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The effect of alkaline water pre-treatment on drying characteristics of apples

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Abstract

The importance of the study presented in this manuscript lies in its being the first detailed analysis of the influence of the alkaline water pre-treatment on apples dehydrated by freeze-drying. The results obtained revealed a significant effect of this pre-treatment on the drying time and the quality of freeze-dried apple cubes determined by both instrumental and sensory tests. Apple cubes of three varieties (*Golden D., Idared* and *Jonagold*) were pre-treated by soaking in alkaline-ionized water (pH 8.5-9, 23°C) before freeze-drying (condenser/heating plate temperature -56/16 °C, pressure 40-44 Pa). The quality of dried samples was determined by instrumental and sensory tests. Hardness was determined in the compressive test performed using texture analyzer. Color parameters L^*, a^* and b^* were measured by a ColorLite sph900 spectrophotometer. Specially trained panel carried out sensory evaluation of the apple samples texture. It was found that the applied pre-treatment increased the drying rate and decreased the drying time of the apples subjected to freeze-drying. The drying curves were fitted using three drying models - polynomial, Page and sigmoid. The models were compared using the coefficient of determination (R^2) and root mean square error (RMSE). The polynomial, Page and sigmoid models exhibited a good fit to the experimental points obtained while freeze-drying. The pre-treated apple cubes demonstrated softer and crispier texture as well as an improved color when compared to control sample, obtained by freeze drying without pre-treatment. This indicates that alkaline water pre-treatment together with the shortening of the drying time allows to obtain a better quality dried product.

Keywords: alkaline-ionized water; apple varieties; color; firmness; freeze-drying kinetics; sensory evaluation.

Abbreviations: *a, b, c, n*_function parameters; a^*_redness; b^*_yellowness; C^*_chroma; db_dry basis; ΔE^*_total color difference; Fc_{max}_maximal compressive force (N); *H*_hardness (points); *k*_drying constant (s^{-1}); K_critical point of drying process; L^*_lightness; *M*_moisture content (kg water/kg dry matter); *MR*_moisture ratio; p_significance level; RMSE_root mean square error; R^2_coefficient of determination; *t*_time (h, s); *T*_temperature (°C); 0, e, t_subscripts indicating initial and equilibrium values as well as values obtained after drying time.

Introduction

Apple (*Malus domestica* L.) is one of the most widely grown fruit crops in the world. Available in fresh and processed forms, apples constitute a rich source of vitamins, organic acids, polyphenols, anthocyanins and minerals. Fresh fruits having high moisture content need to be processed to extend their shelf life and to prevent them from microbial spoilage. Dehydration is one of the processing methods widely applied to a variety of fruits. Currently, dehydrating is a frequent practice since dried apples are components of numerous processed food products, such as snacks, integral breakfast foods, etc. (Vega-Gálvez et al., 2012). Freeze-drying has been used for a wide variety of products and is a commonly applied drying method, especially for high-value products (Jayaraman and Gupta, 1992). Compared to other dehydration methods, freeze-drying has an important quality, being able to retain original structure, texture, shape, color, negligible loss of nutrients and aroma, low bulk density, high porosity, retention of organoleptic properties, and excellent rehydration capability due to a porous structure of the product (Cui et al., 2008). However, freeze-drying is a very expensive method, not always applicable to foodstuffs and marked by a very long drying process. Grabowski et al. (2002) reported that when drying cranberries, freeze-drying had the lowest energy efficiency when compared to vacuum-drying and various air-dryers. Flink (1977) indicated that on an industrial scale, the running cost of freeze-drying processes is from four to five times higher than spray drying, and eight to ten times higher than a single-stage evaporator. This is partly due to very slow mass and heat transfer rates which can be achieved under vacuum to provide heat of sublimation without exceeding the triple point (Duan et al., 2007). In general, using some pre-treatment operations can decrease the high-energy consumption and long drying time characteristic for freeze-drying. Recently, different methods have been used to improve the quality of dried food products and increase the drying rate, e.g. soaking in chemical solutions (sugar, metabisulfite, potassium carbonate, potassium hydroxide, sodium hydroxide, sodium chloride, ethyl oleate, calcium carbonate, sulphuration, olive oil, citric acid), blanching in hot water, or physical pre-treatment by using low temperatures, microwaves, pulsed electric field, infrared radiation (Chayjan et al., 2011; Doymaz and Pala, 2002; Hiranvarachat et al., 2011; Huang et al., 2009; Karabulut et al., 2007; Minaei et al., 2011; Pan et al., 2008; Ponting, 1973; Santos-Sánchez et al., 2012; Tarhan, 2007; Vega-Galvez et al., 2008). The alkaline-ionized water pre-treatment can possibly contribute to reducing the drying time and to accelerating the drying rate. However, there is no relevant literature concerning alkaline-ionized pre-treatment of apples before freeze-drying. Mathematical modeling may appear significant in the design and control of process parameters during drying. Therefore, performing simulations with the use of precise models can contribute to the optimization of the procedure (Khraisheh et al., 2000). In most studies semi-empirical and theoretical models were used as a tool to predict the thin-layer drying kinetics of food products, as this allows to obtain a good fit with the experimental data (Sacilik and Elicin, 2006). Texture and color are the main sensory properties of food that influence consumer acceptability of a product. The color plays a crucial role in the assessment of external quality in food industries research. The thermal treatments during the preservation processes can affect the color of fruits. Changes in natural coloration, such as browning of apples, occur as a result of chemical reactions. These reactions can have both enzymatic and non-enzymatic character (Venir et al., 2007). Feng and Tang (1998) found that microwave drying caused little reduction in the color of diced apples, whereas hot-air drying much greater. Krokida et al. (2001) reported that hot air, vacuum and microwave methods used to dry apples were found to significantly affect the three basic color parameters, while freeze-dried and osmotically treated apple samples kept their color intact. The texture of dehydrated fruits is a carrier of knowledge regarding the changes which have taken place in their structure and mechanical properties. Numerous publications indicate that drying strongly affects rheological properties of the dried material. Jakubczyk et al. (1997) showed that convective drying of apple cubes reduced their hardness by more than half in comparison to fresh material. The texture properties of dried apple are influenced by the condition of cellular system in terms of cell wall structure, turgor pressure and soluble solid phase inside the tissue, dependent on different interactions with water (Contreras et al., 2005). Chong and Law (2011) found that the critical moisture content, which contributed to case hardening of dried product, significantly affected the textural attributes of the product. The present work is aimed at studying the effects of pre-treatment with alkaline-ionized water on the drying kinetics and quality attributes of apple cubes, such as texture, color and sensory properties.

Results

Effect of pre-treatment on drying kinetics

The moisture content of fresh apples of *Golden Delicious*, *Idared* and *Jonagold* varieties were 5.84, 5.41 and 4.72 kg water kg dry matter^{-1} respectively, which corresponds to 85.4, 84.4 and 82.5% wet basis, respectively. The dimensionless moisture ratio (MR) and drying rate changes during freeze-drying of pre-treated and untreated apple samples are presented in Fig. 1 and 2, while adequate drying times necessary to obtain the final moisture contents are compiled in Table 1. The final moisture content, achieved when no change of weight was found in the subsequent measurements, ranged from 0.31 to 0.34 kg water kg dry matter^{-1} for untreated samples, and from 0.23 to 0.28 kg water kg dry matter^{-1} for pre-treated samples. The pre-treatment was found to have a significant influence on freeze-drying time (Table 1). Namely, the time necessary to obtain final moisture content of untreated and pre-treated samples was 24 and 20 hours, respectively. Table 2 shows the drying models coefficients and the comparison criteria used to assess the quality of fit. The R^2 values changed between 0.9976 and 0.9998, while RMSE values ranged from 4.482×10^{-3} to 8.612×10^{-2}. These values show that there is a good agreement between the experimental data and thin-layer modeling equations. This indicates that all models could be acceptable if used to describe the drying kinetics of apple cubes. However, the highest value of coefficient of determination ($R^2>0.999$) and the lowest value of the root mean square error ($RMSE<7.47\times10^{-3}$) were found for third-degree polynomial model. Accordingly, the polynomial model was selected as the best model to represent freeze-drying of apple cubes, followed by the sigmoid model.

Effect of pre-treatment on dried apple firmness

The firmness of apple cubes was evaluated by a compression test, and the results are summarized in Table 1. The fresh apple samples of different varieties presented similar hardness ranging from 4.788 to 4.812 N, which is significantly higher when compared to the hardness of freeze-dried samples obtained from fruits of *Idared* and *Jonagold* varieties. In these cases the reduction of firmness exceeded 50%. However, both fresh and processed *Golden* samples exhibited similar firmness. ANOVA Duncan test shows statistical differences between the values of hardness obtained for pre-treated and untreated samples. It was seen that alkaline pre-treatment could significantly decrease the hardness of apple slabs, as the reduction in hardness caused by pre-treatment reached 43.5% and 73.5% for *Idared* and *Jonagold* samples, respectively. On the other hand, in the case of the *Golden* samples the pre-treatment did not show any significant difference in the hardness.

Effect of pre-treatment on surface color

Color parameters of fresh apple cubes and freeze-dried samples are presented in Table 1. Taking into account only the fresh fruit, it was noted that *Golden* apples were characterized by the brightest color (L^*=67.09), while *Jonagold* by the darkest (L^*=60.39). Freeze-drying considerably increased the brightness of all apple samples. Furthermore, pre-treated *Jonagold* samples were significantly brighter than adequate samples without pre-treatment. On the other hand, pre-treated *Golden* and *Idared* cubes were duller in comparison to untreated samples. Fresh *Golden, Idared* and *Jonagold* samples showed negative a^* values amounting to -0.33, -0.6 and -0.55, respectively. Freeze-drying changed the values of this color parameter in a different way. Namely, all pre-treated samples scored positive a^* values, indicating that their color was shifted towards redness. On the other hand, a^* values of untreated *Golden* and *Idared* samples were even lower (-0.42 and -0.93, respectively) than those measured for adequate fresh samples. This indicates that the color of these samples remained in the greenness area, unlike the color of untreated *Jonagold* samples characterized by the highest a^* value reaching 2.05. The values of b^* parameter determined for fresh *Golden, Idared* and *Jonagold* samples

Table 1. Drying time, moisture content, hardness and color parameters of apple samples.

Sample	Treatments	Drying time (h)	Moisture content (kg water kg dm^{-1})	Hardness (N)	Color parameters							
					L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE^*	C^*
Golden	Fresh		5.84	4.797^{a}	67.09^{a}	-0.33^{a}	9.23^{a}	-	-	-	-	9.24^{a}
	Pre-treated	20^{a}	0.23	5.142^{b}	80.18^{b}	0.18^{a}	17.48^{b}	13.09^{a}	0.51^{b}	8.25^{a}	15.48^{a}	17.48^{b}
	Untreated	23^{b}	0.34	4.933^{ab}	82.46^{b}	-0.42^{a}	23.14^{c}	15.37^{a}	-0.09^{a}	13.91^{b}	20.73^{b}	23.14^{c}
Idared	Fresh		5.41	4.788^{c}	63.39^{a}	-0.6^{a}	8.68^{a}	-	-	-	-	8.7^{a}
	Pre-treated	20^{a}	0.26	1.223^{a}	66.73^{a}	1.11^{b}	11.06^{a}	3.34^{a}	1.71^{b}	2.38^{a}	4.44^{a}	11.11^{b}
	Untreated	24^{b}	0.31	2.168^{b}	84.98^{b}	-0.93^{a}	11.09^{a}	21.59^{b}	-0.33^{a}	2.41^{a}	21.73^{b}	11.13^{b}
Jonagold	Fresh		4.72	4.812^{c}	60.39^{a}	-0.55^{a}	10.03^{a}	-	-	-	-	10.04^{a}
	Pre-treated	20^{a}	0.28	0.588^{a}	77.84^{c}	1.59^{b}	21.49^{b}	17.45^{b}	2.14^{a}	11.46^{a}	20.98^{a}	21.55^{b}
	Untreated	24^{b}	0.34	2.222^{b}	68.70^{b}	2.05^{c}	24.61^{b}	8.31^{a}	2.60^{b}	14.58^{a}	16.98^{a}	24.69^{b}

^{a,b,c} Different letters in the same column within the same section (fresh, pretreated and untreated) indicate a significant difference at $p<0.05$, according to the Duncan test.

Table 2. Effects of drying conditions on the coefficients of the models describing the drying kinetics of apple samples.

Variety	Treatment	Drying model	Model parameters						
			a	b	c	k	n	R^2	RMSE
Golden	+	Third-degree polynomial	0.0002367	-0.006791	-0.006905			0.9996	0.007466
	–		0.0001691	-0.005467	-0.004206			0.9998	0.005268
Idared	+		0.0002574	-0.007363	-0.003158			0.9998	0.005233
	–		0.0001397	-0.004785	-0.004827			0.9997	0.006508
Jonagold	+		0.0002173	-0.006054	-0.01273			0.9998	0.00533
	–		0.000117	-0.004109	-0.007199			0.9998	0.004482
Golden	+	Sigmoid	-0.0378	1.109	9.630	0.2747		0.9994	0.009579
	–		-0.03483	1.116	10.93	0.2367		0.9998	0.004865
Idared	+		-0.01898	1.089	9.507	0.2872		0.9995	0.008376
	–		-0.01837	1.096	11.42	0.229		0.9993	0.009962
Jonagold	+		-0.02683	1.149	9.041	0.2488		0.9994	0.009125
	–		-0.0185	1.128	11.59	0.2029		0.9997	0.006358
Golden	+	Page				0.00563	2.121	0.9976	0.01768
	–					0.004563	2.086	0.9987	0.01182
Idared	+					0.005305	2.144	0.9988	0.01238
	–					0.00417	2.077	0.9983	0.01434
Jonagold	+					0.008327	2.957	0.999	0.011
	–					0.004869	2.98	0.9993	0.08612

+ with pre-treatment, – without treatment (control).

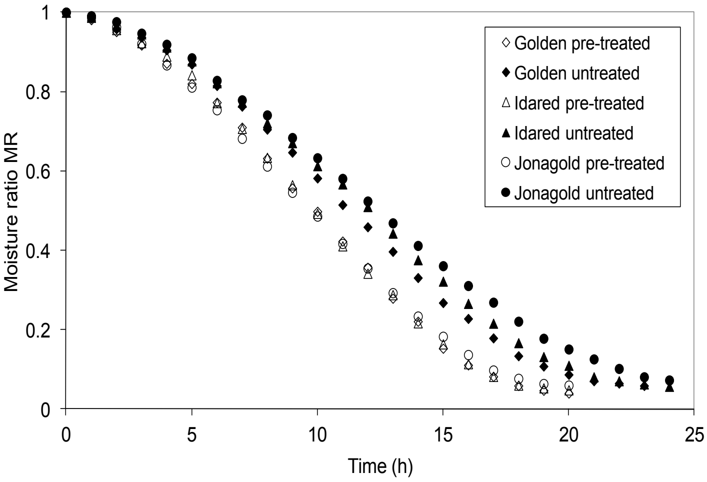

Fig 1. Moisture ratio (*MR*) changes during freeze-drying of pre-treated and untreated apple samples.

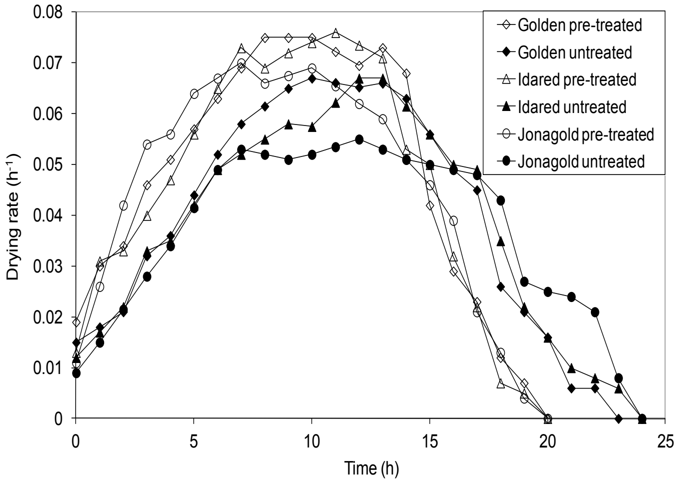

Fig 2. Drying rate changes during freeze-drying of pre-treated and untreated apple samples.

amounting to 9.23, 8.68 and 10.03, respectively, indicated the superiority of yellowness. Freeze-drying increased the value of this parameter, particularly when alkaline pre-treatment was applied. Namely, the treatment increased the values of *b** up to 23.14, 11.09 and 24.61 for *Golden*, *Idared* and *Jonagold* samples, respectively. The alterations of *L**, *a** and *b** values caused by the processing of fresh apple cubes were confirmed by the values of *ΔL**, *Δa** and *Δb**. Positive values of the latest indicated that the color position was enhanced by the processing, while negative values demonstrated that it was shifted to the opposite direction. The highest brightening was found for untreated *Idared* samples (*ΔL**=21.59). On the other hand, the greatest shifting towards redness and greenness was stated for untreated *Jonagold* samples (*Δa**=2.60) and untreated *Idared* samples (*Δa**=-0.33), respectively. Furthermore, untreated *Jonagold* samples showed the greatest shifting towards yellowness (*Δb**=14.58). All alkaline pre-treated samples exhibited lower *Δb** values when compared to untreated samples.

Effect of pre-treatment on sensory attributes

The results of the sensory assessment of the texture of apples subjected to alkaline pre-treatment prior to freeze-drying are shown in Fig. 3. The sensory evaluation of hardness of lyophilized apple samples ranged from 6.9 to 8.9 points, being considerably the highest in case of *Golden* apples. The alkaline water pre-treatment contributed to a reduction in the hardness of *Idared* and *Jonagold* apple samples, and a slight increase for *Golden* samples. However, these changes were not significant. *Jonagold* and *Golden* untreated apples gained higher scores for gumminess (from 4.8 to 5.8) than *Idared* samples (2.4). Alkaline pre-treatment prior to drying insignificantly reduced the gumminess of freeze-dried apples. Despite the introduction of pre-treatment, all freeze-dried apple samples were characterized by very low fibrousness. Sensory analysis of apple tooth-pack showed that all dried samples exhibited a low tendency to be stuck in molars. The pre-treatment technique had no effect on the tooth-pack, however a trend towards higher scores was observed in case of *Golden Delicious* variety.

Discussion

Drying characteristics and modeling

The results indicating that the freeze-drying time for apples may reach 24 hours (Table 1) are in agreement with Cui et al. (2008). In order to reduce moisture content of *Red Fuji* apple from 87.31% to 7% authors applied 30 °C heating plate temperature and 200 Pa pressure in the drying chamber. Similar drying characteristics were also reported by Pan et al. (2008) for a freeze-dried banana. The results obtained also showed that the overall time of the freeze-drying process preceded by alkaline pre-treatment was 4 hours shorter than that without pre-treatment. This indicates that the difference in freeze-drying time was close to 17%. Since, however, untreated samples of *Golden* apples required one hour less to obtain final moisture content, the drying time in this case was reduced up to 13%. This one-hour difference in the drying time could result from some intrinsic properties of *Golden* apple samples. Shorter drying time found for pre-treated apple cubes constitutes also a clear evidence of an increased drying rate (Fig. 2). The drying rate was increasing within the first nine to ten hours for the pre-treated samples, reaching maximal values ranging from 0.07 to 0.076 h^{-1}. The period of increasing drying rate was extended by another two hours for untreated samples. However, the maximal values for these samples were lower, ranging from 0.055 to 0.067 h^{-1}. Consequently, their falling drying rate period was also two hours longer. The alkaline-ionized water may have facilitated the structural changes in apple cubes, and this way improved the process of sublimation. More in-depth studies need to be carried out to further characterize and explain the influence of alkaline water pre-treatment on the freeze-drying kinetics of apples. The models presented in Table 3 can be successfully used to predict the experimental values of the moisture ratio. Our previous results indicate that in the case of freeze-drying, the polynomial model gives the most accurate fit (Antal et al., 2011), however the advantage of the sigmoid model lying in the fact that its parameters have physical interpretation (Figiel, 2009) must also be stressed. Namely, when compared to untreated samples, higher values of drying constant *k* found for pre-treated samples, (Table 2) corresponded to a higher drying rate (Fig. 2). Additionally, the maximum values of the drying rate were achieved earlier in the bending point, due to the lower values of parameter *c*.

Table 3. Mathematical models applied to the drying curves of apple cubes

Model name	Equation
Page	$MR = e^{-k \cdot t^n}$
Sigmoid	$MR = a + \frac{b}{1 + e^{k \cdot (t-c)}}$
Third-degree polynomial	$MR = a \cdot t^3 + b \cdot t^2 + c \cdot t + 1$

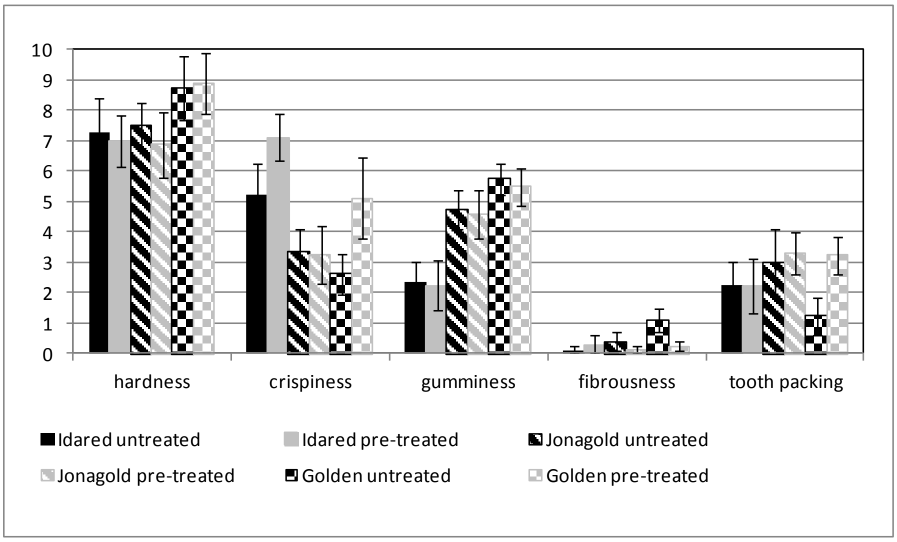

Fig 3. Sensory evaluation of texture attributes of the apple samples subjected to alkaline pre-treatment prior to freeze-drying.

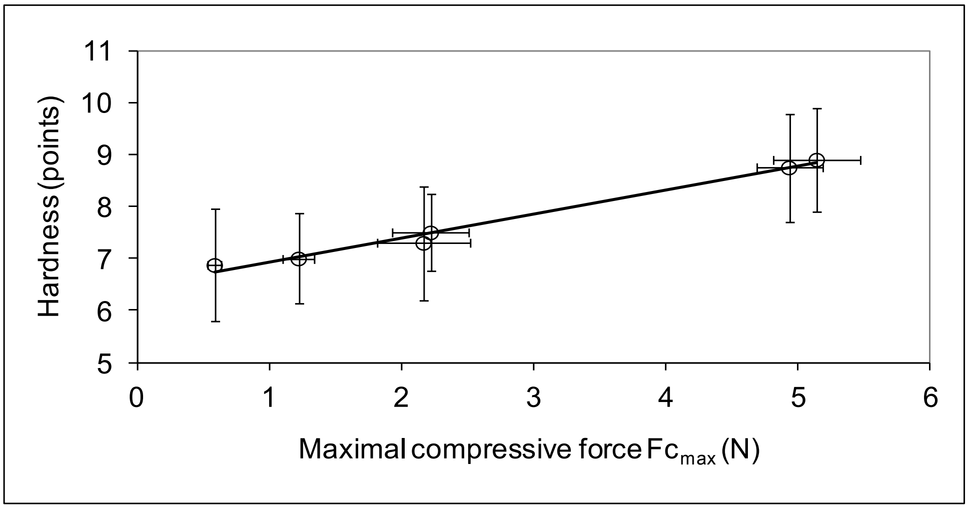

Fig 4. Relationship between the results concerning hardness determined in compressive test and sensory evaluation of freeze-dried apple samples.

Hardness of the dried apple cubes

The tissue hardness reduction is considered a positive modification caused by the process of freeze-drying due to the improved cell structure strength, high porosity and elasticity (Lin et al., 1998). Cui et al. (2008) determined that freeze-dried apple slices were the softest among the samples obtained by microwave drying, hot air drying, and microwave-freeze drying. Huang et al. (2011) found that microwave freeze-drying, microwave-vacuum drying and vacuum-drying exerted only a minimal effect on the changes in the texture of apple chips, while freeze drying caused the greatest reduction in the hardness of the dried product. It can be therefore concluded, that the same structural changes caused by alkaline-ionized pre-treatment, which improved the process of sublimation during freeze-drying, led to the reduced hardness of *Idared* and *Jonagold* dried samples (Table 1). The effect of alkaline pre-treatment is more significant when taking into consideration lower moisture content of pre-treated samples, which usually favors mechanical strength of the dried material (Figiel, 2010). Taking this into account, the unexpected high hardness of pre-treated *Golden* sample may be explained by the dominating effect of an extremely low final moisture content maintained by this sample (Table 1).

Changes of apple samples color

The results of our study revealed that freeze-drying considerably increased the brightness of all apple samples (Table 1). Similarly, Deng and Zhao (2008), Guiné and Barroca (2012), Pan et al. (2008) and Wang et al. (2010) indicated that the freeze-dried food samples (potato, apple, banana, pumpkin and green pepper) were significantly lighter than the fresh ones. According to Nindo et al. (2003), freeze-drying contributed to a higher retention of asparagus color (highest L^* and lowest ΔE^* values) when compared to spouted bed drying, tray drying, combined microwave and spouted bed drying, and refractance window drying. According to Chiralt and Talens (2005), higher L^* values indicated a decrease in the degree of browning in fruits, what may have resulted from a decline in the polyphenol oxidase activity responsible for generating dark pigments. Moreover, Hammami and René (1997) reported that higher working pressure (P>108 Pa) and higher plate temperature of a freeze dryer (T>60 °C) facilitated a slight decrease in the L^* value, which can be attributed to the appearance of a dark brown color at the surface of the fruit. In order to avoid the loss of brightness of processed samples, in our study we applied safe freeze-drying parameters, i.e. heating plate temperature: 16 °C, pressure of vacuum pump: 40-44 Pa. We found that pre-treatment increased the values of a^* parameters for all samples (Table 1). Higher values of a^* could be ascribed to an increased concentration of pigments (Hiranvarachat et al., 2011; Schweiggert et al., 2005). On the other hand, the positive effect of freeze-drying on b^* values, enhancing the samples' yellowness, was confirmed by the findings of Krokida and Philippopoulos (2004). It has to be noted, however, that all alkaline pre-treated samples exhibited lower Δb^* values when compared to untreated samples. Deng and Zhao (2008) revealed that b^* values of the freeze-dried apple samples were almost identical to those determined for fresh samples, what can find its explanation in the absence of the Millard reaction at low temperatures. Eventually, the highest color alteration indicated by ΔE^* values of 21.73 was found for untreated *Idared* samples. The pre-treated samples of the same variety demonstrated the lowest values of ΔE^* (4.44), which proved the best color retention. This stems from the L^* value of pre-treated *Idared* samples being closer to the L^* value of fresh samples. The chroma (C^*) values corresponded to b^* values for all the samples studied, what resulted from relatively low values of parameter a^*, used in the calculation of C^* (Eq. 7). The freeze-drying process led to a vivid color of apple cubes influenced by their high yellowness. However, alkaline pre-treated samples had a slightly lower C^* value in comparison to untreated samples.

Sensory assessment of pre-treated apples

The changes in hardness of freeze-dried apple samples caused by alkaline pre-treatment were not significant (Fig. 3). Similarly, the study of Deng and Zhao (2008) pointed to no considerable effect of *Fuji* apples osmotic pre-treatment on the hardness of the final freeze-dried product. Our study revealed a very high correlation ($R^2=0.9869$) between the hardness values determined in the compressive test and sensory evaluation of freeze-dried apple samples (Fig. 4). Consequently, the relationship between the maximal compressive force and sensory hardness can be described by a linear Eq. (1):

$$H = 0.441 \times F_{c\max} + 6.499 \qquad (1)$$

Such correlation, indicating a greater acceptability of harder samples, finds its justification in the fact that the samples were obtained exclusively by freeze-drying, providing considerably higher softness of the dried product than other drying methods. In such case, an improved impression of the texture may be associated with the increase in the hardness.

Nevertheless, it is the crispiness that seems to be the most important parameter influencing the quality of the texture of a dried product. High crispness is one of the most desired attributes of dried food products, usually consumed as snacks. Huang et al. (2011) showed that by the application of different drying techniques, crispness of dried products could be modified. Apples (Fig. 3) subjected to freeze-drying in that study were characterized by medium (5.0 points, *Idared*) or low crispness (below 3.0 points, *Jonagold* and *Golden*). In the current study, application of the pre-treatment technique resulted in significantly higher crispness of *Idared* and *Golden* apples, which could contribute to the improvement of the overall quality of the final product. However, the use of pre-treatment technology had no effect on the crispness of *Jonagold* apple samples, what corresponds to the results obtained by Deng and Zhao (2008) for *Fuji* apples.

Materials and Methods

Preparation of apple samples

Fresh apples of three varieties (*Golden Delicious, Idared* and *Jonagold*) were stored in a refrigerator at 5 °C until the analysis. After washing and wiping with blotting paper, the fruits were diced into cubes of approximately 10 mm thickness with a stainless steel knife. The apple cubes were immersed in alkaline-ionized water (pH 8.5-9) for 30 min at 23 °C. Within the course of trials it was established that shorter soaking time (less than 30 min) did not have an effect on the drying rate. Upon the soaking time, samples were drained on a perforated tray and wiped with blotting paper. The equipment producing alkaline-ionized water consists mainly of an electrode, a polypropylene fibrous filter, granulometric activated carbon filter element and secondary ultra filter. Untreated apple cubes were prepared as control without immersion.

Drying procedure

The pressure in a freeze-dryer (Armfield FT33, Armfield LTD, Ringwood, England) was maintained at 40-44 Pa. The condenser temperature was set at –56°C with the heating plate temperature maintained at 16 °C. The samples (250 g) were placed in a single layer on the tray and placed in the drying chamber. During dehydration, the mass of samples was recorded at 1 min intervals. Drying was terminated when no further mass changes were observed. The dehydrated samples were packed immediately into polyethylene bags. Drying kinetics was determined by measuring the moisture loss of apple cubes within time. Drying experiments were conducted in triplicate and mean values of the moisture ratio were used for obtaining the drying curves.

Moisture content

The initial and final moisture content of apples was determined using a hot-air oven (model LP-306, Labor-MIM, Budapest, Hungary) at temperature of 105 °C. The samples were taken out from the drier when constant weight was achieved. The weight of dried samples was measured with the use of a digital scale with the range of 0–500 g and accuracy of ±0.1 g (model JKH-500, Jadever Co., Taiwan). The measurement was carried out in triplicate.

Mathematical modeling

The freeze-drying curves obtained were fitted with three thin-layer models: Page, sigmoid and third-degree polynomial model (Table 3). The Page's equation has been widely used to describe drying kinetics of apples dehydrated by different methods (Sacilik and Elicin, 2006). The parameters of the sigmoid model have an intuitive physical meaning. Parameter *a* corresponds to the asymptotic value of moisture content during drying. Parameter *b* is a theoretical interval of moisture content values. Parameter *c* stands for the time coordinate of the inflexion point in the drying curve. This point can be, therefore, treated as the critical point K, which divides the drying process into the period of increasing drying rate (before K) and decreasing drying rate (beyond K). Thus, the K point constitutes the extreme of the drying rate function (Figiel, 2009). The *k* parameter is the drying constant for the Page and sigmoid model. The lower *k* values for a given model the longer the drying process. The values of *a, b, c* parameters of the third-degree polynomial model depend on the characteristics of the material, including the variety, freezing rate, ripeness, and tendency to lose water (Antal et al., 2011).

The moisture ratio (MR) of apple samples during drying was calculated using the following Eq. 2:

$$MR = \frac{M_t - M_e}{M_0 - M_e} \tag{2}$$

The good-fitting model was selected by the use of coefficient of determination (R^2) and Root Mean Square Error (RMSE). Model fit is better if the value of R^2 is closer to unity, and the RMSE value is closer to zero.

Compressive test

The hardness of apple samples was determined by Texture Analyzer (model CT3-4500, Brookfield Engineering Laboratories, Middleboro, USA). Compressive test was carried out to generate a plot of force (N) vs. time (s). The apple cubes 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 test was performed in 8 replicates for fresh and dried apple samples.

Color measurement

Surface color of both fresh and treated apple samples was determined with a ColorLite sph900 spectrophotometer (ColorLite GmbH, Katlenburg-Lindau, Germany). CIELab color values (L^*, a^*, b^*) were measured at 5 different points (random locations) and the average values were calculated for each sample. L^* parameter corresponds to lightness, a^* represents redness/greenness and b^* refers to yellowness/blueness.

The total color difference (ΔE^*) was subsequently determined using the Eq. 3. This was calculated according to Hunter (1975) as:

$$\Delta E^* = \sqrt[2]{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{3}$$

ΔL^*, Δa^* and Δb^* values contribute to the total color change (Eq. 4, 5, 6):

$$\Delta L^* = \left(L^*_t - L^*_0\right) \tag{4}$$

$$\Delta a^* = \left(a^*_t - a^*_0\right) \tag{5}$$

$$\Delta b^* = \left(b^*_t - b^*_0\right) \tag{6}$$

The fresh apple cubes were used as a reference, and higher values of ΔE^* denote greater color change from the reference material.

The chroma value C^* was calculated accordingly to the Eq. 7:

$$C^* = \sqrt{(a^*)^2 + (b^*)^2} \tag{7}$$

The C^* value represents color saturation of the samples which varies from dull (low value) to vivid color (high value).

Sensory evaluation

The sensory evaluation of dried apple samples was carried out by a specially trained panel, consisting of eight members. Evaluators were asked to indicate their preferences towards each sample, basing on the quality of texture features. 10-point hedonic scale was applied for all the attributes evaluated. The responses were as follows: like very much (9-10), like (7-8), neutral (5-6), dislike (3-4) and dislike very much (1-2). Samples were served to the panel in separate disposable plastic containers with a three-digit code. All analyzes were conducted in triplicate.

Statistical analysis

All data were processed statistically applying the one-way analysis of variance (ANOVA). PASW Statistics version 18.0 software (SPSS Inc., Chicago, IL, USA) was used to perform all statistical calculations. Differences among mean values were subjected to ANOVA and Duncan test. The results obtained demonstrated that mean values were significantly different when $p<0.05$. Table Curve 2D Windows v. 2.03 (Jandle Scientific, San Rafael, CA, USA) allowed for mathematical modeling with the best R^2 and the lowest RMSE.

Conclusions

Alkaline water pre-treatment was found to have a significant effect on the freeze-drying time, texture, and color of apple samples. The drying time of alkaline pre-treated apple samples was reduced by 13-17%, what may constitute a crucial factor for reducing the processing cost of a given material. The third-degree polynomial model was determined to have given the best fit, with higher coefficient of determination (R^2) and lower root mean square error (RMSE) values, followed by the sigmoid model. However, for freeze-drying the sigmoid model provided more practical information regarding the time coordinate *c* of the critical point, which divides the drying kinetics into two periods. Furthermore, it was shown that alkaline pre-treatment influenced the sensory attributes of samples. Apple cubes pre-treated with alkaline water had softer and crispier texture than the untreated samples (except *Golden D.*), what stemmed from the softening of the cellular structure. The results of the sensory evaluation obtained for the hardness were confirmed in the compressive test. In addition, it was found that all chromatic parameters of the samples were affected by the treatment. The retention of the surface color of pre-treated apple samples was related to a relatively short drying time, low working pressure, low heating plate temperature and an increase in the color pigment. It was determined that the total color difference (ΔE^*), b^* value and chroma (C^*) of pre-treated apple cubes were enhanced in comparison to control samples. On the other hand, without the pre-treatment, freeze-drying proved an effective method for improving the L^* and a^* color values.

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