, naturally occurring nutrient and antioxidant (Dow et al., 2012). In pink grapefruit varieties, β-carotene (pro-vitamin A) and lycopene are responsible for the colour, also contributing to the antioxidant capacity of the fruit (Xu et al., 2006). Despite the high functional value of grapefruit and the advances in the scientific knowledge of consumers regarding the binomial health-diet, the consumption of grapefruit is low, probably due to its strong, bitter taste. In this sense it would be interesting to obtain processed grapefruit products that, while maintaining most of their functional value, could be mixed with other foods or added as an ingredient.

Powdered fruit consumption could be nutritionally equivalent to that of fresh fruit in smaller serving sizes, ranging from 30 to 43 g depending on the fruit. Epidemiological studies have found an association between fruit consumption, both fresh and dehydrated, and the prevention of diseases probably due to fruits being excellent sources of phytochemical compounds in the diet (Blasa et al., 2010). The powdered fruit market also has the advantage of being much more stable than that of fresh fruit, benefiting from the fact that the product is available all year round and is easier to store and distribute. Nevertheless,

the process used to obtain the powder must ensure the maximum preservation of the bioactive or functional fruit compounds.

Spray drying is a technique that allows powder to be obtained from fruit. It is a rapid dehydration method with intensive water evaporation on the surface of the droplets which keeps them cool until the dry state is reached, so leading to high quality powders (Fang and Bhandari, 2012). It is the most commonly used encapsulation method in the food industry (Rajam and Anandharamakrishnan, 2015). The properties of spray-dried powders are mainly affected by the process conditions, such as the air inlet and outlet temperatures, the air flow rate, the type of atomizer and the feed properties (Igual et al., 2014). This method has a number of advantages, some of which are the production of free flowing powders with a controlled particle size, rapid drying and easy scale up (Rajam and Anandharamakrishnan, 2015). Freeze drying may also be used to obtain powdered foods. Freeze drying involves the removal of water by sublimation of the frozen material, usually under low applied pressure. This technique is considered as a benchmark for powders of high quality, since one of its main advantages is to preserve attributes such as taste, nutrients, color or flavor. Nevertheless, in some previous studies, losses of food vitamins, antioxidant compounds and nutritional or functional value due to freeze-drying have been reported (Shofian et al., 2011). Besides, the main disadvantage of this technique is its high cost, both in terms of time and energy. Nevertheless, the application of pre-treatment for the purposes of removing some of the water present in the food contributes to a reduction of the cost involved (Benlloch-Tinoco et al., 2013; Donsi et al., 2001; Fahloul et al., 2009).

When a dehydration process is shorter than that needed for the crystallization of solutes, an amorphous matrix is obtained, which can be found in a glassy or rubbery state, depending on the glass transition temperature (Tg). Powdered foods in the rubbery state may suffer structural collapse phenomena, quickly exhibiting stickiness and caking problems (Adhikari et al., 2003; Gabas et al., 2007). Fruits, with a high content of both

organic acids and low molecular weight sugars, have a low Tg and, for dehydrated products, the rubbery state prevails under the usual storage conditions (Roos, 1995). In order to increase the Tg and promote the much easier-to-handle and stable glassy state, adding high molecular weight additives to the product before drying is a widely-used alternative (Truong et al., 2005; Yousefi et al., 2011). Both spray and freeze-drying processes lead to amorphous fruit powders. The addition of carriers is particularly necessary in the case of spray drying so as to avoid the adhesion of dust particles, not only to each other but also in the team, in order to increase product yield and avoid operational problems (Yousefi et al., 2011; Gabas et al., 2007). Some of the materials commonly used to increase the Tg can, at the same time, act as encapsulating agents. Arabic gum, a natural plant exudate of Acacia trees, has been the encapsulating agent of choice for many years because it is an excellent emulsifier, has a bland flavor and prevents water adsorption, oxidation and the volatilization of compounds (Gabas et al., 2007; Rascón et al., 2011; Singthong et al., 2009). This solute also contributes to an increase in the Tg and reduces the hygroscopicity, thus increasing the stability of the fruit powder. Bamboo fibre is extracted from the plant Bambusoideae subfamily and is mainly composed of hemicellulose, cellulose, pectin and lignin (Liu et al., 2012). Despite the fact that this solute has not been used with this purpose in mind, its high molecular weight makes it a possible candidate to increase the Tg, with the added value of being a healthy vegetable fiber.

The aim of this study was to compare freeze drying and spray drying as drying technologies in order to obtain grapefruit powder with the highest content of bioactive compounds, such as the total phenolics, total carotenoids and vitamin C, and the highest functional value measured through the antioxidant capacity. Moreover, yield information together with the water content, hygroscopicity, colour and porosity of the powder have also been considered.

2. Materials and methods

2.1. Raw material

This study was carried out with grapefruit (*Citrus paradise* var. Star Ruby*)* purchased in a local supermarket (Valencia, Spain). Two different batches were used in the study, one for all freeze-drying and one for all spray-drying experiments. The grapefruits were washed and peeled with the careful removal of the albedo. Arabic gum (AG, Scharlau, Spain) and bamboo fibre (BF, VITACEL®, Rosenberg, Germany) were added to the grapefruit pulp.

2.2. Freeze-drying (FD). Preparation of feed mixture and process conditions

The peeled grapefruits were cut and ground in a bench top electrical food processor (Thermomix TM 21, Vorwerk, Spain). The ground grapefruits were mixed with AG and/or BF and adjusted to a final water content according to the generated experimental design, commented on below, obtained from the response surface methodology (RSM) (Table 1). The samples were placed in aluminium plates (approximately 250 g, 0.5 cm thick, per plate) and immediately frozen at -45 ºC (Liebherr Mediline, LCT2325) for 48 h before freeze-drying in a Telstar Lioalfa-6 Lyophyliser at 0.021 Pa and -59 ºC for 24h. The obtained cakes were ground (Kenwood, CH 580) and sieved to obtain powder with a particle size of under 0.7 mm. The powder was vacuum packed and stored in a test cabinet at 10 ºC and 20 % relative humidity (Nüve, TK 120).

2.3. Spray-drying (SD). Preparation of feed mixture and process conditions.

The peeled grapefruits were liquidized in an electrical food processor (DeLonghi, Spain). The obtained juice was mixed with a water solution containing AG and/or BF. The solutes were added to water according to the generated experimental design, commented on

below, obtained from the RSM (Table 2). Each one of these solutions (400 g) was added to 400 g of the grapefruit juice and stirred for 30 min till homogeneity. After that, the mixture was fed into a Büchi B-290 (Switzerland) mini spray dryer with the following operating conditions: aspirator rate 90% (35 m^3/h); atomisation air rotameter 40 mm (473 L/h) with a co-current flow; pump rate 30% (9 mL/min). The drying air inlet temperature was varied according to the experimental design (Table 2). After the completion of the experiment, and when the air inlet temperature fell below 50 ºC, the samples were collected from the product collection vessel and immediately vacuum packed and stored in a test cabinet at 10 ºC, 20 % relative humidity (Nüve, TK 120).

2.4. Analytical determinations

2.4.1. Ground grapefruit (GG) and liquidized grapefruit (LG) were characterized, in triplicate, as to their water content (x_w), soluble solids (x_s), bioactive compounds (total phenolics, vitamin C, total carotenoids) and antioxidant capacity. The mass fraction of water was obtained by drying the samples in a vacuum oven (Vaciotem, J.P. Selecta) at 60ºC ± 1ºC under p < 100 mm Hg until constant weight (AOAC 2000, method 934.06). The mass fraction of soluble solids was obtained at 20°C by measuring the °Brix (Refracto 30 PX, Mettler Toledo at 20ºC) of the previously homogenized samples. The content of bioactive compounds was determined following the methodology described in the next section (2.4.2).

In order to make the results of GG and LG comparable, those of the liquidized sample were referred to the corresponding ground fruit (Eq. 1).

$$m_i^{GG} = m_i^{LG} \frac{m^{LG}}{m^{GG}} \quad (1)$$

where: m_i^{GG} is the mass of each compound in the ground grapefruit (w/w), m_i^{LG} is the mass of each compound analysed in the liquidized grapefruit (w/w) and m^{LG} is the mass of liquidized grapefruit (g) obtained from a determined mass (g) of ground grapefruit (m^{GG}).

2.4.2. Powdered samples

The response variables considered for each obtained powder were analyzed in triplicate. The analysis of the total quantity of phenols (TP) was based on the Folin-Ciocalteu reagent. For the extraction, 35 g of the sample were homogenized (T25D Ultra-turrax, IKA, Germany) for 5 min with 40 mL of methanol, 10 mL of HCl (6 N) and NaF (2 mM) to prevent the phenolic degradation caused by polyphenol oxidase action. The homogenate was centrifuged at 12.857xg and 4ºC for 10 min (Eppendorf centrifuge 5804R, Germany). For quantification purposes, 15 mL of distilled water and 1.25 mL of Folin Ciocalteu reagent (Sigma-Aldrich, Germany) were added to 250 μL of the supernatant. The samples were mixed and allowed to stand for 8 min in darkness before 3.75 mL of 7.5 % sodium carbonate aqueous solution was added. Water was added to adjust the final volume to 25 mL. The samples were allowed to stand for 2 h at room temperature before absorbance was measured at 765 nm in a UV-visible spectrophotometer (Thermo Electron Corporation, USA). The total phenolic content was expressed as mg of gallic acid equivalents (GAE) per gram of sample, using a standard curve range of 0-800 mg of gallic acid (Sigma-Aldrich, Germany)/L.

Vitamin C (VC) was determined by HPLC (Jasco, Italy). To quantify the total vitamin C content, dehydroascorbic acid was the reduced to ascorbic acid by mixing 0.5 g sample with 2 mL of a 20 g/L DL-dithiothreitol solution for 2 h at room temperature and in darkness (Igual et al., 2014). Afterwards, 1 g of this mixture was extracted with 9 mL 0.1% oxalic acid for 3 min and immediately filtered through a 0.45 μm membrane filter before injection (Xu et al., 2008). The HPLC conditions were: Ultrabase-C18, 5 μm (4.6x250 mm) column

(Análisis Vínicos, Spain); mobile phase 0.1 % oxalic acid, volume injection 20 μL, flow rate 1mL/min, detection at 243 nm and at 25 ºC. AA standard solution (Panreac, Spain) was prepared. The VC content was calculated as mg/g sample.

The total quantity of carotenoids (TC) present in the samples was extracted following the methodology recommended by Olives Barba et al., (2006). Briefly, 5 g of the sample were mixed with 100 mL of hexane/acetone/ethanol (50:25:25, v/v/v) for 30 min. Distilled water (15 mL) was added and an upper layer aliquot of 0.6 mL was dried under a stream of liquid nitrogen. The residue was dissolved with tetrahydrofuran/acetonitrile/methanol (15:30:55 v/v/v) solution to a final volume of 1 mL. The spectrophotometric AOAC reference method (2000) was used for quantification. The sample absorbance was measured at 446 nm in a UV-visible spectrophotometer (Thermo Electron Corporation, USA). The total carotenoid content was expressed as mg of β-carotene (Fluka-Biochemika, USA).

The antioxidant capacity (AOA) was assessed by using the free radical scavenging activity of the samples evaluated with the stable radical 2,2-diphenyl-1-picryl-hydrazyl-hydrate (DPPH, Igual et al., 2014). Briefly, the samples were homogenized and centrifuged (Eppendorf centrifuge 5804R, Germany) at 12,857xg and 4 ºC for 10 min. 0.1 mL of supernatant diluted in methanol was added to 3.9 mL of DPPH diluted in methanol (0.030 g/L, Sigma-Aldrich, Germany). At 25 ºC, the same spectrophotometer mentioned before was used to measure the absorbance at 515 nm at 0.25 min intervals until the reaction reached the steady state. Appropriately diluted samples were used on the day of preparation. The percentage of DPPH was calculated following equation (2). The final results were converted to mmol trolox equivalents (TE), using a trolox (Sigma-Aldrich, Germany) calibration curve in the range 6.25-150 mM.

$$\%DPPH = \frac{(A_{control} - A_{sample})}{A_{control}} * 100 \qquad (2)$$

where $A_{control}$ is the absorbance of the control (initial time) and A_{sample} the absorbance of the sample at the steady state.

The water content was obtained as previously described in section 2.4.1. For the hygroscopicity (Hg), about 2 g of each powder were placed in a Petri dish at 25 °C in an airtight plastic container containing a Na_2SO_4 saturated solution (81% RH). After 24 h, each sample was weighed and hygroscopicity was expressed as the g of water gained by the sample.

The colour of the powder was measured in a previously compressed sample as described by Telis and Martínez-Navarrete (2010) by using a Minolta CM-2002 Camera Co. (Japan). From the CIE L*a*b* colour coordinates obtained with a D65 illuminant and 10º observer, the Lightness (L*) of the samples and, in the case of the freeze-dried samples, the total colour difference (ΔE*) with respect to a freeze-dried grapefruit sample without added solutes or water, were considered. The aim of this measurement was to evaluate the effect of added solutes on the colour of the obtained powder. This ΔE* study was not carried out with the spray-dried samples as it is very difficult in this case to obtain a powdered fruit sample without solutes added acting as a process carrier.

The porosity (ε) was calculated from the true and bulk densities (Eq. 3). The true density (ρ) of a mixture was calculated from its individual components. In this case, water and carbohydrates, their own and added, were considered to be the main components of the samples (Eq. 4). For the purposes of bulk density (ρ_b) determination, approximately 2 g of the powder were transferred to a 10 mL graduated test tube and stirred for 10 seconds at 1600 rpm in a Vortex (Velp WX F202A0230, Italy). The bulk density was calculated by dividing the mass of the powder by the volume occupied in the tube after stirring.

$$\varepsilon = \frac{\rho - \rho_b}{\rho} \quad (3)$$

$$\frac{1}{\rho} = \frac{x_w}{\rho_w} + \frac{x_{CH}}{\rho_{CH}} \quad (4)$$

where ε is the porosity; ρ and ρ_b are the true and bulk densities, respectively; x and ρ are the mass fraction and density, respectively, of water ($_w$) and carbohydrates ($_{CH}$) of the mixture, with ρ_w (20 ºC) 0,9976 g/cc and ρ_{HC} (20 ºC) 1,4246 g/cc (Okos, 1986).

For spray-dried samples, the process yield was also considered, taking into account both the product yield (Y_P, Ec. 5) and the drying yield (Y_D, Ec. 6, 7).

$$Y_P = 100\frac{m_p^{wb}}{m_f^{wb}} \quad (5)$$

$$Y_D = 100 - Y_P - Y_L \quad (6)$$

$$Y_L = 100\frac{m_f^{db} - m_p^{db} + \left(m_f^{db} - m_p^{db}\right)x_{w_p^{db}}}{m_f^{wb}} \quad (7)$$

where m_p is the mass of the obtained powder from a determined mass of feed (m_f) in wet (wb) or dry (db) basis, Y_L is the loss yield and $x_{w_p^{db}}$ is the water content of the powder in dry basis.

As each sample had a different composition of added solutes (Tables 1 and 2), all the compositional results were referred to the grapefruit's own solutes (GS) (Eq. 8 and Eq. 9) to make the results comparable.

$$m_i = \frac{m_i^p}{(1 - x_w^p)(x_{GS/TS})} \quad (8)$$

$$x_{GS/TS} = \frac{m_g(1 - x_w^g)}{m_{AG} + m_{BF} \pm m_g(1 - x_w^g)} \quad (9)$$

where: m_i is the mass of each analysed compound referred to grapefruit solutes (mg/g GS), m_i^p is the mass of each compound analysed in the powder (mg/g), x_w^p is the water content of the powder (g_{water}/g_{powder}), $x_{GS/TS}$ is the mass fraction of grapefruit solutes (GS) to

total solutes (TS), m_g, m_{AG} and m_{BF} are the mass of grinded or liquidized grapefruit, arabic gum and bamboo fibre, respectively, in the sample and x_w^g is the water content of the grinded or liquidized grapefruit (w/w).

2.5. Experimental Design and Statistical analysis

For this study, RSM was used to evaluate the effect of three independent process variables on different response variables, mainly related to the functional, nutritional and physical quality of the powder. In the case of FD, the feed inlet moisture (70-90 g water/100g feed, x_1), arabic gum concentration (4-12 g AG/100g feed, x_2), and bamboo fibre concentration (0-2 g BF/100g feed, x_3) were selected as independent variables. In order to reach the feed inlet moisture level, water was added or microwave energy (Moulinex 5141 AFW2, Spain) was applied to dehydrate the samples. The independent variables for SD were the inlet air temperature (120-180 °C, x_1), arabic gum (4-12 g AG/100g liquidized grapefruit, x_2) and bamboo fibre concentration (0-2 g BF/100g liquidized grapefruit, x_3). The value ranges considered for the independent variables respond to previous studies (Agudelo et al., 2014; Igual et al., 2014; Kha et al., 2010; Quek et al., 2007). Twenty three experimental runs were generated for each process based on the corresponding central composite design rotable and orthogonal (Tables 1 and 2). The experiments were randomized.

Both an analysis of variance and a regression surface analysis were conducted to define the statistical significance of the model terms and to fit a regression relationship relating the experimental data to the independent variables. The generalized polynomial model proposed for predicting the response variables as a function of the independent variables was given by Eq. (10):

$$Y_i = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x^2_1 + \beta_{22} x^2_2 + \beta_{33} x^2_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (10)$$

where Y_i is the response value predicted by the model; β_0 is a constant; β_1, β_2, and β_3 are the regression coefficients for the linear effects; β_{11}, β_{22}, and β_{33} are the regression coefficients for the quadratic effects; and β_{12}, β_{13}, and β_{23} are the regression coefficients for the interaction effects. In this model, x_1, x_2, and x_3 are the independent variables.

The terms which were statistically non-significant ($p>0.05$) were dropped from the initial model, and the experimental data were refitted only to significant ($p<0.05$) independent variable effects in order to obtain the final reduced model (Mirhosseini et al., 2009). The lack of fit of every selected final model ($p>0.05$) confirmed the suitability of the fitted model and the non-significance of the Durbin-Watson proved that there was no significant autocorrelation or serial correlation. The goodness of the fit of the final reduced models to the experimental data was evaluated from the coefficient of determination adjusted (R^2_{adj}) and the standard error of estimate (EE) between the predicted and experimental values.

For the multiple response optimization, a response optimizer was used to determine the combination of input variable settings that jointly optimized the significant response variables. Through this optimization procedure, a combined level of the considered freeze-drying or spray-drying independent variables was obtained to produce the grapefruit powder with the largest quantity of phenols and carotenoids and the highest vitamin C content and antioxidant capacity. Furthermore, in order to discover the significant differences ($p<0.05$) between the FD and SD processes, an analysis of variance (ANOVA) was performed considering the losses of each compound caused by each process. All the statistical analyses were conducted using Statgraphics Plus 5.1 (Statgraphics Plus 5.1. for Windows, 2000).

3. Results and Discussion

The freeze-drying process works with the whole or ground fruit, while the spray drying requires an input feedstock with a low viscosity and small particle size. For this reason, the grapefruit was liquidized and diluted to obtain a fluid which meets the conditions of the spray drier. The water and soluble solute (SS) content of GG were 0.8760±0.0007 or 0.8848±0.0005 g_{water}/g GG and 0.109±0.006 or 0.104±0.002 g_{ss}/g GG for the two batches used for freeze-drying and spray-drying, respectively. As regards vitamin C and total carotenoid content, also significant differences ($p<0.05$) were found between batches (Table 3). Differences between batches are in the range of what may be expected when working with fruit. Nevertheless, the great amount of fruit needed to carry out all the 23 experimental runs described for freeze-drying and the 23 for spray drying, prevents the possibility of working with one unique batch of fruit unless a part of it is frozen before being processed. In order not to include an additional variable in the work, the same batch was used for each one of the processes. This allows the powders obtained by each process to be compared with each other. For the purposes of comparing both processes, the losses of the analyzed compound caused by each drying technique were considered. The water and SS content of LG (0.8912±0.0005 g_{water}/g LG and 0.107 g_{ss}/g LG) were slightly higher than those of the corresponding GG.

From these values, the insoluble solute content can be obtained which was, as expected, higher in GG (0.011 w/w) than in LG (0.0018 w/w) due to the extensive removal of solid components from the fruit, mainly the fiber, when liquidizing. Liquidizing caused additional significant changes ($p<0.05$) in the functional value of the grapefruit juice (Table 3). When referred to the corresponding ground grapefruit (Eq. 1), a lower content of vitamin C and total phenolics and carotenoids was observed in the liquidized fruit, which also exhibited a milder antioxidant activity. The experimental results of the different powders obtained by FD and SD are shown in Tables 1 and 2, respectively. The reduced end surface response

models corresponding to the significant correlation of each response variable with the independent variables are reported in Tables 4 and 5.

The total phenolic content of FD powders varied between 192 and 574 $mg_{GAE}/100g_{GS}$. As shown in Tables 1 and 4, the water content of the sample coming into the freeze-drier was observed to have no effect on TP content. The positive linear and the negative quadratic effect of the AG and BF content (Table 4) lead to intermediate levels of both solutes being the most convenient with which to obtain a product with a greater amount of phenolic compounds (Fig. 1a). The TP content of SD powders varied between 100 and 504 mg GAE $/100g_{GS}$ (Table 2). In this case, only the temperature showed a positive linear and negative quadratic effect on total phenols so that intermediate temperatures favour the extraction of these compounds (Fig. 1b). The same behaviour has been observed by Sharma et al. (2015) working with dehydrated onion.

The content of vitamin C ranged from 439 to 831 $mg/100g_{GS}$ in FD samples (Table 1) and from 314 to 700 $mg/100g_{GS}$ in SD powders (Table 2). In the case of FD powders, a positive effect of increasing the water and AG content of the sample coming into the freeze-drier was observed, while the positive effect of BF was offset by the strong negative quadratic effect (Table 4). In this way, the powder with the greatest VC content was obtained when the sample was processed with the highest water and AG content and with an intermediate BF content. Figure 2a shows the change in the VC content of the FD powder, dependent on the added solutes, for an intermediate water content. In SD samples, the increase in temperature caused a clear decrease in the VC content of the powders while a protective effect of BF was observed up to an intermediate content of this solute (Table 5). The effect of vitamin C degradation caused by the high temperature applied during spray drying was also observed by Langrish (2009) and Solval et al. (2012) and the protective effect of AG by Ali et al. (2010), among others.

The total carotenoids of the FD samples ranged from 9 to 34 mg/100g_{GS} (Table 1). They were positively affected by all the independent variables, while some negative quadratic effects and interactions were detected (Table 4). As a result, an increase in the water content prior to freeze-drying together with an intermediate-high BF content and a low amount of AG lead to the highest carotenoid content in the obtained powder (Fig. 2b). As shown in Table 2, the TC of the SD samples varied between 0 and 30.2 mg β-carotene/100 g_{GS} and they were not significantly ($p>0.05$) affected by any of the independent variables considered. Kha et al. (2010) also found no statistical difference in TC of spray-dried gag fruit at temperatures between 140 ºC and 200 ºC.

The antioxidant capacities of the extracts obtained with methanol was evaluated by DPPH method. Despite this procedure allows to evaluate the hydrophilic antioxidant activity, rather than the total antioxidant activity, hydrophilic phenols and ascorbic acid are the major compounds of fruits contributing to AOA (Boeing et al., 2014; Pulido et al., 2003). FD and SD samples showed values between 12.1 - 194 mmol and 42 - 184 TE /100g_{GS}, respectively (Tables 1 and 2). In this case, AOA was promoted when the sample coming into the freeze-drier had the highest water content and an intermediate AG concentration, with no significant effect of BF (Table 4). Despite the corresponding response surface plot, taking into account the regression coefficients shown in Table 4, for AOA has not been included to avoid increasing in excess the number of figures in the manuscript, this behavior of AG, similar to that previously described in the case of TP (Fig. 1a), is due to the positive linear effect and the negative quadratic effect shown. As for the SD powder, only a significant ($p<0.05$) negative linear effect of AG was observed. No significant correlation between AOA and the bioactive compounds was found.

From the above results, it seems that the presence of solutes is of greater necessity as protection for the bioactive compounds, especially vitamin C and phenols, during the long freeze-drying process than during the short spray-drying process, where the temperature

is a critical variable. Bamboo fibre may play a steric role while AG interacts with water, both of which avoid contact between the different substrates involved in deteriorative reactions.

The water content of FD and SD powders varied between 2.5 – 7.92 g water /100 g_{GS} and 1.68 – 15.53 g water /100 g_{GS}, respectively (Tables 1 and 2). These values correspond to 1.1 – 4.2 g water /100 g FD powder, which are normal values for a freeze-dried product (Benlloch-Tinoco et al., 2013) and 0.8 – 7.8 g water /100 g SD powder (Igual et al., 2014). A clear negative effect of the water content of the sample coming into the freeze drier or the temperature used for spray-drying was observed (Tables 4 and 5, respectively). The greater the x_w or the T, the lower the water content of the powders. The same effect of T has been observed for other fruits and vegetables and it has been related to a higher rate of heat transfer into particles, causing faster and intense water removal (Kha et al., 2010; Quek et al., 2007). As for FD, the greater water content prior to the freezing of the samples leads to a more diluted system, which eases the water to crystallize and sublimate (Fabra et al., 2009). FD samples also exhibited an interaction with the added solutes (Fig. 3a). If only AG is added, the greater the AG content the greater the powder water content. This could be linked to a cryoprotective role played by AG, leading to a smaller amount of ice formed during the freezing step prior to freeze-drying (Benlloch-Tinoco et al., 2013; Mosquera et al., 2012). Nevertheless, when BF is added the powder water content decreases. A steric role of BF preventing the interaction of water with the gum could justify this result. In this way, the powders with the lowest water content were obtained when the greatest amount of both solutes was added.

The hygroscopicity of all the powders was increased after AG addition and, in the case of the SD powders, intermediate temperatures and BF content lead to the greatest Hg (Fig. 3b). The porosity of the FD or SD powders increased when BF or AG, respectively, were added up to an intermediate level; moreover, a positive effect of the water content of the

sample coming into the freeze drier was observed (Tables 4 and 5). A greater porosity corresponds to a more free-flowing powder. The colour of the samples was affected by the solute content because of its white colour, which increased the luminosity of the powders (Tables 4 and 5), although as observed by Kha et al. (2010), L* was not significantly influenced by spray drying T. Despite the drying yield of all the SD samples being high (between 87 and 93 g water evaporated/100 g feed), the product yield was very low in every case (between 1 and 7 g powder/100 g feed), due to the composition of the fruits, as described in the introduction section. A clear increase in Y_P was observed when AG was added and T was increased (Fig. 3c).

The powdered grapefruit products with the best functional quality should be those with the maximum amount of the analyzed bioactive compounds and antioxidant activity. As regards the other analyzed properties, a powder with a low x_w, Hg, L*, ΔE and a high ε and Y_P would be preferred. In this sense, the response variables that were significantly ($p<0.05$) correlated with the independent variables were maximized or minimized for both FD and SD processes in an optimization of multiple response. In the case of FD, the optimum combination of the independent variables with which to obtain the best powder were 90 g water/100g feed, 4 g AG/100g grapefruit pulp + solutes and 0.56 g BF/100g grapefruit pulp + solutes. For spray-drying, the best grapefruit powder will be obtained by adding 4 g AG and 2 g BF to 100g liquidized grapefruit and using an inlet air temperature of 120°C.

For the purposes of knowing which of the two processes, freeze-drying or spray-drying, has the greatest effect on both the content of bioactive compounds and the antioxidant activity of the obtained powders, a statistical comparison was carried out. As commented on above, due to the differences found between the batches used for each process, the comparison was made between the losses caused by each drying technique (Eq. 11). Data from Tables 1 to 3 were used to this end. No significant differences ($p>0.05$) were

observed in the case of TP and AOA, while the losses in VC and TC were greater ($p<0.05$) in the case of the SD process.

$$\Delta_i = \frac{m_{i(G)} - m_{i(P)}}{m_{i(G)}} \quad (11)$$

where Δ_i is the relative variation of each analysed compound; $m_{i(G)}$ is the mass of each analysed compound referred to grapefruit solutes(mg/g GS) in the ground (for FD) or liquidized (for SD) grapefruit; $m_{i(P)}$ is the mass of each analysed compound referred to grapefruit solutes (mg/g GS) in the powder.

4. Conclusion

Freeze-drying may be proposed as a better technology than spray drying with which to obtain grapefruit powder with the highest vitamin C and total carotenoid content. The liquidizing step, which is necessary before spray drying, leads to a loss not only in the insoluble solutes of the fruit, which include fibre and carotenoids, but also in vitamin C, phenolics and antioxidant activity. Moreover, vitamin C and carotenoids turned out to be more sensitive to the high temperatures used in SD, despite the presence of added potential microencapsulating agents. Nevertheless, the use of these agents in SD is necessary in order to increase the product yield. The freeze-dried powders with the highest functional quality were those obtained from grapefruit pulp with approximately 6 g water + 4 g AG + 0.6 g BF/100 g grapefruit pulp. The water and solutes added improve the preservation of total phenols, vitamin C and total carotenoids and decrease the water content of the more free-flowing obtained powders.

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Figure 1. Response surface for the total phenol (TP) content of the freeze-dried (a) and spray-dried (b) powders. Values of TP are referred to grapefruit's own solutes (GS) as a function of arabic gum (AG) and bamboo fibre (BF) content (g/100 $g_{pulp+solutes\ or\ liquidized}$) when the water content of the feed is 80 g/100 g (a) or as a function of arabic gum (AG) and temperature (ºC) when BF is 1 g/100 $g_{liquidized}$ (b).

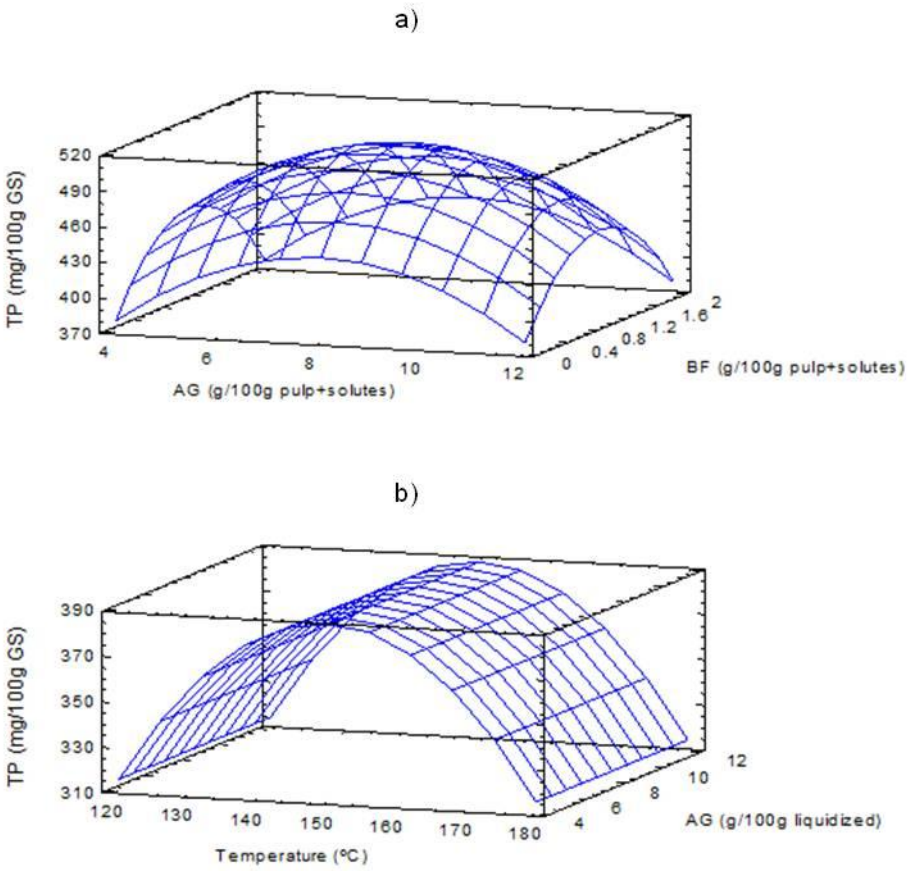

Figure 2. Response surface for the vitamin C (VC) (a) and total carotenoid (TC) content (b) of the freeze-dried powders. Values are referred to grapefruit's own solutes (GS) as a function of arabic gum (AG) and bamboo fibre (BF) content (g/100 $g_{pulp+solutes}$) or water content (g/100 g). An intermediate value of the variable that does not appear is always considered.

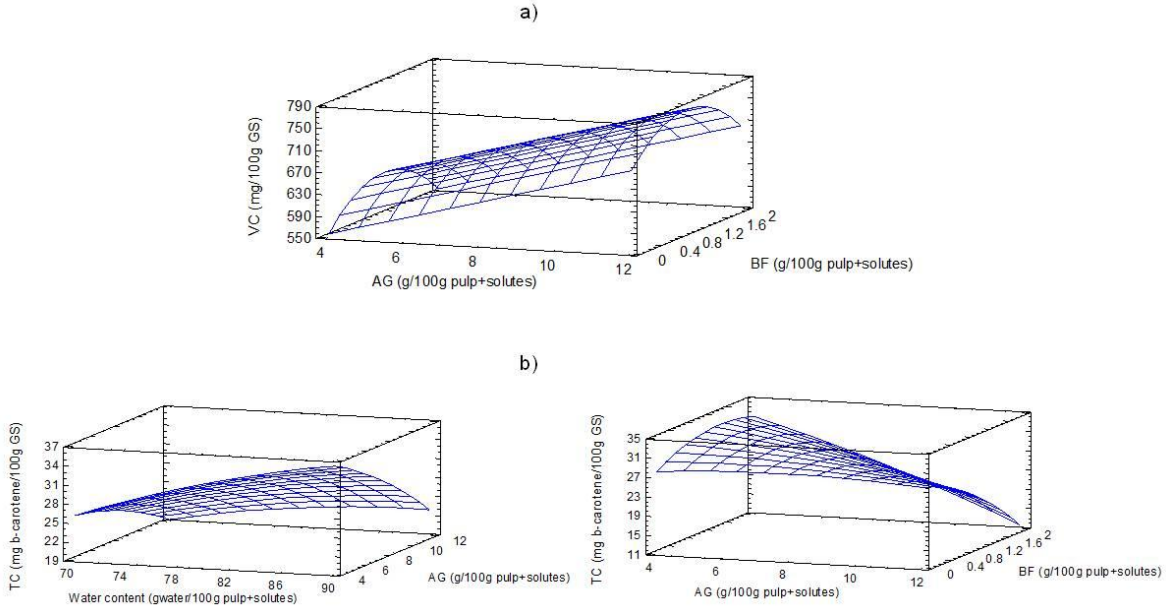

Figure 3. Response surface for the water content (x_w) of the freeze-dried powders (a) and the hygroscopicity (Hg) (b) or product yield (Y_P) (c) of the spray-dried powders. Values are referred to grapefruit's own solutes (GS) as a function of arabic gum (AG) and bamboo fibre (BF) content (g/100 $g_{pulp+solutes\ or\ liquidized}$) or temperature (ºC). An intermediate value of the variable that does not appear is always considered.

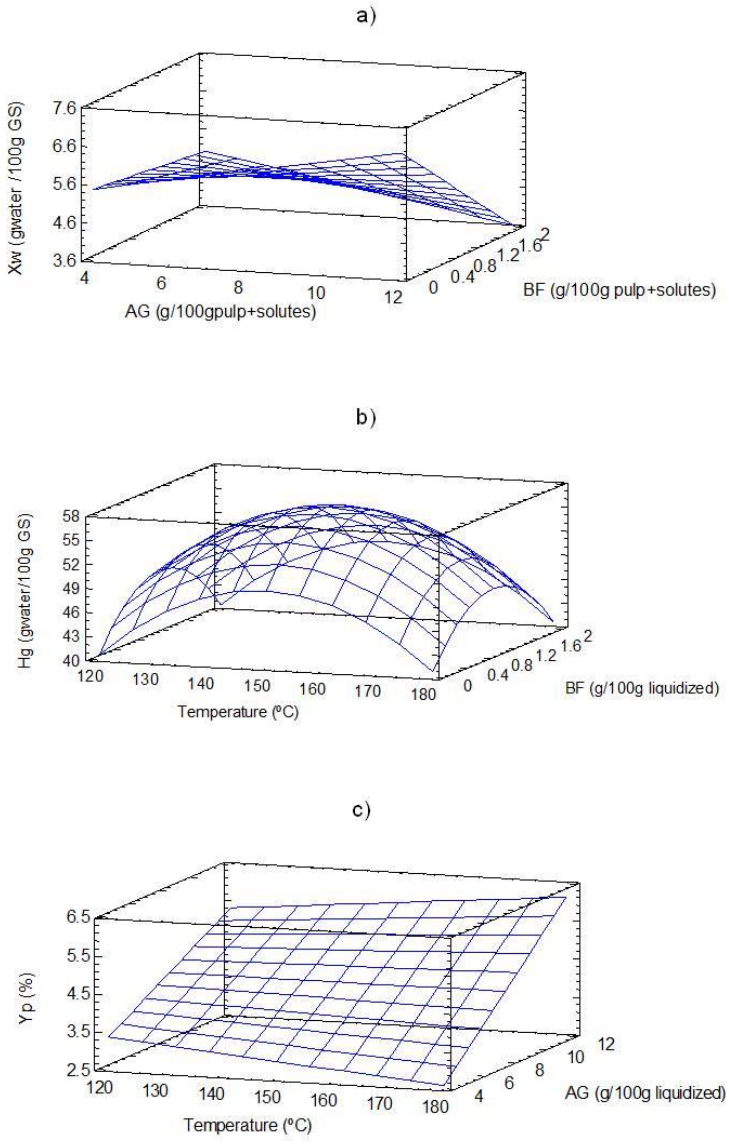

Table 1. Matrix of the central composite design of freeze dried powder. Where x_1, x_2 and x_3 are the feed water content ($g_{water}/100g_{feed}$), arabic gum (g/100g $_{pulp+solutes}$) and bamboo fibre (g/100g $_{pulp+solutes}$), respectively, and the experimental results (with standard deviation in brackets) are *TP*: Total phenolic content (mg GAE/100 g_{GS}), *VC*: Vitamin C content (mg/100 g_{GS}), *TC*: Total carotenoid content (mg β-carotene/100 g_{GS}), *A0A*: Antioxidant capacity (mmol TE/100 g_{GS}), x_w: Water content ($g_{water}/100\ g_{GS}$), H_g: Hygroscopicity ($g_{water}/100\ g_{GS}$), ε: Porosity (air volume/total volume), L*: Lightness and ΔE^*: Colour difference with respect to the freeze-dried fresh fruit. GS are the grapefruit's own solutes.

Run	X_1	X_2	X_3	TP	VC	TC	AOA	x_w	H_g	ε	L*	ΔE*
1	80	8	1	531 (16)	759 (11)	29 (2)	136 (9)	4.7 (0.2)	44 (2)	74.8 (1.2)	79.7 (0.8)	10.4 (0.5)
2	80	8	1	509 (5)	630 (17)	29.1 (0.8)	146 (15)	3.646 (0.005)	42.5 (0.2)	73.1 (0.2)	81.01 (0.14)	11.54 (0.13)
3	80	8	1	543.9 (1.2)	700 (7)	29.3 (0.5)	143 (3)	4.976 (0.102)	43 (3)	78.3 (0.9)	80.2 (0.2)	10.3 (0.5)
4	80	8	1	482 (10)	720 (8)	30.9 (0.6)	102 (21)	6.24 (0.07)	42 (3)	66.7 (0.8)	80.1 (0.3)	10 (3)
5	80	8	1	519 (5)	771 (32)	28.3 (0.2)	145.1 (3.5)	3.87 (0.05)	46 (3)	76.1 (0.9)	80.2 (0.7)	11.7 (0.8)
6	80	8	1	473 (4)	719 (23)	28.5 (0.2)	143 (9)	5.15 (0.08)	43 (2)	75.7 (0.4)	80.1 (0.4)	10.3 (0.7)
7	80	8	1	570 (12)	716 (19)	27.3 (0.5)	127 (6)	5.38 (0.06)	60 (5)	72 (2)	78.2 (0.3)	8.6 (0.2)
8	80	8	1	574 (0)	749 (10)	29.4 (0.2)	130 (12)	4.5 (0.3)	47.46 (1.02)	79.65 (0.02)	80.5 (0.3)	10.9 (0.5)
9	80	8	1	461 (6)	676 (42)	27.4 (2.2)	132 (9)	5.9 (0.3)	53 (6)	68.2 (1.2)	78.4 (0.9)	8.1 (0.9)
10	80	1.27	1	228.6 (3.5)	506 (18)	34 (5)	134 (12)	4.936 (0.103)	38 (5)	69.2 (0.9)	68.8 (0.6)	6.7 (1.2)
11	70	4	0	433 (32)	466 (5)	23 (2)	69 (14)	5.14 (0.07)	33 (2)	62 (3)	74.3 (0.3)	2.9 (0.3)
12	90	4	0	570 (3)	728 (18)	31.9 (0.8)	144 (24)	6.44 (0.02)	34 (2)	75 (2)	72.1 (0.3)	2.9 (0.4)
13	70	4	2	458 (13)	458 (26)	25 (2)	72 (5)	7.1 (0.2)	38 (3)	69.4 (0.5)	77.1 (0.4)	6.3 (0.4)
14	90	4	2	419 (4)	679 (26)	33.15 (1.12)	145 (10)	4.31 (0.06)	54 (2)	84.9 (0.2)	80.3 (0.5)	10.2 (0.7)
15	80	8	0	192 (5)	738 (39)	26.3 (0.2)	161 (7)	5.46 (0.06)	50 (4)	65 (2)	78.9 (1.2)	8.6 (1.4)
16	63.18	8	1	546 (3)	600 (3)	18.3 (1.2)	119 (12)	7.92 (0.06)	75.1 (0.8)	54.8 (0.6)	75.2 (0.8)	5.4 (0.8)
17	96.82	8	1	547 (7)	677 (8)	33.9 (0.5)	194 (8)	4.18 (0.12)	43.1 (0.6)	91 (2)	82 (2)	16 (2)
18	80	8	2.68	358 (5)	439 (8)	17 (2)	137 (6)	2.7 (0.4)	70(4)	72.9 (1.2)	79.9 (0.2)	10.5 (0.2)
19	70	12	0	201 (2)	662 (4)	26 (6)	12.13 (1.15)	7.72 (0.12)	60 (5)	57.11 (0.09)	77.4 (0.2)	7.5 (0.2)
20	90	12	0	426 (11)	792.1 (0.3)	29 (4)	32 (4)	5.8 (0.9)	58 (3)	88.5 (0.4)	83.5 (0.4)	15.6 (0.3)
21	70	12	2	316 (3)	525 (13)	9 (2)	35.3 (0.8)	5.1 (0.2)	60 (2)	67.8 (0.8)	80.3 (0.3)	11.6 (0.3)
22	90	12	2	344 (5)	789 (2)	11 (2)	68 (11)	2.5 (0.2)	61.3(1.3)	89.1 (0.9)	81.9 (0.3)	13.7 (0.4)
23	80	14.72	1	398 (0)	831 (35)	17 (10)	61.4 (1.5)	5.6 (2.5)	54 (2)	78.832 (0.007)	82.9 (0.3)	15.1 (0.5)

Table 2. Matrix of the central composite design of spray dried powder. Where x_1, x_2 and x_3 are the temperature (ºC), arabic gum (g/100g $_{liquidized}$) and bamboo fibre (g/100g $_{liquidized}$), respectively, and the experimental results (with standard deviation in brackets) are *TP*: Total phenolic content (mg GAE/100 g_{GS}), *VC*: Vitamin C content (mg/100 g_{GS}), *TC*: Total carotenoid content (mg β-carotene/100 g_{GS}), *A0A*: Antioxidant capacity (mmol TE/100 g_{GS}), x_w: Water content (g_{water}/100 g_{GS}), Y_P: Product yield (g powder/100 g feed), Y_D: Drying yield (g water/100 g feed), H_g: Hygroscopicity (g_{water}/100 g_{GS}), ε: Porosity (air volume/total volume) and L*: Lightness. GS are the grapefruit's own solutes.

Run	X_1	X_2	X_3	TP	VC	TC	AOA	X_w	Y_P	Y_D	H_g	ε	L*
1	150	8	1	353.9 (1.2)	586 (3)	9.6 (0.6)	174 (11)	3.55 (0.08)	3.70	90.08	66.2 (0.7)	75.77 (0)	90.4 (0.5)
2	150	8	1	328.9 (1.2)	572 (0.5)	10.2 (0.2)	161 (4)	3.9 (0.2)	4.15	90.11	56.2 (0.6)	75.92 (0.06)	90.2 (0.6)
3	150	8	1	343 (2)	569 (2)	9.8 (0.8)	139 (9)	3.26 (0.04)	3.92	90.11	55.9 (0.9)	77.53 (0)	90.40 (0.12)
4	150	8	1	442 (12)	553 (8)	18.9 (2.7)	97 (2)	4.33 (0.14)	4.12	90.15	54.9 (0.4)	77.4 (0.2)	90.2 (0.7)
5	150	8	1	404 (19)	543.11 (0.09)	21 (3)	95.2 (0.4)	3.5 (0.4)	4.45	90.26	53.9 (0.7)	77.7 (0.2)	89.1 (0.6)
6	150	8	1	396 (5)	559 (11)	10.5 (0.2)	137 (2)	2.22 (0)	4.56	90.21	63.5 (1.4)	76.1 (0.9)	90.6 (0.5)
7	150	8	1	391 (27)	530.9 (0.4)	20 (2)	94 (2)	2.6 (0.2)	4.09	90.22	58.1 (0.3)	78.2 (0.9)	90.48 (0.12)
8	150	8	1	320 (5)	563 (2)	15.6 (0.2)	130 (6)	5.5 (0.2)	5.10	89.93	41 (2)	76.57 (0.08)	88.1 (0.2)
9	150	8	1	308 (2)	543.5 (0.3)	10.6 (0.3)	120 (2)	3.4 (0)	4.95	90.15	67.1 (0.5)	78.11 (0.2)	89.3 (0.2)
10	150	1.27	1	503 (5)	526 (7)	3.2 (0.6)	152.4 (0.7)	6.8 (1.5)	0.99	93.30	46 (4)	53 (2)	49.6 (0.9)
11	120	4	0	133 (8)	516 (6)	18.3 (1.7)	133 (3)	7.6 (0.2)	4.02	92.31	29.6 (0.4)	73.31 (0.02)	83.6 (0.2)
12	180	4	0	347 (3)	314 (13)	30.2 (1.2)	125.67 (0.03)	4.23 (0.03)	3.18	92.65	24.9 (1.2)	73.95 (0.05)	83.8 (0.4)
13	120	4	2	332 (5)	535 (36)	6.6 (0.2)	181.2 (1.2)	3.81 (0.05)	3.84	92.15	25.9 (0.3)	70.2 (0.2)	81 (2)
14	180	4	2	365 (9)	365 (4)	13 (2)	184 (5)	4.81 (0.09)	3.59	91.59	25.92 (0.08)	84.1 (0.9)	85.69 (0.07)
15	150	8	0	411 (9)	486 (6)	7.1 (0.5)	104 (6)	8.95 (0.12)	5.11	90.37	41 (0.2)	80.22 (0.12)	88.8 (0.2)
16	100	8	1	100 (6)	700 (5)	12 (2)	91 (16)	15.53 (0.03)	4.28	89.43	39 (2)	72.9 (0.2)	87.9 (0.5)
17	200	8	1	239 (2)	431 (18)	0.00 (0.12)	142 (2)	1.91 (0.15)	4.64	90.21	33.083 (0.012)	78.8 (0.2)	89.16 (0.12)
18	150	8	2.68	504 (6)	583 (11)	10.9 (0.2)	85 (8)	5.8 (0.3)	4.64	89.25	49.4(0.4)	79.14 (0.2)	88.5 (0.2)
19	120	12	0	356 (10)	529 (44)	18 (6)	86.5 (0.8)	4.1 (0.2)	5.83	88.37	40.08 (0.16)	72.59 (0.08)	89.49 (0.07)
20	180	12	0	334 (15)	353 (43)	9.1 (0.8)	42 (9)	1.683 (0.009)	6.69	88.72	53.34 (0.09)	71.9 (1.2)	88.6 (0.4)
21	120	12	2	370 (8)	615 (20)	0.7 (0.9)	134 (4)	3.82 (0.05)	5.25	87.60	39.8 (0.5)	76.31 (0.3)	90.24 (0.05)
22	180	12	2	352 (7)	384 (4)	12 (4)	71.3 (0.7)	2.69 (0.14)	6.39	87.71	44.7 (0.2)	69.47 (0.06)	89.1 (0.4)
23	150	14.72	1	308 (10)	608 (5)	6 (3)	81 (11)	4.04 (0.03)	6.66	86.88	65.6 (0.8)	72.87 (0.12)	90.25 (0.14)

Table 3

Characterization of the two grapefruit batches used for freeze-drying (FD) or spray-drying (SD). Mean values and standard deviation of each compound referred to 100 g of the ground (GG) or liquidized (LG) grapefruit and to 100 g of grapefruit's own solutes (GS) (Eq. 8 and 9). Values of LG are also referred to the corresponding ground fruit (Eq. 1).

	FD		SD			
	GG (per 100_{GG})	GG (per 100_{GS})	GG (per 100_{GG})	LG (per 100_{GL})	LG (per 100_{GG})	LG (per 100_{GS})
Vitamin C (mg)	106.20 ± 0.9^{A}	856.5±0.9	79.3 ± 1.2^{Ba}	83.5±1.2	48.1 ± 1.0^{b}	773±10
Total phenolic content (mg)	52.9 ± 0.9^{A}	427±7	53.9 ± 0.8^{Aa}	37.8±0.2	21.85 ± 0.07^{b}	351±2
Total carotenoid content (mg)	5.37 ± 0.04^{A}	43.3±0.4	4.75 ± 0.12^{Ba}	4.12±0.09	2.38 ± 0.06^{b}	38.2±0.9
Antioxidant capacity (mmol)	15.5 ± 0.2^{A}	125±2	15.5 ± 0.3^{Aa}	14.02±0.05	8.08 ± 0.03^{b}	129.7±0.5

Different superscripts within the same row indicate significant differences ($p<0.05$) between both batches (A or B) and between grinded or liquidized (a or b)

Table 4

Regression coefficients, adjusted determination coefficient (R^2) and standard error of the estimate (EE) for the final reduced models of freeze-dried powders.

Regression coefficient	TP	VC	TC	AOA	x_w	H_g	ε	L*	ΔE
Constant					12.3439	34.33	-8.9	52.47	-16.0026
β_o	193.11	-40.80	-97.86	-110.11					
Linear									
β_1		6.57	2.41	2.42	-0.095		0.98	0.15	0.23
β_2	62.28	18.04	4.19	18.56	0.18	1.95		2.31	0.73
β_3	139.68	140.83	11.41		0.53		3.11	3.58	1.29
Square									
β_1^2			-0.011						
β_2^2	-3.89		-0.069	-1.62				-0.076	
β_3^2	-69.84	-70.41	-2.49						
Interactions									
β_{12}			-0.039						
β_{13}									
β_{23}			-1.20		-0.18			-0.3037	
R^2 adj	34.41	60.45	93.24	59.25	58.54	28.12	71.73	78.756	74.49
EE	95.38	72.18	1.78	30.08	0.88	9.34	5.04	1.76	1.77

β_i: estimated regression coefficient for the main linear effects, β^2_i: estimated regression coefficient for the quadratic effects, β_{ij}: estimated regression coefficient for the interaction effects. Subscripts i=1: water content of the sample incoming to the freeze-drier ($g_{water}/100g_{pulp+solutes}$); i=2: gum arabic (g/100g $_{pulp+solutes}$); i=3: bamboo fibre (g/100g $_{pulp+solutes}$). *TP*: Total phenolic content (mg GAE/100 g_{GS}), *VC*: Vitamin C content (mg/100 g_{GS}), *TC*: Total carotenoid content (mg β-carotene/100 g_{GS}), *A0A*: Antioxidant capacity (mmol TE/100 g_{GS}), x_w: Water content ($g_{water}/100\ g_{GS}$), H_g: Hygroscopicity ($g_{water}/100\ g_{GS}$), ε: Porosity (air volume/total volume), L*: Lightness and ΔE^*: Colour difference with respect to the freeze-dried fresh fruit. GS are the grapefruit's own solutes.

Table 5

Regression coefficients, adjusted determination coefficient (R^2) and standard error of the estimate (EE) for the final reduced models of spray-dried powders.

Regression coefficient	**TP**	**VC**	**AOA**	**x_w**	**Y_P**	**Y_D**	**H_g**	**ε**	**L***
Constant									
β_o	-1448.15	902.536	180.229	15.9937	5.76247	93.1724	-189.57	0.588	52.7685
Linear									
β_1	24.4936	-3.00206		-0.075	-0.026	0.00854	2.99		
β_2			-7.51		-0.1348	-0.496	1.84	0.047	7.639
β_3		143.071			-0.6343	0.3122	14.67		
Square									
β_1^2	-0.081						-0.009		
β_2^2								-0.0029	-0.3723
β_3^2		-50.4189			0.3171		-7.339		
Interactions									
β_{12}					0.0322				
β_{13}						-0.0047			
β_{23}									
R^2 adj	41.63	72.61	37.50	33.3	84.60	98.86	64.58	44.39	72.80
EE	71.69	48.63	29.47	2.4	0.48	0.19	7.99	0.04	4.40

β_i: estimated regression coefficient for the main linear effects, β^2_i: estimated regression coefficient for the quadratic effects, β_{ij}: estimated regression coefficient for the interaction effects. Subscripts i=1: temperature (ºC); i=2: gum arabic (g/100g $_{\text{liquidized grapefruit}}$); i=3: bamboo fibre (g/100g $_{\text{liquidized grapefruit}}$). *TP*: Total phenolic content (mg GAE/100 g_{GS}), *VC*: Vitamin C content (mg/100 g_{GS}), *A0A*: Antioxidant capacity (mmol TE/100 g_{GS}), x_w: Water content (g_{water}/100 g_{GS}), Y_P: Product yield (g powder/100 g feed), Y_D: Drying yield (g water/100 g feed), H_g: Hygroscopicity (g_{water}/100 g_{GS}), ε: Porosity (air volume/total volume) and L*: Lightness. GS are the grapefruit's own solutes.