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# Quality of a powdered grapefruit product formulated with biopolymers obtained by freeze-drying and spray-drying

**Luis A. Egas-Astudillo** | **Nuria Martínez-Navarrete** | **María del Mar Camacho**

María del Mar Camacho, Food Technology Department, Food Investigation and Innovation Group, Universitat Politècnica de València, Camino de Vera Valencia, Spain

**Correspondence**
María del Mar Camacho, Food Technology Department, Food Investigation and Innovation Group, Universitat Politècnica de València, Camino de Vera s/n, 46022, Valencia, Spain.
Email: mdmcamvi@tal.upv.es

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**Abstract:** Freeze-drying and spray-drying are two techniques used to produce dehydrated food products. Both techniques are easy to use and offer high sensory, nutritive value, and functional quality to foods. However, both processes become difficult for foods with high sugar and acid content, such as fruits. This is because these products, once dehydrated, moisten quickly, causing a change in their physical properties, mainly in the mechanical aspects related to the start of a caking phenomenon. Therefore, incorporating high molecular weight biopolymers that act as facilitators or processors, prevent the structural collapse of the product. The aim of this study was to select the best process, between freeze-drying or spray-drying, to obtain a powdered grapefruit product with the higher quality. The impact of the biopolymers used to stabilize the powdered product was also tested. The properties analyzed were the solubility, wettability, hygroscopicity, porosity, and color of the powder together with the flow behavior, both in air and water. The results of this study show that using the freeze-drying technique, products have a better flow behavior, greater porosity, and a color more like fresh grapefruit. Biopolymers, especially when in combination, have a positive effect on the quality parameters studied.

**Practical Application:** The results of this study allow freeze-drying to be proposed as a process to obtain a grapefruit product with better properties, both powdered and rehydrated, than that obtained by spray-drying. On the other hand, although the incorporation of biopolymers is necessary to facilitate the process and stabilize the product, no significant differences have been found between the different formulations tested, although it seems that their combination favours some of the properties of the powder, such as solubility, hygroscopicity, wetting time and dispersibility.

**KEYWORDS**
color, hygroscopicity, porosity, solubility, viscosity, wettability

## 1 | INTRODUCTION

Grapefruit (*Citrus paradisi*) of the variety Star Ruby is a citrus well studied for being a source of bioactive molecules such as vitamin C (Vanderslice et al., 1990), eriocitrin, and naringin among the phenolics (Uckoo et al., 2012; Zhang et al., 2011) or alpha and beta carotenoids (Holden et al., 1999; Hung et al., 2017; Peterson et al., 2006), compounds that seem to confer this fruit's biomedical properties (Cristóbal-Luna et al., 2018). Previous studies report that grapefruit juice has several biomedical activities, in relation to the cardiovascular system (Díaz-Juárez et al., 2009), metabolic syndrome (Fujioka et al., 2006), cholesterol, and low-density lipoprotein levels (Dow et al., 2012). The juice inhibits DNA damage (Alvarez-Gonzalez et al., 2011) while decreasing gastric lesions and onset of diarrhea. The grapefruit also promotes the benefits of glutathione in the body because of its antioxidant and anti-inflammatory properties (Cristóbal-Luna et al., 2018; Khan et al. Feroz, 2016).

Despite the goodness of fruit in general and grapefruit in particular, there is a problem related to the consumption of these foods. Fruit intake is below the RDA, which may be due to its perishable nature in relation to new lifestyles. From this point of view, the design of more stable and easy-to-use fruit products could stimulate their consumption among the population. Both freeze-drying and spray-drying are two techniques easy to manage and are used to produce powdered products with high sensory, nutritive, value, and functional quality. Fruit powder, dehydrated or previously rehydrated, allows for incorporation in juice formulations, infusions, desserts, dairy products, salads, ice cream, among other products. It has the advantages of product storage stability and logistical improvements, such as increased product packing density and transportation. However, both processes are difficult when applied to foods with a high sugar and acid content such as fruits. Main grapefruit composition is about 89 g water/100 g and 10°Brix, the main soluble solids in this fruit being sucrose, fructose, glucose, and citric acid, in mass ratios of 45.5, 21.2, 18.0 and 15.3, respectively (Fabra et al., 2009). The normal water content of dehydrated powdered foods is in the range 3% to 5%. So, the soluble solids in the powdered grapefruit increase from 88% to 86%, which in fact is a very high sugar and acid content. The parameter that defines the loss of quality of these products when dehydrated, a consequence of their wetting, is the change in their mechanical properties, related to the start of the caking phenomena. These sample changes occur from the moment the glass transition begins and are previous to the color changes, associated with their non-enzymatic browning. Changes also occur before chemical and microbiological reactions take place, responsible for their deterioration. The glass transition supposes the change from the stable glassy to the more instable rubbery state of material and occurs above the so-called glass transition temperature (Tg), dependent on the water content and solutes composition. Therefore, keeping the powder products in a glassy state is essential to make sure their quality and stability. The critical viscosity that determines the start of caking phenomena in mixtures of sucrose and fructose, sugars present in fruits, occurs at approximately 20°C above the Tg (Roos, 1995).

The low values of critical water content and water activity required for the glass transition of powdered fruit products make it necessary to incorporate high molecular weight biopolymers. For example, according to the data published by Silva-Espinoza et al. (2020), the Tg of the orange puree freeze-dried to 3 g water/100 g product is 11.4°C and increases to 20.32°C when gum Arabic (GA) and bamboo fiber (BF) (ratio 100:5:1) were added. This increase is enough to ensure the product stability during storage at room temperature. Examples of different biopolymers to be added to increase the Tg including gum Arabic, maltodextrins, starches, gelatine, methylcellulose, alginates, pectin, and mixtures of them (Telis & Martínez-Navarrete, 2009; Silva-Espinoza et al., 2020). Certain other biopolymers, such as proteins, insoluble fiber or inorganic compounds as silicon dioxide or tricalcium phosphate, delay the products' caking phenomena through steric activity (Barbosa-Canovas et al., 2005ÿ Gabas et al., 2007; Sablani et al., 2008; Silva et al., 2006; Telis & Martínez-Navarrete, 2009). Proteins can minimize the stickiness in dried products by modifying the surface properties of the droplets/spray-drying particles (Bhusari et al., 2014). The functional properties of biopolymers encompass any physicochemical property that exerts an effect on the characteristics of the foods to which they have been applied during their production, processing, storage, and/or consumption, thus contributing to their final quality (Dehnad et al., 2016). These properties include the water retention capacity of the food, the emulsifying properties, solubility, viscosity, porosity, swelling, elasticity, adsorption, among others (Zogzas et al., 1994; Fazaeli et al., 2012).

Agudelo et al. (2017), in a previous study, optimized the formulation of a grapefruit puree or liquidized added with GA and BF as to obtain, in each case, a powdered product with the best nutritional and sensory quality, established on the basis of its color, mechanical properties, hygroscopicity, solubility, total phenols, flavonoids, vitamin C and antioxidant activity, and even with the highest dry matter yield. This study allowed the authors to propose a different mix of biopolymers depending on the dehydration process, this being (4.2 g GA + 0. 58 g FB)/100 g of puree, in the case of freeze-drying, and (4 g GA + 2 g FB)/100 g of liquidized, in the case of spray-drying. Taking this result into account, the objective of the present study was to compare the quality of the best grapefruit powdered product that can be obtained by freeze-drying with the best one that can be obtained by spray-drying, in order to propose the most suitable process to obtain a grapefruit powder product of

the highest quality. On the other hand, in this study, we also tested the possibility of replacing GA with n-octenyl succinic anhydride modified starch (OSA) and BF with whey protein isolate (WPI), as these compounds are also widely used in the food industry and are more economical and seem to show suitable properties for the matrices under study (Adhikari et al., 2009; Sweedman et al., 2013). Specifically, OSA is cheaper than GA and is characterized by its high solubility and low viscosity (Dokić et al., 2012). Both GA and OSA permit an increase in the Tg of the freeze-dried fruit, without any of them being more or less effective than the other (Silva-Espinoza et al., 2020).

## 2 | MATERIALS AND METHODS

### 2.1 | Raw materials

The grapefruit (*Citrus paradisi*) of the Star Ruby pigmented variety, used for this study, was purchased from a local market (Valencia, Spain). The water and soluble solids content of the processed fruit batch were 87.6 ± 0.4 g water/100 g sample and 11.47 ± 0.12°Brix, respectively. To increase the physical stability of the dehydrated products, different biopolymers of high molecular weight were used: GA (Scharlab), whey protein hydrolysate isolate (WPI) (Lacprodan® DI-9212), OSA (Roquette® Cleargum CO 01), and BF (Vitacel® BAF 200).

### 2.2 | Preparation of the samples and drying conditions

The grapefruit was manually peeled and, after removing the albedo (white connective tissue) and the central axis, it was crushed (CG) or liquefied (LG) for subsequent freeze-drying (FD) or spray-drying (SD), respectively, as described below.

#### 2.2.1 | Freeze-drying

The peeled grapefruit was crushed for 40 s at speed 4 and for another 40 s at speed 9 in a food processor, Thermomix Vorwerk TM-21 (Spain). The water and soluble solids of the puree were 89.1 g water/100 g sample and 10.6°Brix, respectively. Addition of biopolymer to the crushed pulp (CG), gave four different formulations: CG (GA + BF) with 4.2 g GA + 0.58 g BF/100 g puree, CG (GA + WPI) with 4.2 g GA + 0.58 g WPI/100 g puree, CG (OSA + BF) with 4.2 g OSA + 0.58 g BF/100 g puree, and CG (OSA + WPI) with 4.2 g OSA + 0.58 g WPI/100 g puree. This ratio of biopolymers was selected based on previous studies where the formulation of the puree or liquidized was optimized for obtaining powdered fruit by freeze-drying or spray-drying, respectively, with good nutritional and sensory quality, established on the basis of its color, mechanical properties, hygroscopicity, solubility, total phenols, flavonoids, vitamin C, and antioxidant activity (Agudelo et al., 2017). The homogenization of the formulated samples was carried out in the same food processor (speed 2 for 300 s). After mixing, each formulation's moisture content was adjusted to 90 g water/100 g mixture (Agudelo et al., 2017). The formulations were then placed in aluminum trays of 23 cm diameter with 0.5 cm of product thickness. The samples were frozen at −45°C for 48 hr in a chest freezer (Liebherr LGT 2325, Germany) and dried at 0.05 mbar of pressure, 25°C shelf temperature and −55°C in the condenser, over 48 hr (Telstar Lyo Quest 55, Spain).

#### 2.2.2 | Spray-drying

An electric juice extractor (DeLonghi KC280, Italy) was used to obtain the liquefied grapefruit (LG, 88 g water/100 g sample and 12°Brix). An exact amount of biopolymer was added to obtain four formulations: LG (GA) with 4 % GA, LG (GA + WPI) with 4% GA and 2% WPI, LG (OSA) with 4% OSA, LG (OSA + WPI) with 4% OSA, and 2% WPI (Agudelo et al., 2017). For formulation incorporation, the biopolymers were previously dissolved in distilled water at the stated concentrations by magnetic stirring (OVAN, BasicMagMix, Spain) at 750 rpm. Subsequently, formulations were mixed with the liquefied pulp in the ratio 1:1, thus giving each of the formulations which ranged between 6,1 and 6,2 °Brix. Immediately afterwards, the samples were frozen at −20 °C (Liebherr GG 5210, Germany) until their subsequent spraying. Twenty-four hours before spray-drying, the samples were removed from the freezer and kept in a refrigerator (Liebherr GKv 6410, Germany) at 4°C, ensuring thawing. The spray-drying of the formulations was carried out in a Mini-Büchi B-290 atomizer, coupled with a nozzle diameter 0.7 mm (BÜCHI, Germany) which provides powder particles with diameters between 2 and 25 micrometers. In all cases, the following conditions were met: aspiration speed of 35 $m^3$/hr, air flow velocity of 473 L/hr, pump flow rate of 9 mL/min, air inlet temperature of 150°C, and air outlet temperature 50°C.

### 2.3 | Analytical determinations in the powder

Freeze-dried and spray-dried powers (PFD and PSD, respectively) were evaluated in relation to their water content ($X_w$), solubility (Sb), wettability (Wt), hygroscopicity (Hg), porosity ($\varepsilon$), and color. The samples obtained after the drying processes were vacuum packed (EDESA VAC-20 SL, Spain), to avoid moisture gain. The cakes obtained by freeze-drying were milled (Thermomix Vorwerk TM-21.

Spain,) at speed 2, for 10 s, obtaining a powder which was sieved (<700 μm) ensuring a homogeneous sample with a mean particle size lower than 260 micrometers (data not shown). The samples from spray-drying were processed as powders.

### 2.3.1 | Water content

Water content ($X_w$) was determined in triplicate, from the weights of the sample before and after subjection to drying in a vacuum oven (Vaciotem, JP Selecta SA, Spain) at 60 ± 1°C and a pressure <100 mmHg, until achieving constant weight.

### 2.3.2 | Water activity

A dew point hygrometer (Decagon, AquaLab CX-3, Pullman, WA, USA) was used to analyze the water activity ($a_w$).

### 2.3.3 | Solubility

The solubility (*Sb*) or mass fraction of soluble solutes regarding the totals was calculated in triplicate, using Equation 1 (Mimouni et al., 2009). To measure the content in total solutes (*ST*) and soluble solutes (SS), 1 g of sample was added to 9 mL distilled water at 20°C under constant magnetic stirring at 750 rpm (OVAN, BasicMag-Mix, Spain) for 5 min. The *ST* were determined by drying a known amount of the rehydrated powder ($m^1_{Rh}$) in a vacuum oven (Vaciotem, J.P. Selecta, Spain) at 60°C and with pressure <100 mm Hg for 24 hr, obtaining the dry weight ($m^{1d}_{Rh}$). To determine *SS*, another part of the rehydrated powder ($m^2_{Rh}$) was centrifuged (GYROZEN 123GR, Korea) at 10,000 rpm for 10 min at 4°C. All the obtained supernatants were weighed and filtered through a syringe with Whatman filter paper no. 1, both the obtained filtrate and the filter were dried under the same conditions described for the *ST* and weighed to obtain the soluble solutes mass ($m^{2d}_{Rh}$):

$$Sb = \frac{SS}{ST} = \frac{m^{2d}_{Rh}/m^2_{Rh}}{m^{1d}_{Rh}/m^1_{Rh}} \quad (1)$$

### 2.3.4 | Wettability

The powder wetting time (*Wt*) was evaluated in triplicate, based on the method proposed by Jinapong et al. (2008) but with modifications. By measuring the time (s) required to achieve complete wetting of a known amount, 1 g of powder was poured gently onto the surface of the water in a container, allowing the powder to submerge spontaneously without agitation (Gea-Niro, 2020), greater wetting time meant less wettability. To achieve a uniform dust discharge, use of a mechanical arm composed of a microcontroller (AT mega328, China), with an operating voltage of 5 V and an oscillator speed of 16 MHz, which controls a servo motor (maximum torque at 4.8 V of 1.6 kg/cm and turning speed at 4.8 V without load of 60°/0.12 s), was responsible for pouring the powder into the container attached to the servo motor shaft. For the analysis, a volume of 100 mL of distilled water at 25°C was placed in a 500 mL beaker of 85 mm diameter. A support that holds the servo motor with the container was placed on the beaker. The height between the container with the sample and the surface of the water was 10 cm. A timer recorded the moistening time.

### 2.3.5 | Hygroscopicity

The hygroscopicity (Hy) was determined by placing 1.5 g of powder in an environment of 81% relative humidity (RH) (created by a saturated solution of $_{Na2SO4}$) at room temperature for 48 hr. Differences in weight delimited the amount of water gained by the sample (Cai & Corke, 2020; Koç et al., 2014). Results were expressed as g of water gained/100 g of dry solids, according to Equation (2) and measurements were made in triplicate, per sample:

$$Hy\ (\%) = \frac{(m_1 - m_2)}{m_2\left(1 - X^p_w\right)}100 \quad (2)$$

where $m_1$ is the hydrated mass (g), $m_2$ is the initial powder mass (g), and $X^p_w$is the initial moisture of the powder (g of water/g of sample).

### 2.3.6 | Porosity

Equation (3) calculates the porosity ($\varepsilon$). In this equation, the real density ($\rho$) was calculated for the water, carbohydrate, and protein composition of the samples (Equation 4). The apparent density (Equation 5) was based on measuring the volume occupied by a known sample quantity after having been subjected to a vibration stage at 1600 rpm for 10 s (Infrared Vortex Mixer, F202A0175, Spain):

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

$$\rho = \frac{1}{\frac{X^p_w}{\rho_w} + \frac{\left(1 - X^p_w\right)\left(\frac{x^F_{CH}}{1 - x^F_w}\right)}{\rho_{CH}} + \frac{\left(1 - X^p_w\right)\left(\frac{x^F_P}{1 - x^F_w}\right)}{\rho_P}} \quad (4)$$

where $X_w^p$ is the moisture of the powder (g water/g powder obtained), $\rho_w$ is the water density (0.9976 g/cc), $\rho_{\mathrm{CH}}$ is the carbohydrates density (1.4246 g/cc), $\rho_p$ is the protein density (1.892 g/cc), $x_p^F$ is the protein mass fraction (WPI added according to the formulation), $x_{CH}^F$ is the carbohydrates mass fraction (by difference), in the crushed or liquefied grapefruit formulated, $x_w^F$ is the water mass fraction in the crushed or liquefied grapefruit formulated:

$$\rho_a = \frac{m^p}{V_f^p} \tag{5}$$

where $m^p$ is the mass of powder (g) and $V_f^p$ is the volume after the vibration stage (cc).

### 2.3.7 | Color

To determine the color of the samples, a spectrophotometer (Minolta CM 2600-D, Japan) was used, with a measuring window of 8 mm diameter. For the measurement, an optical glass (CR-A51, Minolta Camera Co., Japan) was placed on the sample, making three measurements per sample. CIE L*a*b* coordinates were obtained, using the illuminant D65, as a reference, and the observer of 10°. The hue angle ($h_{\mathrm{ab}}$*) and chroma ($C_{\mathrm{ab}}$*) were calculated from Equations (6) and (7):

$$h_{ab}{}^* = \arctan\left(b^*/a^*\right) \tag{6}$$

$$C_{ab}{}^* = \left(a^{*2} + b^{*2}\right)^{0.5} \tag{7}$$

## 2.4 | Rheological analysis of liquid samples

Both PFD and PSD powders were rehydrated at the moisture level of formulated CG and LG, respectively to obtain the CG-Rh and LG-Rh samples. The amount of water required to rehydrate was calculated with a material balance (Equations 8 and 9), based on the moisture content of the powders and the humidity required to arrive to ($X_w^f$), it was calculated for the two processes of the sample formulations. The procedure was carried out in 50 mL beakers provided with a double jacket, connected to a water bath set to 20°C (VWR North 1162A, Radnor, PA, USA), with constant magnetic stirring (OVAN, BasicMagMix, Spain) for 5 min at 750 rpm:

$$m^{\mathrm{Rh}} = m^p + m^w \tag{8}$$

$$m^{p*}\left(1 - X_w^p\right) = m^{\mathrm{Rh}*}\left(1 - X_w^f\right) \tag{9}$$

where $m^{\mathrm{Rh}}$ is the rehydrated product mass (g), $m^{\mathrm{w}}$ is the mass of water added (g), $m^{\mathrm{p}}$ is the mass of grapefruit powder (g), $X_w^f$ is the moisture of the formulated sample (g water/g sample formulated, this being 0.90 and 0.84 in the case of CG and LG samples, respectively), and $X_w^p$ is the moisture of grapefruit powder (g water/g powder).

The flow curves of the rehydrated samples were obtained by applying a shear sweep from 0 to 150 $s^{-1}$ at constant temperature of 20°C (Viscotherm VT 10, Physica, Germany). A rheometer (Rheolab MC 1, Paar Physica, Germany) with concentric cylinder geometry Z1 DIN was used for LG and LG-Rh, while a Z2 DIN was used for samples CG and CG-Rh.

## 2.5 | Statistical analysis

Statistics included an analysis of variance (ANOVA), applying the LSD test (least significant difference) to 95%. Factorial multivariate analysis was applied to study the relationships between the samples and their properties. Minitab® software 16.2.2 was used for the statistical analysis.

# 3 | RESULTS AND DISCUSSION

## 3.1 | Comparison between powder products obtained by freeze and spray drying

Table 1 shows the water content, $a_{\mathrm{w}}$ and physical parameters of freeze- and spray-dried samples and their formulations. Most of the powders presented normal water content for these types of products, although the freeze-dried products had the lowest moisture content ($p < 0.05$). The low values of $a_{\mathrm{w}}$ indicate the strict relative humidity conditions required for the storage of these powders. The water activity increased when biopolymers were added, related to the greater water content shown by the formulated powders.

A significant increase in solubility was observed with the incorporation of biopolymer ($p < 0.05$), especially related to the high solubility of GA and OSA (Dokić et al., 2012). On the other hand, the higher solubility showed by spray-dried products may be related to the different composition of CG and LG used to obtain PFD and PSD, respectively. The greater presence of fiber in the purees than in the liquidized may offer an important barrier to the solubility of the powder. The spray-dried samples had a longer wetting time ($p < 0.05$) than the freeze-dried. The

**TABLE 1** Mean values and standard deviation, in parentheses, of water content ($X_w$ (g water/100 g powder)), water activity ($a_w$), solubility (*Sb* (%)), wetting time (*Wt* (s)), hygroscopicity (*Hy* (%)), and porosity ($\varepsilon$ (%)) of the freeze-dried (PFD), and spray-dried (PSD) powders. Obtained from the crushed grapefruit (CG) and liquefied grapefruit (LG), respectively. Formulated with gum arabic (GA), bamboo fiber (BF), whey protein isolate (WPI), and anhydrous *n*-octenyl starch (OSA)

| Samples | $X_w$ | $a_w$ | *Sb* | *Wt* | *Hy* | $\varepsilon$ |
|---|---|---|---|---|---|---|
| PFDCG | 1.1(0.5) a | 0.020(0.003) a | 83.4(0.01) a | 57(2) b | 27.4(0.4) f | 74(0.6) f |
| PFD(GA+BF) | 2.5(0.3) c | 0.147(0.002) d | 84.60(0.010) b | 12.6(0.3) a | 23.9(1.1) cd | 66.6(0.6) cd |
| PFD(GA+WPI) | 2.24(0.08) c | 0.090(0.001) b | 83.8(0.004) ab | 17.4(0.8) a | 23.7b(1.0) bcd | 68.9(0.2) de |
| PFD(OSA+BF) | 1.7(0.2) b | 0.167(0.019) d | 86.16(0.004) c | 15.6(0.9) a | 21.9(0.4) ab | 71.1(1.7) ef |
| PFD(OSA+WPI) | 1.9(0.1) bc | 0.101(0.002) b | 89.6(0.002) d | 15.9(1.1) a | 21.8(0.3) a | 69.0(1.4) de |
| PSD (GA) | 2.86(0.10) d | 0.119(0.003) c | 94.4(0.004) e | 294(6) e | 26.6(1.3) ef | 61.1(0.5) ab |
| PSD(GA+WPI) | 3.47(0.12) e | 0.248(0.017) e | 94.80(0.0010) ef | 223(11) d | 24.5(0.3) cd | 66.0(1.3) cd |
| PSD(OSA) | 4.1(0.8) e | 0.281(0.013) e | 96.70(0.0010) g | 149(11) c | 25,2(1.2) de | 64(4) bc |
| PSD(OSA+WPI) | 1.5(0.2) b | 0.105(0.002) b | 95.3(0.002) f | 216(15) d | 23.9(1.5) abc | 58(4) a |

*Note*: Different letters in columns show significant difference between samples for each of the parameters ($p < 0.05$).

commented smaller particle size because of spray-drying process, related to the larger available surface area contact with water, would justify this result.

Incorporating biopolymer in the CG caused a decrease in the hygroscopicity of the corresponding powder products ($p < 0.05$). However, the higher values of Hy in the spray-dried products can be related, with their smaller particle size and greater surface area availability, allowing for the adsorption of water (Tonon et al., 2008).

The freeze-dried products showed greater porosity than those spray-dried ($p < 0.05$). The same results in freeze-dried and spray-dried mango powders were also previously found (Caparino et al., 2012). Karam et al. (2016) show that freeze-dried materials, compared to products obtained by other dehydration methods, are characterized by having the lowest values of bulk density and greater porosity because of the pores generated by sublimation of the formed ice and characteristic of the technique.

As regards the color, all the powders obtained by freeze-drying were darker (lightness between 74,4 and 77,5) than the spray-dried ones ($L^*$ 90,4 to 91,8). Figure 1 shows the chromatic coordinates $a^*$ and $b^*$. In this figure, the angle described by the sample position to the positive $a^*$ axis corresponds to the hue angle and the smaller angle shown by the powders obtained by freeze-drying is related with a more orange color. On the other hand, the greater distance from these samples position to the grid origin ($a^* = 0$, $b^* = 0$) is related to their greater chroma. Despite the slight lower water content of FD samples, the lower natural grapefruit fiber content of the spray-dried products, together with their smaller particle size and an effect of temperature during this stage on the carotenes, responsible for the typical color of this product, can justify the differences observed.

The relationship between the processes and the studied properties of the powdered products can be easily

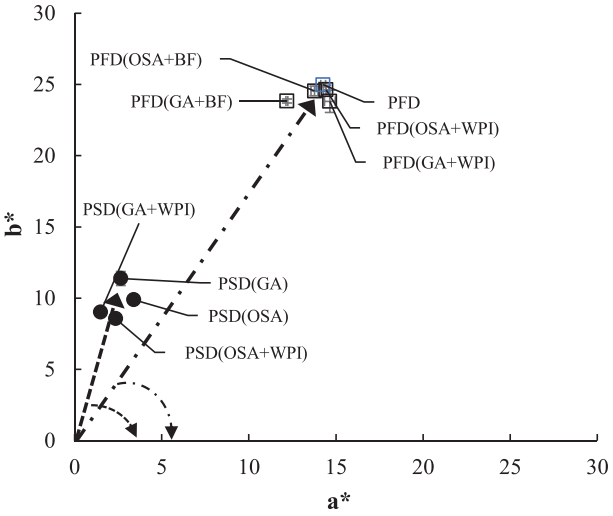


**FIGURE 1** Color coordinates and attributes $a^*$, $b^*$, $C_{ab}^*$ (chroma) and $h_{ab}^*$ (hue angle) in the spray-dried (PSD (○)) and freeze-dried samples (PFD (□)), without formulating, and formulated with gum arabic (GA), bamboo fiber (BF), whey protein isolate (WPI), and anhydrous n-octenyl succinic modified starch (OSA). $h_{ab}^*$ and $C_{ab}^*$ are shown with arrows

observed with a factorial analysis, carried out with the analyzed parameter values corresponding to all the samples (Figure 2). The first two factors accounted for 93% of the total variability. The first factor (F1) represents 81.5% of the variability and is associated with *Wt* ($r = 0.95$), *Sb* ($r = 0.93$), $\varepsilon$ ($r = -0.80$), $L^*$ ($r = 0.99$), $a^*$ ($r = -0.99$), $b^*$ ($r = -0.99$), $h_{ab}^*$ ($r = 0.97$), and $C_{ab}^*$ ($r = -0.99$). The second factor (F2) is associated with *Hy* ($r = 0.95$). Two different groups are observed corresponding to the freeze-dried samples (negative values of F1) and to those spray-dried (positive values of F1). In addition, with freeze-dried powders, we can differentiate between those that do not have biopolymers (greater values of F2) and those that do (lower

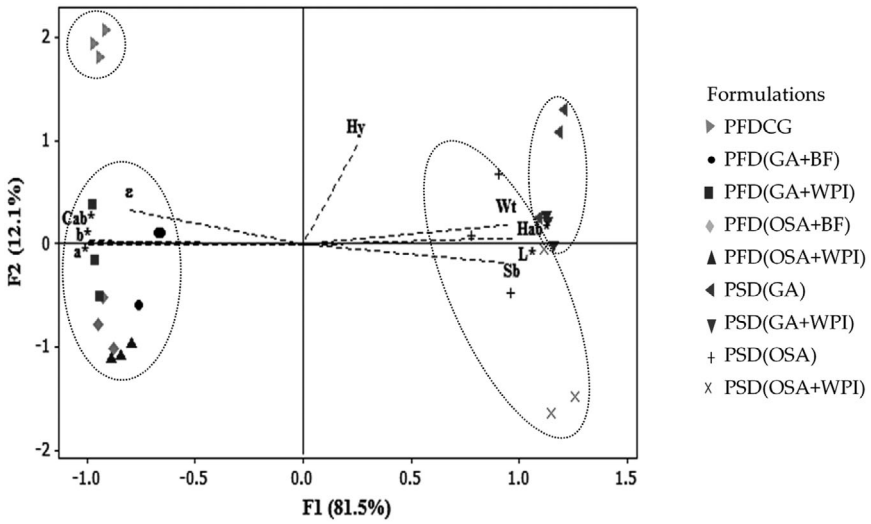


**FIGURE 2** Factorial multivariate analysis (FA) of the powders obtained by freeze-drying (PFD) and spray-drying (PSD). Bi plot factorial with physical properties; solubility (*Sb*), wetting time (*Wt*), hygroscopicity (*Hy*), and porosity (*ε*). Formulations with gum Arabic, bamboo fiber (BF), whey protein isolate (WPI), and anhydrous *n*-octenyl succinic modified starch (OSA)

values of F2). For the spray-dried samples, two groups are observed, although with less clarity. Those that incorporate OSA in their formulation and those that incorporate GA. Therefore, this method discriminates both the process (F1) and the formulation (F2). In relation to the properties evaluated, high values of porosity, coordinates $a^*$, $b^*$, and chroma were associated with freeze-dried powders. However, high values of solubility, wettability, lightness, and hue angle were associated with spray-dried powders. Therefore, a high value of wetting time expresses greater hydrophobicity of its particles with a lower surface tension. Finally, high values of hygroscopicity were related to spray-dried powders containing GA and freeze-dried powders without biopolymers.

## 3.2 | Rehydration of freeze and spray-dried grapefruit powder

The grapefruit powder obtained by freeze and spray-drying was rehydrated to the moisture level of CG and LG formulations to obtain samples CG-Rh and LG-Rh, adding the water lost during the relative processes (Section 2.3).

The influence of rehydration on the rheological behavior analysis in all the samples was studied. Flow curves of the CG-Rh and LG-Rh formulated samples showed a pseudoplastic and Newtonian behavior, respectively. For CG-Rh, the curves were fitted to the Ostwald-de Waele model (Equation 10) to obtain the flow behavior index ($n$) and consistency index ($k$). With these two parameters, the apparent viscosity (Equation 11) was calculated at shear rate 100 $s^{-1}$. This procedure was performed in triplicate. For LG-Rh, the curves showed a Newtonian behavior, with $n = 1$ and $k$ being the Newtonian viscosity in Equation 10):

$$\sigma = k \times (\dot{\gamma})^n \quad (10)$$

**TABLE 2** Mean values and standard deviation, in parentheses, of the flow behavior index ($n$), consistency index ($k$), and apparent viscosity ($\eta_{ap}$) in rehydrated samples of freeze-dried grapefruit formulated with gum Arabic (GA), bamboo fiber (BF), whey protein isolate (WPI), and anhydrous *n*-octenyl succinic modified starch (OSA)

| Sample | $n$ | $k$ (Pa $s^n$) | $\eta_{ap}$ (Pa s) |
|---|---|---|---|
| CG-Rh | 0.372(0.002) a | 6.46(0.17) c | 0.359(0.006) d |
| CG-Rh(GA+BF) | 0.429(0.006) d | 2.17(0.08) a | 0.157(0.007) b |
| CG-Rh(GA+WPI) | 0.402(0.009) b | 2.8(0.2) b | 0.181(0.007) c |
| CG-Rh(OSA+BF) | 0.424(0.003) cd | 2.20(0.08) a | 0.155(0.006) b |
| CG-Rh(OSA+WPI) | 0.418(0.004) c | 2.23(0.10) a | 0.153(0.004) b |

*Note*: Different letters in columns show significant difference ($p < 0.05$).

$$\eta_{ap} = k \times (100)^{n-1} \quad (11)$$

where $\sigma$ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate ($s^{-1}$), $n$ is the flow behavior index, $k$ is the consistency index (Pa $s^n$), and $\eta_{ap}$ is the apparent viscosity (Pa s).

The viscosity of the LG samples was between 0.0028 ± 0.0001 to 0.0035 ± 0.0002 Pa s with no significant differences between them. Table 2 shows the rheological parameters obtained from fitting the Ostwald-de Waele model to CG (Equation 10). The apparent viscosity values calculated at 100 $s^{-1}$ shear rate (Equation 11) for CG samples are also shown. The correlation coefficient ($R^2$ between 0.998 and 0.959) shows that the adjustment was statistically significant in all cases. For CG-Rh, the values of n were less than 1, as expected, confirming the pseudoplastic behavior. The freeze-dried formulated samples showed lower viscosity when rehydrated than those without biopolymers added. The Newtonian behavior of the LG-Rh samples and the lesser consistency than the freeze-dried rehydrated ones may be also related to the presence of fiber in the latter.

## 4 | CONCLUSION

The results of this study allow us to propose freeze-drying as a process to obtain a grapefruit product with better properties, both in powder and rehydrated form, than the one obtained by spray-drying. The freeze-dried powders showed lesser wetting time and lesser hygroscopicity but greater porosity, although they also presented lower solubility. In addition, the powders obtained by freeze-drying were darker, more orange and less viscous when rehydrated. The lower natural grapefruit fiber content of the spray-dried products, together with their smaller particle size and an effect of temperature during this process on the carotenes, responsible for the typical color of this product, can justify the differences observed. On the other hand, although the incorporation of biopolymers is necessary to facilitate the process and stabilize the product, no significant differences have been found between the different formulations tested.

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## AUTHOR CONTRIBUTIONS

Nuria Martínez-Navarrete and María del Mar Camacho conceived and designed the study. Luis A. Egas-Astudillo conducted the experiments. Nuria Martínez-Navarrete, Luis A. Egas-Astudillo and María del Mar Camacho wrote the paper. Nuria Martínez-Navarrete and María del Mar Camacho reviewed and edited the manuscript. All the authors read and approved the manuscript.

## CONFLICTS OF INTEREST

The authors declare no conflict of interest

## ORCID

*María del Mar Camacho* https://orcid.org/0000-0002-2342-2105

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