

Description of atmospheric freeze-drying process of organic apples using thermo-physical properties

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Abstract

This study discusses the influence of temperature and total moisture content on ice fraction in organic apples during atmospheric freeze-drying process. The ice formation of glass transition events were described by Clausius-Clapeyron and Gordon Taylor equations. The obtained data is essential for design the drying process and for understanding the limiting factors.

Keywords: *ice fraction, organic apples, atmospheric freeze/drying, glass transition*

1. Introduction

Atmospheric freeze drying (AFD) of apples results in improved quality of the product which is reflected in better appearance, high porosity and better color, when compared with conventional drying [1, 2]. However, the properties of the foods with high moisture content can vary significantly when dehumidifying at the selected freezing temperatures. Extensive research was previously conducted to model and explain physical phenomena of AFD of apples [3-5]. The studies revealed high amount of unfrozen moisture when drying at -5.0 and -10.0 °C. However, ice development in apples during AFD process is still unclear. Thus, it is of a great importance to gain a deeper understanding of the thermal properties of apples during drying to further decrease undesired changes of product properties. The aim of current study was the investigation of the development of thermal properties and ice content at different freeze-drying temperatures. Such comparisons will give the essential information to understand factors, which influence the process and limits the AFD process. The same principle can be applied to design the drying regimes of other organic foods, which contain significant amount of sugars (fruits and berries).

2. Materials and Methods

2.1 DSC analysis

Raw and vacuum-frozen samples were used for experiments. The desired moisture content of vacuum freeze-dried samples was obtained by equilibration in climate camera at defined conditions. The DSC analysis was done with DSC Q 2000 (TA instruments, USA) equipped with a Liquid Nitrogen Cooling System. Helium was chosen as a purge gas at 25 mL/min, according to TA's instrument recommendations. The reference sample was an empty hermetically sealed aluminum pan. The samples with masses between 13.0 mg and 20.0 mg were placed into aluminum pans with hermetic lids. Samples were cooled and equilibrated for 5 minutes at -150.0 °C; the cooling rate was 10.0 °C/min. The annealing procedure was applied at -50.0 °C. This was done to avoid cold crystallization during scanning. Then the samples were heated up to 150.0 °C with the heating rate of 10.0 °C/min.

2.2 Determination of glass transition

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, end and inflection points. It should be noted, that the glass transition in seaweeds with high moisture content is relatively weak. Thus, the inflection point was determined as a negative peak of the derived heat flow curve [6].



2.3 Determination of end of freezing and initial freezing point

The onset of ice melting (or end of freezing point), was determined by analyzing the DSC heating curve. The freezing point was estimated as a minimum value of the ice melting endothermic peak on the DSC heat flow curve.

2.4 Determination of ice fraction and unfreezable water

The amount of unfreezable water and ice fraction was detected by the DSC melting curve analysis. The DSC melting peaks were integrated with the sigmoidal tangent baseline function from the onset of ice melting point. The ice fraction was determined as a ratio of melting energy to latent heat of fusion of pure ice. As soon as melting energy of ice is a function of temperature, the empirical equation suggested by Riedel^[7] was used for correction of obtained values. The amount of unfreezable water was obtained as the difference between the total water fraction in the product and the ice fraction.

2.5 State diagram

The thermal transitions can be introduced using the state diagram. A typical state diagram consists of two curves: the freezing curve and the glass transition curve. The freezing curve represents the influence of a solid matter content on the reduction of the freezing point. In this investigation it was obtained from the data of the freezing point of semi-dried apples with different moisture contents. The decrease of the freezing point δ (°C) was modeled with the Clausius-Clapeyron equation modified for food by Schwartzberg^[8], equation (1):

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

where β – molar freezing point constant, 1860 (kg K)/(kg mol); M – molecular mass, kg/kmol; B – ratio of unfreezable water to the total solids content, kg/kg; R – molecular mass ratio of water and solids, kDa/kDa; x_s – solid fraction kg/kg w.b.

The glass transition curve shows the influence of the solid content on the glass transition temperature ($T_{g,i}$). It was modeled with the Gordon-Taylor equation^[9], equation (2):

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

where, x_s – solid fraction kg/kg w.b.; k – system's constant in Gordon-Taylor equation; $T_{g,i,s}$ – glass transition of pure solids; $T_{g,i,w}$ – glass transition of pure water.

2.6 Statistical analysis

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.

3. Results and Discussion

3.1 Thermo-physical properties of apples

The DSC heat flow curve for fresh apples revealed the following endothermic processes: glass transition of unfreezable solution, and melting of freezable water. The unfreezable solution consists of solids and unfreezable water. It is also referred to as maximal freeze concentrated solution [10]. One of the remarkable properties of this solution is its high viscosity. The ice formation is usually not detected when the solids concentration exceeds the value of the maximal freeze concentrated solution. The example of the thermal transitions in apples is introduced on Figure 1a,b.

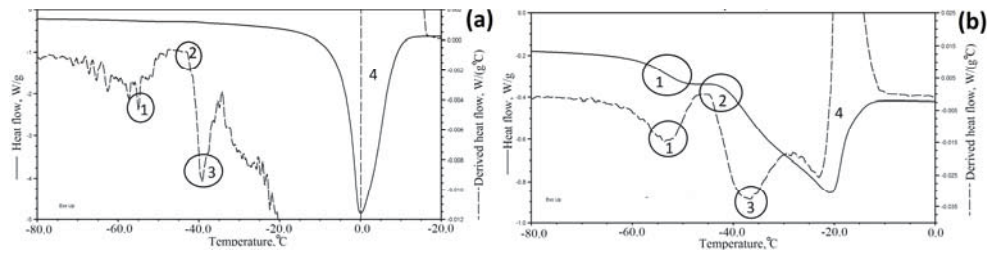


Fig. 1 Example of thermal transitions in apples: raw (left) and dried (right): 1- inflection point of glass transition, 2- end of freezing (insipient point of ice melting); 3- eutectic point; 4- ice melting peak.

Glass transition of fresh apples was relatively weak due to a high content of freezable water, but it was easily detected on the derived heat flow curve ($T_{g,i} = -55.08$ °C, Figure 1a, left, dashed line). At the same time, decreasing of amount of freezable water by drying (semi-dried blanched apples, Figure 1b) made the glass transition shift visible on the heat flow curve, $T_{g,i} = -53.42$ °C. All the apple samples, which showed an ice melting peak, formed the same maximal freeze concentration of 79.0 % solids w.b. irrespective of the moisture content. Thus, the glass transition shift was detected in the same temperature range ($T_{g,i}$ between -55.5 and -53.0 °C) as for fresh blanched apples. As soon as the temperature of glass transition is a function of average molecular weight of the system. Such a dependence was determined before for other types of foods [6].

At the same time, the samples, which did not show an ice melting peak (the concentration of solids ≥ 79.0 % w.b.), showed a different trend. The glass transition strongly depended on the moisture content: it increased within decreasing of the moisture in the sample. This study determined the inflection point of glass transition of dried apples (0.5 (0.3) % d.b.) in

the range between 38.0 and 46.0 °C. Such a deviation can be explained by accumulation of moisture during sample preparation for DSC. Water molecules work as plasticizers and even a small amount of moisture can decrease glass transition temperature significantly [10]. A recent study revealed the glass transition for dried apples in the range between 33.0 and 84.0 °C [11], when the glass transition was affected by drying temperature from 30.0 to 60.0 °C. However, this study did not show such a dependence for AFD conditions.

The melting peak (solid line, Figure 1a,b) of the freezable water occurred in very narrow temperature range, which indicated the high amount of free water in the product. However, the incipient point of melting (end of equilibrium freezing) was detected at a temperature of -44.2(1.2) °C. The eutectic point was detected on the DSC heat flow curve in the temperature range between -39.2 and 37.4 °C. It was introduced as a weak bend of the melting peak line and as a negative peak on the derived heat flow curve (in the range between -39.11 and -37.40 °C), see Figure 1a,b.

Integration of the melting peak from the incipient point of melting with respect to Riedel's equation [12] allowed to calculate the amount of frozen matter vs. temperature, Figure 2a. The amount of unfreezable water, which was calculated as a difference between total water content and the ice fraction, was found at 3.7 (0.3) % w.b. Thus, apples include solid fraction, freezable and unfreezable water. Most of the freezable water was in crystalline form in the temperature range between -3.0 and -10.0 °C, Figure 2a. Such temperatures is a typical range for the AFD process [3, 13]. At the same time, the moisture content of unfrozen solution at these temperatures was also very high and varies in the range between 60.0 and 43.0% w.b., Figure 2b. This significantly influenced the drying process. The retreating of the ice front from the surface to the inner parts of the product with the formation of a porous zone, which phenomena is widely used for modelling of AFD process, [13] will not occur in such a case. The process of evaporation of the unfrozen moisture and ice melting due to depression of freezing point is much more likely to occur.

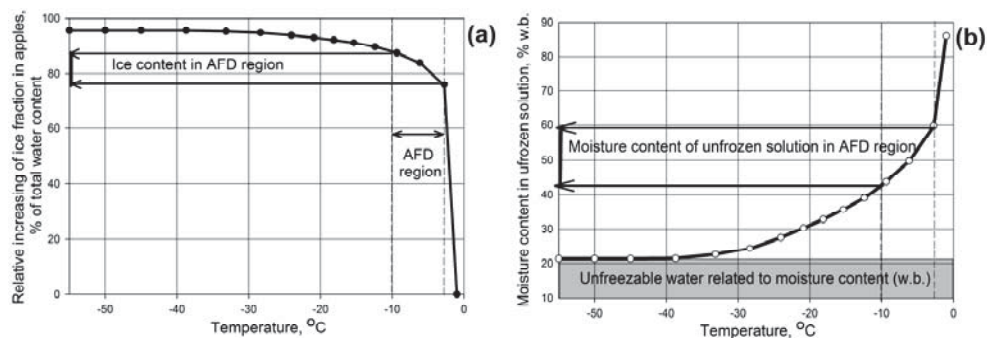


Fig. 2 Ice content increasing in apples (left), Moisture content in unfrozen solution(right)

3.2 The state diagram for organic apples

The state diagram, which is constructed on the basis of equations (1) and (2), is introduced in Figure 3. The inflection point of glass transition was used for the modeling. These two lines split the diagram area into four regions with respect to solid content and temperature. The amorphous region appears above the freezing point depression line (Clausius-Clapeyron's equation: $R=5.48 \cdot 10^{-5}$; $B=12.78 \cdot 10^{-2}$); this region is common for atmospheric convection drying of foods. The region of ice and amorphous unfrozen solution is situated between the freezing point depression line and glass transition line. The region of the glassy state can be found below the glass transition line (Gordon-Taylor equation: $k=4.19$; $T_{gi,s}=42.09 \text{ } ^\circ\text{C}$).

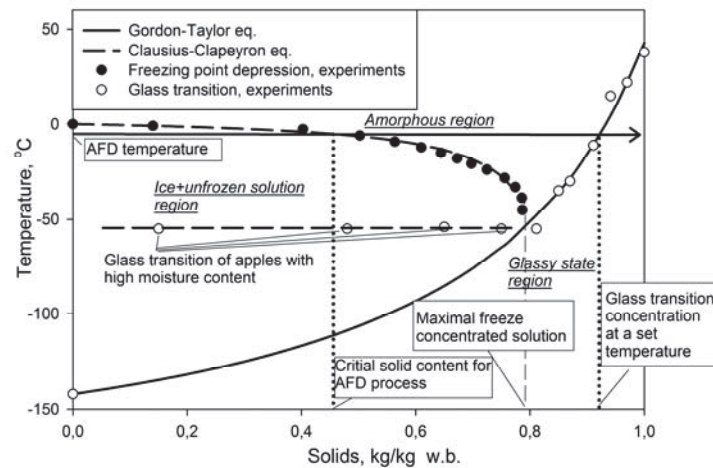


Fig. 3 State diagram for apples: experimental results and modelling ($F(\text{Ratio}) > 600$; $\text{Prob}(F) = 0$)

The application of the state diagram, Figure 3, allows to predict indirectly the amount of ice during drying at different processing temperatures with respect to the moisture content. Further, the natural limitation of the AFD process can be determined. The minimum AFD temperature is influenced by the formation of maximal freeze concentration, when further decreasing of the temperature does not influence on ice content in the product. The overall amount of ice at any time of the drying process can be easily determined knowing the actual moisture content and the critical solid content, which is a function of the drying temperature, equation (3):

$$x_{ics,t} = x_{w,t} - (1 - x_{s,critt,T}) \quad (3)$$

where, $x_{ice,\tau}$ – ice content at any time of the AFD process (kg/kg w.b.); $x_{w,\tau}$ – water content at any time of AFD process (kg/kg w.b.); $x_{s,crit,T}$ – critical solid content at the AFD drying temperature (kg/kg w.b.).

Critical solid content is the maximum available concentration of solids in unfrozen solution at freezing temperature. It can be determined using equation (1) or Figure 3. Due to this, it is possible to control AFD process using the weight reduction as a reference. For example, Duang et al., [14] suggested to decrease the temperature of the drying air from -5.0 to -10.0 °C to avoid ice melting during atmospheric freeze-drying.

The full melting of ice will occur when the concentration of the solid fraction reaches the critical solids content at a given freezing temperature, Figure 3 (dotted line). At such conditions, the process became the typical low temperature convection drying. Another important issue is glass transition of the samples, when the amorphous solution will solidify. Such a phenomenon depends on the solid fraction and temperature (Gordon-Taylor equation). The subsequent increase of temperature before reaching the glass transition concentration at a given temperature is essential to decrease the drying time. The viscosity of an amorphous solution in the vicinity of the glass transition reaches 10^{12} Pa*s [15]. This can decrease the drying rate significantly. At the same time, crossing the glass transition line will make the product crispy and brittle, as soon as the viscous-elastic characteristics of the product disappear in the region [6].

4. Conclusions

The temperature of glass transition of fresh and dried apples was determined at -55.08 and -53.42 °C respectively. The inflection point of glass transition of dried apples was detected in the range between 38.0 and 46.0 °C. Both fresh and dried apple samples showed the same maximal freeze concentration of 79.0 % solids w.b. irrespective of the moisture content. The incipient point of melting was found at -44.2(1.2) °C. The eutectic point was detected in the temperature range between -39.2 and 37.4 °C. The amount of unfreezable water was determined at 3.7 (0.3) % w.b. The moisture content of unfrozen solution varied in the range between 60.0 and 43.0% w.b. at -3.0 and -10.0 respectively. The process of AFD should be held in the temperature range below the melting temperature with respect of moisture content, but the temperature should be increased after the ice melting. The region of glass transition should be avoided for rapid and efficient drying.

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