Thermophysical properties of frozen parsley: A state diagram representation

Published Version:
Iaccheri E., Cevoli C., Dalla Rosa M., Fabbri A. (2021). Thermophysical properties of frozen parsley: A state diagram representation. JOURNAL OF FOOD PROCESS ENGINEERING, 44(4), 1-7 [10.1111/jfpe.13651].

Availability:
This version is available at: https://hdl.handle.net/11585/792052 since: 2022-02-03

Published:

DOI: http://doi.org/10.1111/jfpe.13651

Thermophysical properties of frozen parsley: a state diagram representation

Eleonora Iaccheri[1], Chiara Cevoli[1,2*], Marco Dalla Rosa[1,2], Angelo Fabbri[1,2]

[1] Interdepartmental Centre for Agri-Food Industrial Research, Alma Mater Studiorum, University of Bologna, Via Quinto Bucci 336, Cesena, Italy

[2] Department of Agricultural and Food Sciences, Alma Mater Studiorum, University of Bologna, Piazza Goidanich 60, Cesena, Italy

**corresponding author: chiara.cevoli3@unibo.it*

Abstract

Sorption behaviour and glass transition of frozen parsley were investigated in order to study the physical modifications, represented as state diagram to figure out information about product behaviour for storage, and supply chain handling. Frozen products may be located in the state diagram in all the possible freezing temperatures to understand the structure state and study feasible corrective actions mainly focused on temperature and solid content.

Parsley was totally dehydrated and equilibrated at selected relative humidity. Sorption behaviour was evaluated by saturated salt slurry method and sorption isotherm fitting, while solid components in terms of mass fraction were investigated by using Differential Scanning Calorimetry. Brunauer-Emmet-Teller (BET) model well fitted with moisture and water activity data (R^2=0.995, *p-level<0.05*). The characteristic ranges of stability, in terms of system mobility and physical modification, are the monolayer values (0.240 water activity; 0.052 kg/kg dry basis) and the critical water activity range (0.424 water activity; 0.078 kg/kg dry basis). Glass transition and melting temperature were used to define parsley state diagram. Different zones figure out a specific physical behaviour: depending on solid content and temperature. Unfrozen water was estimated as monolayer BET value 0.84 kg/kg wet basis and extrapolated from state diagram 0.984 kg/kg wet basis.

Practical Applications

Frozen high-quality product and energy efficiency can be obtained by a correct temperature management. Thermophysical properties of parsley represented in a state diagram are reported in the typical solute and temperature range of freezing process and storage. These data can relate physical structure and temperature, allowing different possible conditions management.

Keywords: frozen parsley; physical properties; state diagram; food chain management

1. Introduction

Parsley is worldwide sold as leafy green herb consumed for its own cooking peculiar flavour, but also widely used as ingredient and drugs (Soysal et al., 2006). Because of its high-water content (78–82%, w/w), parsley is ordinarily processed in order to inhibit microorganism growth and prevent degradation (Doymaz et al., 2006). Minimally processed parsley could stay fresh for a period of 23 days (Catunescu et al., 2012), but the long-lasting operation induced by freezing produce a peerless shelf lifetime (Tolba et al., 2008).

The characterization of biological food tissues is a complicated task, accounting for inhomogeneous arrangement, distribution of cell sizes and shapes, their state and local solute concentrations (Canatella et al., 2004). Water content and temperature are the most important parameters for physical properties assessment of biological products. The role of water in the physical stability of multicomponent system is critical, particularly regarding mechanical properties (such as crispness, softness, etc.) and structure characteristics (crystallization, collapse, etc.). Basically, amorphous, and semi-crystalline polymers, that during their industrial processing undergone a fast cooling from environmental temperatures, end up in a meta-stable state (Priestley et al., 2005). These modifications over a storage time can show themselves through physical properties changes, such toughness, strength, density, and specific heat (Miles, 1991). Thermophysical properties of foods are mainly dependent on chemical composition, time, and temperature. Considering freezing aspects, enthalpy and specific heat capacity of frozen foods are parameters mainly affected by the latent heat of ice fusion (Miles, 1991). Thus, understanding of water/ice equilibrium and phase transition is the basis to understand physical properties of frozen foods. In summary, the whole interpretation of the food frozen system can be simplified and resumed to a two-phase system liquid and dissolved and undissolved solids, with water and dry matter taken as the main components (Fikiin and Fikiin, 1999). Freezing may be subdivided in several stages. The precooling stage, in which the material is cooled from an initial temperature to the initial freezing point, that is the highest temperature at which ice may exist in a food in thermal equilibrium (Miles, 1991). It should be considered that not all the water can be converted into ice at this transition temperature (Roos, 2012), so a phase change period is present as crystallization of the majority part of water required time (Miles, 1991). Finally, a further reduction of temperature is of central importance to freeze water, the so-called tempering stage in which food during time reaches a final established temperature. The quantity of ice increases as a function of decreasing temperature until a plateau, when this phenomenon goes more slowly. Hence, water and ice rate in every foodstuff is highly time dependent (Miles, 1991). Considering the differences between water and ice physical properties, water phase transitions rule frozen food modifications. Thus, the main physical changes occurring during frozen conditions depending on moisture migration and ice recrystallization (Roos, 2012)

An easy way to show these phases, correspondent to different physical properties of a frozen food, is depicting a stability map able to describe relations among water in the amorphous and crystalline phase, solute freeze concentration and the residual unfrozen water, highlighting the critical zones. In this way, different states of a food as a function of soluble solids and temperature of state transition were displayed to build up a state diagram. In literature, food stability has been formerly reported as a function of thermo physical modifications due to a second order thermodynamic transition, such as glass transition, in which the material undergoes a change in phase but not in state (Roos, 1991) Particularly, the concept of food state diagram based on glass transition and freezing curve has been proposed in the '90s by Roos and Karel, and since then by several other authors (Roos, 1991; Sá and sereno, 1994; Figueiredo et al., 1999; Rantanen et al., 2000; Melton et al., 2002; Rahman, 2004; Rahman, 2006 Rahman, 2009; Guizani et al., 2010; Rahman, 2012; Zhao et al., 2015; Suresh et al., 2017).

Frozen products could be located in the state diagram as a function of solids content and temperature. Based on the location in a defined zone it is possible to estimate the stability of the foodstuff and develop strategies for storage design and management. The objective of this work is to explore the concepts of state diagram and glass transition to figure out the thermophysical properties of frozen parsley.

2. Material and methods

2.1 Samples preparation

Frozen parsley was purchased in a commercial supermarket in Cesena, Italy. Frozen parsley was chosen to investigate the humidity influence and physical properties of a disintegrated cellular structure, in order to well evaluate the possible behaviour of products under storage and distribution conditions. Three packages were employed, and the ingredients of the final product were parsley and sunflower oil (maximum 3%, for preservation purposes). Short time after purchasing, the products was de-frozen at environmental temperature, 22°C ±1, then water content and glass transition for de-frozen parsley was stated at 4.57 kg/kg dry basis and -48.64°C, respectively.

All the samples were then conditioned for about 30 days into a desiccator containing phosphorus pentoxide (P_2O_5) in order to dehydrate and stabilize the samples to the minimum water activity, about 0. Hereafter samples were rehydrated as reported in the following subsection.

2.2 Sorption isotherm

Traditional saturated salt slurry method (DES) was carried out for sorption isotherms assessment. DES method consists in the achievement of a defined hydration level of samples, imposed by salt solution saturation. The salt solution produces a relative humidity of the closed environment, and time is required to the samples to reach a thermodynamic equilibrium with the surrounding atmosphere. Dehydrated parsley samples were positioned inside a hermetically closed desiccator containing, on the bottom, different saturated salt solutions (LiCl, $KC_2H_3O_2$, $MgCl_2$, K_2CO_3, NaBr, and NaCl). The thermodynamic equilibrium was evaluated by weighting samples three consecutive times, considering a steadiness at $\Delta_{weight} < 0.0005$.

Water activity of the equilibrated samples was measured by a dewpoint hygrometer, mod. Aqualab (Decagon Devices Inc., Pullman, WA). Moisture was evaluated by oven method (AOAC 934.06, dry oven at 70°C until steady weight) and hereafter expressed as water content on dry basis for moisture sorption isotherms and as solid content on wet basis for state diagram representation. All the analyses were conducted at least in triplicates. BET equation was chosen to fit experimental data of water content and water activity:

$$X = \frac{V_m \, C \, a_w}{(1-a_w)(1+(C-1)a_w)} \quad (1)$$

X is the water content (kg/kg dry basis), *Vm* is the water content of the monolayer (kg/kg dry basis) and C is the constant related to monolayer sorption heat. According to the literature, BET equation is the best ways to determine the sorption behaviour in mid-low water activity range, particularly it well estimates monolayer moisture content, fundamental parameter for product stability defining the quantity of water un-available for physical structure modifications (Ross, 1991).

2.3 Differential Scanning Calorimetry

The glass transition temperature (T_g) and the initial freezing point were evaluated in triplicate by using a DSC mod. Q20 (TA Instrument, Germany). The DSC was connected to a low-temperature cooling unit mod. System90 (TA Instrument, Germany). For calibration, the same heating rate used for sample measurement was applied under a dry nitrogen gas flux of 50 mL/min. Heat flow was calibrated using the heat of fusion of indium (ΔH 28.71 J/g). Each sample (about 1 mg) was weighed in 50 µl hermetic aluminium pans and then loaded into the DSC instrument at room temperature, using an empty pan for reference. Samples were equilibrated at -35°C for 10 min, and then two heat-cool cycles were applied from -90 to 80°C at 5°C/min. Variations of heat flux (V), displayed as thermogram base line deviations in terms of peak and step changes of the baseline, were evaluated by using the automatic tool of the Software TA-Universal analyser (TA Instrument, Germany).

2.4 Glass transition fitting

The Gordon and Taylor model (eq. 2) was applied to experimental data:

$$Tg = \frac{Tg_s\, X_s + k\, Tg_w\, X_w}{X_s + k\, X_w} \qquad (2)$$

T_g, T_{gs} and T_{gw} are the glass transition temperatures of the sample, solid and water, respectively, instead X_s and X_w are the percentage of solid and water content in the sample, and k is the calculated parameter. The T_{gw} was taken as -135°C, according to average value of the literature data (Roos, 1995). Gordon and Taylor equation describes the composition dependence of the transition temperature of amorphous components, and it is usually used for T_g prediction (Gordon and Taylor, 1952).

3.Results and discussion

The influence of water on molecular mobility is pronounced on system where moisture content is restricted, such as frozen parsley. Prediction of the physical state was based on water mobility assessment in temperature and humidity domains, and also on modelling water plasticization, thus T_g

depression with increasing water content. Sorption data and T_g determination allow the description of changes in physical state that may occur during processing and storage conditions.

Thermal properties of parsley were obtained by using DSC. The annealing conditions selected, holding samples at -35°C, allowed the maximum ice formation leading to a maximum solid part concentration since water solidified alone creating a soluble solid amorphous concentrated phase. Two examples of parsley thermograms are shown in figure 1.

Thermogram of sample equilibrated at 69% of relative humidity (RH) (Fig. 1a) showed ice formation on freezing and rewarming. Ice formation is a first order state transition of water, the passage from liquid to solid and vice versa, it is detected by maximum value of peak correspondent to melting temperature (T_m) and crystallization temperature (T_c). Sample equilibrated at 17% of RH (Fig. 1b) reported no ice formation. Ice melting was found for samples equilibrated at RH higher than 24%. No ice formation means unfrozen water presence, water unavailable to solidified alone. Un-freezable water is the amount of water remaining unfrozen as un-crystallized free water or bound to the solid matrix even at low temperature (Raman et al. 2006). Different state of water could be measured in several way, such as sorption isotherms with monolayer, multilayer concepts or unfreezeable water estimated by DSC (Raman et al. 2006). Several authors estimated un-freezable water content comparing DSC endotherms of samples having freezable water from the plot of meting enthalpy (Roos, 1991). This procedure was used for crackers (Given, 1991), strawberry (Roos, 1987), dates (Rahman, 2004), sucrose (Ablett et al., 1992), cabbage (Paakkonen & Plit 1991) and garlic (Rahman et al., 2005a).

In table 1 the averaged value of temperature for both glass transition and melting point of water in parsley at each a_w levels are reported.

T_g ranges from -5.02 to -46.71°C and, as expected, T_g decrease with water content increase. Melting point at 0.172 a_w was not detected, due to water unavailability according to literature (Duckworth & Smith, 1963).

Linear relation between T_g and a_w can be calculated in addition to sorption isotherm to build a stability map useful for predicting T_g of materials stored at various conditions (figure 2).

The sorption isotherm of parsley at 22°C was fitted with BET model with a good determination coefficient (R^2=0.995, RMSE=0.02, *p-level<0.05*) confirming that the model well described the low moisture region of sorption profiles. The calculated monolayer value *Xm* corresponded to an a_w of 0.24 and a water content of 0.052 kg/kg dry basis. BET monolayer was previously reported as un-freezable water and contributed to metastability of frozen product evaluation (Labuza et al., 1972; Rahman, 2009; Ross, 2012). The monolayer value is the limit under which water is strictly bound to the matrix, hence represent the most stable zone in terms of moisture mobility.

The linear relation created by using experimental data of T_g and a_w was used to calculate the critical a_w value. This critical value was calculated by using the used storage temperature of frozen product (-26°C) and correspond to a water activity of 0.424. According to sorption isotherm the corresponding water content expressed on dry basis is 0.079 kg/kg. Above this critical value physical modifications begin, such as loss of crispness, stickiness of powder and hard candies, recrystallization of amorphous sugars causing caking, mechanical modification including collapse phenomena, loss of porosity as well as diffusion (Gordon and Taylor, 1952; Labuza et al., 1972; Ross, 2012).

Actually, this map can give important indications about product stability. Despite this, equilibrium freezing conditions influenced by the amount of ice formed on temperature and composition are missing information. Freezing curve and glass transition data were implemented in a state diagram to draw several regions with different physical states, as previously reported in literature (Raman 2004, Raman et al. 2006).

State diagram of parsley is shown in figure 3. The state diagram was built starting from temperature and solid content data. T_{gw} and T_{gs} are glass transition of water and totally dried product, respectively. Glass transition of the product at different solid contents are reported, with grey dot, in between and fitted with Gordon Taylor equation (eq. 2). The Gordon and Taylor model show good coefficient of determination value (R^2=0.958, RMSE=0.17, *p-level<0.05*). The value of the calculated k parameter is 3.78, comparable to literature k values of foodstuff (Sá and Sereno, 1994).

The melting temperatures of onset and end point were added to figure out different zone of solute, solution, and solid presence. The freezing curve is created from T_{mw}^{I} and T_{m}^{end} of the product at the higher hydration level (a_w 0.693). B is the melting temperature at the end freezing point. The intersection of vertical interpolation from B to the Tg curve is the point A. The point A is known as unfrozen water. The extrapolated solid content is 0.84 kg/kg wet basis. Similar solid contents were reported in literature for date flesh and garlic (Rahman, 2006, 2005), even if attention to wet or dry basis should be paid to avoid misinterpretation. The calculated solid content of monolayer Xm of the BET equation, other expression of unfrozen water is 0.948 kg/kg wet basis, as expected in agree with state diagram. BET-monolayer solid content value is used as un-freezable water quantification and it can be determined by using different methods. As several works reported (Rahman 2006, 2009, 2012), parsley un-freezable water calculated with BET-monolayer value is higher than that of the extrapolated from the state diagram. These stability values are of utmost importance for process and storage management, as parameters influencing product stability. Several authors (Roos and Karel, 1991; Sá and Sereno, 1994), reports the temperature storage dependence on product degradation. Particularly, it suggests a simple index based on $T_{storage}$-T_g. In this way if T_g correspond to storage temperature no degradation occurs. For frozen food stored at about -26°C this corresponds roughly to the moisture content of the critical water activity, well under the typical frozen product. As guess, frozen vegetables are not totally stable, with time dependent chemical-physical modifications.

Conclusions

The present study maps the phase modification of liquid, rubbery, glassy, and crystal components of parsley by means of a stability map and a state diagram as a function of water content, solid content, and temperature.

The sorption profile of parsley was assessed and integrated with glass transition temperature to draw a stability map. Thermophysical properties of parsley, such as glass transition and melting point, were measured. The temperature ranges from 20 to -135 allowing an easily visualization of the typical process and storage temperatures of freezing. Different zone delineated in the state diagram are characterized by different physical structures of parsley characterized as a function of water and temperature. Considering the supply cold chain of frozen products, the state diagram could provide useful data in terms of critical temperature strictly related to the product physical modification and hence the final quality.

Further work should be done to extend the solid content range and implement the state diagram with deliquescent point data, to provide information also referring to the drying process.

Acknowledgements: This work was supported by CoACh project - Cold management in Agro-food Chains: solutions for process digitalization (Grant number (CUP): CUP D41F18000060009), co-funded by the Emilia-Romagna Region through the POR FESR 2014e2020 funds (European Regional Development Fund).

References

Ablett, S., Izzard, M. J., & Lillford, P. J. (1992). Differential scanning calorimetric study of frozen sucrose and glycerol solutions. Journal of the Chemical Society Faraday Transactions, 88(6), 789–794.

Canatella, P.J., Black, M.M., Bonnichsen, D.M., McKenna, C., Prausnitz, M.R., (2004). Tissue Electroporation: Quantification and Analysis of Heterogeneous Transport in Multicellular Environments. Biophysical Journal, 86, 3260–3268. https://doi.org/10.1016/S0006-3495(04)74374-X.

Catunescu, G.M., Tofana, M., Crina, M., David, A. (2012). Sensory Evaluation of Minimally Processed Parsley (Petroselinum crispum), Dill (Anethum graveolens) and Lovage (Levisticum officinale) Stored at Refrigeration Temperatures. Bull. Univ. Agric. Sci. Vet. Med. Cluj-Napoca - Agric. 69, 205–212. https://doi.org/10.15835/buasvmcn-agr:8762.

Doymaz, I., Tugrul, N., Pala, M. (2006). Drying characteristics of dill and parsley leaves. Journal of Food Engineering, 77, 559–565. https://doi.org/10.1016/j.jfoodeng.2005.06.070.

Duckworth, R. B., & Smith, G. M. (1963). The environment for chemical change in dried and frozen foods. Proceedings of the Nutrition Society, 22, 182–189.

Figueiredo, A.M., Sereno, A.M., Sa, M.M. (1999). Glass transitions and state diagrams for fresh and processed apple, Thermochimica Acta, 329, 31–38.

Fikiin A.K., Fikiin, G.A. (1999). Predictive equations for thermophysical properties and enthalpy during cooling and freezing of food materials, Journal of Food Engineering, 40, 1–6. https://doi.org/10.1016/S0260-8774(99)00026-6.

Gordon, M, Taylor, J. S., (1952). Ideal copolymers and the second-order transitions of synthetic rubbers. I. Non-crystalline copolymers, Journal of Applied Chemistry, 2, 493-500. https://doi.org/10.1002/jctb.5010020901.

Given, P.S., (1991). Molecular behavior of water in a flour–water baked model system. Levine, and L. Slade (Eds.), Water relationships in food, vol 302, 465–483, New York: Plenum Press.

Guizani, N., Al-Saidi, G.S., Rahman, M.S., Bornaz, S., Al-Alawi, A.A. (2010). State diagram of dates: Glass transition, freezing curve and maximal-freeze-concentration condition, Journal of Food Engineering, 99, 92–97. https://doi.org/10.1016/j.jfoodeng.2010.02.003.

Labuza, T.P., McNally, L., Gallagher, D., Hawkes, J., Hurtado, F. (1972). Stability of intermediate moisture foods, Journal of Food Science, 37, 154–159. https://doi.org/10.1111/j.1365-2621.1972.tb03408.x.

Melton, L.D., Rahman, M.S., Bai, Y., Perera, C.O., Smith, B. (2002). State diagram of apple slices: glass transition and freezing curves, Food Research international, 34, 89–95. https://doi.org/10.1016/s0963-9969(00)00128-9.

Miles, C.A. (1991). The Thermophysical Properties of Frozen Foods. Springer Series in Applied Biology, 45–65. https://doi.org/10.1007/978-1-4471-3446-6_4.

Paakkonen, K., & Plit, L. (1991a). Equilibrium water content and the state of water in dehydrated white cabbage. Journal of Food Science, 56(6), 1597–1599.

Priestley, R.D., Ellison, C.J., Broadbelt, L.J., Torkelson, J.M. (2005). Materials Science: Structural relaxation of polymer glasses at surfaces, interfaces, and in between, Science, 80, 456–459. https://doi.org/10.1126/science.1112217.

Rahman, M.S. (2004). State diagram of date flesh using differential scanning calorimetry (DSC), International Journal of Food Properties, 7, 407–428. https://doi.org/10.1081/JFP-200032930.

Rahman, M.S., Sablani S.S., Al-Hasbi N., Al-Maskri S., Al-Belushi R. (2005). State diagram of freeze-dried garlic powder by differential scanning calorimetry and cooling curve methods. Journal of food science, 70 (2), E 135-141, https://doi.org/10.1111/j.1365-2621.2005.tb07086.x

Rahman, M.S. (2006). State diagram of foods: Its potential use in food processing and product stability. Trends Food Sci. Technol. 17, 129–141. https://doi.org/10.1016/j.tifs.2005.09.009.

Rahman, M.S. (2009). Food stability beyond water activity and glass transtion: Macro-micro region concept in the state diagram, International Journal of Food Properties. 12, 726–740. https://doi.org/10.1080/10942910802628107

Rahman, M.S. (2012). Applications of macro-micro region concept in the state diagram and critical temperature concepts in determining the food stability, Food Chemistry, 132, 1679–1685. https://doi.org/10.1016/j.foodchem.2011.09.092

Rantanen, J., Räsänen, E., Tenhunen, J., Känsäkoski, M., Mannermaa, J.P., Yliruusi, J. (2000). In-line moisture measurement during granulation with a four-wavelength near infrared sensor: An evaluation of particle size and binder effects, European Journal of Pharmaceutics and Biopharmaceutics, 50, 271–276. https://doi.org/10.1016/S0939-6411(00)00096-5.

Roos, Y. H. (1987). Effect of moisture on the thermal behavior of strawberries studied using differential scabbing calorimetry. Journal of Food Science, 52(1), 146–149.

Roos, Y., Karel, M. (1991). Applying state diagrams to food processing and development. Food Technology. PubMed 45 (12): 66, 68-71, 107.

Roos, Y.H. (2012). Materials Science of Freezing and Frozen Foods. Food Mater. Wiley Online Library. Sci. Eng. 373–386. https://doi.org/10.1002/9781118373903.ch14

Sá, M.M., Sereno, A.M. (1994). Glass transitions and state diagrams for typical natural fruits and vegetables, Thermochimica Acta, 246, 285–297. https://doi.org/10.1016/0040-6031(94)80096-0.

Guizani, N., Al-Saidi, G.S., Rahman, M.S., Bornaz, S., Al-Alawi, A.A., 2010. State diagram of dates: Glass transition, freezing curve and maximal-freeze-concentration condition. J. Food Eng. 99, 92–97. https://doi.org/10.1016/j.jfoodeng.2010.02.003

Melton, L.D., Rahman, M.S., Bai, Y., Perera, C.O., Smith, B., 2002. State diagram of apple slices: glass transition and freezing curves. Food Res. Int. 34, 89–95. https://doi.org/10.1016/s0963-9969(00)00128-9

Rahman, M.S., 2012. Applications of macro-micro region concept in the state diagram and critical temperature concepts in determining the food stability. Food Chem. 132, 1679–1685. https://doi.org/10.1016/j.foodchem.2011.09.092

Rahman, M.S., 2006. State diagram of foods: Its potential use in food processing and product stability. Trends Food Sci. Technol. 17, 129–141. https://doi.org/10.1016/j.tifs.2005.09.009

Roos, Y., Karel, M., 1991. Applying state diagrams to food processing and development. Food Technol. 45.

Sá, M.M., Sereno, A.M., 1994. Glass transitions and state diagrams for typical natural fruits and vegetables. Thermochim. Acta 246, 285–297. https://doi.org/10.1016/0040-6031(94)80096-0

Soysal, Y., 2006. Microwave Drying of Parsley : Modelling , Kinetics , and Energy Aspects 93, 403–413. https://doi.org/10.1016/j.biosystemseng.2006.01.017

Suresh, S., Al-Habsi, N., Guizani, N., Rahman, M.S. (2017). Thermal characteristics and state diagram of freeze-dried broccoli: Freezing curve, maximal-freeze-concentration condition, glass line and solids-melting, Thermochimica Act, 655, 129–136. https://doi.org/10.1016/j.tca.2017.06.015

Tolba, K.H., Youssef, S.M., Abd-Elwahab, E.S. (2008). Physicochemical Properties and Its Application of Dill (an-Ethum Graveolens) and Parsley (Petroselinum Sativum) and Their Essential Oils, Arab Universities Journal of Agricultural Science, 16, 379–387. https://doi.org/10.21608/ajs.2008.14953

Zhao, J.H., Liu, F., Wen, X., Xiao, H.W., Ni, Y.Y. (2015). State diagram for freeze-dried mango: Freezing curve, glass transition line and maximal-freeze-concentration condition, Journal of Food engineering, 157, 49–56. https://doi.org/10.1016/j.jfoodeng.2015.02.016