EFFECT OF PRE-TREATMENT ON THE CHARACTERISTICS OF DRIED APPLE VARIETIES USING ALKALINE-IONIZED WATER

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Abstract

The effect of alkaline-ionized water (pH 8,5-9) dipping pre-treatment on drying kinetics of apple varieties ('Idared', 'Golden') under vacuum freeze-drying conditions has been studied. It was observed that the pre-treatment affected the drying time. The drying time was shorter for treated with alkaline-ionized water solution compared to the untreated. The experimental moisture loss data were fitted empirical thin-layer drying models, namely Page, Sigmoid and third-degree polynomial. All the models were compared using two statistical parameters, i.e. coefficient of determination (R^2) and root mean square error (RMSE). The rehydration ratio of the pre-treated apples was higher than of the untreated samples. The apple cubes treated with alkaline water had softer texture than the untreated products.

Key words: pre-treatment, apple, freeze-drying, drying kinetics, rehydration, firmness

INTRODUCTION

Fruits, vegetables and foodstuffs are commonly pre-treated prior to industrial drying in an attempt to speed up the drying process and improve the quality of dried product. Pre-treatments are the necessary pre-requisites for successful dehydration process. Pre-treatments check the undesirable physical, chemical and qualitative changes that may occur during the drying process.

Freeze-drying is a one of the most implemented emerging technologies used to obtain high quality and high value dried foods.

Freeze-dried strawberries are found to be of excellent colour and flavour, with high rehydration capacity (Shishehgarha et al., 2002). In this method shrinkage is eliminated or minimized, and near-perfect preservation results are obtained (Moreira et al., 1998). However, freeze-drying is an expensive method, has long drying time and the high cost of process limit its application to industrial scale (Shishehgarha et al., 2002). Lyophilizing is a very slow process, it is necessary to increase water transport from samples. That is why prior to drying alkaline-ionized water pre-treatment used to increase the drying rate, decrease the freeze-drying time, while preserving the physical, chemical qualities of the final product. No published work seems to have been carried out on the effects of pre-treatment of alkaline-ionized water on freeze-drying kinetics.

Alkaline-ionized water obtained by the electrolysis of tap water is widely used in various fields: medicine (Jin et al., 2006), food industry (Huang et al., 2008) and agriculture (Shirahata et al., 1997). The alkaline water can reduce the presence of bacterium in organic matter (meat, fruits, vegetables) and can decrease blood-glucose levels, improve uric acid levels, hepatic and allergic disorders, hypertension etc.

Drying methods also affect the behaviour of dehydrated product during rehydration. Krokida et al. (1999) studied the viscoelastic behaviour of dehydrated products during rehydration. They found that freeze-dried products showed the highest hysteresis after rehydration, losing their elasticity and becoming more viscous.

In concerns texture, this implies knowledge about changes in the 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 dependent on the behaviour of cellular system (cell wall structure, turgor pressure) and soluble solid phase inside the tissue, both with different interactions with water (Contreras et al., 2005).

In the present study, the following objectives were studied: To investigate the influences of alkaline-ionized water in the apple varieties freeze-drying. To investigate a suitable empirical thin-layer drying model for describing the drying process. To determine the rehydration and hardness characteristics of apple varieties of freeze-dried.

MATERIAL AND METHOD

Fresh material and preparation

The apple is an important raw material for many food products and apple plantations are cultivated in many countries of the world. Apples of the Idared and Golden Delicious variety were purchased from a local market in Nyíregyháza, Hungary and stored at +5 °C. Before starting each experiment apples were cleaned and diced into 1cm×1cm×1cm cubes. The initial and final moisture content of apples was determined by the gravimetric method using a laboratory drying chamber (LABOR-MIM, LP-306, Hungary). The moisture content of the product was calculated and expressed on a dry weight basis. The dry matter content of fresh, Idared and Golden were 5.41 and 5.84 kg water kg dry matter^{-1}, respectively (84.4 and 85.4% of wet basis, respectively). Triplicate samples were used for the determination of moisture content and the average values were reported.

Pre-treatment methods

Prior to freeze-drying apple samples were pre-treated by the following pre-treatment methods – to reduce the FD time: soaking in alkaline-ionized water (pH 8,5-9, temperature 23 °C) for 30 min and untreated sample (control sample). The untreated samples as control were just washed with tap water to take away dust and prior to drying, under the same conditions. The pH of the water was measured using a pH indicator. Each sample utilized in the experiment weighed 250 g. The Fig. 1 shows the alkaline water making machine. The setup mainly consists of electrode, a polypropylene fibrous filter, granulometric activated carbon filter element and secondary ultra filter.

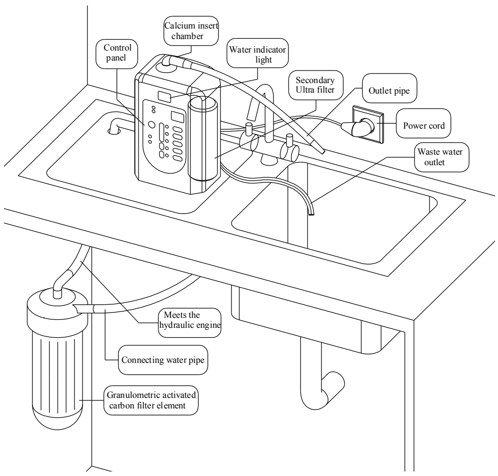


Fig. 1 Alkaline-ionized water making equipment

Freeze-drying procedure

The drying of apple samples was investigated in a laboratory vacuum freeze-dryer (Armfield FT33, England) this installed in the Department of Vehicle and Agricultural Engineering of College of Nyíregyháza, Hungary. The temperature of the condenser was set at -56 °C. The product was dried at 44 Pa with the heating plate maintained at 16 °C.

The apple samples (250 g) were placed in a single layer over the tray and inserted into the drying cabinet of the freeze-drier. The moisture loss is recorded during drying by a specially developed weighing unit. This weighing unit consists of a load cell (5000 ±0,1 g), scale instrument and DATPump software (Emalog, Hungary). Moisture loss was recorded at 1h intervals. The drying was stopped when the moisture content of samples reached to 5-6% (wet basis). Drying experiments were conducted in triplicate and average values reported. The drying data from the drying tests were then expressed as dimensionless moisture ratio (MR) versus drying time.

Determination of drying characteristics

Various types of empirical thin-layer models have been used to describe drying of food materials. The freeze-drying curves obtained were fitted with 3 different thin-layer drying moisture ratio models, namely, the Page model, the Sigmoid model and third-degree polynomial.

Page model is an empirical modification of Lewis model to overcome its shortcomings. It was successfully used to describe the drying characteristics of some food products (Page, 1949). The model is given as (1):

$$MR=\exp(-k\cdot t^n) \quad (1)$$

The Sigmoid model developed by Figiel (2009), which can be described the vacuum-microwave drying kinetics (2):

$$MR = a + \frac{b}{1+e^{k\cdot(t-c)}} \quad (2)$$

Another model, which is used for thin-layer drying studies, is the third-degree polynomial (3). The model was successfully used to describe the freeze-drying characteristics of fruits and vegetables (Antal, 2010):

$$MR=at^3+bt^2+ct+1 \quad (3)$$

However, the moisture ratio (MR) was simplified to M/M_0 instead of $(M-M_e)/(M_0-M_e)$. The values of M_e are relatively small compared to M or M_0. For the analysis it was assumed that the M_e was equal to zero (Pala et al., 1996).

The sample moisture content M was calculated on a dry basis (db) according to Equation (4):

$$M = \frac{W_t - W_k}{W_k} \quad (4)$$

The drying model with the highest R^2 and lowest RMSE was chosen as the best model to describe the thin-layer drying behaviour of untreated and treated apples.

Rehydration procedure

Rehydration of dried apple samples was done in water at 35 and 70 °C. The mass of apples corresponding to 0,5 g of dried samples were placed in 400 ml water. The process was terminated at 0.5, 5, 10, 15, 30, 60 min, the samples were taken out and blotted with tissue paper to eliminate excess water on the surface. During the experiment, the permanent temperature of the liquid was ensured by means of liquid supply. The water temperature was measured with Testo (Germany) nickel-chrome-nickel thermocouple (-200 - 600 ±0,3 °C). The experiments were replicated three times. The weights of dried and rehydrated samples were measured with an electronic digital balance (Precisa HA 60, Switzerland) having a sensitivity of 0,001 g. The rehydration ratio (RR) was calculated as follows (5) (Lin et al., 1998):

$$RR = \frac{W_r}{W_d} \tag{5}$$

Determination of texture

The hardness of apple samples was determined by texture analyzer (model CT3-4500, Brookfield Engineering Laboratories, Middleboro, US).

Compressive test was carried out to generate a plot of force (N) vs. time (s) was used to obtain hardness values. The parameters that have been used were the following: 4,5 kg force load cell, 1 mm/s test speed, 20 mm travel distance and 4 mm diameter of cylindrical probe. The maximum depth of penetration was 2 mm and trigger force was 10 g. A 115 mm diameter compression plate (rotary base table) was used to compress the apple cubes.

The samples were kept in a room temperature at 20°C until analysis. The texture test was performed 8 times in fresh and treated apples, the average values were presented. The penetrometer measurements are reported in Newtons (N).

Statistical analysis

Mean separation was obtained by Tukey's test (significance level $p<0,05$) and one-way analysis of variance (ANOVA) was conducted on the mean values to determine the significance of any differences between the pre-treated samples. The results were carried out using PASW Statistics 18 software. Table Curve 2D Windows v. 2.03 enabled mathematical modelling with the best coefficient of determination (R^2) and the lowest root means square error (RMSE).

RESULTS AND DISCUSSIONS

Effect of pre-treatments on drying kinetics

Figs. 2-3 show the drying curves for apple dehydration under various pre-treatments. The initial drying rate of apples from alkaline treatment was higher than the untreated. Hence, the overall drying rates due to alkaline treatment were faster than no-treated. The reason this behaviour can be due to softening and increasing of permeability of the apple cells tissue by the alkaline treatment which facilitated the water removal. To reach a final water content 0,31 kg water kg dry matter^{-1} (dry basis) in untreated Idared apple, 24 h of drying was needed, while Idared treated with alkaline water reached 0,26 kg water kg dry matter^{-1} (dry basis) after 20 h. The difference in the drying time was close to 17%.

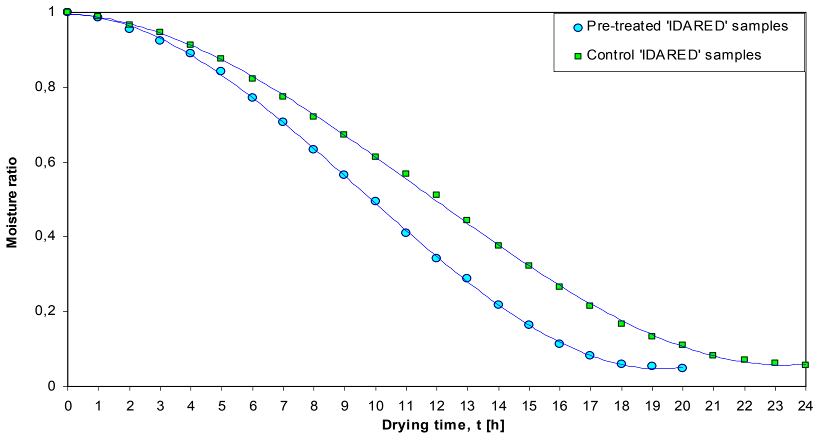


Fig. 2 Effect of pre-treatment/control on freeze-drying time of Idared apple

While the freeze-drying process took 23 h with the non-treated Golden samples (0,34 kg/kg, dry basis), dipping the Golden samples in alkaline water solution (0,23 kg/kg, dry basis) had a significant influence on the drying time decrease. Pre-treated in alkaline water reduced the drying time up to 13%.

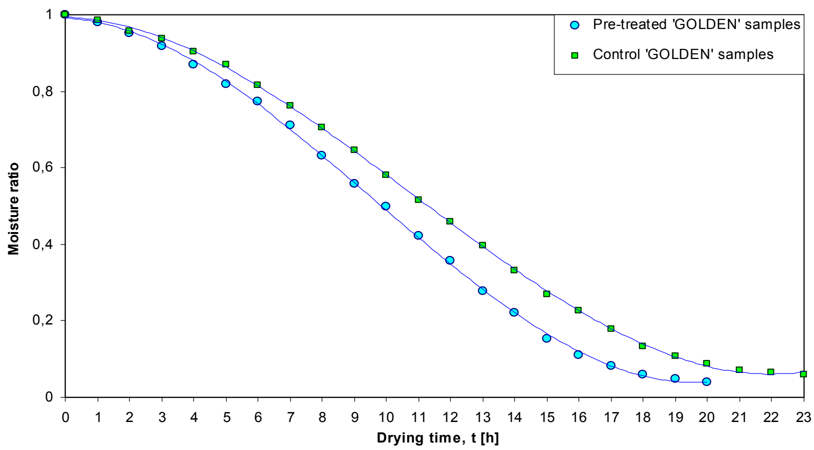


Fig. 3 Effect of pre-treatment/control on freeze-drying time of Golden Delicious apple

From Table 1. it can be seen that there is significant effect of alkaline-ionized water on drying time. The difference in drying time (untreated: 23 and 24 h) can be due to the difference in some intrinsic properties of apple varieties.

Table 1

The drying time to reach final moisture content

Pre-treatment methods	Drying time [h]	
	Idared	*Golden D.*
Alkaline-ionized water	20^a	20^a
Untreated/control	24^c	23^b

[a, b]Different letters in the same column indicate that values are significantly different (p<0,05)

The results showed that the alkaline-ionized water has a significant effect in accelerating the drying process and also effective to reduce drying time.

Table 2. shows that all fitted curves matched well with the experimental values and reports the model parameters. The R^2 values were higher then 0,90 in all cases. The third-degree polynomial had the highest R^2 value, the lowest RMSE value. This model described best the drying behaviour of Idared and Golden apple samples. Figs. 2-3. compare experimental data with the predicted ones using the third-degree polynomial for apple samples.

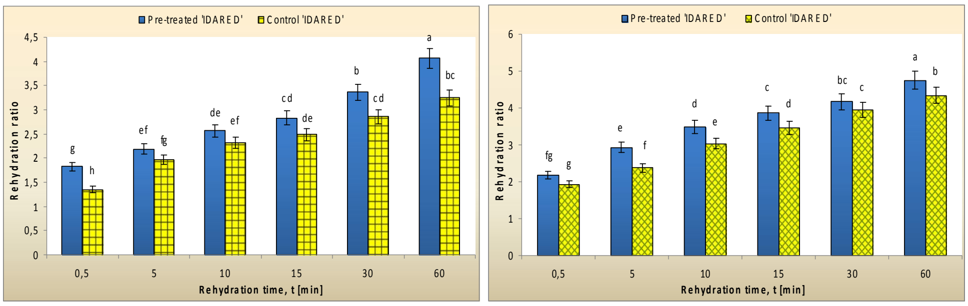
Table 2

Curve fitting criteria for the various models and parameters for pre-treated apple varieties

Apple varieties	Model name	Model parameters				
		a	b	c	k	n
Idared Treated	Polynomial	0,00025	-0,0073	-0,0031	-	-
	Page	-	-	-	0,0053	2,144
	Sigmoid	-0,0189	1,089	9,507	0,2872	-
Idared Untreated	Polynomial	0,00013	-0,0047	-0,0048	-	-
	Page	-	-	-	0,00417	2,077
	Sigmoid	-0,0183	1,096	11,42	0,229	-
Golden D. Treated	Polynomial	0,00023	-0,0067	-0,0069	-	-
	Page	-	-	-	0,00563	2,121
	Sigmoid	-0,0378	1,109	9,63	0,2747	-
Golden D. Untreated	Polynomial	0,000166	-0,00546	-0,0042	-	-
	Page	-	-	-	0,00456	2,086
	Sigmoid	-0,03483	1,116	10,93	0,2367	-

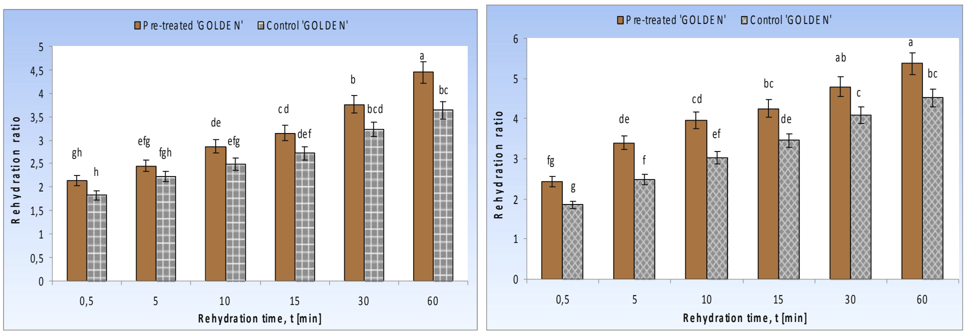
Effect of pre-treatments on rehydration ratio

The rehydration ratios of apples pre-treated by different methods are given in Figs 4-5. In untreated apple samples and apples treated by alkaline water the rehydration ratios were significantly difference. At 70 °C apples had much better rehydration capabilities than the water dipped at 35 °C.



a, b, c, d, e, f, g, h – groups which differed statistically significantly ($p<0,05$) from one another according to different pre-treatments

Fig. 4 Rehydration ratio of different pre-treatments Idared samples at 35 and 70 °C



a, b, c, d, e, f, g, h – groups which differed statistically significantly ($p<0,05$) from one another according to different pre-treatments

Fig. 5 Rehydration ratio of different pre-treatments Golden samples at 35 and 70 °C

Raw Idared dried by freeze-drying increased in mass during rehydration by more than 4-fold, while Idared treated with alkaline water increased 4,7-fold. Freeze-dried Golden samples increased in weight during rehydration by more than 4,5-fold, while Golden treated with alkaline water increased 5,4-fold.

Effect of pretreatment on hardness

The firmness of the apple cubes was evaluated by a compression test and the results are summarized in Table 3.

Table 3

Hardness parameters of apple varieties

Variety	Treatment	Hardness (N)
	Fresh	$4{,}788^{c}$
	Pre-treated	$1{,}223^{a}$
Idared	Control	$2{,}168^{b}$
	Fresh	$4{,}797^{a}$
	Pre-treated	$5{,}042^{b}$
Golden D.	Control	$4{,}833^{ab}$

^{a,b,c} Mean separation between rows based on probability of significant difference ($p<0,05$). Values with the same superscript show no significant difference. ANNOVA Duncan test applies between treatments.

The fresh apple presented a hardness of 4,788-4,797 N, which is significantly high compared to the hardness values of all treatments, except that the firmness of the fresh *Golden* samples were equal to the untreated ones. It was observed that lyophilisation has a positive influence on textural behaviour. This tissue hardness reduction due to the improved cell structure strength, high porosity and elasticity, porous structure of freeze dried samples (Lin et al., 1998).

ANOVA Duncan test shows statistical differences between hardness values of the different treatments (pretreated and untreated). It was seen that alkaline pretreatment could significantly decrease the hardness of apple slabs. Withdrawn the *Golden* samples, where the treatments did not showed a significant difference on the hardness. For example, the reduction in hardness from the untreated *Idared* to that pretreated *Idared* samples was 43,5%.

It can be concluded, that the structural changes caused by alkaline-ionized pretreatment, which improved the process of sublimation during lyophilisation led to less hardness of *Idared* dried samples.

CONCLUSIONS

The effects of alkaline-ionized water as pre-treatment on the drying kinetics, hardness and rehydration capacity were studied. With alkaline water treated apple varieties have shorter drying time compared to untreated. Samples that were pre-treated reached lower final moisture content compared with untreated samples. Several models were tested to model the drying kinetics. Among these 3 models, the third-degree polynomial is very accurate to predict the drying behaviour of the pre-treated apple varieties.

It was found that rehydration properties of alkaline water treated dried products are improved compared to no-treated samples. The apple cubes treated with alkaline water had softer and crispier texture than the untreated products (except *Golden D.*). The reduction of hardness of the pretreated apple was due to the softening of cellular structure.

Pre-treatment is necessary for successful dehydration process. This will have a strong impact on the production cost of freeze-drying. For future jobs, the influence of alkaline pre-treatment in freeze-drying will be tested deeply, modifying pH values and soaking time. Further studies should be conducted to determine the effect of alkaline pretreatment on microstructure of dried food samples. Additional opportunity to reduce the processing time of the freeze-drying process, the utilisation of combined (hot-air + freeze-drying, thermal vacuum drying + freeze-drying) processes are proposed.

NOMENCLATURE

a, b, c, d, n	function parameters	-
k	drying constant	1/s
M	moisture content on a dry basis at any time	kg water kg dry matter^{-1}
M_e	equilibrium moisture content on a dry basis	kg water kg dry matter^{-1}
M_0	initial moisture content on a dry basis	kg water kg dry matter^{-1}
MR	moisture ratio	-
RR	rehydration ratio	-
t	time	min, h
W_d	weight of dry sample used for rehydration	g
W_k	sample dry weight	kg
W_r	weight of the rehydrated sample	g
W_t	sample weight at a specific time	kg
Superscript		
a, b, c, d, e, f, g, h	indicate significant differences	-

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