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ASSESSMENT OF FREEZING PRE-TREATMENTS FOR THE FREEZE DRIED OF APPLE SLICES

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Abstract: The effect of freezing rate on the quality of dried Jonagold and Idared was studied. Apple slices underwent various pre-treatments, i.e. freezing in household freezer (freezing rate: 0,5 °C/min), contact plate freezing (2 °C/min) and vacuum-freezing (3 °C/min). The quality of the freeze dried product was then evaluated in terms of water activity, hardness, color and rehydration. The freezing in household freezer (slow freezing rate) significantly reduces the duration of the freeze drying process and consequently the process costs. The slow freezing rate allows the growth of large ice crystals at the beginning of the freeze-drying process, this fact should consequently lead to larger pores and injured cell walls and thus to shorter freeze drying time. Quality of the freezing in household freezer product was assessed as higher than the quality of the other freezing pre-treated material. Slow freezing rate resulted softer texture and higher rehydration capacity, than that of other pre-treated samples. In all cases, slow freezing lead to lower final moisture content, total color difference and water activity.

Keywords: Apple, Freezing, Freeze drying, Drying time, Quality assessment.

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INTRODUCTION

Freeze drying is a dehydrating process for the long term preservation of heat sensitive food and other biological materials based on the phenomena of sublimation. The freeze drying process consists of three stages (1) freezing of the material, (2) a first drying stage, where sublimation of the frozen free water occurs, and (3) a second drying stage, where the bound frozen water is eliminated by desorption (Reyes et al., 2010). Freezing is a previous operation in freeze drying in which develop the structure and therefore predetermine the properties of dried material (Ceballos et al., 2012). Freezing plays an important role in material preservation and dehydration (Jackel et al., 2008). Freezing method, freezing temperature and freezing time are very important parameters in the initial stage (Wang et al., 2012). In terms of the drying kinetics, physical pre-treatment such as freezing, change the physical properties of the sample cell structure, which in turn alter the rate of moisture removal (Eshtiaghi et al., 1994).

Generally the faster the freezing rate, the smaller the ice crystals and hence, the longer the primary drying period. This has the advantage of giving a higher final product quality (Ghio et al., 2000). Araki et al. (2001) observed that a slower freezing rate, which leads to larger ice crystals, resulted in higher permeability in the frozen samples. Therefore, it is important to control the size of the ice crystals during freezing because it affects the quality of the freeze dried product. It can influence damage cell walls, porosity and hence drying kinetics as well as rehydration characteristics of freeze dried products. The reduce the freeze drying costs; one alternative is to evaluating adequate freezing rate.

Apples are an important raw material for many food products and apple plantations are cultivated all over the world in many countries. The apples are consumed either fresh or in the form of various processed such as juice, jam and marmalade, dried apples, etc (Doymaz, 2009).

This research aimes to improve the quality of freeze dried apple by various freezing rate (0.5, 2 and 3 °C/min). The effect of freezing pre-treatments on the drying time and some quality attributes of dried apple slices viz. moisture content, water activity, color, texture and rehydration are investigated.

MATERIALS AND METHODS

Material

Fresh apples (var. *Jonagold* and *Idared) (Malus domestica* Borkh.*)* were purchased from a local market and stored at 5 °C. Prior to an experiment

apple was washed with tap water, peeled and sliced to a thickness of 5 mm using a hand slicer. The initial moisture content of *Jonagold* and *Idared* apple slices were 86,5%, wb. (6,4 kg water/kg dry matter, db.) and 87,6%, wb. (7,064 kg water/kg dry matter, db.). The moisture content – before and after treatment – was determined by gravimetric method. At regular time intervals during the processes, samples were taken out and dried in the oven for 3–4 h at 105 °C until a constant weight was achieved. Weighing was performed using a digital balance, and then moisture content (wet basis (wb.), dry basis (db.)) was calculated. The tests were performed in triplicate. All apple samples were randomly divided into groups for each treatment.

Freezing pre-treatments

The freezing of the apple samples, achieved when using three different freezing equipment, where: (1) freezing in household freezer (freezing rate: 0,5 °C/min, cooling down to -25 °C), (2) freezing in contact plate freezer (freezing rate: 2 °C/min, to -25 °C) and (3) freezing in chamber of vacuum freezer (freezing rate: 3 °C/min, to -25 °C). Two freezing rates (medium and slow) were used to freeze apple slices in order to determine changes in apple quality characteristics. The thermocouples were inserted in the top, in the middle and in the bottom of the sample in order to obtain a good and reproducibility results. After pre-treatments, the samples were dried in the vacuum-freeze drier. In every drying experiment, about 200 g apple slices were pre-treated. All measurements were performed in triplicate.

Freeze drying

The experiment was conducted using a laboratory scale freeze drier (FT33, Armfield Ltd, Ringwood, England) equipped with a computerized data acquisition system. The moisture loss is recorded during drying by a specially developed weighing unit. The weighing unit consists of a load (model PAB-01, 500±0.1 g) and registering instrument (model ES-138, Emalog, Budapest, Hungary). The product was dried for a period of 22-24 h at 45-82 Pa with the heating plate kept at 18°C. The condenser temperature was kept at –50 to –55°C. The experiments were replicated three times and the average of the moisture content at each value was used.

Water activity

Water activity (a_w) is defined as the ratio of the vapour pressure of water in the food to the vapour pressure of pure water at the same temperature (McLaughlin and Magee, 1998). Water activity indicates how tightly the

water is bound in the food, from a structural and chemical point of view, and hence describes the availability of the water to participate in chemical and biochemical reactions. The water activity scale extends from 0 (bone dry) to 1.0 (pure water) but most foods have a water activity level in the range of 0.2 for very dry foods to 0.99 for moist fresh foods.
The water activity of apple slices was measured at 25 °C, using a temperature-controlled Novasina Labmaster (model CH-8853, Novasina AG, Switzerland). The determination was performed in triplicate.

Color

Color is an important quality attribute in a food to most consumers. Color of apple slices was measured by ColorLite sph900 spectrophotometer (ColorLite GmbH, Germany) before and after drying. The color meter was calibrated against a standard calibration plate of a white surface and set to CIE $L^*a^*b^*$. The color parameters (L^*, a^*, b^*) were measured at 5 different points and the average was calculated for each sample. The color brightness coordinate L^* measures the whiteness value of a color and ranges from black at 0 to white at 100. The chromaticity coordinate a^* measures red when positive and green when negative, and chromaticity coordinate b^* measures yellow when positive and blue when negative. In addition, total color difference (ΔE) was calculated using Eq. (1):

$$\Delta E = \sqrt{(L - L_0)^2 + (a - a_0)^2 + (b - b_0)^2} \quad (1)$$

where L_0, a_0 and b_0 are the control values for fresh apple.

Textural characteristics

Measurements of the texture of apple slices were carried out using a texture analyzer (CT3-4500, Brookfield Engineering Laboratories, Middleboro, USA). The parameters of the test were as follows: 4.5 kg force load cell, 1 mm/s test speed, 10 g trigger force. The samples were placed on a hollow planar base, and afterwards were compressed with 4 mm cylindrical probe. The depth of penetration was 2 mm. The maximal compressive force recorded during the test was defined as hardness. The average value of maximum firmness for each treatment was then calculated and the results were expressed as Newtons.

Rehydration

The rehydration indicate the physical and chemical changes during freezing and drying as influenced by processing conditions, sample pre-treatment and

composition (Feng and Tang, 1998). The rehydration test was done by measuring the weight gain of dehydrated samples (ca. 2g) that were immersed in 250 ml of distilled water at a constant temperature of 25°C. Samples were withdrawn at 1, 5, 15, 30, 60 and 90 min, drained, wrapped in absorbent tissue to remove surface water, and weighed on an analytical balance (JKH-500, Jadever, Taiwan). The rehydration rate (RR) was calculated from the sample weight before and after rehydration. The rehydration measurements were made in triplicate for all the samples and average values were reported.

Statistical analysis

All data were subjected to the analysis of variance (ANOVA) using SPSS software and are presented as mean values with standard deviations. Differences between mean values were established using Duncan's multiple range tests at a confidence level of 95% ($p \leq 0,05$). All experiments were performed in triplicate.

RESULTS AND DISCUSSIONS

Influence of cooling pre-treatments on drying time

Curves of product temperature versus freezing-drying time for pre-treated apple samples are shown in Figure 1. According to the results in Figure 1, freezing pre-treatment is an important parameter that affects the drying time. Freezing time for fresh apple slices varied from 13, 19 to 70 min, when temperature in the core of samples decreased from 14 to -25 °C (vertical broken line).

The overall freeze and drying process, depicted in Figure 1, starts with a freezing step (the end of this running is labelled with a vertical broken line), followed by the first drying step, in which mainly the frozen water is removed by sublimation. A second drying step follows, in which bound water (unfrozen) is removed by desorption. In order to reduce the drying time in the first drying stage (sublimation), the size of ice crystals should be large (black line). Increase in drying rate is observed when fast freezing is used, probably due to the generation of smaller crystals in the first case, which is adverse for drying time (triangular-black line).

Finally, it can be observed that the rate of freezing of samples affects the drying kinetics. Nail and Gatlin (1993) affirmed that the greatest resistance of vapour transport occurs across the dried product layer where water molecules

have to pass the pores and channels, depending on the size of ice crystals. Thus, the slow freezing treatment increases the ice crystal mean size, improving the water vapour mass transfer, gives higher permeability of the dried layer and consequently reducing the primary drying times.

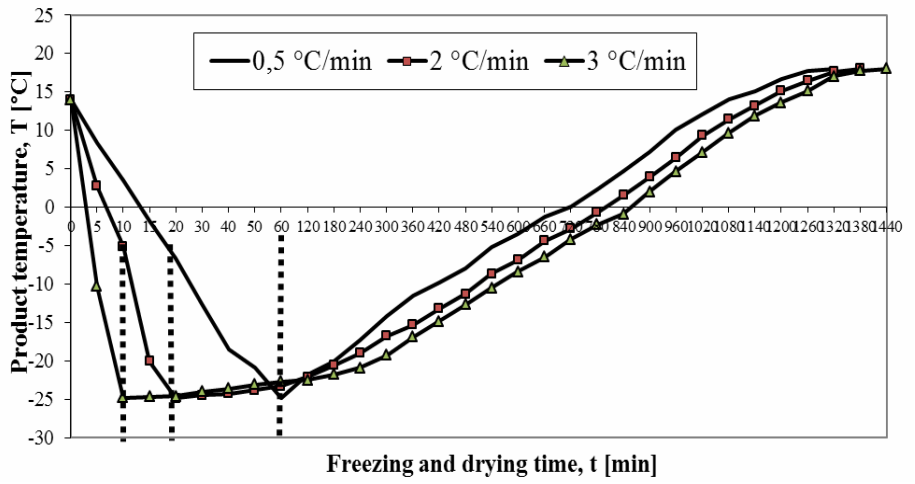

Figure 1. Temperature profile within *Jonagold* slices during freezing and sublimation process

We did not arrange plotting the running of the temperature curves of *Idared* apple, because it is very similar to the *Jonagold*.

Samples frozen in household freezer prior to freeze drying were found to have a significantly shorter drying time compared to pre-treated ones by vacuum-freezing samples. The drying time of frozen apple slices (0,5 °C/min) was close to those of frozen in contact plate freezer (2 °C/min). In our present work, it was shown that slow freezing rate (0,5 °C/min) reduced the drying time by 8,3 % and 4,1 %, than faster freezing rate (3 °C/min) (Table 1.).

According to Rovero et al. (2001) increasing the porosity and the permeability of the dry matrix will increase the sublimation rate so that slower freezing rate, the shorter drying time. The slow freezing tends to disrupt cell walls, allowing the moisture to escape more easily. We stated in previous study, that the cell size was of plant largely depending on the freezing rates. The higher the freezing rate, the smaller the cell size during the freezing step (Antal, 2013). In Table 1 it can be noticed that final water content was also favoured by lower freezing rates.

Table 1. Effect of freezing pre-treatments on the freeze drying time and final moisture content

Pre-treatments	Freezing in household freezer (0,5 °C/min)	Freezing in contact plate freezer(2 °C/min)	Freezing in vacuum freezer (3 °C/min)
Drying time, t (h)			
Jonagold	22[a]	23[ab]	24[b]
Idared	23[a]	23[a]	24[b]
Final moisture content, w (%, wb) Final moisture content, M (kg water/kg dry matter, db)			
Jonagold	4,72 0,177	4,93 0,192	5,25 0,281
Idared	5,16 0,213	5,30 0,229	4,97 0,145

[ab] different superscripts in the same row mean that the values are significantly different ($p \leq 0,05$)

According to the results in Table 1, the freezing pre-treatments had an effect on the moisture content of apple slices. The least moisture content of apple was observed for freezing in household and vacuum freezer (*Jonagold* and *Idared*).

Quality assessment of treated apple samples

The a_w of apple samples at various pre-treatments can be observed in Table 2. The value of water activity was highest in raw material, followed by freezing in different equipments. The a_w of slow frozen apple slices was lowest compared to that of other pre-treatment (except of freezing in contact freezer at *Jonagold*).

The important feature to consider is that all values of water activity are below 0.5, which indicates that the growth of moulds, bacteria, and yeast is not promoted, and enzymatic reactions are not likely to occur.

Table 2. Effect of freezing rates on water activity (a_w) of apple slices

Freezing in household freezer (0,5 °C/min)		Freezing in contact plate freezer (2 °C/min)	Freezing in vacuum freezer (3 °C/min)	Raw material
Water activity, a_w (dimensionless)				
Jonagold	0,464[ab]	0,458[a]	0,472[b]	0,975[c]
Idared	0,438[a]	0,461[b]	0,454[b]	0,981[c]

[abc] different superscripts in the same row mean that the values are significantly different ($p \leq 0,05$)

Table 3 shows the evaluated mechanical parameters obtained from the compression test. The slow freezing rate (household freezer) provided the texture of *Jonagold* apple similar to those of the frozen in contact freezer. The hardness values of *Idared* apple obtained for freezing in household freezer were the lowest of all samples. Slightly lower values were measured in the *Jonagold* slices between household and vacuum freezing. From our investigations it is clear that the vacuum freezer method was the worst. The firmness of frozen and dried apple tissue strongly depends on physical (cell wall) and chemical changes due to the freezing speed.

Table 3. Effect of freezing pre-treatments on hardness of apples

Freezing in household freezer (0,5 °C/min)		Freezing in contact plate freezer (2 °C/min)	Freezing in vacuum freezer (3 °C/min)	Raw material
Hardness – Compressive force, F_c (N)				
Jonagold	5,677[a]	5,591[a]	6,127[b]	8,221[c]
Idared	4,344[a]	5,481[b]	5,755[c]	7,436[d]

[abcd] different superscripts in the same row mean that the values are significantly different ($p \leq 0,05$)

Table 4 shows that the treatment with slow freezing has better color parameters (L and ΔE) than those of other pre-treatments. When the samples were frozen in household freezer the lightness (L^*) and color difference (ΔE) of apple were significantly lower than those underwent faster freezing. The rate of freezing has a marked effect in the brightness of the dried samples: quick frozen apple slices maintained a whiter color than those frozen more slowly (Ceballos et al., 2012). Nevertheless, the effect of higher freezing rate on the redness (a*) and yellowness (b^*) was not significantly different among pre-treated samples.

The higher *L* values represented decreasing in the degree of browning in frozen and dried samples, probably due to freezing process provoked a decrease in polyphenol oxidase activity responsible for browning. Vacuum freeze treatment showed the largest increase in *L* value from 65,54 to 76,55 and from 73,81 to 83,34 at *Jonagold* and *Idared* samples.

It was stated that the permeability of the rehydrated cell wall depended on the applied cooling rate. Rehydration curves of pre-treated apple slices at different rehydration time are shown in Figure 2. It can be seen that the

rehydration rate of pre-treated *Idared* and *Jonagold* samples with slow freezing (0,5 °C/min) resulted in the highest rehydration, compared to faster frozen samples. This might be due to a smaller pore size left by faster freezing (2 and 3 °C/min), which is filled up slowly with a distilled water.

Table 4. Effect of freezing rates on color attributes of apple samples

Pre-treatment	Freezing in household freezer (0,5 °C/min)				Freezing in contact plate freezer (2 °C/min)				Freezing in vacuum freezer (3 °C/min)			
Color	L^*	a*	b^*	ΔE	L^*	a*	b^*	ΔE	L^*	a*	b^*	ΔE
Jonagold	$69,4^a$	$2,3^a$	$19,2^a$	$9,7^a$	$71,9^b$	$2,4^a$	$21,1^{ab}$	$12,0^b$	$76,5^c$	$2,5^{ab}$	$20,2^a$	$14,3^c$
Idared	$76,4^a$	$1,5^a$	$13,6^a$	$7,3^a$	$81,7^b$	$1,2^a$	$14,5^a$	$11,3^b$	$83,3^{bc}$	$1,1^a$	$15,4^{ab}$	$16,8^c$

^{abc} different superscripts in the same row mean that the values are significantly different ($p \leq 0,05$)

The rehydration ratio increased within the initial period, but the rate slowed gradually. Similar results have been reported for red apple (Doymaz, 2010). The values of rehydration rate (RR) of frozen apple samples at 25°C and 90 min are listed in Table 5. From the results, it is observed that the rehydration capacity in household freezer cooled samples was higher than contact plate freezer and vacuum freezer frozen ones. There was no significant difference in the rehydration rate in case of faster freezing rates (at *Jonagold*). The freeze dried product has excellent rehydration capacity (RR is more than 4,00). It is due to the structural rigidity of the frozen product, which can prevent the collapse of the solid matrix remaining after drying (Beaudry et al., 2004).

Table 5. Effect of freezing rates on rehydration rate (RR) of apple cubes

Pre-treatment	Freezing in household freezer (0,5 °C/min)	Freezing in contact plate freezer (2 °C/min)	Freezing in vacuum freezer (3 °C/min)
Rehydration rate, RR (-) at 90 min (soaking time, end of wetting process)			
Jonagold	$4,62^a$	$4,13^b$	$4,02^b$
Idared	$5,23^a$	$4,51^b$	$4,27^c$

^{abc} different superscripts in the same row mean that the values are significantly different ($p \leq 0,05$)

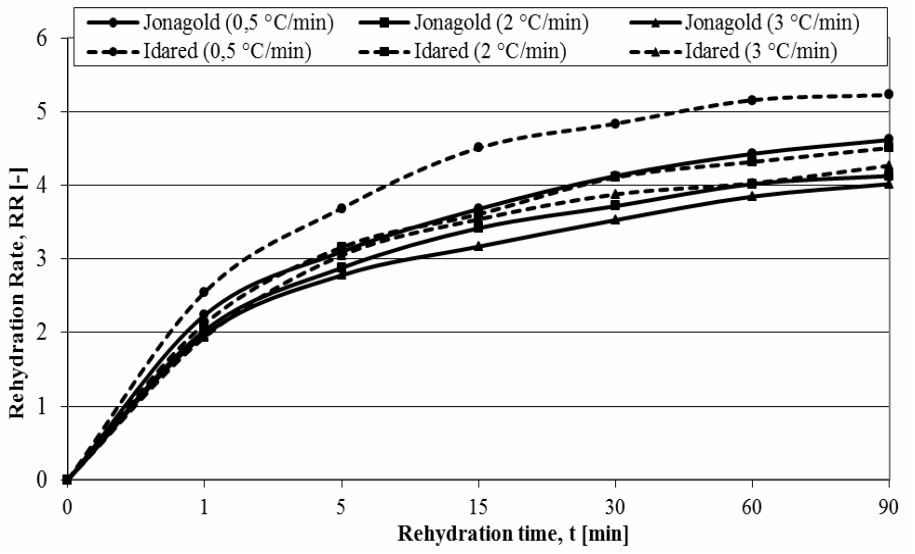

Figure 2. Rehydration rate of pre-treated apple samples in wetting medium at 25 °C

CONCLUSIONS

The effect of freezing pre-treatments on drying time and quality of apple varieties using freeze drying was studied. It was observed that the lower cooling rate leading shorter drying time of the samples (enhancing the moisture transfer). The drying time of *Jonagold* and *Idared* samples was reduced by 8,3 and 4,1% when using household freezer. It was observed that these values are negligible in terms of freeze drying. The freezing in household freezer caused lower final moisture content in dried samples. Samples pre-treated with slow freezing (0,5 °C/min) have higher rehydration rates and better color (L^* and ΔE) compared to faster frozen (2 and 3 °C/min) apple samples. Similarly, the water activity and firmness of slow frozen apple slices were superior, than the pre-treated ones with other freezing methods.

Smaller crystals provide an advantage in frozen food products (microstructure), whereas larger crystals useful for running time of lyophilisation. The slow freezing reduces the duration of the freeze-drying process and consequently the process costs.

Slow freezing rate causes severe changes in product microstructure and the final product presented broken surfaces, membrane rupture and cell wall

degradation (Tregunno and Goff, 1996). Pikal (2007) noted that a shorter freezing time is essential in reducing product degradation. It is therefore recommended that relatively fast freezing (up to 3 °C/min) prior to drying should be conducted as a method for producing dried apple pieces.

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