



Freezing pre-treatments on the intensification of the drying process of vegetables with different structures

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ABSTRACT

The effect of different freezing pre-treatments on the drying kinetics (50 °C and 1 m/s), and quality of vegetables with different structures such as beetroot, apple and eggplant has been studied. Samples cubes of 0.01 m edge were frozen at temperatures of −20 °C, −80 °C, or by immersion in liquid nitrogen (−196 °C). Then, frozen samples were dried at 50 °C and 1.0 m/s. Freezing pre-treatments promoted a significant ($p < 0.05$) increment of the drying rate, leading a reduction of the drying time up to 17, 27, and 34% in beetroot, apple and eggplant, respectively. A diffusion model was proposed to identify both the effective diffusion (D_e) and the external mass transfer (h_m) coefficients during convective drying. The identified D_e in untreated (non-frozen samples) beetroot, apple and eggplant was of $4.2 \pm 0.1 \times 10^{-10}$, $4.7 \pm 0.1 \times 10^{-10}$ and $5.1 \pm 0.3 \times 10^{-10}$ m²/s, respectively. This coefficient was significantly higher in treated samples. Increments ranged from 18 to 31%, from 42 to 64%, and from 18 to 72% in beetroot, apple and eggplant, respectively and in all cases the higher figure was observed when samples were frozen at −20 °C. The identified h_m was of $7.0 \pm 0.5 \times 10^{-4}$, $4.2 \pm 0.2 \times 10^{-4}$ and $2.3 \pm 0.2 \times 10^{-4}$ kg water/(m² s) for beetroot, apple and eggplant drying, respectively. Regarding quality parameters, colour change and microstructure were deeply affected by both the freezing pre-treatment and the drying process. The extension of this effect varied accordingly to the porosity of the sample. The eggplant colour and microstructure, with a higher porosity, was the most affected, particularly by freezing pre-treatment at −20 °C.

1. Introduction

As many other vegetables, beetroot (*Beta vulgaris var. conditiva*), apple (*Malus domestica var. Granny Smith*) and eggplant (*Solanum melongena var. black enorme*) are prone to spoilage due to their high moisture content (> 6 kg water/kg dm) (Figiel, 2010; Morales-Soto et al., 2014; Sabarez et al., 2012). Consequently, they are perishable products which could maintain their storage stability and extend their shelf life, if the optimal postharvest technologies are applied (Sousa-Gallagher et al., 2016). The shelf-life can be profitably prolonged through drying of the product.

Drying is one of the most common processes used to improve food stability. Drying process application decreases the water activity of the material, reduces microbiological and enzymatic activity and minimizes physical and chemical reactions during storage (Russo et al., 2013). However, convective drying requires a long processing time. Hence many different pre-treatment methodologies have been proposed in the literature to intensify the drying process (Dandamrongrak et al., 2002). Among them, freezing pre-treatment has been reported to

enhance the mass transfer process in vegetables and, therefore, promote higher drying rates (Lewicki, 2006). It seems that freezing process modifies the structure and results in better water diffusion since it contributes to an easier water removal and, consequently, shorter drying times. Compared with untreated samples, significant drying time shortening was reported by Dandamrongrak et al. (2002) when drying banana at 50 °C and 3.1 m/s (46% shorter) after a freezing pre-treatment carried out at −34 °C. Arévalo-Pinedo and Xidieh Murr (2007) observed a reduction by 24–32% in the drying time (50 and 70 °C and 5 kPa) of carrot and pumpkin, after samples were frozen at −20 °C. Zielinska et al. (2015) and Ando et al. (2016) studied the effect of freezing pre-treatment at −20 °C on the drying kinetics of blueberries and carrots, respectively. Both studies reported reductions of the drying time by 13–20% (60–80 °C) and by 40% (60 °C and 0.81 m/s), respectively. Drying of cape gooseberry (60 °C and 2 m/s) was shortened by freezing pre-treatment of the samples at −18 °C (13%) and by liquid nitrogen immersion (20%) (Junqueira et al., 2017). As far as we are concerned, only two studies related to the products used in this work (beetroot, apple and eggplant) were found in the literature. The

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Nomenclature

D_e	effective water diffusion coefficient (m^2/s)
dm	dry matter (kg)
F20	frozen sample at -20°C
F80	frozen sample at -80°C
FLN	frozen sample by liquid nitrogen immersion
h_m	external mass transfer coefficient ($\text{kg}/\text{m}^2 \text{ s}$)
L	half of the length of the cube (m)
n	number of experimental data
MRE	mean relative error (%)
S_x	moisture content standard deviation (sample) (kg water/kg dm)
S_{yx}	moisture content standard deviation (calculated) (kg water/kg dm)
t	time (h)

U	untreated sample (non-frozen)
var	percentage of explained variance (%)
W	moisture content (kg water/kg dm)
x,y,z	spatial coordinates (m)
ρ_{dm}	dry matter density ($\text{kg dm}/\text{m}^3$)
φ	relative humidity

Subscripts

0	initial
∞	drying air
cal	calculated
e	equilibrium
exp	experimental
l	local

application of freezing pre-treatments at -20°C and -30°C promoted a reduction of the drying time by 32% in beetroot (70°C and 2 m/s) (Shynkaryk et al., 2008), and by 28% in apple (60°C and 1.2 m/s) (Ramírez et al., 2011), respectively.

Regarding energy consumption, freezing pre-treatment has been reported to decrease specific energy consumption by up to 27% in comparison with drying without pre-treatment when blueberries were frozen (at -20°C) prior to drying at 60 and 80°C (Zielinska et al., 2015). Furthermore, mass transfer process intensification could be evaluated by modelling the experimental drying kinetics. Using the slope method on empirical models, Dandamrongrak et al. (2002) observed an increment of 187% in the water diffusivity figure, compared with untreated sample, when banana was frozen at -34°C prior to drying (50°C and 3.1 m/s). Moreover, by using the Page empirical model, Junqueira et al. (2017) observed an increment of 111 and 135% in k parameter when cape gooseberries were dried (60°C and 2 m/s) after a freezing pre-treatment at -18°C and by liquid nitrogen immersion, respectively, compared with untreated sample. However, in order to properly study the mass transfer, a phenomenological model (Ramírez et al., 2011) can be used by the application of Fick's law of diffusion which might be considered the main transport mechanism (Rodríguez et al., 2014). Arévalo-Pinedo and Xidieh Murr (2007) found an increment of 3–77% in effective diffusivity figure of carrot and pumpkin during drying (50 – 70°C and 5 – 25 kPa) when freezing pre-treatment was applied at -20°C .

Physical aspect and texture of vegetables arise from the structural organization at different levels; from molecular to tissue level that determine different physical characteristics (Chassagne-Berces et al., 2009). Tissue structure disorders due to ice crystals formation during freezing process would lead to physico-chemical changes of the material. The quality of the frozen and dried product would depend on the extension of such changes. In order to evaluate the influence of freezing at the tissular and cellular level, the colour change has been considered a quality parameter which represents the macroscopic changes caused by freezing treatments and microscopy has become a useful tool (Chassagne-Berces et al., 2009). Unfortunately, only few studies of different freezing treatments have been found and only for one product at a time: apple (Chassagne-Berces et al., 2009), carrot (Kidmose and Martens, 1999), and strawberry (Delgado and Rubiolo, 2005), or for different products but subjected to only one freezing treatment (green asparagus, zucchini and green beans frozen at -40°C) (Paciulli et al., 2015). The only exception found was the study of Chassagne-Berces et al. (2010) which evaluated the effect of different freezing treatments (-20°C , -80°C and liquid nitrogen immersion) on mangoes and apples of different varieties and ripeness.

In general it is accepted that less migration of water and less breakage of cell walls, therefore better preservation of the food

structure, is caused by fast freezing which induces the production of a large number of small ice crystals (Chassagne-Berces et al., 2009). However, breakage of the product due to ice density differences with water can be provoked by too fast freezing (Chassagne-Berces et al., 2009). Thus, there is still a claim for a better understanding of the complex mechanisms that take place during freezing which are not only affected by the freezing velocity but also by the structure of the sample submitted to freezing process. Beetroot, apple and eggplant represent a diversity of cell patterns and tissue structures that could be found among vegetables. The porosity of these products ranged from low figures in the case of beetroot (0.043), to middle-high figures in the case of apple (0.500) and eggplant (0.641) (Boukouvalas et al., 2006).

Therefore, the purpose of this study was to evaluate the effect of different freezing pre-treatments (-20°C , -80°C and liquid nitrogen immersion) on the drying kinetics (at 50°C and 1 m/s), by the identification of the effective diffusion (D_e) and the mass transfer (h_m) coefficients, and on the quality of the frozen and subsequently dried product by the study of the colour change and the microstructure of beetroot, apple and eggplant.

2. Materials and methods**2.1. Sample processing**

Beetroot (*Beta vulgaris* var. conditiva), apple (*Malus domestica* var. Granny Smith) and eggplant (*Solanum melongena* var. black enorma) were obtained from a local market in Palma de Mallorca, Spain. They were selected according to their solid content, being of 9.0 ± 2.0 , 12.3 ± 0.9 and $5.1 \pm 0.6^\circ\text{Bx}$, for beetroot, apple and eggplant, respectively. Moreover, eggplants were selected with hardness of 71 ± 4 Shore units to assure the homogeneity of the sample ripeness, as flesh hardness is considered an eggplant maturity characteristic (Gajewski and Arasimowicz, 2004). After selection, they were washed, peeled and cut into cubes (0.01 m edge) not including seeds. Two sets of experiments were carried out. In set U (untreated, non-frozen), samples were directly dried meanwhile in set F (frozen), samples were frozen under different conditions summarized in Table 1 and directly placed into the preheated drier without thawing in order to avoid moisture losses which were observed by Ramírez et al. (2011). Samples were placed on a stainless steel tray at F20 and F80 freezing pre-treatments, and in a stainless steel tray at FLN freezing pre-treatment. Freezing velocities were calculated by monitoring the sample temperature according to Chassagne-Berces et al. (2010) methodology and they are summarized in Table 1. Thus, F20 and F80 freezing pre-treatments corresponded to low-medium freezing velocities and FLN freezing pre-treatment corresponded to an instant freezing process (Chassagne-Berces et al., 2010).

In order to avoid sample physical-chemical properties degradation

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