J Therm Anal Calorim (2010) 102:383–390
DOI 10.1007/s10973-009-0544-z

Osmo-dehydration of apple pulp studied by means of classical and Knudsen thermogravimetric approach

Paola Pani · Marco Signorelli · Alberto Schiraldi · Danila Torreggiani

Received: 7 August 2009 / Accepted: 2 October 2009 / Published online: 3 November 2009

Abstract Classical thermogravimetry and its modification with Knudsen cells were employed to quantitatively investigate the osmo-dehydration of apple pulp samples. The data allowed realization of the complex mechanism of the process, which is not a mere solvent depletion, since it also implies sugar exchanges between the apple tissue and the hypertonic syrup used to dehydrate the fruit. The comparison between different hypertonic syrups, all at the same water activity, showed that maltose is more effective than either sucrose or a mixture of sugars that mimics the saccharide content of the apple. The conclusions are supported by a thermodynamic analysis of the aqueous solutions of these sugars at a concentration level as large as that of the hypertonic syrups used for the osmo-dehydration process.

Keywords Osmo-dehydration · Apple · Water · Thermogravimetry

Introduction

One of the major problems in fruit storage and processing is the accurate modelling of the migration and location of water. Water is indeed a major component of the system, accounting for about 80% of the overall mass and substantially affecting texture, sensory quality, shelf stability and process compliance [1].

P. Pani (✉) · M. Signorelli · A. Schiraldi
DISTAM University of Milan, Via Celoria 2, 20133 Milan, Italy
e-mail: paola.pani@unimi.it

D. Torreggiani
CRA-IAA, Via Venezian 26, 20133 Milan, Italy

The moisture content of biological materials is partitioned in different fractions and states, depending on the kind of tissutal compartment and the solutes therein hosted. Water is largely engaged in the solvation of solutes, therefore, affecting both their excluded volume and molecular mobility. Due to the presence of extracellular biopolymers, cell membranes and other physical barriers, water molecules of the various moisture fractions have different mobilities, as evidenced by means of NMR relaxometry [2, 3], and are perpetually involved in exchanges between different states.

Water in fruits and vegetables is largely mobile and its thermodynamic activity, a_W, is close to unity, which makes their degradation easy because of microbial spoilage and oxidation [4, 5]. For this reason, dehydration of fruits and vegetables is crucial when they have to be preserved for long periods and/or used as ingredients in the preparation of special foods.

In order to avoid non-enzymatic browning and allow preservation of a number of bioactive components (mainly vitamins and aromatic compounds), any thermal treatment can be deleterious. Mild dehydration techniques, such as low temperature convection drying, freeze drying, etc., should therefore be preferred, possibly in combination with an osmotic treatment, a technique applied as a tool to obtain intermediate and end products of improved quality.

Osmo-dehydration implies draining of the endogenous moisture of the fruit under the driving force of a sugar concentration gradient. The fruit is poured into a hypertonic solution of simple sugars, which sucks out most of the fruit moisture. The result is a partially dried material that is still rather soft, as part of its moisture is retained, making the final product microbiologically unstable. A much drier and stable product is, instead, obtained combining the osmotic treatment with heat drying.

Cell walls and other tissutal sieves do not behave like an actual semipermeable membrane. This means that some fruit solutes (sugars, organic acids, minerals, salts, etc.) are leached into the hypertonic solution and partially replaced by its sugars. Some sugars of the syrup may not actively migrate into the cell, but simply penetrate the intra-cellular spaces. This impregnation effect can be important, and the term 'dewatering—impregnation—soaking in concentrated solution' proposed by Raoult-Wack and Guilbert [6] seems to be more suitable than osmotic dehydration.

Modifying the extent of the partial dehydration and the syrup composition during an osmotic treatment of fruit or vegetable product can not only diversify the end product but also improve chemical, physical and functional properties [7]. Although effective moisture diffusivity decreases normally in osmotically treated fruits, there are some quality characteristics that are better retained than in fresh-dried ones. Several studies have been performed to monitor these changes. Lewicki et al. [8], for example, proved that syrups added with calcium chloride allow improvement of texture and mechanical resilience of tomatoes undergoing osmotic dehydration. Osmotic agents, especially mono- and di-saccharides, play an important role also as protective compounds. Ferrando and Spiess [9] investigated the impact of different disaccharides on cellular shrinkage and cell viability through onion epidermis and strawberry cortex tissue during osmotic treatment. Taking into account the nature and the sugar concentration, they observed that maltose and trehalose had a protective effect on the plasma membrane of onion epidermis cell, maintaining its barrier properties. Parenchymatic cells of strawberry tissue were, instead, not susceptible to any protection effect, no matter the kind of disaccharide employed.

The antioxidant properties of simple carbohydrates in a food system are well known [10]. Lo Scalzo et al. [11] evaluated the influence of carbohydrate addition on stability of phenolics and radical scavenging activity during frozen storage of blueberry juice, showing a significant increase of hydroxyl radical scavenging activity in the juices added with sugar, but no influence on anthocyanin content.

The rate of several collapse phenomena, such as recrystallization of freeze-dried sugars or structural collapse, is governed by the glass transition temperature (T_g). Physical changes are related to viscosity, which, in amorphous materials, such as dried fruits, decreases with increasing $(T - T_g)$ following the WLF-type temperature dependence [1, 12, 13]. Being the physical state of dehydrated food materials one of the rate-defining factors of diffusion-controlled deteriorative changes, such as non-enzymatic browning and phenolase activity [14], the modification of sugar composition in a fruit tissue can also affect the stability of these characteristics. As shown in apricot cubes pre-treated in different sugar solutions [15, 16], the lower ascorbic acid degradation can be related to the higher T_g values of these fruits with respect to the untreated ones: the smaller $(T - T_g)$ values are a consequence of a less severe structural collapse on drying.

All these findings show that the choice of the osmotic syrup plays a very important role, and the specific effect of the solution, such as a_W-lowering capacity, has to be taken into account in a fruit dehydration process.

This article contributes to explain the complex mechanism of water removal from a heterogeneous system such as fruit tissues. It aims to get some information about the changes of a_W, or relative humidity, RH, in apple pulp samples during an osmo-dehydration process in different sugar solutions, by means of classical and Knudsen thermogravimetry (TG), which appeared very suitable to investigate water displacements in food [17] and release of other volatiles from different materials [18]. The conclusions of this study are supported by ad hoc Knudsen TG investigations aimed at determining the thermodynamic activity of water and solutes of the aqueous solutions of the different sugars used as osmotic agents.

Materials

Fuji cultivar apples were purchased at a local store, peeled, cut into spheres ($d = 1.5$ cm) and osmo-dehydrated.

One hour osmotic treatment was performed at room temperature ($\sim$25 °C) with three different sugar syrups of given water activity ($a_W = 0.90$), namely, 63% maltose, 59% sucrose and a 50% mixture (15.6% sucrose, 22% glucose and 62.5% fructose, that reproduced the sugar content of the apple pulp). All the above % concentrations are mass fractions. The hypertonic syrup was continuously recirculated through a peristaltic pump, and the fruit-syrup ratio was kept at 1/8 (w/w) ratio. Since the volume of the syrup was much larger than that of the apple spheres, any dilution of the hypertonic syrup was considered negligible.

At the end of process, the apple samples were accurately and rapidly washed with cold water and weighed. Weight changes of the apple samples were split in: water loss (WL), solid gain (SG) and weight reduction (WR), referred to 100 g of fresh product. Calculations were performed according to the following equations:

$$\mathrm{WL} = \frac{w_{wo} - (w_t - w_{st})}{(w_{wo} + w_{so})}; \quad \mathrm{SG} = \frac{(w_{st} - w_{so})}{(w_{wo} + w_{so})};$$
$$\mathrm{WR} = \mathrm{WL} - \mathrm{SG},$$

where w_{wo}, w_t, w_{so} and w_{st} stand for fruit moisture before treatment; fruit mass after treatment; dry matter before treatment and dry matter after treatment, respectively.

Samples of these apple spheres were used for classical and Knudsen TG.

Classical TG analysis was performed also on apple pulp samples previously osmo-dehydrated to various extents (30 min, 1, 2, 3, 4, 5, 6 and 24 h), to obtain traces at different dehydration levels.

Methods

The instrument for classical and Knudsen TG investigations was a SETARAM TG-DSC111, Lyon, France, which allowed the simultaneous output of TG trace, namely mass-loss versus T, its time derivative DTG and the relevant thermal effect. The sample mass ranged between 10 and 40 mg, and the experimental runs were performed heating from 25 to 140 °C at 5 °C/min heating rate.

The TG trace directly records the mass loss of a sample that undergoes heating at a given rate. When coupled with DSC, the mass loss can be reliably attributed to the release of water if the mass-loss-rate/heat flux ratio has a value of about 2.2 J g^{-1}, namely, the vapourization enthalpy of water [19]. This is the case of the TG traces recorded from salt and sugar solutions, vegetables, fruits and other water rich samples. The mass-loss-rate is the time derivative of the TG trace, currently expressed with the acronym DTG. The DTG trace related to the dehydration of an aqueous solution shows a single broad peak with a maximum around 100 °C (Fig. 1). When the sample is not a simple aqueous solution, since it may be referred to as a multi-phase system, the release of water is governed by the diffusion through phase boundaries, and the relevant DTG trace shows a clearly shouldered peak (Fig. 2).

The Knudsen TG approach was designed by Schiraldi and Fessas [19] to directly determine water activity. The standard thermobalance cells are replaced with Knudsen cells, namely closed cells, the cover of which is pierced

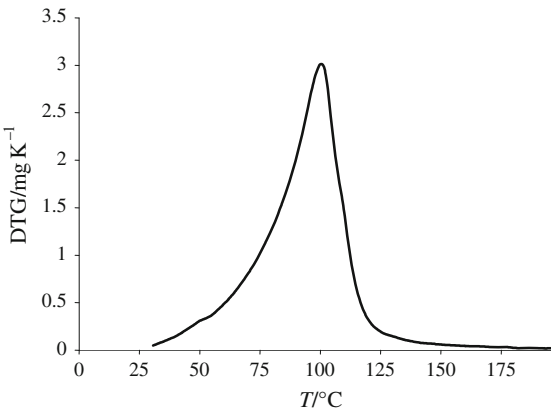

Fig. 1 DTG trace from an aqueous starch suspension

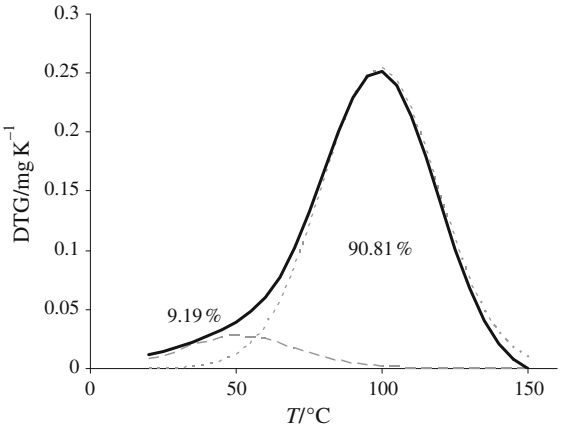

Fig. 2 DTG trace from a sample of apple pulp

with a laser beam so as to form a narrow orifice (20 μm) through which water molecules can diffuse at a rate, J, which, in strictly isothermal conditions and under dynamic vacuum ($p_{ext} \approx 0$), is directly proportional to the water partial pressure, p_W, within the cell,

$$J = \frac{dm_W}{dt} = \propto (p_W - p_{ext}) \approx Kp_W,$$

where K is a constant that depends on the temperature and the size of the Knudsen orifice.

A separate experiment carried out with a pure water sample, at the same temperature and vacuum conditions, produces a flat DTG trace that corresponds to the vapour pressure of pure water, p_W^* (Fig. 3).

The p_W/p_W^* ratio is a good approximation for the value of water activity, a_W, or RH of the sample considered. Since the sample is undergoing dehydration during the Knudsen TG run, the p_W/p_W^* ratio decreases (in absolute value) during the experiment (Fig. 4), so as to allow a direct record of the residual moisture mass versus RH, namely, a desorption isotherm (Fig. 5).

As long as the starting sample can be supposed to exist in an equilibrium state (namely, its various water fractions have the same water activity), the Knudsen TG allows estimation of the actual RH of the sample considered [19, 20].

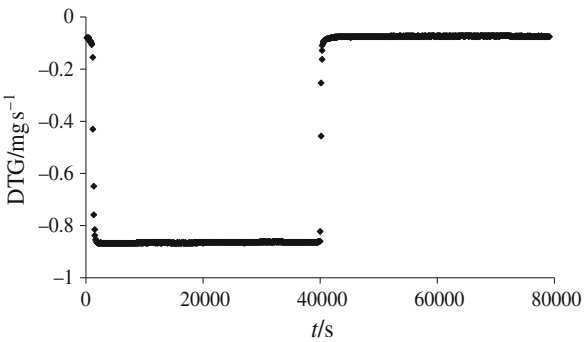

Fig. 3 Knudsen DTG trace of a pure water sample

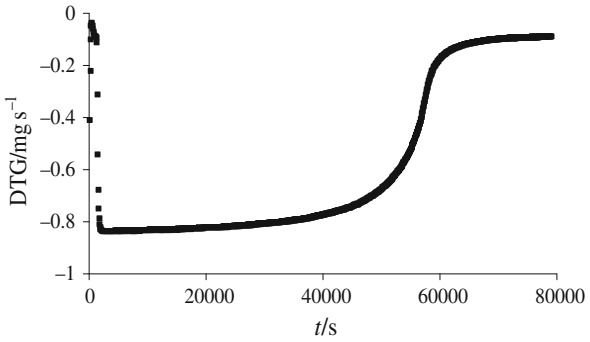

Fig. 4 Knudsen DTG trace from a sample of apple pulp

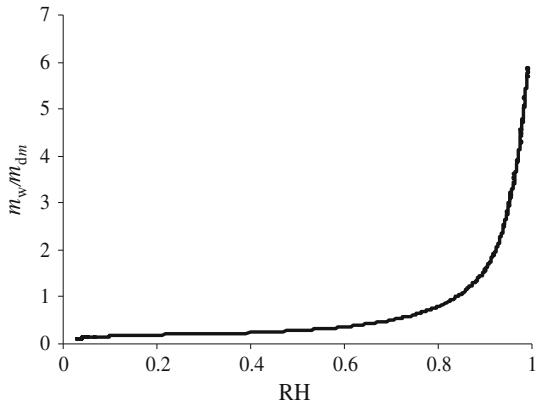

Fig. 5 Desorption isotherm drawn from Knudsen DTG trace of a sample of apple

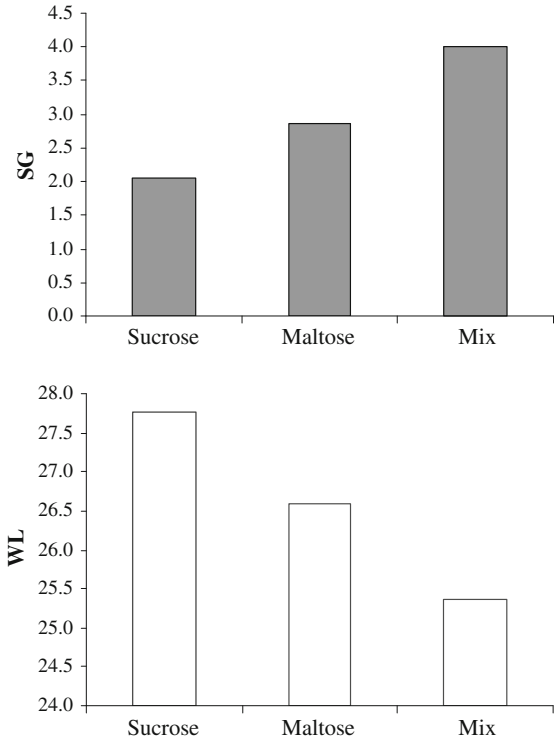

Fig. 6 Solid gain (SG) and water loss (WL), referred to 100 g of fresh apple samples, after 1 h treatment with different hypertonic solutions (sucrose, maltose and mix)

Results and discussion

The solid–liquid exchanges of the apple pulp after 1 h dehydration is reported in Fig. 6.

Although all the hypertonic sugar syrups had the same water activity, $a_W = 0.90$, the WL of the apple pulp samples after the treatment was rather different following the order sucrose > maltose > mixture. At the same time, the sugar content of the apple pulp (SG referred to 100 g of fresh product) increased in the reversed order.

This finding is a major evidence of the fact that the process may not be referred to as a true osmotic migration of the solvent. The proportion of the fruit sugars was indeed modified, which supported the conclusion that some of them were leached out being partially replaced by the sugar of the hypertonic syrup used for the treatment.

Since the molecular mobility of water and small molecular mass solutes may be supposed to be large enough to comply with concentration gradients, the overall process must progress obeying the principle of a negative drop of the chemical potential of every compound. In particular, water activity may be supposed to decrease within the apple pulp, while changes relevant to the hypertonic syrup are negligible because of its much larger mass and volume. However, this is not the case, indeed, as shown in TG experiments.

Classical TG traces (in the form of DTG) of apple pulp samples which had been osmo-dehydrated to various extents (30 min, 1, 2, 3, 4, 5, 6 and 24 h) showed a shouldered signal which was deconvoluted in a couple of gaussian peaks (see below), each related to a given water fraction within the sample. The maxima of these gaussian peaks occurred at different temperatures. This finding can be explained taking into account that the vapourization of water takes place just at the surface of the sample and therefore, produces a water activity gradient across the sample. Water migrates from the core to the surface through the phase boundaries, namely, cell membranes, polymer domains, etc., aiming at levelling its chemical potential. If this migration encounters severe hurtles or is limited by the viscosity of the system, then the separation of the DTG peaks is larger, and the respective vapourization temperatures reflect the differences of water activity in the various compartments or phases of the sample [19], namely,

$$T_{vap} \approx \frac{\Delta_{vap}H}{A + R \ln a_W}.$$

When only short-range displacements are allowed, for instance, as in bread dough [19, 20], each of the DTG peaks

may reflect the actual location of water in the sample before the TG run. If the temperature scan experienced by the sample allows water to easily overcome the constraints through the phase boundaries, then the DTG peaks simply reflect transient water activity gradients produced by the fast release of water at the sample surface. If so, the relevant information may not be used to quantify the amounts of the water fractions within the sample before the TG run.

This is the case of the TG traces collected from apple samples. Figure 7 reports a typical DTG trace of apple pulp which can be mathematically deconvoluted in two gaussian peaks for samples treated with different sugar hypertonic solutions and examined at different treatment stages. The two main peaks in the DTG traces can be referred to as water that is free to evaporate from the core to the surface of the sample (water 1), and as water bound within the apple microstructure (water 2), respectively. According to the percent areas beneath these DTG peaks, the content of free water in osmo-dehydrated samples was larger than in the fresh ones, probably indicating the release of some bounded water from the intracellular compartments, due to the modification of cellular structure caused by the dehydration. There were no significant differences in the water distribution between samples treated with the three kinds of hypertonic syrups, no matter the duration of the osmo-dehydration (Table 1).

This finding was in line with the results of separate investigations (still in progress at the Institute of Food Research, Norwich, UK) aimed to garner direct evidence of different water domains by means of NMR relaxometry and NMR Imaging. Some preliminary results showed that during the osmo-dehydration span (24 h) both relaxation times T1 and T2 shifted towards smaller values, indicating a decrease of ^{1}H mobility, and that the ^{1}H T1 distributions changed towards a bimodal shape (mainly in samples dehydrated with maltose syrup), which could stand for distinct proton populations characterized by different mobility [21].

The Knudsen desorption isotherms of apple pulp after 1 h osmotic dehydration were determined to get some information about the occurred changes of the RH.

The starting sample in an equilibrium state, the Knudsen TG, would allow evaluation of the actual RH. Unfortunately, there is a major limitation in the above statement. As a matter of facts, the faster water displacements at the sample surface are the main responsible for the water partial pressure in the head space of the Knudsen cell. The pressure drop across the Knudsen orifice triggers a core-to-surface water displacement within the sample and produces a water activity gradient that tends to compensate the water removal form the surface. Because of the dehydration, the sample approaches the so-called critical water activity [22], namely, the RH level that corresponds to the glass

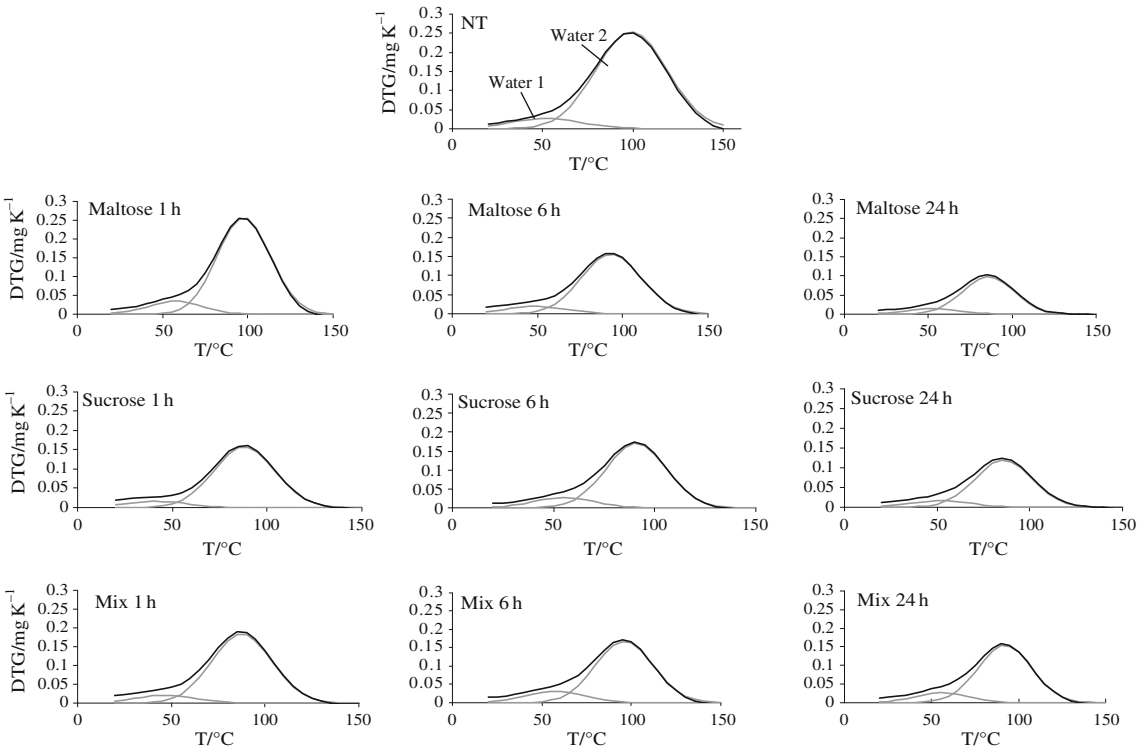

Fig. 7 DTG traces from apple pulp samples untreated (NT) and osmo-dehydrated with a maltose, sucrose and mix solution for 1, 6 and 24 h

Table 1 Percent distribution of the two gaussian contributions (water 1 and water 2) indicating the two kinds of water in apple pulp samples after 1, 6 and 24 h of immersion in different hypertonic solutions (sucrose, maltose and mix)

Time of treatment/h	Maltose		Sucrose		Mix	
	Water 1/%	Water 2/%	Water 1/%	Water 2/%	Water 1/%	Water 2/%
0	9.19	90.81	9.19	90.81	9.19	90.81
1	11.80	88.19	8.51	91.48	9.51	90.49
6	10.59	89.41	13.46	86.54	15.39	84.61
24	12.15	87.85	12.31	87.69	14.67	85.33

transition range of the sample at the room temperature (at which the experiment is being carried out).

Since in this moisture range, the molecular mobility is dramatically reduced, any further dehydration is practically hindered. The Knudsen dehydration is therefore only partial, being related to the water fraction that can find an easy access to the sample surface. The desorption isotherm below the critical water activity is meaningless [23], but the rest of it, namely the curve recorded at higher moisture levels, is reliable and may be used to directly compare different samples [24].

The residual moisture kept by the sample at the end of the Knudsen dehydration can be determined by rising the temperature and recording the further drop of the sample mass. This may be referred to as the water fraction that has no easy access to the sample surface at room temperature.

The situation can be described in an easy way for the dehydration of a solution of a simple sugar, looking at its phase diagram (Fig. 8).

The solubility curve of the sugar has to be matched with the descending trend of the glass transition. This means that any isothermal dehydration can be represented with an horizontal straight line that crosses either curve: the first intercept corresponds to the solubility of the sugar at the temperature considered, while the second intercept is the glass transition threshold that cannot be trespassed [22, 23]; the corresponding moisture level represents the residual water that is kept by the sample and cannot be removed unless the temperature is raised up.

Limiting the analysis of data at the desorption trends observed at high moisture contents, the three hypertonic syrups produced the following effects (Fig. 9): the moisture content was substantially reduced after 1 h treatment, although with different effect on the RH value.

At a given moisture content, the RH of apple pulp treated with maltose was lower than that of non-treated (NT) samples. The opposite was instead observed for treatments with sucrose and mix syrup. This finding suggests that osmo-dehydration actually implies not only water withdrawing, but also some sugar exchange between the apple pulp and the dehydrating sugar syrup.

The available data do not allow a clear explanation, although some tentative arguments may be advanced. Fresh apple pulp does not contain maltose. Because of the drop of the maltose chemical potential, some maltose of the hypertonic syrup migrates toward the apple tissues partially replacing some of the endogenous sugars and fixing more tightly the residual moisture (see below); this can explain why the relevant RH is lower than that of the residual moisture of non-treated apple pulp. The same holds for the sucrose, but its binding power for water is lower than that of the endogenous sugars thus producing an osmo-dehydrated pulp with higher RH with respect to non-treated

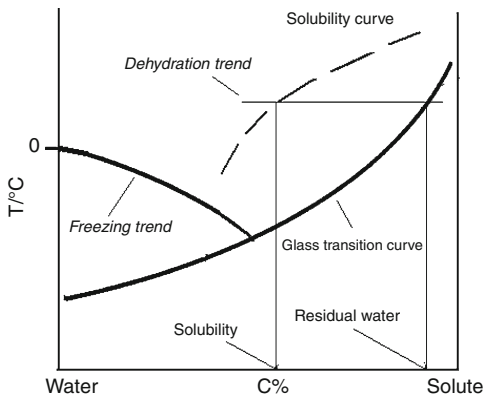

Fig. 8 Schematic representation of the phase diagram of an aqueous sugar. The isothermal dehydration path crosses the solubility and the glass transition curve

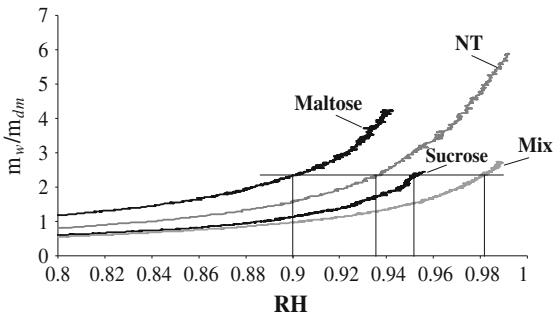

Fig. 9 Desorption isotherms of apple pulp after 1 h osmo-dehydration with different hypertonic syrups. NT stands for non-treated sample

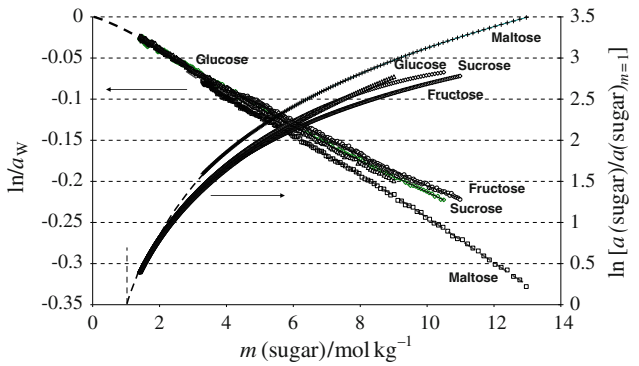

Fig. 10 Water activity (from Knudsen TG data) and sugar activity (calculated via Gibbs–Duhem equation). The reference for the latter was an ideal one molal solution

pulp. The behaviour of the mix syrup would finally be intermediate between the two above.

A support of this tentative explanation comes from the desorption isotherms of the aqueous solutions of maltose, sucrose, glucose and fructose. The a_W data have been replotted (Fig. 10) versus the sugar molality, m. The a_W versus m trend can be used to get the corresponding trend of the thermodynamic activity of sugar via the Gibbs–Duhem equation, namely,

$$\mathrm{d}\ln a_S = -\frac{X_W}{(1-X)_W}\mathrm{d}\ln a_W = -\frac{\text{water mass}}{n_S \times M_W}$$

$$\mathrm{d}\ln a_W = -\frac{m_W}{m}\mathrm{d}\ln a_W,$$

where $m_W = (10^3/18)$ mol kg^{-1} and X_W stands for the water molar fraction. The integration of the above equation can be spanned between $m = 1$ and m, therefore allowing evaluation of the thermodynamic activity of the sugar, a_S, referred to an 'ideal' $m = 1$ solution [25], namely, $[a_S/(a_S)_{m=1}]$ (Fig. 10).

For $a_W = 0.9$ (namely, the water activity of the hypertonic syrups used for the osmo-dehydration treatment), the molality of the sugar ranges around $m = 5$. At this concentration, the thermodynamic activity of the sugar, a_S, is significantly larger for maltose than for the other sugars.

This can justify the different behaviour of maltose which, for a given water activity value, has a larger chemical potential than the other sugars considered.

Conclusions

Osmo-dehydration of apple pulp is much more than a mere solvent depletion process as it implies exchanges of the sugar between the fruit pulp and the hypertonic syrup used in the process. This is the reason why different syrups produce different end products and, therefore, are to be appropriately selected in view of the desired properties of dehydrated fruit. This also means that osmo-dehydration will have different effects on different fruits, according to the nature of their pulp and their endogenous sugar content. Any modelling of this treatment, therefore, demands a previous knowledge of these peculiarities of the product to be dehydrated. Since temperature may not be raised to much, because of the thermo-lability of many fruit components, osmo-dehydration is severely limited by the glass transition threshold, with the consequence that some residual moisture remains within the fruit pulp producing a relatively large RH environment where microbial flora can develop.

The quantitative evaluation of the moisture loss and the relevant residual RH can be achieved via classical and Knudsen thermogravimetry that allowed to recognize maltose that migrates from the hypertonic syrup towards the apple pulp where it fixes water so as to reduce the RH of the fruit more than the other sugars considered in this study. Such a behaviour can be explained taking into account that, at a given sugar concentration, the thermodynamic activity of maltose is larger than that of the other sugars.

References

1. Slade L, Levine H. Beyond water activity: recent advances based on an alternative approach to the assessment of food quality and safety. Critical Rev Food Sci Nutr. 1991;30:115–360.
2. Hills BP. Magnetic resonance imaging in food science. New York: Wiley; 1998.
3. Fullerton GD, Cameron IL. Relaxation of biological tissues. In: Wehrli FW, Shaw D, Kneeland JB, editors. Biomedical magnetic resonance imaging—Principles, methodology and applications. New York: CH Publishers Inc.; 1998. p. 115.
4. Labuza TP, Acott KA, Tatini SR, Lee R, Flink J, MacCall W. Water activity determination: a collaborative study of different methods. J Food Sci. 1976;41:910–7.
5. Chirife J, Bruera MP. Water activity, water glass dynamics, and the control of microbiological growth in foods. Critical Rev Food Sci Nutr. 1996;36:465–513.
6. Raoult-Wack AL, Guilbert S. La Déshydratation Osmotique ou procédé de Déshydratation-imprégnation par Immersion dans des solutions concentrées. In: Les Cahiers de L'Ensbana, L'eau dans les procédés de transformation et de conservation des aliments 1990; 7: 171–192.
7. Torreggiani D, Bertolo G. Osmotic pre-treatments in fruit processing: chemical, physical and structural effects. J Food Eng. 2001;49:247–53.
8. Lewicki PP, Vu Le H, Pomaranska-Laznka W. Effect of pretreatment on convective drying of tomatoes. J Food Eng. 2002;54:141–6.
9. Ferrando M, Spiess WEL. Cellular response of plant tissue during the osmotic treatment with sucrose, maltose and trehalose solutions. J Food Eng. 2001;49:115–27.
10. Morelli R, Russo-Volpe S, Bruno N, Lo Scalzo R. Fenton-dependent damage to carbohydrates: free radical scavenging activity of some simple sugars. J Agr Food Chem. 2003;51:7418–25.
11. Lo Scalzo R, Giussani E, Brambilla A, Torreggiani D. Effect of fruit blanching and carbohydrate addition on phenolics and

radical scavenging activity of blueberry juice during frozen storage. Proceedings of XXIII international conference on polyphenols, Winnipeg, Manitoba, Canada, August 22–25, 2006; p. 423–424.
12. Levi G, Karel M. Volumetric shrinkage in freeze-dried carbohydrates above their glass transition temperature. Food Res Intern. 1995;28:151–4.
13. Roos HY, Karel M. Crystallization of lactose. J Food Sci. 1992;57:775–7.
14. Karmas R, Buera MP, Karel M. Effect of glass transition on rates of non enzymatic browning in food system. J Agr Food Chem. 1992;40:873–9.
15. Torreggiani D, Bertolo G. Present and future in process control and optimization of osmotic dehydration. In: Taylor SL, editors. Advances in food and nutrition research, vol. 48. San Diego: Elsevier; 2004. p. 174–225.
16. Forni E, Sormani A, Scalise S, Torreggiani D. The influence of sugar composition on the colour stability of osmodehydrofrozen intermediated moisture apricots. Food Res Intern. 1997;30:87–94.
17. Fessas D, Signorelli M, Pagani A, Mariotti M, Iametti S, Schiraldi A. Guidelines for buckwheat enriched bread: thermal analysis approach. J Therm Anal Calorim. 2008;9:9–16.
18. Clausen P, Signorelli M, Schreiber A, Hughes E, Plummer CJG, Fessas D, Schiraldi A, Månson JAE. Equilibrium desorption isotherms of water, ethanol, ethyl acetate and toluene on a sodium smectite clay. J Therm Anal Calorim. (published online 09 July 2009).
19. Fessas D, Schiraldi A. Water properties in wheat flour dough, I: classical thermogravimetry approach. Food Chem. 2001;72:237–44.
20. Schiraldi A, Fessas D. Classical and Knudsen thermogravimetry to check states and displacements of water in food system. J Therm Anal Calorim. 2003;71:221–31.
21. Pani P, Curti E, Torreggiani D, Schiraldi A. Multidisciplinary model of apple dehydration. In: Book of abstracts of 5th conference on water in food, Nürtingen, Germany, April 6–8, 2008.
22. Roos HY. Phase transitions in foods. San Diego: Academic Press Inc.; 1995.
23. Slade L, Levine H. Glass transition and water–food interactions. Adv Food Nutr Res. 1995;38:103–269.
24. Fessas D, Schiraldi A. Water properties in wheat flour dough II: classical and Knudsen thermogravimetry approach. Food Chem. 2005;90:61–8.
25. Pitzer KS, Peiper JC, Busey RH. Thermodynamic properties of aqueous sodium chloride solutions. J Phys Chem Ref Data. 1984;13:1–102.