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Study On Drying and Glass Transition of Appless

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Abstract

The atmospheric freeze-drying process of organic apples and their thermophysical parameters (phase transitions and ice formation) was investigated. The experiments were conducted at -10.0, -5.0 and 3.0 °C drying temperatures. The dynamic mode of drying was proposed based on thermophysical parameters. The state diagram of material was obtained using Clausius-Clapeyron and Gordon-Taylor equations. Analysis of drying kinetics revealed at -10.0 °C drying resulted in a significantly longer process, in comparison to temperatures. The aim of this study was to gain a deeper understanding of the changes of thermal properties of apples during drying in view of decreasing undesired changes of product properties.

Keywords: Freeze-drying; apples; State diagram; Sorption; Ice content

Introduction

Dried fruits are very popular snacks in European countries, e.g., in Germany the overall annual consumption lies at more than 116 000 tons. In the organic food sector in particular, consumers are increasingly health conscious and expect processing to be as little detrimental to the valuable components as possible. Therefore, it is of utmost importance to gain a deeper understanding of the thermal properties of apples during drying to further decrease undesired changes of product properties.

Production of dried organic food is mostly carried out by small and medium sized enterprises (SME) which are currently facing several challenges. The consumers required high quality products as a precondition for successful marketing but there is a lack of corresponding processing knowledge and awareness by the producers. At the same time, the competition on the market forces strictly controls the costs. Atmospheric freeze drying has the potential to preserve organic products, like apples, with a superior quality by cost effective processing, strengthen hereby the market position of SME. Health-conscious consumers and expect processing to be as little detrimental to the valuable components as low as possible. Therefore, it is of utmost importance to gain a deeper understanding of the thermal properties of apples during drying to further decrease undesired changes of product properties. Hence deeper understanding of the thermal properties of apples during drying to minimize detrimental effects and increase the valuable components as possible is of utmost importance to the producer.

Many researchers investigated drying kinetics of freeze-drying with respect to temperature, relative humidity, and type of additional treatment (infra-red treatment, ultra-sound etc.). Atmospheric freeze drying (AFD) is a process for apples to give better quality of the product which is reflected in better appearance, high porosity, and better color, when compared with convective freeze drying [1,2]. Many studies revealed high amounts of unfrozen moisture when drying at -5.0 and -10.0 °C. Also, geometric parameters of the product behave the drying process and influence on shrinkage and porosity of the final products [3]. Foods with high moisture can show differences in properties when dehumidifying at freezing temperatures. Changes in water activity, freezing point, porosity, shrinkage, and glass transition will influence the drying parameters of foods [4]. Previously extensive research was done to model and explain physical phenomena of AFD of apples [5,6]. These studies revealed high amounts of unfrozen moisture when drying at -5.0 and -10.0 °C. Also, geometric parameters behavior during the drying process and influence on shrinkage and porosity of the final product [3]. Organic apples possibly have higher moisture content and need to be investigated. Current experiments investigated drying kinetics and quality of material with against their thermal parameters and formation of ice at different drying conditions. Comparisons provide valuable information to understand factors which influence the process and could have in the planning of future industrial applications. The same principle can be applied to design the drying schemes for other nonorganic foods, which contain higher amounts of sugar content. The quality factors analysis is based on the experimental determination of basic thermodynamics (state diagrams, water sorption isotherm) and physical properties (ice content) of the apples.

Materials and Methods

Experiment description.

Organic apples Royal Gala Malus domestica Borkh of the variety Suedtirol, were purchased on the local market in Trondheim (Norway). Apples were purchased from the same supplier to maximize reproducibility of results. After purchasing they were kept in a plastic container before experimentation to equilibrate the moisture content at 8 ± 0.5 °C for 1 month prior to experimentation. Initial moisture content of the apples was determined at 86.0 + 0.2°C. The apples were cut (with skin, 5 mm thickness, diameter 55 + 5 mm) and steam blanched for 1.0 min at 100.0 °C, before experiments. The Blanching process is necessary to deactivate enzymes, avoid browning, and increase mass transfer of apples during drying [7, 8]. The blanched apple slices were frozen at -56.0 °C in a chest freezer (MDF chest freezer, Sanyo, Japan) before AFD process. The slices were placed in one layer on the plastic tray and transferred to the chest freezer. Complete freezing of the samples (temperature -56.0 ± 1.0 °C) was achieved within 2 hours. After freezing the product was immediately delivered to the drying chamber. The drying was conducted on shelves in an insulated drying chamber (laboratory test unit at NTNU, Norway) with a closed loop air circulation equipped with heat pump. The drying chamber had internal dimensions of 1000.0 mm x 600.0 mm x 300.0 mm and slots for 3 shelves, the distance between shelves was 150.0 mm Figure 1.

Figure 1: AFD Drying set up.

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Experimental variations

Temperature: +20.0, +3.0, -5.0 and -10.0 °C. The temperatures of -5.0 and -10.0 °C are selected for and the most representative of the AFD process. The temperatures of +20.0 and +3.0 °C were used for comparison of drying mode on drying kinetics, colour and sorption properties of the material. Some experiments were conducted at -5.0 to -10.0 °C. This way was selected according to DSC findings of ice in apples.

a) Relative humidity of air was kept at 45.0 ± 3.0 %.

b) Drying air velocity for all cases was 1.5 ± 0.2 m s-1.

Dehydration was terminated when moisture slightly below 20 % d.b. because it was found that the drying rate of apple slices was extremely low at moisture contents below this value. The dry basis (d.b.) moisture content was determined by vacuum drying at 70.0 °C for 17.0 hours using Alpha 2-4 LSC Plus vacuum-freeze dryer with a LyoCube 4-8 chamber (Martin Christ GmbH, Germany). This method was applied to fresh and dried apples to obtain samples of extremely low water content for the DSC investigations.

Drying kinetics

The drying kinetics were analyzed by Newton model [9], equation (1):

$$MR = \exp(-kt) \qquad (1)$$

The more accurate way to represent dehydration is by effective moisture diffusivity. It was derived from the dehydration kinetics of the analytical solution of the Fick's second law of diffusion (infinite slab) [10], equation (2):

$$MR = \frac{8}{\pi}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-(2n+1)^2\pi^2 Deff^{t}}{4(h)^2}\right) \qquad (2)$$

In other investigations a modification of the Weibull distribution model is used for analyzing the comparative drying behavior of products in AFD [11]. The modified Weibull model gives an accurate mathematical description of the drying rate. However, the determination of the effective diffusion (Equation (2) is more common in food technology since it is independent from the shape factor used in the Weibull approach. Deff was determined by plotting of experimental drying data in terms of ln (MR) versus drying time (t). The slope of this quasi-linear curve was used to obtain the values of the effective diffusion coefficient. This method considers constant diffusion. Of course, the model will overestimate the MR decreasing in the beginning of the process. This was considered by many researchers to describe the drying process.

Sorption and desorption properties

Equilibrium moisture content of foods with respect to relative humidity and temperature of air is essential for the design of the drying process and the storage conditions. Sorption isotherms were determined at 25.0 °C by equilibration of the dried samples (1.5-3.0 g) in a sealed container (KMF 240, Binder, Tuttlingen, Germany) maintaining a set mode continuously (temperature ±0.1 °C; RH ±1.5%) until the weight of the sample stabilized (±0.001 g). Relative humidity was altered stepwise in the range between 20.0 and 80.0 %. The same procedure was used for preparation of the samples with different moisture content for differential scanning calorimetry (DSC) investigation for the determination of state diagram.

DSC experimentation

It was carried out with a DSC Q 2000 (TA instruments, USA) comprised with a Liquid Nitrogen Cooling System. The heat capacity was calibrated with a Sapphire in the range of –150.0 and 180.0 °C. Purge gas was Helium at 25 mL min-1, according to TA's instrument advice. The reference sample used was an empty hermetically sealed aluminum pan. The samples of 3.0 mg and 20.0 mg were put into aluminum pans and closed with hermetic lids using Tzero® DSC Sample Encapsulation Press (TA Instruments, USA) before placed into the DSC cell by an autosampler. Samples were cooled and equilibrated for 5 minutes at –150.0 °C; with cooling rate of 10.0 °C min-1. Subsequently they were heated to 150.0 °C with a heating rate of 10.0 °C min^{-1}. Samples with higher moisture content (higher than 25.0 % w.b.) were annealed for 15 minutes at –50.0 °C before cooling down to -150.0 °C. This was done to avoid cold crystallization during scanning. Afterwards the samples were heated to 80.0 °C with a heating rate of 10.0 °C min^{-1}.

Glass transition and incipient melting point

The glass transition was found by TA Universal Analysis 2000 version 4.5A software (TA instruments, USA). It was characterized by the onset, end, and inflection points. In samples the inflection point was determined as a negative peak of the derived heat flow curve and end of freezing was detected by DSC heating curve [11]. Determination of ice content and unfrozen water the amount of ice content and unfrozen water was found by the analysis of DSC melting curve. It seems pertinent and adequate. The DSC melting peaks were integrated with the sigmoidal tangent baseline function from the incipient point of melting to the full melting of ice. Straight baselines were drawn from each limit, and an S-shaped curve was drawn to connect the two baselines before and after the transition. The shape of the curve was obtained by considering the slope of the heating curve before and after the ice melting peak. The perpendicular drop function was used with temperature steps of 2.0 °C to determine the melting energy for the specific temperature range. The amount of ice (kg/kg), which melts in a defined temperature range (ΔT = 2.0 °C for this study), was calculated as the ratio of melting energy to latent heat of fusion. It should be noted that latent heat of fusion is a function of temperature (LT, kJ kg-1), which decreases with decreasing of the melting temperature. The correction of the latent heat of melting

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of ice with the temperature significant in the small temperature range of experiments, i.e., between -5°C and 10°C. This correction seems symbolic and negligible. Thus, Riedel's correlation was used [12] for corrections in Equation (3):

$$L_T = 333.5 + 2.05 * T - 4.19 * 10^{-3} T^2 \quad (3)$$

The correction is significant when the un-freezable water content is determined. This dependence was used not only for those two temperatures.

State diagram

The thermal transitions can be found using the state diagram. A typical state diagram consists of the freezing curve (the influence of a solid matter content on the reduction of the freezing point) and the glass transition curve. Freezing point of semi-dried apples with different moisture contents were obtained. The decrease of the freezing point behavior was characterized with the Clausius-Clapeyron equation modified for food [13] Equation (4):

$$\delta = -\frac{\beta}{M_W} \ln\left(\frac{1 - x_s - Bx_s}{1 - x_s - Bx_s + Rx_s}\right) \quad (4)$$

Influence of the solid content on the glass transition temperature was modeled with the Gordon-Taylor equation [13], Equation (5):

$$T_{gi} = \frac{x_s T_{gi.s} + kx_w T_{gi.w}}{x_s + kx_w} \quad (5)$$

Statistical analysis

The analysis of variance (ANOVA: single test and two-factor test with replication) was used for the data. The difference was considered significant at p<0.05 and experiments were conducted in six replicates. A regression analysis was carried out with a software Data Fit 8.1 by Oakdale Engineering. The quality was represented by: F-Ratio, Prob (F) and R2. 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. R2 is the coefficient of multiple determinations. The standard deviation is introduced in the brackets after the values given in the text.

Results and Discussion

Thermo-physical properties of apples

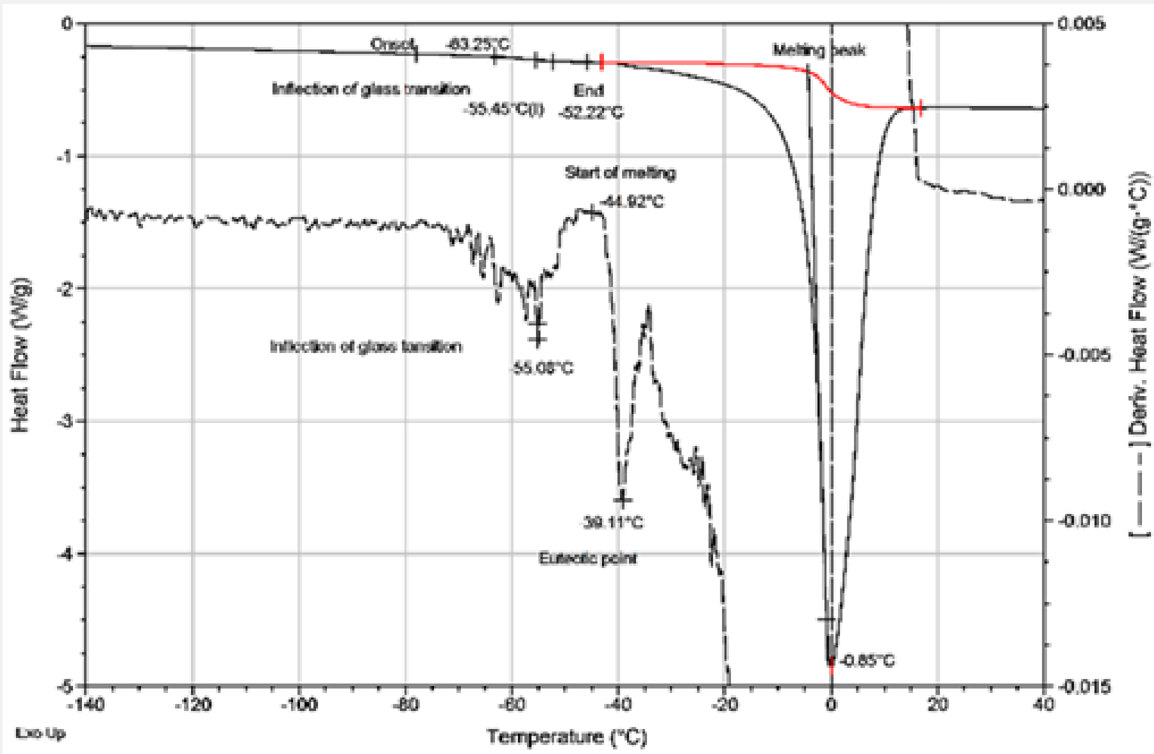

Figure 2(a): Main thermal transitions of fresh blanched apples (a) and semi-dried blanched apples.

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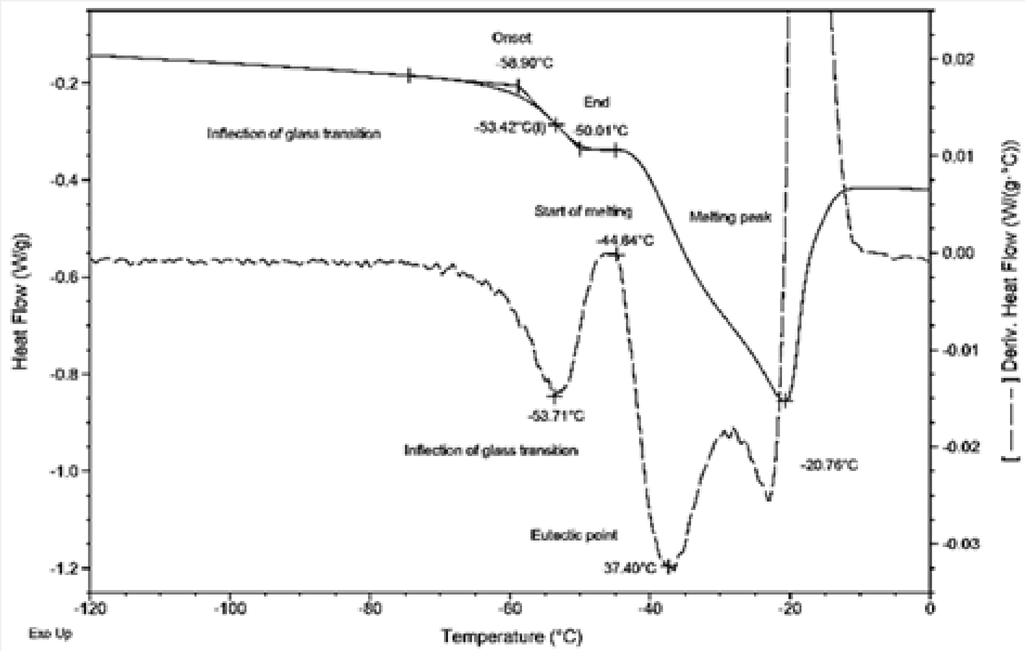

Figure 2(b): DSC heat flow curve (solid) and its derivation by temperature (dashed).

DSC heat flow curve for fresh apples revealed following endothermic processes: glass transition of maximal freeze concentrated solution and melting of freezable water. Maximal is a traditionally accepted term to describe such critical concentrations of water in the product. The maximal freeze concentrated solution is formed by unfreezable water and water-soluble solids (at equilibrium freezing) [14]. Figure 2 shows thermal transitions of apples. Figure 2(a) is for fresh blanched apples and Figure 2(b) for semi-dried blanched apples. Glass transition of fresh apples was weak (more water content), but it was easily observed on the deviated heat flow curve (Tg,i = -55.08 °C on Figure 2(a). At the same time, decreasing amount of freezable water (semi-dried blanched apples on Figure 2(b) shift visible on the heat flow curve, Tg,i = -53.42 °C. All the apple samples showed ice melting peaks, formed the same maximal freeze concentration irrespective of the moisture content. Thus, the glass transition shift was detected in the same temperature range (Tg,i between -55.5 and -53.0 °C) as for fresh blanched apples.

At the same time, the samples, which did not show ice melting peak (the concentration of water is equal or below maximal freeze concentration), showed different trends. The glass transition strongly depended on moisture content: it increased with decreasing moisture in the samples. Carbohydrate content (mono and di-saccharides) influenced the detected phase transitions in apples as soon as protein content is very low. Inflection points of glass transition of dried apples (0.5 (0.3) % d.b.) in the range between at 38.0 and 46.0 °C. Such deviation can be explained by accumulation of moisture during sample preparation for the DSC. Water molecules work as plasticizers and even small amount of moisture can decrease glass transition temperature significantly [15, 16]. The observed temperature ranges of glass transition of dried apples correspond to glass transition behaviour of mixture of simple sugars. When the glass transition decreased within increasing of drying temperature from 30.0 to 60.0 °C. It may occur due to degradation of sugars during drying process. However, this study did not show such dependence behaviour. The melting peak (solid line) of the freezable water in quite narrow temperature range, which indicated high amount free water in the product. However, the incipient point of melting (end of equilibrium freezing) was detected at temperature of -44.2 °C. Eutectic point was detected on DSC heat flow curve in the temperature range -39.2 and 37.4 °C. It was introduced as a weak bend of the melting peak line (negative peak on the derived heat flow curve (-39.11 and -37.40 °C)). It should be noted that some authors reported this phenomenon as a second glass transition [17] . However, in this study such event occurred in the vicinity of the incipient point of melting irrespective of the moisture content and it was not detected for all the samples with low moisture contents.

Integration of the melting peak from the incipient melting with Riedel's equation [18] calculate amount of frozen matter. Results calculations are in Figure 3(a) as variation and Figure 3(b) shows physical interpretation. Most of the freezable water was in crystalline form between -3.0 and -10.0 °C (the typical range for AFD process) [5, 18]. At the same time, the moisture

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content of unfrozen solution was also very high and varies in the range between 60.0 and 43.0%. This influenced the drying process. The retreating of ice front from surface to the inner parts of product with formation of porous zone [19] will not occur at given conditions. The drying process at temperatures between -10.0 and -3.0 °C will result in evaporation of unfrozen water with subsequent melting of ice crystals on the surface and inner parts of product. This process is shown in Figure 3(a, b) as graph and schematic. Ice crystals on the surface are covered with thin layers of brine at such temperatures [20]. In such case moisture gradient will appear in the product rather than in the dry zone. It should be noted that the actual temperature of the product will be different from the drying air temperature. Such differences are influenced by geometry, nature, and chemical composition of product.

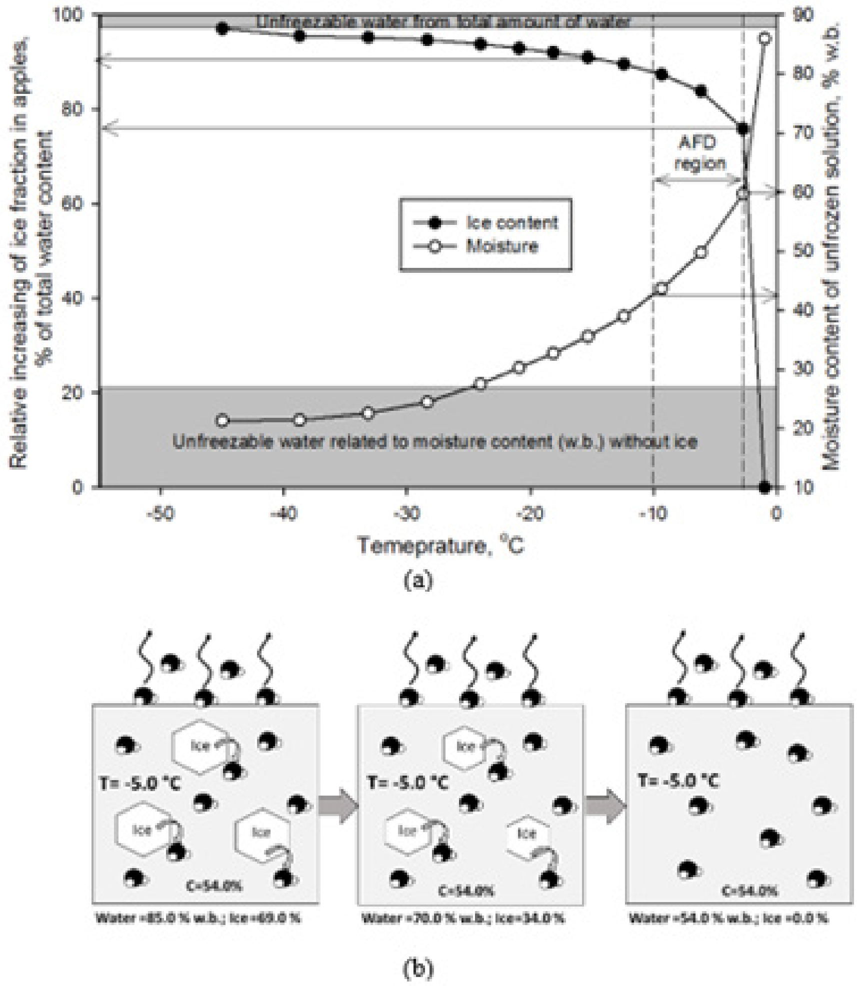

Figure 3: Ice and moisture of unfrozen solution at temperature.

State diagram for organic apples

The inflection glass transition was used for the modelling. The parameters of the models are given in (Table 1). The application of state diagram, Figure 4, predict quantity of ice formation during drying with respect to moisture content. To decrease the drying air from -5.0 to -10.0 °C to avoid ice melting during atmospheric freeze-drying [21]. However, such manipulation with drying temperature will postpone full melting of ice in the product. The full melting of the ice will occur when the concentration of solid fraction reaches equilibrium solids content at a given freezing temperature, Figure 3 (dashed line). Another important issue is glass transition of samples when the freeze concentrated solution will solidify. Such phenomena depend on solid fraction and temperature. Subsequent increasing of temperature will help to avoid unnecessary glass transition during drying.

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Table 1: 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	$5.48*10^{-5}$	$12.78*10^{-2}$
Grodon-Taylor	502.0	$2*10^{-5}$	0.99	k	$T_{gi.s}$
				4.19	42.902

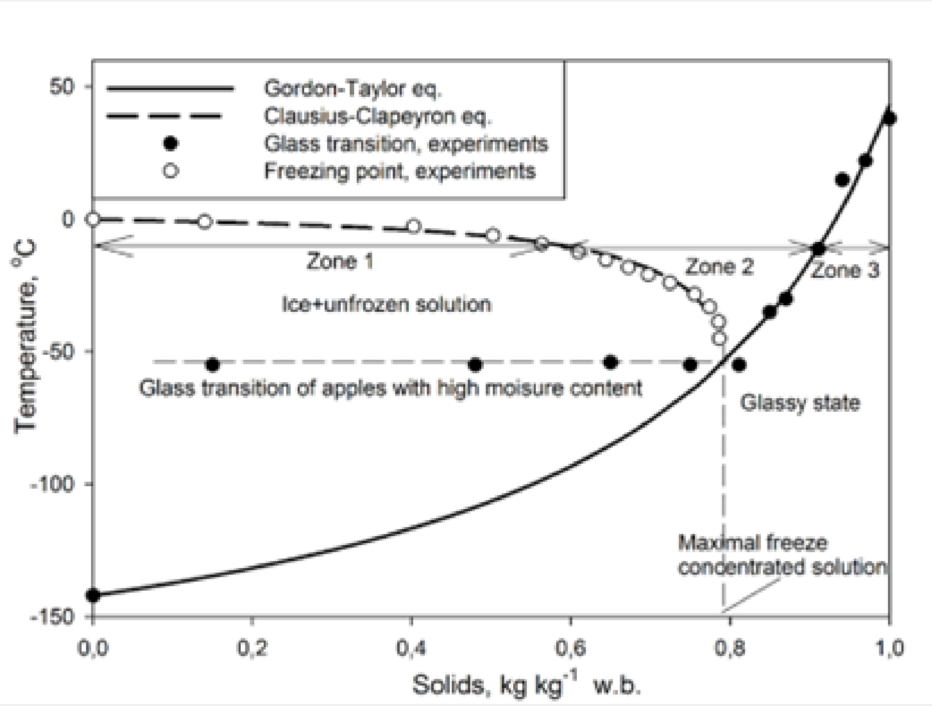

Figure 4: State diagram for organic apples.

The phenomena in Figure 4 can be described as follows. Drying at -10.0 °C, can be divided into three different zones. The product will retain its shape in "Zone 1" where the product will have approximately the same liquid content due to the decreasing of moisture content will be compensated by melting ice (following Clausius-Clapeyron line). The temperature of the product will be slightly lower, when compared with drying air temperature. The real value will strongly depend on system design parameters: air flow, RH, distribution of product etc. The shrinkage development will be observed, when the product comes to "Zone 2", after -10.0 °C, to avoid shrinkage is to decrease the drying temperature (for ice formation) or to increase the temperature for acceleration of the drying rate. The "Zone 3" and vicinity of the "Zone 3" is not beneficial for drying, because this is the zone glass transition. The viscosity in vicinity of the glass transition reaches 1012 Pa*s [22]. This will decrease the drying rate significantly and shows crossing the glass transition line make the product crispy and brittle, as soon as viscous-elastic characteristics of the product disappear in the region. However, the moisture gradient in thick apple slices will create the situation when all the three zones will appear simultaneously during the freeze-drying.

Drying kinetics of organic apples

Figure 5 shows the influence of temperature and drying method on the colour of the apples. Main characteristics of the drying process with respect to phase transition, which happens during the dewatering of the samples, are presented on Figure 6 as drying rate Figure 6(a) and ice content Figure 6(b). The drying kinetics was investigated for blanched fresh apples at drying temperatures of -10.0, -5.0, +3.0 (as a reference sample). In addition, dynamic drying was applied to understand the influence of ice formation of the drying process. The term "dynamic" was

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used to characterize the step change of drying temperature during the drying process. Dynamic means change in temperature during the drying process, which influences the ice content in the product. The drying air temperature was decreased from -5.0 to -10.0 °C after 15.0 hours of drying (MR=0.41). The low temperature convective drying at +3.0 °C was used as a reference to compare and clarify the main influencing factors.

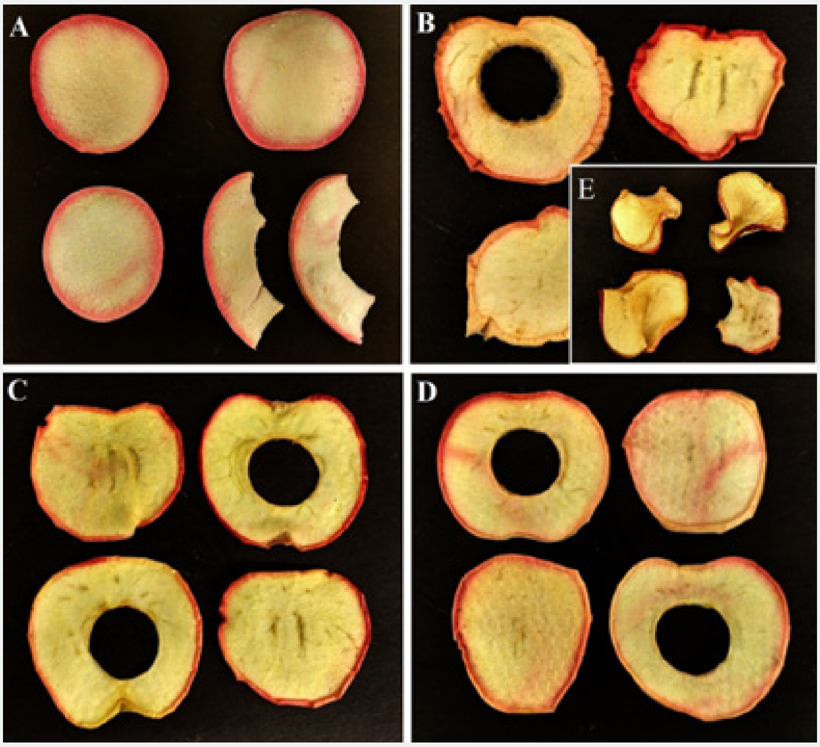

Figure 5: Influence of temperature and drying method on color and quality of apple slices: A – vacuum freeze-drying; B – drying at +3.0 °C; C – drying at -5.0 °C; D – drying at -10.0 °C; E – drying at +20.0 °C.

All the investigated regimes showed falling drying rate. The same observation was made in the investigations other agricultural products [23] where the drying rate was continuously falling already in the beginning of drying, even for products with high moisture content [24] which approves statement that diffusion can be considered as the dominant mechanism of moisture transfer during the atmospheric freeze-drying of apple slices. Drying at +3.0 °C showed typical quasi-linear decreasing of drying rate, which was reported for convective drying of apples before [25,26]. At the same time, drying at -5.0 and -10.0 °C showed quasi-constant drying rate in the MR range between 1.0 and 0.7. This can indicate the absence of shrinkage and constant transport of moisture from inner parts to the surface of the apple slice in the case of AFD. The structure of the samples was maintained by presence of ice crystals, which fraction was higher for samples dried at -10.0 °C (75.7 %) comparing with -5.0 °C (70.7%). The moisture content in the unfrozen solution is maintained at 57.0 and 40.0 % w.b. due to continuous melting of ice. The balance was interrupted when the moisture ratio reached value of 0.7. This can be explained by full melting of ice in the surface layer of the apple slices, the moisture gradient appeared within the thickness. The high difference between drying rate of apples at -5.0 and -10.0 °C, which was observed in this study, was reported before [27]. It influenced by drying properties of air, temperature and concentration of solids which was determined at 43.0 and 60.0 % w.b. (see Figure 2 and 3). Seems to be that concentration of sugars can be the dominant factor, which influences moisture diffusivity. Viscosity increases exponentially with the increasing of sugar content [28] and this phenomenon can reduce transport of water molecules through the product significantly Figure 5.

At the same time, drying at -5.0, -10.0 °C, looking at dynamics of drying showed non-linear falling drying rate, which can be split into two parts. The first part, which was detected in the MR range between 1.0 and 0.6, can be considered as a quasi-constant drying rate, Figure 5(b). This can indicate the absence of a moisture gradient due to melting of ice. The moisture content in the unfrozen solution was maintained at 57.0 and 40.0 % w.b. respectively. The balance was interrupted when the moisture ratio reached the value of 0.7 and 0.6 for drying at -5.0 and -10.0 °C. Such a transition can be explained by the full melting of ice in the surface layers of the apple slices. Thus, the moisture gradient

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appeared within the thickness and the drying rate showed the same trend as for drying at +3.0 °C. It is remarkable that the drying rate doesnot show a significant difference (p>0.05) between drying temperatures of +3.0 and -5.0 °C, when the MR was below 0.5. That period was characterized by the development of shrinkage in the apple slices, which was reflected in reduction of thickness of apple slices.

In the beginning of the AFD process, the structure of the samples was maintained by presence of ice crystals, the fraction of which was higher for samples dried at -10.0 °C (75.7 %) compared to -5.0 °C (70.7%). The reduction of the ice fraction accelerated together with decreasing of MR. The application of dynamic regime resulted in a subsequent increasing of the ice fraction from 41.0 to 45.0 % calculated values, dashed line on Figure 6(a). The decreasing of temperature to -10.0 °C resulted also in a slight slowdown of the drying process (average values), when compared with drying at -5.0 °C. This can be observed in the drying rate curve Figure 6(b) or the drying kinetic curve Figure 6(b).

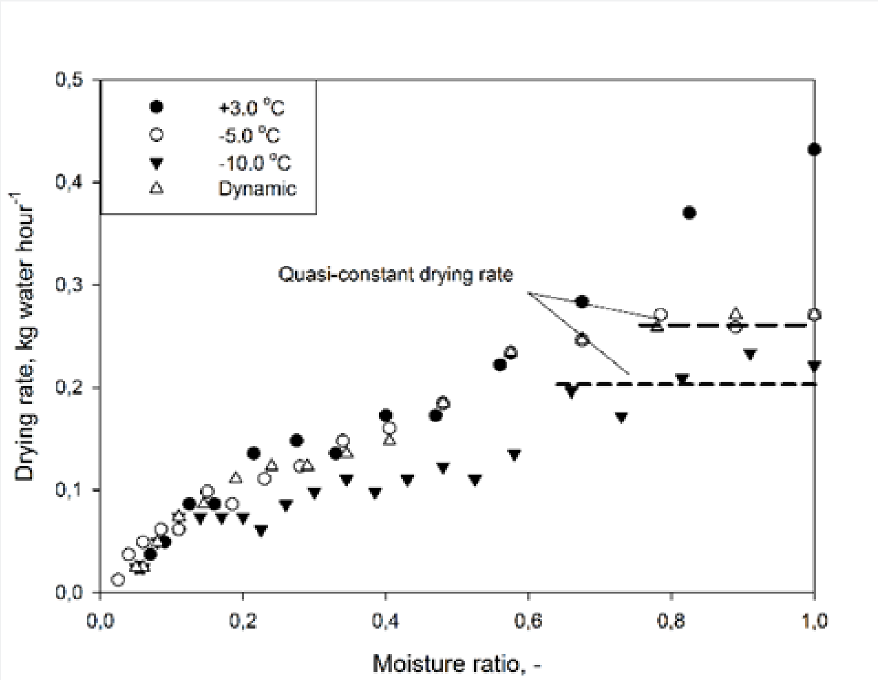

Figure 6(a): Drying rate of organic apples with respect to drying temperature.

However, the statistical difference between drying at -5.0 °C and the dynamic drying was negligible (p>0.05) due to a relatively high variation in results between the parallel experiments. The drying kinetics was modelled using Newton model and solution of the Fick's second law of diffusion (infinite slab), (Table 2). The effective diffusivity values, which were obtained in this study were relatively low, varying from 1.53 to 2.14 *10-10 m^2/s for the atmospheric freeze-drying process (Table 2). Other research devoted to different regimes of AFD of apples at -5.0 °C determined the effective diffusion value in the range between 3.44*10-11 and 1.40*10-10 m^2/s [2]. Sample sizes were similar as in the current study (40x12x4 mm). The same trend was observed before, when branched apples dried faster during AFD, when compared with freshly frozen.

Average effective moisture diffusivity and the drying constant increased with increasing temperature. A recent study revealed the effective moisture diffusivity (5 mm thick slabs) for convective drying of apples at 3.22*10-9 m^2/s at 40.0 °C and air velocity of 0.5 m/s(33) . The increase of temperature to 65.0 °C results in an alteration of moisture diffusivity up to 7.3*10-8 m^2/s [27]. The normal range of moisture diffusivity for foods was found to be between 10-9 and 10-12 m^2/s [29]. The values of effective moisture diffusivities lay far below the values of the high temperature drying process. However, it provides gentle and energetically effective treatment of the product [1, 2]. Dehumidifying of the apple slices during AFD was not uniform, melting of ice on the edges was much higher. Thus, effective diffusion coefficient can be considered as an apparent diffusion. The drying process in the dynamic mode was faster, when compared with AFD at -10.0 °C. At the same time, there was no statistically significant difference in drying time, and drying rates between dynamic process and drying at -5.0 °C.

The drying rate decreased for all the drying temperatures at MR below 0.5. That period was characterized by the development

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of shrinkage in the apple slices, which was reflected in reduction of thickness of apple slices. All the ice melted in the apple slices at MR of 0.18 (26.0 hours) and 0.12 (41.8 hours) when drying at -5.0 and -10.0 °C respectively, Figure 4(b). The dynamics of drying was used to understand the influence of ice formation of the drying process. As it can be observed on Figure 6(b), the air temperature was decreased from -5.0 to -10.0 °C after 15.0 hours of drying (MR=0.41) when the ice fraction decreased to 40.0 %. It resulted in subsequent increasing of ice fraction to 45.0 % at 17.5th hour of drying calculated values, dashed line on Figure 6(b), while no stagnation or interruption of the process was observed on drying kinetic curve or drying rate. The decrease to -10.0 °C also in slight slowdown the drying process (average values), when compared at -5.0 °C. Probably, decreasing temperature and ice formation redistributed moisture in the samples due to osmosis. However, statistical difference between MRs was negligible (p>0.05) due to relatively high variation in results between parallel experiments. The drying kinetics was modelled using Newton model and using analytical solution of the Fick's second law of diffusion (infinite slab), (Table 2).

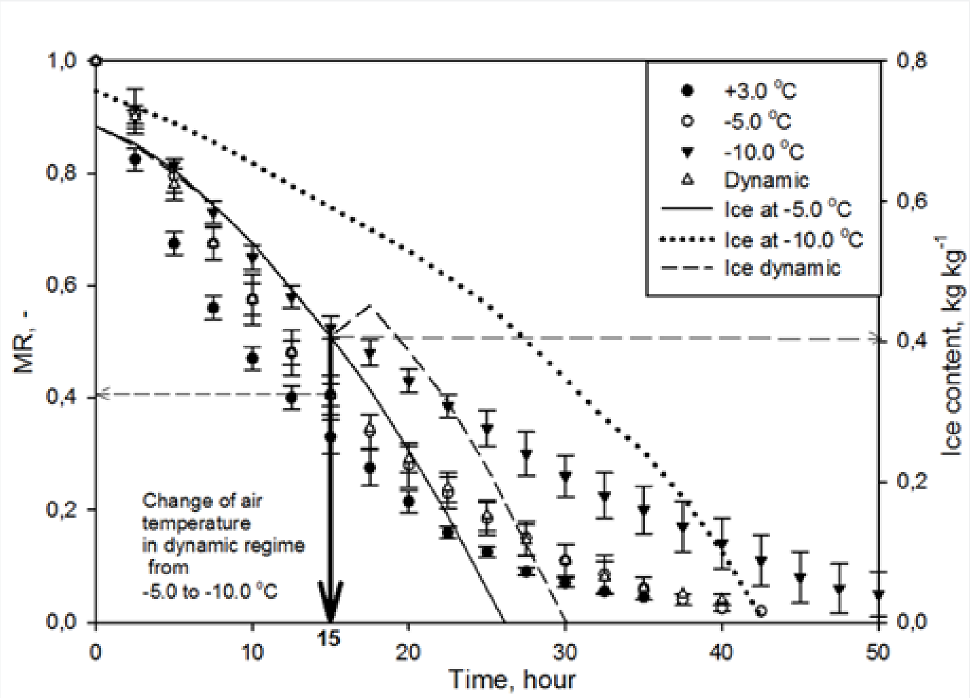

Figure 6(b): Drying kinetics (dots) and ice content development during drying (line) with respect to drying temperatures (b). The lines reflect average data.

Table 2: 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 °C Dynamic drying	0.0608	1.7	>0.99	>2224.0	0
The values are introduced with a confidence interval of 95.0 %					

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The effective diffusivity values, which were obtained in this study were relatively low. At can be seen form (Table 2), effective moisture diffusivity varied in the range between 1.3 and 1.8 $*10^{-10}$ m^2 s^{-1} for atmospheric freeze-drying process. At the same, the research devoted to different designs of AFD of apples at -5.0 °C determined the value between $3.44*10^{-11}$ and $1.40*10^{-10}$ m^2/s [1]. The same trend was observed before, when branched apples dried faster during AFD, when compared with freshly frozen.

The recent study revealed moisture diffusivity for convective drying of apples at $3.22*10^{-9}$ m^2/s at 40.0 °C and air velocity of 0.5 m s^{-1} [30]. Further increasing of temperature to 80.0 °C results in alteration of moisture diffusivity up to $7*10^{-8}$ m^2/s. The normal range of moisture diffusivity for foods was found between 10^{-9} and 10^{-12} m^2/s [31]. It should be noted, that dehumidifying of the apple slices was not uniform and the ice melting on the edges of the apples slices was much higher, when compared with their middle part. Thus, the effective diffusion coefficient in this study can be considered as a relative value.

Sorption isotherms of organic apples

Sorption characteristics were determined for apples, which were dried at -10.0, -5.0, dynamic regime, +3.0 and +20.0 °C, with the aim to determine the influence of drying mode on structural properties of final product. It showed sigmoid shape (type III, Brunauer's classification), which is typical for products with high sugar content Figure 7. The same dependencies were detected in past research [16, 19, 31]. The sharp increasing of moisture content at high relative humidity (RH>60.0 %) is explained by the effect of solute–solvent interactions associated with sugar dissolution.

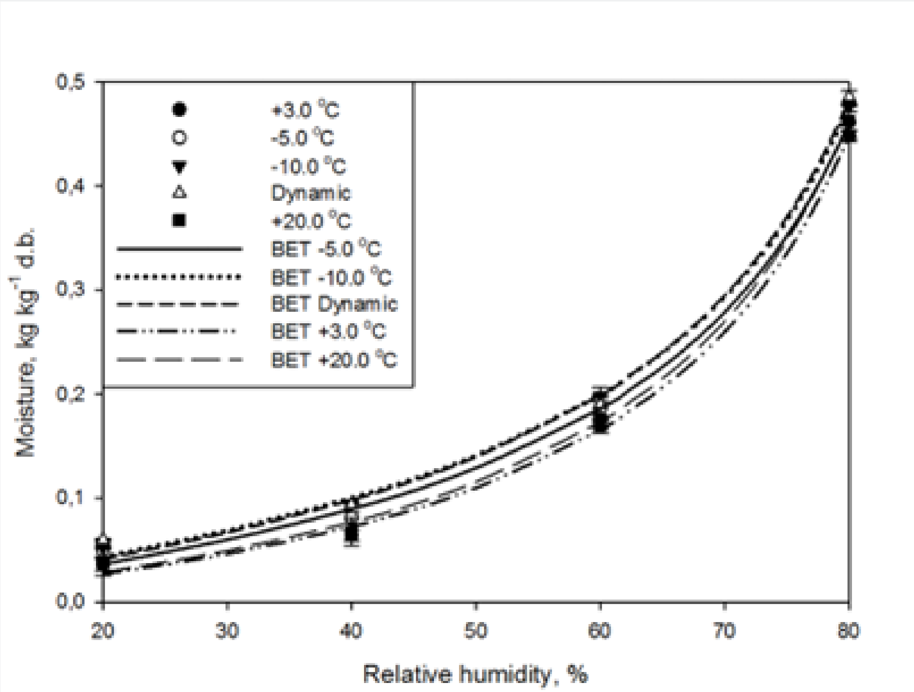

Figure 7: Sorption characteristics of organic apples at 25.0 °C with respect to drying method.

The higher sorption was detected for apples dried at -10.0 °C and dynamic regime ($p<0.05$). Sorption properties was observed between the AFD (group) and convective dried samples ($p<0.05$). Sorption properties of AFD samples increased with decreasing of drying temperature from -5.0 to -10.0 °C. Dynamic mode of drying had the same impact as drying at -10.0 °C ($p>0.05$). Sorption characteristics were modelled using Brunauer-Emmett-Teller (BET) Equation. Moisture monolayer content was determined in the narrow range between 0.108 and 0.116 kg kg^{-1} d.b.. This was lower compared with vacuum dried apple at 70.0 °C, 0.137 kg kg^{-1} d.b. [31]. The study devoted to transition and sorption characteristics of freeze-dried and osmotic dried apples (Golden Delicious) determined monolayer moisture content at 0.112 and 0.081 kg kg^{-1} d.b. respectively [32]. The apples (Golden Delicious) were equilibrated at 30.0 °C and showed monolayer moisture contents at 0.092. Seems to be that low atmospheric drying temperature drying and AFD influence positively on sorption characteristics of final product.

Conclusion

The atmospheric freeze-drying process (AFD) of organic apples thermophysical properties was investigated. The

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experiments were conducted at -10.0, -5.0 and 3.0 (reference) °C drying temperatures. The dynamic mode of drying was also proposed based on the analysis of thermophysical properties with the aim to investigate its influence on quality of the dried apples. The inflection point of glass transition of blanched fresh apples was determined in the range between -55.0 and -53.0 °C. The onset of ice melting of blanched fresh apples was found at -44.2(1.2) °C, when unfreezable water content reached 3.7 (0.3) % w.b. The state diagram of organic apples was obtained using Clausius-Clapeyron and Gordon-Taylor equations. The study revised the amount of unfrozen water content with respect to drying temperatures and moisture content. Initial ice content, when drying at -10.0 and -5.0 °C, was measured at 75.7 and 70.7% respectively. At the same time, significant amounts of moisture were unfrozen at these temperatures. The water concentration in unfrozen solution reached 60.0 and 43.0 % w.b respectively. Thus, the drying process was governed by diffusion process and ice melting phenomena when the so-called ice front does not appear within the thickness of the product. Analysis of drying kinetics revealed at -10.0 °C resulted in significantly longer process. At the same time, sorption characteristics and lightness were much better for samples dried at -10.0 °C, when compared with other samples. The effective diffusivity values, which were obtained in this study were relatively low, varying from 1.3 to 1.8 *10-10 m^2/s for -5.0 and -10.0 °C respectively. Application of dynamic regime provided the effective diffusivity value at 1.7 *10-10 m^2/s and the quality, which was comparable with drying at -10.0 °C. Similar studies could improve the planning of processes and design of the drying process for any food material.

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Nomenclature

- **a)** AFD atmospheric freeze-drying
- **b)** a* redness (CIE L*a*b* color space)
- **c)** B ratio of unfreezable water to the total solids content, kg/kg
- **d)** b* yellowness (CIE L*a*b* color space)
- **e)** C* chrominance (CIE L*C*h* color space)
- **f)** Deff coefficient of effective moisture diffusivity, m^2/s
- **g)** d.b. dry basis, kg/kg
- **h)** DSC differential scanning calorimeter
- **i)** h half thickness of apple slice, m
- **j)** h* hue angle (CIE L*C*h* color space), °
- **k)** k system's constant in Gordon-Taylor equation
- **l)** L latent heat of fusion kJ/kg
- **m)** L* lightness (CIE L*C*h* color space)
- **n)** M molecular mass, kg/kmol
- **o)** MR moisture ratio, -
- **p)** n number of terms
- **q)** R molecular mass ratio of water and solids, kDa/kDa
- **r)** RH relative humidity of air, %
- **s)** SME small and medium sized enterprises
- **t)** T temperature, °C
- **u)** w.b. wet basis kg/kg
- **v)** x mass fraction kg/kg
- **w)** z drying constant, 1/sec

Greek symbols

- **a.** β molar freezing point constant, 1860 (kg K)/(kg mol)
- **b.** ΔE total color difference
- **c.** δ depression of freezing point, °C
- **d.** τ time, min or hours

Subscripts

- **I.** crit critical
- **II.** gi inflection at glass transition
- **III.** s solids
- **IV.** T temperature
- **V.** vac vacuum sample
- **VI.** w water
- τ time, min or hours.

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