STATE DIAGRAMS IN LOW TEMPERATURE AND ATMOSPHERIC FREEZE DRYING OF ORGANIC FRUIT PRODUCTS

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ABSTRACT

The influence of environmental parameters on freeze-drying of blanched organic apples was investigated. The changes of material when dried were also studied since the reduction of moisture content during drying decreases the freezing point significantly which influences the process efficiency and final product quality. The process of freeze-drying was described with the help of state diagram in order to study the dependencies between moisture content and freezing point depression as well as the nature of shrinkage. The processes of ice formation in apples were described by modified Clausius-Clapeyron equation. The processes of glass transition was described by Gordon-Taylor equation.
The drying methodology for organic apples was proposed.

INTRODUCTION

Significant amount of research investigate the drying kinetics for freeze-drying process with respect to temperature, relative humidity and type of additional treatment (infra-red treatment, ultra-sound etc.). However, the properties of the foods with high moisture content can vary significantly when dehumidifying. The decreasing of water activity, freezing point and porosity, appearance of shrinkage and phenomena of glass transition will influence a lot on the drying properties of the foods (Rahman, 2009).
The aim of this study is the investigation of drying kinetics and quality of organic apples with respect to their thermal properties and ice content at different freeze-drying temperature. Such comparisons will give the essential information. This can be applied to design the drying regimes for organic foods, which contain significant amount of sugars (fruits and berries).

MATERIALS AND METHODS

Description of drying experiments

The organic apples (Royal Gala, Sudtirol) were purchased on the local market and then stored at temperature of 10.0 °C before experiments. The apples were sliced (with skin, 5 mm thickness) and blanched for 1.0 min in steam (100.0 °C) before drying and any other tests. The sliced and blanched apples were place on shelves into the drying chamber. The drying was performed at different temperatures: +20.0, +3.0, -5.0 and -10.0 °C. Additional experiments were done with varied temperature of the air from -5.0 to -15.0 °C. This mode was suggested based on DSC investigations of ice content in the apples at different temperatures.

Air velocity was chosen at 1.5-2.0 m/s, relative humidity of the drying air on the inlet to the drying chamber varied in the range between 20.0 and 40.0%.

Sorption isotherms were found for samples, which were dried at different temperatures, by equilibrating of them in a climate chamber (KMF 240, Binder, Tuttlingen, Germany).

DSC analysis

The DSC analysis was done with a DSC Q 2000 (TA instruments, USA) equipped with a Liquid Nitrogen Cooling System. Samples were cooled and equilibrated for 5 minutes at –150.0 °C; the cooling rate was 10.0 °C min^{-1}. Then the samples were heated up to 150.0 °C (depending on moisture content) with the heating rate of 10.0 °C min^{-1}.

The glass transition, freezing and melting temperatures and unfreezable water determination

The incipient melting point (“end of freezing”), T'_m, was detected by analyzing the DSC heating curve (Tolstorebrov et.al., 2014). The freezing point was estimated as the minimum value of the ice melting endothermic peak on the DSC heat flow curve.

The glass transition was determined with TA Universal Analysis 2000 version 4.5A software (TA instruments, USA). The glass transition is characterized with the following parameters: the onset (T_{go}), end (T_{ge}) and inflection (T_{gi}) points. It should be noted, that the glass transition in apples is relatively weak. Thus, the inflection point was determined as a negative peak of the derived heat flow curve. The amount of unfreezable water was detected by the DSC melting curve analysis, (Tolstorebrov et al.,, 2014)

Statistical analysis

The analysis of variance (ANOVA: single test and two-factor test with replication) was applied to analyze the obtained data. The difference was considered significant at $p<0.05$.

A regression analysis was done with a software DataFit 8.1 program (Oakdale Engineering). The quality of the regression was evaluated with the following parameters: F-Ratio, Prob(F) and R^2. F-Ratio is the ratio of the mean regression sum of the squares divided by the mean error sum of the squares. Prob(F) is the probability that the null hypothesis is true. R^2 is the coefficient of multiple determinations. The standard deviation is introduced in the brackets after the values given in the text.

RESULTS AND DISCUSSION

Influence of drying temperature on color of organic apples

The color was analyzed for organic apples which were dried at +20.0, +3.0, -5.0, 10.0 ºC, also, vacuum freeze-drying method was used. The vacuum freeze-drying and drying at 20.0 ºC as a reference were both used in parallel to understand the influence of temperature on the quality of the apples in comparison. The example of the influences is introduced on Figure 1.

The drying at +20.0 °C resulted in the highest shrinkage and color alteration, when compared with the other samples. The visual quality of the apples, which were dried at +3.0 and -5.0 °C was similar: some shrink and browning were detected. While, drying at -10.0 resulted in a better quality, when compared with other samples (except of freeze-dried). However, all the samples were significantly different from the freeze-dried reference. The color analysis in L*C*h* scale is introduced in Table 1.

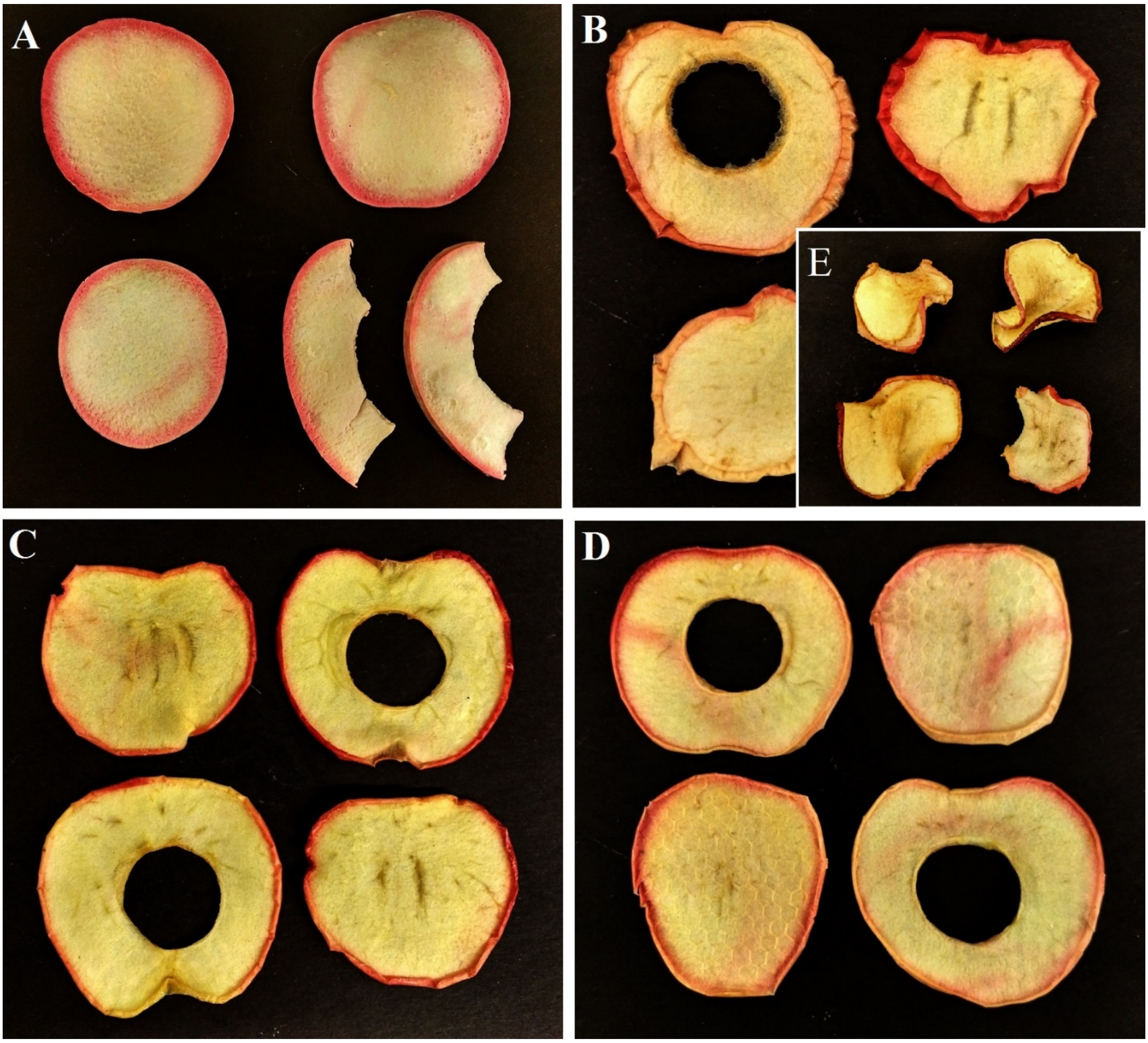

Figure 1 Influence of temperature and drying method on color and quality of apple slices: A – vacuum freeze-drying; B – drying at +3.0 °C; C – drying at -5.0 °C; D – drying at -10.0 °C; E – drying at +20.0 °C.

Table 1. Color parameters of raw and blanched apples before and after drying

Drying temperature, °C	Color parameters		
	L* (-)	C* (-)	h*, °
+20.0	67.52 (1.39)[a]	36.88 (2.98)[c]	74.71 (1.11)[e]
+3.0	70.21 (1.70)[a]	28.03 (1.13)[d]	80,41 (4.17)[e]
-5.0	71.58 (2.17)[b]	27,89 (3.03)[d]	85,43 (1.99)[e]
-10.0	73.37 (1.89)[b]	33,94 (3.25)[c]	84,33 (7.19)[e,f]
-5.0→-10.0→-15.0 °C	73.3 (1.5)[c]	33.9 (2.0)[c]	90.0 (1.73)[f]
Vacuum-freeze drying	79,95 (1.83)	13,22 (1.04)	75,45 (7.01)[e]

The freeze-dried samples showed the higher lightness (L*), when compared with the samples dried at temperatures above 0 °C. This caused by enzymatic browning reactions, which depends on temperature and time of drying (Vega-Gálvez et al., 2012). At the same time, hue (h*) was the same for all the samples. This can be explained by the high deviation of this parameter during measurements, because the color of the samples was not homogenous. Chrominance (C*) was high for all the samples when compared with vacuum-freeze dried reference.

The alteration of structure and color of the organic apples after drying showed that the decreasing of the drying temperature to +3.0 °C could maintain the color and quality of the product, which was similar of comparable with freeze-dried samples. However, drying at -10.0 °C was much more gentle comparing with other methods (except of vacuum-freeze drying)

Sorption isotherms of organic apples

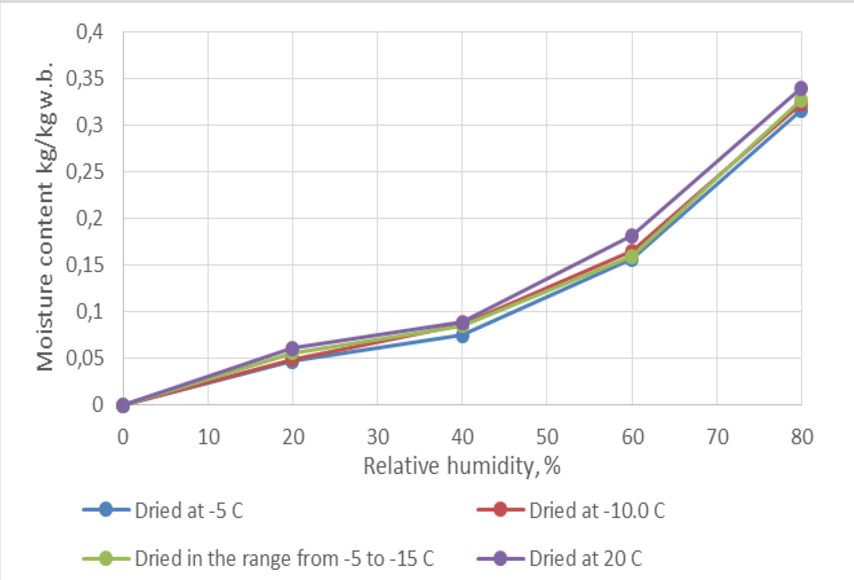

Figure 2 Sorption isotherms for blanched apples at 25.0 °C.

The moisture sorption behavior of dried apples showed sigmoid shape (type III, Brunauer's classification), which is typical for products with high sugar content, Figure 2. The same dependencies were detected before for other types of apples (Kaymak-Ertekin & Gedik, 2004; Mrad et. al.,, 2012). A sharp increase of moisture content at high relative humidity is explained by the effect of solute–solvent interactions associated with sugar dissolution.

Statistical difference in sorption properties was observed between all the investigated samples ($p<0.05$). However, the difference was found in a range of 2-3 % of moisture content. Thus, we can conclude that drying temperature in the range between -10.0 and +20.0 °C does not influence significantly on the structural properties (for ex. porosity) of the apples. However, apples, which were dried at +20.0 showed a significant degree of shrinkage when compared with others. It should be noted, that the relative humidity in the range between 20.0 and 40.0% resulted in a slight increase of the equilibrium moisture content, thus the relative humidity of drying air can be increased up to 40.0 % without significant reduction of drying rate.

Thermo-physical properties of apples

Typical behavior of DSC heat flow curve is introduced on Figure 3. The melting peak (green line) occurred in a quite narrow temperature range. However, the freezing of concentrated solution happened at a temperature far below -20.0 °C and full solidification of all the freezable moisture happened at -46.23 (2.0) °C (End of freezing point on Figure 3). The unfreezable moisture forms maximal freeze concentrated solution with soluble solids, which underwent glass transition at temperature -54.32 (3.0). Glass transition of fresh apples was relatively weak (due to high amount of other matter), but it was easily detected on the derivate heat flow curve (point -54.32 °C on Figure 3, blue line). The decreasing amount of freezable water (semi-dried blanched apples) made the glass transition shift more visible on the heat flow curve. It was detected in the same temperature range as for fresh blanched apples as soon as these two types of sample had the same maximal freeze concentration of solids.

Phase transitions of apples depend on a carbohydrate content. Due to this, the glass transition of absolutely dry matter is much lower, when compared with, for example, fish (in the range between 150.0 and 162.0 °C) (Tolstorebrov et al., 2014). Due to the same reason, the glass transition of apples with high moisture content was relatively high, when compared with fresh fish tissues. The resent study revealed the glass transition for dried apples in the range between 33.0 and 84.0 °C (Mrad et al., 2012), when the glass transition varied with the drying method due to unknown reasons. This study determined the inflection point of glass transition at 38.0 and 46.0 °C. This temperature range corresponds to glass transition behavior of mixture of simple sugars such as glucose, fructose and sucrose (the main compounds of apples). The glass transition of fructose was in the range between 18.0 and 25.0 °C depending on the thermal history of the sample. However, the presence of sucrose and glucose increases the glass transition temperature to higher values (up to 40.0 °C, when sucrose is around 50.0 %) (Truong et. al., 2004).

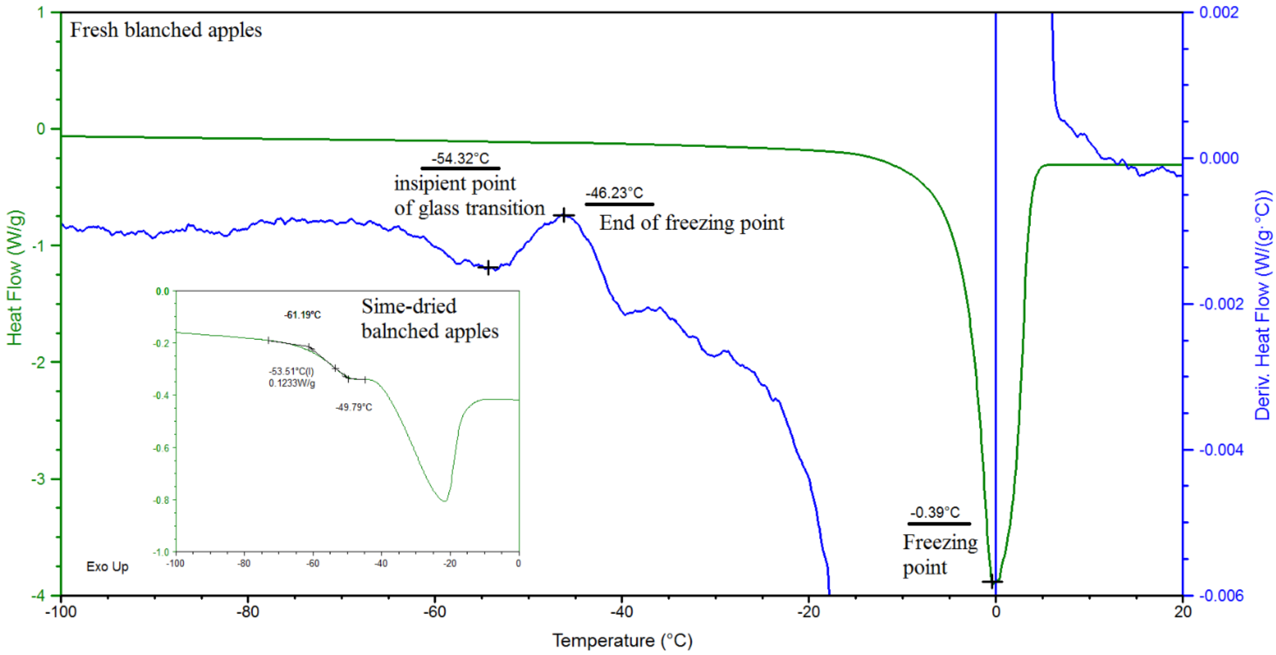

Figure 3. DSC heat flow curve (green) and its derivation by temperature (blue) and main thermal transitions of fresh blanched apples and semi-dried blanched apples.

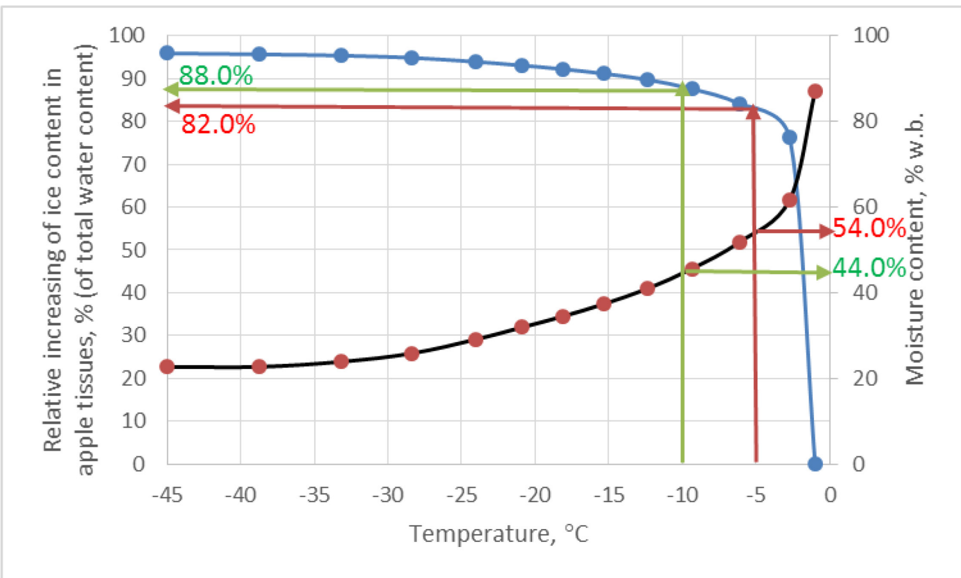

Figure 4. Development of ice and moisture content with respect to the drying temperature.

Integration of the melting peak from the "End of freezing point" (insipient point of melting) with respect to Riedel's equation (Riedel, 1956) gave an opportunity to calculate amount of frozen matter vs. temperature. The result of the integration is introduced on the Figure 4. It is shown, that amount of all freezable moisture reached 82.0 and 88.0 % at -5.0 -10.0 °C respectively (blue line on diagram). At the same time, these values can be introduced as the moisture content vs. temperature (considering that ice is insoluble and excluded from the system). The moisture content of fresh blanched apples decreases to 44.0 and 54.0 % at -5.0 and -10.0 °C respectively. Such high moisture content was explained by unfreezable moisture content, which was detected in the range between 3.0 and 4.0 % w.b., and by remains of unfrozen fraction of moisture, which still exists in the temperature range between -10.0 and -46.0 °C.
The data of moisture content at different freeze-temperatures is essential, because it help to understand at which point the drying object will start to melt during freeze-drying. For the given case, it is visible, that the product will be absolutely unfrozen when the moisture content will be decreased to 44.0 % w.b. (for freeze-drying at -10.0 °C). This fact explains the insignificant difference in quality and color between drying temperatures, which was discusses previously.

The state diagram for organic apples

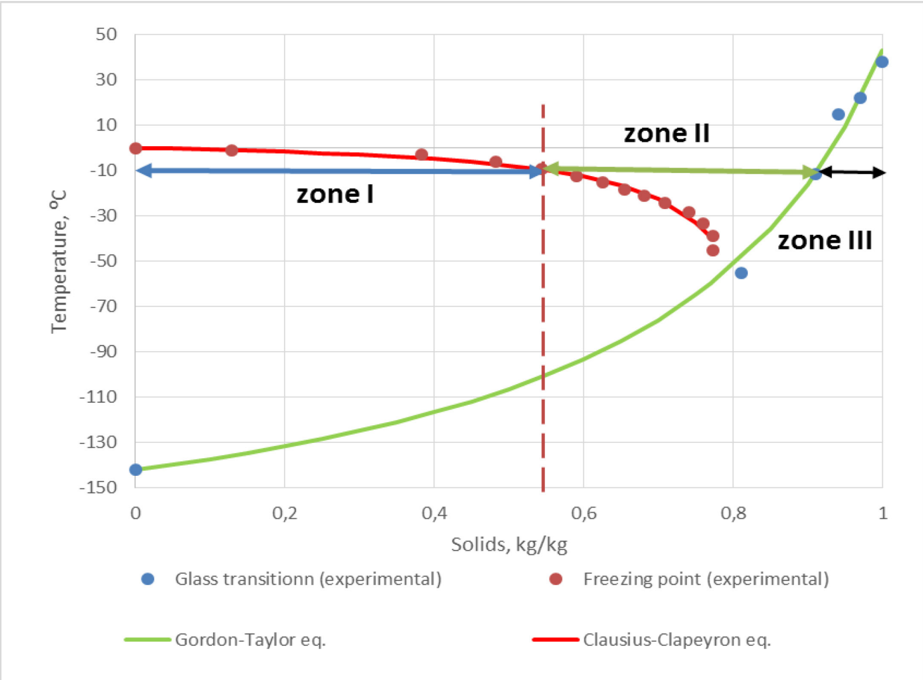

Figure 5. State diagram for blanched apples.

A typical state diagram consists of two curves: the freezing curve and the glass transition curve. The freezing curve represents the influence of the solid matter content on reducing the freezing point. In this investigation it was obtained from the data of the freezing point of the apples samples with different moisture contents. The decreasing of the freezing point was modeled with the Clausius-Clapeyron equation modified for food by Chen (Chen, 1986), Equation 1:

$$\delta = -\frac{\beta}{M_w} \ln\left(\frac{1-x_s-Bx_s}{1-x_s-Bx_s+Rx_s}\right) \quad (1)$$

The glass transition curve shows the influence of solid content on glass transition temperature. and it was modeled with the Gordon-Taylor equation (Gordon & Taylor, 1952), Equation 2:

$$T_{gi} = \frac{x_s T_{gi.s} + k x_w T_{gi.w}}{x_s + k x_w} \quad (2)$$

The inflection glass transition points values were used for modeling. The parameters of the models are introduced in Table 2.

Table 2. Parameters and coefficients of the regression models

Equation	Statistical analysis			Coefficients	
	F-ratio	Prob(F)	R^2	R	B
Clausius-Clapeyron	698.14	0	0.98	$6.51*10^{-5}$	$12.78*10^{-2}$
Grodon-Taylor	502.0	$2*10^{-5}$	0.99	k	$T_{gi.s}$
				4.19	42.902

The application of freeze-drying looks very promising. It will give an opportunity to detect amount of ice at different processing temperatures, understand the desirable low temperature condition to avoid glass transition and provide effective drying regimes. When drying at -10.0 °C, the state diagram region can be split into three different regions. The product will retain its shape in the zone I (blue arrows). At this stage, the product will have approximately the same liquid content related to dry matter, because the decreasing of moisture content will be compensated by the ice melting due to the decreasing of the freezing point (following Clausius-Clapeyron line). The shrink development will be observed, when the product comes to zone II, when all the ice have been melted at the drying temperature of -10.0 °C. The solution for avoidance shrinkage is to decrease the drying temperature (for ice formation) or to increase the temperature for acceleration of the drying rate. The zone III and vicinity of the zone III is not beneficial for drying, because this is the zone glass transition. The formation of maximal freeze concentrated solution happens, which is very viscous (up to 10^{12} Pa*s). This will decrease the drying rate significantly. At the same time, crossing the glass transition line will make the product crispy and brittle, as soon as viscous-elastic characteristics of the product disappears in the region. However, the moisture gradient in apples slices will create the situation when all the three zone will be presented simultaneously during the freeze-drying, especially in the middle and final periods.

Drying kinetics of organic apples

The drying kinetics was investigated for blanched fresh apples at different drying temperatures, Figure 6. One dynamic regime was applied based on the DSC investigation of thermal properties of apples at different temperatures. The drying temperature in this case varied from -5.0 below to -15.0 °C following the freezing point line that ensured the ice presence in the product on the final stages of drying.

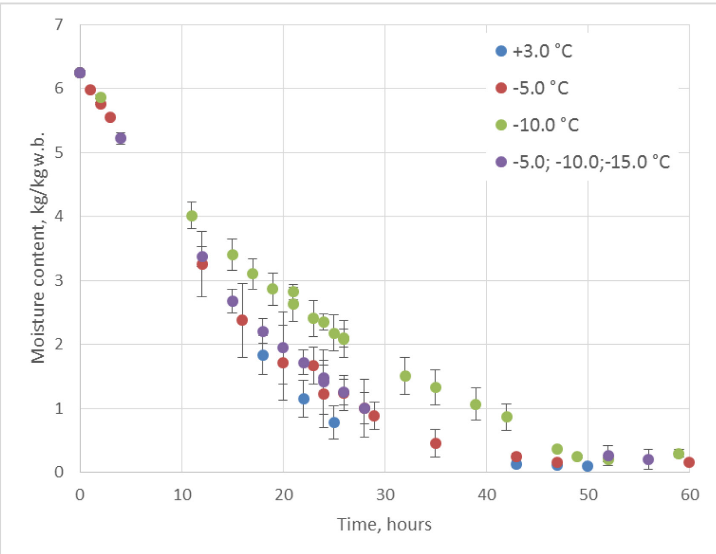

Figure 6. Drying kinetics of blanched apples with respect to temperature.

The decreasing of drying temperature resulted in a longer drying time and the lowest rate of drying was predictably observed for -10.0 °C air temperature. At the same, the dynamic regime of drying, when the temperature varied form -5.0 to -15.0 °C did not show significant difference, when compared with drying at -5.0 °C. Nevertheless, quality of the apples was equivalent to the samples, which were dried at -10.0 °C. Probably, the drying rate was maintained by lower shrinkage of the samples at the later drying stages. This compensated the negative influence of temperature on the moisture diffusion.

The drying behaviors were modelled using Newton model, as soon as the apple slices can be considered as a plane,

Equation 3:

$$MR = \exp(-k\tau) \quad (3)$$

where k - drying constant , hour^{-1}.
The more precise way to characterize the drying behaviors is determination of the effective moisture diffusivity. This property of material can be derived from the drying kinetics via analytical solution of the Fick's second law of diffusion (infinite slab), Equation 4:

$$MR = \frac{8}{\pi}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-(2n+1)^2\pi^2 D_{eff}\tau}{4(h)^2}\right) \quad (4)$$

where D_{eff} – effective moisture diffusivity , m^2 s^{-1}; τ – drying time, sec; h – half-thickness of seaweed layer, m; n – number of terms (as positive integer, 35 for this study).
Table 3 introduces the empirical drying coefficients for Equation 3 and effective diffusivity for Equation 4.

Table 3. Coefficients for Newton and Fick's second law of diffusion equations, organic apples drying

Drying temperature, °C	**k, hour^{-1}**	**D_{eff}*10^{10}, m^2/s**	**Statistical analysis**		
			R^2	**F(Ratio)**	**Prob(F)**
+3.0 °C	0.0733	2.0	0.98	845.0	0
-5.0 °C	0.0645	1.8	0.99	2759.0	0
-10.0 °C	0.0455	1.3	0.98	1266.0	0
-5.0→-10.0→-15.0 °C	0.0608	1.7	0.99	2224.0	0

The average values of effective moisture diffusivity and drying constant increased with increasing of the drying temperature. The effective diffusivity was detected in the normal range of moisture diffusivity for foods between 10^{-9} and 10^{-12} m^2/s (Onwude et.al, 2016). The resent study revealed effective moisture diffusivity for apples of 3.22*10^{-9} m^2/s at 40.0 °C.
However, the values of effective moisture diffusivity and empirical drying constant of apples for dynamic drying was higher, when compared to those dried at -5.0 °C. Probably, manipulation with drying temperature and maintenance of the ice in the product at low moisture content improves the porosity structure of the product and this enhanced the drying rate. It should be noted, that dehumidifying of the apple slices was not uniform and the drying rate on the edges of the apples slices was much higher, when compared with their middle part. This resulted in intensive melting of the apple slice edges and presence of frozen part in the middle. Thus, the effective diffusion coefficient can be considered as a relative value, which can describe the drying process only partly.

CONCLUSIONS

The analysis of thermal properties and state diagram of the blanched organic apples gave an opportunity to investigate the dynamic drying process when the drying temperatures was regulated with respect to the moisture content of the product (by weight lose). This approach can be promising for the design of the freeze-drying process which will provide a better quality of the product.

ACKNOWLEDGEMENTS

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