Impact of shelf temperature on the temperature evolution of a grapefruit puree during freeze-drying

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Abstract

Fruits are foods with a high nutritional and functional value. Freeze-drying supplies products of high quality and added value. Therefore, although it is a slow and energy-costly process, it seems appropriate to optimize it for the purposes of obtaining fruit products. In this sense, it is of utmost importance to know the end point of the process as accurately as possible. While many kinetic models have been described to predict the evolution of the water content over time, their application is impractical because they do not permit the on-line monitoring of the process. It is also important to quantify how much shorter the process will be if applying temperature, while always guaranteeing the quality of the product. In this study, the use of the evolution of the temperature of the sample to identify the drying end point in-line has been investigated. The impact of the shelf temperature has been considered.

Keywords: primary drying, secondary drying, heating rate, target temperature

1. Introduction

Since freeze-drying is a drying technique based on the sublimation of water from a previously frozen product, the freezing stage will condition the quantity and size of the ice crystals formed and, therefore, the ease of their subsequent elimination which, in turn, will influence the characteristics of the product obtained. On the other hand, the conditions during the drying stage will also affect their duration and the quality of the product. Drying takes place in two stages, primary and secondary drying. In the former the sublimation of ice occurs and so it is necessary for the sample to remain below the triple point of water during drying, which is p = 610.4 Pa and T = 0.0099 ºC (Roos, 1995). Once most of the ice is removed, it is necessary to remove the bound water by further supplying heat to the product to accelerate the secondary drying.

The target of the process is to get the desired water content in the final product at the lowest process time. Suitable process analytical technologies (PAT) have been described as to follow in conventional freeze-dryers the drying stages, thus evaluating in-line if the desired quality is obtained in the final product (Davide Fissore, Roberto Pisano & Antonello A. Barresi (2018) Process analytical technology for monitoring pharmaceuticals freeze-drying – A comprehensive review, Drying Technology, 36:15, 1839-1865, DOI: 10.1080/07373937.2018.1440590; Patel, Doen and Pikal).

The various techniques proposed can be catalogued depending on the monitored variable being the product temperature, the pressure inside the chamber or even a specific physical property of the product. Any of these techniques has specific problems that also depend on the product in question and even the sample size. In-line temperature recording has been widely used for monitoring freeze-drying, especially primary drying, in pharmaceutical applications (Refs). However, there are not many references focused on

recording the evolution of food temperature during freeze-drying as a tool for monitoring the process (Pikal fresa???).

During the freeze-drying, the latent heat of sublimation must be provided. This allows work to be done at moderate temperatures, in order to shorten the process, without the sample changing its temperature during this stage. However, once the sublimation is finished, the temperature of the product will begin to increase and its quality could be compromised. Considering both aspects, it is necessary to study the cost/benefit ratio of the increase in temperature during drying, always in relation to the working pressure. In the case of dehydrated fruit products, structural collapse is one of the main quality aspects to be considered.

Collapse is a phenomenon that includes different time-dependent structural transformations that occur in amorphous food and other biological materials at temperatures above their glass transition temperature (Tg). In many cases, during the drying of a food, an amorphous non-thermodynamic equilibrium state may be reached, which could be rubbery or glassy depending on how the temperature is related to its Tg. The glassy state is related to a higher viscosity of the matrix that ensures greater stability. The loss of viscosity associated with the rubbery state is related to the loss of the structure of the dehydrated product, which involves significant textural changes and the development of stickiness and caking phenomena in the case of powdered products.

However, it has been described that the critical viscosity that determines this structural collapse is reached at a temperature higher than Tg, this being the critical temperature for the structural collapse (Tc). For example, in mixtures of sucrose and fructose, major sugars in fruits, this occurs at approximately 20 °C above the temperature at the end of the glass transition (Roos, 1995). The Tg depends on the composition of the sample, so that it increases when the average molecular weight of the solutes increases and when the

water content decreases. The Tg of dehydrated grapefruit presents low values, in the order of the conventional storage and consumption temperatures of these products (Telis and Martínez-Navarrete, 2009). That is why this particular product, and fruit in general, is in a rubbery state under these conditions, with the quality problem that this implies. To avoid this problem, the incorporation of high molecular weight biopolymers in their formulation has been shown to be an effective technique for increasing Tg (Telis and Martínez-Navarrete, 2012). However, while these compounds will improve aspects related to the rheological behavior of the product, they can also affect other properties of the product, such as its color, as well as the process kinetics.

Considering all these aspects, it is important to select the drying temperature during freeze-drying (Davide Fissore, Roberto Pisano & Antonello A. Barresi (2018) Process analytical technology for monitoring pharmaceuticals freeze-drying – A comprehensive review, Drying Technology, 36:15, 1839-1865, DOI: 10.1080/07373937.2018.1440590). It should not exceed the ice melting temperature for the duration of primary drying. In addition, even when there is no ice left, care must be taken not to exceed the aforementioned critical temperature responsible for the structural collapse of the formulated sample, taking into account its water content at each moment of the process. The Tg of the anhydrous grapefruit is around 45ºC and increases to almost 75ºC when gum Arabic is added to the grapefruit solutes in a 1:1 ratio (Fabra et al., 2009; Telis and Martínez-Navarrete, 2009). So, in the worst-case scenario where no biopolymers have been added and assuming the afore mentioned Tc value being 20 ºC above the Tg, the Tg of the anhydrous grapefruit without added biopolymers would be close to 65 °C. According to the data published by Telis and Martínez-Navarrete (2009), the Tg of grapefruit juice dehydrated to 3 g water/100 g product decreases to 25 ºC, so that its Tc will be close to 45 ºC. Considering the greater Tg of the formulated grapefruit and that

3% is a usual water content in freeze-dried products, 40 °C was selected as the maximum freeze-drying temperature for this study, ensuring the absence of ice melting and structural collapse at all times. In fact, some previous experiments carried out before starting the work plan contemplated in this study confirmed both extremes.

The objective of this study was to delve deeper into the fundamentals of food freeze-drying, taking as a tool the evolution of the temperature of the product throughout the process. The study was carried out using grapefruit puree, formulated, or not, with gum Arabic and bamboo fiber, and heating, or not, the shelves of the freeze-dryer to 40 ºC.

2. Materials and methods

2.1. Sample preparation.

Grapefruit (*Citrus paradisi*) of the pigmented variety Star Ruby obtained from a local market (Valencia, Spain) was used for the study. The fruits were selected according to their size, firmness and absence of physical damage. Two high molecular weight biopolymers were added as carriers: gum Arabic (GA, Scharlab, Spain) and Bamboo Fiber (BF, Vitacel® BAF 200, Spain).

The grapefruit was manually detached from its flavedo, albedo and central axis. It was chopped and crushed at speed 4 for 40 s, followed by speed 9 for 40 s, in a Thermomix Vorwerk TM-21 robot (Spain).The obtained puree was subdivided into two parts: one remained as such, while the biopolymers (Bp) were added to the other according to a previously established ratio (Agudelo et al., 2017): (4.2 g GA + 0.58g BF) / 100g grapefruit puree. The mix was homogenized by means of the same Thermomix described above at speed 2 for 300 s. In this way, two types of samples were obtained: one without added biopolymers (G) and another with (GB). In both cases, the water (60 ± 1 ° C and

pressure <100 mm Hg, JP Selecta vacuum oven, Spain) and soluble solid (Mettler Toledo 30 PX Refractometer, Spain) content was analyzed.

2.2. Process conditions

2.2.1. Freezing

The samples (G and CB) were distributed in aluminum trays of 5.8 cm in diameter and 1 cm high, with an approximate weight of 27 g per container. A total of 6 trays per sample were frozen. A Liebherr LGT 2325 freezer chest (Germany) was used and the samples were kept inside for 6 hours at -45 ° C. During the freezing, the temperature evolution was recorded every 30 s, by means of a wireless system consisting of a data transmitter, Datanet Logger DNL910A Fourtec (Spain), to which a K-type thermocouple of 0.5 mm diameter is attached (Thermocoax, Spain) and a Datanet Repeater DNR900 Fourtec data receiver (Spain) connected to a computer. The thermocouple was placed in the geometric center of the sample at a height of 0.5 cm. The temperature was registered in 2 trays of each sample per drying experiment, as described below.

2.2.2. Freeze-drying

The frozen samples were dried in a standard cylindrical chamber (diameter 215 x 300 mm height) of acrylic material, with three heated shelves, coupled to a freeze-dryer (Telstar Lyo Quest-55, Spain). In both cases, the chamber pressure was maintained at 0.05 mbar. Two different shelf temperatures were tested: the room temperature (20 ºC, RT samples) and 40 °C (samples labelled 40). In each case the process time was adjusted to obtain a product with ≈3 g water/g sample, known the appropriate product quality with this water content (Table 1, Egas-Astudillo et al., 2018). In this way, four different drying experiments were designed (G, GB, G40 and GB40) and carried out in duplicate. In each experiment, 2 sample trays with thermocouple and 1 without it, prepared as described in

149 section 2.2.1 and placed on the central shelf, were dried. The evolution of the temperature
150 of the samples was recorded in a similar way to that explained in the previous point.
151 2.2. Water content
152 The water content of all the freeze-dried samples was determined in triplicate by drying
153 the samples at 60 ± 1 ° C and pressure <100 mm Hg (JP Selecta vacuum oven, Spain).
154 2.3. Statistical analysis
155 In order to analyze the significant differences ($p < 0.05$) between processes and samples,
156 an analysis of the variance (ANOVA) was performed applying the LSD (least significant
157 difference) test at 95%. The software program Minitab® 16.2.2 was used.
158
159 3. Results and discussion
160 The water and soluble solid content of the grapefruit puree used for the study was
161 87.39±0.02 g water/100 g puree and 11.2±0.2, respectively. These values changed to
162 83.59±0.03 g water/100 g puree and 15.4±0.4 ºBrix when the Bp were added. The water
163 content of the freeze-dried samples appears in Table 1. As can be observed, in all cases it
164 was close to the expected 3 g water/g sample.
165 3.1. Evolution of the temperature of the product along the freezing
166 Figure 1 shows, as an example, a curve with the evolution of the temperature of (G) and
167 (GB) during freezing. As expected, these curves permitted the identification of the 4 steps
168 that are generally observed during the freezing of a food (James and James, 2014). First,
169 the cooling of the sample occurs before the start of ice crystal formation (step S1), the
170 slope of this section being proportional to the cooling rate of the product, taking into
171 account the equipment used and the thermal and geometric properties of the sample
172 (Heldman and Hartel, 1997). When the water phase transition begins, at a temperature
173 dependent on the quantity and type of solutes present in the food, a very important

174 decrease of the slope is observed. The second step (S2) is extended until the formation of
175 ice in the sample ends. In conventional freezers, the elimination of the extra heat released
176 during the exothermic crystallization of water does not allow the sample to continue
177 cooling at the same speed as before the start of freezing. During the next step (S3), the
178 cooling rate of the product that is now frozen increases again, until the temperature of the
179 freezer is reached (S4). It should be remembered at this point that not all the water present
180 in a food is freezable. The progressive cryoconcentration of the liquid fraction of the food
181 causes its freezing temperature to decrease. Both factors lead to a significant increase in
182 the viscosity of the unfrozen matrix that ends up limiting the molecular mobility of the
183 water that still remains in the liquid state, preventing its crystallization. Thus, the
184 maximally cryoconcentrated residual solution, in an amorphous state, is trapped between
185 the ice crystals. This structure ensures the food system is highly stable, precisely through
186 the immobilization of the residual liquid water and the low temperature.
187 In addition to these 4 stages, in some cases a subcooling of the sample may be observed
188 (Fig. 1), which occurs when the cooling rate is higher than that of crystallization, so that
189 the product remains at a temperature lower than the onset freezing temperature for a short
190 time. The subcooled product is in a meta-stable state of non-thermodynamic equilibrium,
191 which could be interpreted as somewhat similar to the activation energy necessary for the
192 nucleation process (Kasper et al., 2013). However, when the crystallization begins, the
193 heat released causes a pointwise increase in the sample temperature until it reaches the
194 value that thermodynamically corresponds to that of water crystallization (Tc).
195 For each of the obtained curves, the slope (ºC/min) and duration (min) of the three cooling
196 steps described above were characterized (Fig. 2). The slope of S1 and S3 will be closely
197 related to the cooling system used and no significant differences were observed among
198 them ($p>0.05$). In no case was the presence of the added biopolymers observed to exert a

significant effect on the cooling rate ($p>0.05$). As regards the subcooling, observed in every sample, no significant differences ($p>0.05$) were observed between the different samples, with the mean value of Tc being -1.7 ± 0.8 ºC. In this way, this may be assumed to be the initial freezing temperature of the grapefruit puree in the freezer used, which was not affected by the presence of GA and BF in the sample.

Despite the fact that the slope of S2 would be, from a strict point of view, the freezing rate of the samples, which in our case varied, on average, between -0.0102 and -0.0496 ºC/min, different studies consider the freezing rate over a wider temperature range (Degner et al., 2013; Bronfenbrener and Rabeea, 2015; Nowak et al., 2016). Taking into account that the duration of each step described above exhibited no significant differences ($p>0.05$) brought about by the presence of biopolymers (Fig. 2), the average general cooling rate of the samples considered in our study was calculated, from 20 to -15 ºC (Degner et al., 2013). This was 0.58 ± 0.07 ºC/min. According to Degner et al. (2013), freezing rate values, calculated over this temperature range, of over 0.11 ºC/min can already be considered as fast freezing.

3.2. Evolution of the temperature of the product during the drying

During the drying step of the freeze-drying process, a first period was identified in which the temperature of the product remained low and constant and a second period in which the temperature of the product increased rapidly until reaching the temperature of the chamber. The first period has been traditionally identified with primary drying, in which sublimation occurs and the second with secondary drying that corresponds to the desorption of the non-frozen water. However, the separation between primary and secondary drying is not always so clear when a food is processed, especially when freezing and drying are carried out using different equipment.

In Fig. 3, an example of how the temperature of each of the samples evolved during the drying stage can be observed. As can be appreciated, the samples are at an initial temperature of approximately -45ºC, the temperature at which they were held in the freezer cabinet. Once the samples are introduced into the freeze-dryer chamber and it is switched-on, the temperature of the sample begins to rise rapidly due to the difference in temperature between the freeze-dryer shelves and the frozen samples. The progressive decrease in the pressure of the freeze-dryer chamber, until it stabilizes at the programmed pressure, causes the temperature of the product to fall again until it stabilizes, remaining at this temperature while sublimation predominates (the primary drying stage). Afterwards, the temperature of the samples begins to increase and the curves acquire more or less pronounced slopes, depending on the drying conditions. In order to find out the state of the sample at that moment, we carried out some tests/a test on top of the experiments contemplated in this study, stopping the drying at that point. As we saw that the sample was still partially frozen, as it has been observed by other authors (Chen et al.[65] and Bosca et al.,[62] en Fissore et al., Drying Tech.), we can confirm that sublimation still occurs during this time, although in all likelihood already overlapping with the desorption of the non-frozen water. The sudden change of temperature may be due to the moving sublimation interface advances that past the thermocouple losing contact with ice at that point in the sample (Fissore et al., Drying Tech). This account a difficulty for the temperature to identify the predominant drying mechanism in this moment. Finally, the temperature of the sample rises more and more slowly until reaching the temperature of the chamber, during what would already be the secondary drying stage, where desorption predominates.

As shown in Fig. 3, in every case the effect of the shelf temperature became evident in the duration of both primary and secondary drying. As expected, heating the shelves to

40 °C implied that the samples reach the temperature of the chamber beforehand, which permitted a shortening of the process time. This was reflected in two ways: in a shorter first stage, as there was a greater amount of heat available for sublimation, and also in a higher rate of sample temperature increase during the second stage.

In an attempt to better identify both stages and the phenomena predominant at each moment, the temperature data of the sample during drying (Tt), from the moment that the freeze-dryer reaches the established pressure, were normalized with respect to the final temperature reached by the sample (Tf). In addition, the sample's rate of temperature change, calculated from the relationship between the sample temperature increase between 2 consecutive data and the corresponding increase in time ($\Delta T/\Delta t$), was analyzed. Figure 4 shows both relationships and their evolution over drying time. The curve $\Delta T/\Delta t$ vs. t, allows a first phase to be identified in which the sample's temperature change rate over time remained constant. This is consistent with the fact that the sublimation of a significant amount of ice in the sample occurs during this time, so that the heat that the frozen sample obtains from the environment is invested in the sublimation and the temperature of the sample is not modified. When the sample has little ice left, the temperature increases faster and faster until it reaches a maximum value. As the sample temperature increases and there is no more ice left, so that evaporation only occurs due to desorption, the sample heating rate over time fell. With this analysis of the temperature curve, primary drying could be identified up to the moment when the maximum value of ($\Delta T/\Delta t$) is reached and, after that, secondary drying occurs.

As was observed in different experiments during this study, the duration of the secondary drying stage is key to obtaining a product of the right quality, because if it is shortened excessively, there is a risk of obtaining a product with more water content than desired. On the other hand, lengthening it too much would mean an unnecessary increase in the

cost of the process. In this sense, it would be important to have a tool with which to identify the precise end point of this second stage. In spite of the fact that different kinetic models have been described based on the evolution of the water content of the samples over time (Togrul and Pehlivan, 2003; Simal et al., 2005; Fahloul et al., 2009; Benlloch-Tinoco et al., 2013; Egas-Astudillo et al., 2018), we wanted to confirm the possibility of using the evolution of the sample temperature to be able to identify the drying end point of our formulated grapefruit puree in-line. Some authors describe to identify this ending point looking for the time instant when the temperature detected becomes equal to the temperature of the heating source (REFs: M.J. Pikal, A. I. Liapis, R. Bruttini, A. Barressi, S.A.Velardi, C. Ratti, H. Sadikoglu. En realidad no se si ninguno de estos dice exactamente eso!; Fissore et al., Drying Tech: éste dice que ahí es donde acaba el primario!). Therefore, the end point of the process could be identified when the value (Tt/Tf)=1 is recorded. Considering this criterion, the duration of the drying process was identified for the different processed samples (Table 1). If this time is compared with that used in this study to obtain a product with a water content of ≈3%, it can be observed that when the drying is carried out at room temperature, it is convenient to increase the time by approximately 15% compared to the predicted one. On the other hand, when the freeze-dryer shelves are heated, the proposed criterion is closer to reality and even ensures the extra drying of the product, so that its quality will never be compromised.

Taking the abovementioned into consideration, the end point of the drying step of the freeze-drying process could be related to the sample reaching a certain target temperature (T). In this sense, when the drying occurs at a temperature lower than T, the sample will never reach it and, therefore, once the temperature of the chamber is reached, the drying will have to be extended for somewhat longer until the sample has obtained the heat necessary for the desorption of the remaining water from the environment. If the drying

298 is done at a temperature higher than T, the process can be stopped even before the sample
299 reaches the temperature of the chamber. In the present work, this temperature seems to
300 be greater than 20 and lower than 40 ºC, without having been able to determine it exactly
301 with the information available. In order to confirm this hypothesis, the programming of a
302 series of experiments is recommended, stopping the process when the sample reaches
303 temperatures in that interval and analyzing its water content.
304 Assuming the drying time based on the aforementioned criteria and establishing the limit
305 between primary and secondary drying when the maximum value of ($\Delta T/\Delta t$) was reached,
306 the duration of these two stages was identified for the different processed samples (Figure
307 5). Secondary drying occupied between 33 and 55% of the total drying time, the longest
308 relative duration being observed for the samples dried at 40 °C, in which process,
309 obviously, sublimation was facilitated. In any case, this indicates that, although
310 sublimation was what occupied most of the drying time, the desorption stage was also an
311 important part of the process. The ANOVA performed to analyze the differences in the
312 duration of each stage as a function of the samples showed that the drying lengthens
313 significantly ($p<0.05$) when performed at room temperature (Fig. 5). This significantly
314 affected the primary drying ($p<0.05$). This significantly affected primary drying ($p<0.05$).
315 In every case, primary drying was longer and secondary drying was shorter when the
316 samples contained Bp in their formulation, although in this case the differences did not
317 become significant ($p>0.05$). These results would seem to indicate a certain contribution
318 of the biopolymers to the formation of a more structured matrix that would hinder the
319 formation of the pores in some way and, therefore, the sublimation of the ice. It would,
320 nevertheless, simultaneously give greater consistency to the porous structure formed,
321 facilitating the exit of the water vapor during desorption.
322

4. Conclusions

The product heating rate during the drying step of the freeze-drying process seems to be a more interesting tool than the temperature itself with which to identify the separation between primary and secondary drying, associated with a greater predominance of the sublimation or desorption of the non-frozen water, respectively. It seems that the continuous recording of the sample temperature during the drying step of the freeze-drying process is able to be used for the purposes of identifying the end point thereof, although it does not necessarily coincide with the moment at which the sample reaches the temperature of the chamber. The target temperature will have to be determined for each specific sample in some previous experiments. In this case, the target would be to reach a temperature of between 20 and 40 ºC.

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393 Table 1. Water content (Xw, g water/100 g sample) and duration of the drying stage of
394 the freeze-drying process of the samples without and with added biopolymers (G and GB,
395 respectively), and dried at room temperature (RT) or at 40 ºC (40).

		t (h)	
Sample	Xw	Tt/Tf=1[(1)]	Xw= 3%[(2)]
GB(RT)	3.0	20.58	23
GB(RT)	2.7	19.13	
G(RT)	3.0	20.58	22.3
G(RT)	3.0	19.23	
GB(40)	2.6	12.88	9.1
GB(40)	2.9	10.79	
G(40)	2.8	12.94	10
G(40)	2.5	10.36	

396 [(1)]Time until the temperature of the sample (Tt) reaches the temperature of the drying chamber (Tf);
397 [(2)]Experimental freeze-drying time ~~predicted to reach 3 g water / 100 g of sample (Egas-Astudillo et al.,~~
398 ~~2018)~~.
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400