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CLASSICAL AND KNUDSEN THERMOGRAVIMETRY TO CHECK STATES AND DISPLACEMENTS OF WATER IN FOOD SYSTEMS

A. Schiraldi[*] *and D. Fessas*

diSTAM, Università di Milano, Italy

Abstract

Water states and displacements can be investigated with thermogravimetry (TG) either in its classical or in the Knudsen version (where standard pans are replaced with Knudsen cells). The case of wheat flour dough is considered in various steps of bread making, namely, mixing, proofing, baking, staling. The split of DTG signals into various components (gaussian functions) support the assumption that the overall dough water is partitioned into various fractions. Few comments are devoted to water displacements during freezing.

Keywords: food, thermogravimetry, water

Introduction

Classical thermogravimetry (TG) is a well established thermal analysis approach in the study of synthetic polymers, as well as organic and inorganic compounds that release some volatile moieties and/or water on heating. FTIR and/or mass spectrometry detectors at the outlet of the thermobalance allow recognition of the chemical nature of the volatiles lost and therefore are necessary (and expensive) appendices when a decomposition process has to be investigated.

Much cheaper and easier to solve is the assessment of the extent of a dehydration process relevant to food systems. Widely available are nowadays TG-DSC instruments that combine TG with DSC and provide both the relevant traces (Fig. 1), namely, mass loss (m) and heat flow, HF ($\mathrm{d}Q/\mathrm{d}t$), *vs.* $T(t)$, the former being also in the derivative form, DTG ($\mathrm{d}m/\mathrm{d}t$).

The HF/DTG ratio allows a simple check of the enthalpy drop related to the mass loss, since $HF/\mathrm{DTG}=\mathrm{d}Q/\mathrm{d}m=\Delta_{vap}H$ (in J g^{-1} units). It is therefore easy to verify that the release of water from food systems is always accompanied by an enthalpy change very close to 2.2 J g^{-1} [1], which is the vaporisation enthalpy of pure water at 0.1 MPa.

This finding is however relevant only to the energetic balance and simply reveals that the nature of links involving water molecules in food systems is always of

* Author for correspondence: E-mail: alberto.schiraldi@unimi.it

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the same type, namely hydrogen bonds. Depending on the specific link between water and substrate, the strength of these bonds can vary within a narrow range and therefore imply differences of $\Delta_{vap}H$ values that cannot be reliably detected with a standard TG-DSC instrument.

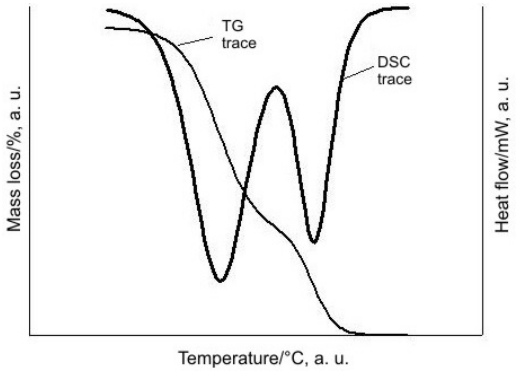

Fig. 1 Simultaneous TG and DSC traces. The latter is slightly shifted toward higher T because of the time lag of the calorimeter

However different states of water can be recognised because of the different temperatures at which water is released during an experimental run, since they are related to the configuration entropy of each state, namely, $T_{vap} \approx -(\Delta_{vap}H)/(R \ln a_W)$, where a_W is the water activity at T_{vap} and R is the gas constant.

DTG curves obtained from food systems indeed show multiple and/or shouldered peaks that can be split into separate contributions through a mathematical deconvolution of the whole trace [1]. This allows evaluation of the mass fraction of each state of water within the system and the corresponding T_{vap}, namely, the temperature of the peak maximum. The same treatment can be applied to the concomitant *HF* trace to draw the enthalpy change relevant to each DTG peak.

The T_{vap} values determined in this way cannot unfortunately be used for any thermodynamic evaluation since they depend on the scan rate applied to record the DTG-*HF* trace. More fundamentally, the multiple and/or shouldered DTG peaks are the overall result of a number of events related to the previous mechanical and/or thermal history of the system.

One has therefore to sketch reality with a simplistic scheme. First, water partition in the system is supposed to be reasonably stable before the experimental run; second, water mobility rises with rising temperature and produces only non-chemical diffusion-limited effects related to the reversible formation of hydrogen bonds; third, structural water remains fixed at its positions until a sufficiently high temperature is reached where its links are loosened and it can move away. In spite of these oversimplifications, many processes that occur in food systems, like starch gelatinization, protein denaturation, formation of physical gels and networks, can be satisfactorily described according to this scheme.

When the standard pans of the thermobalance are replaced with Knudsen cells, which communicate with a low pressure (10^{-4} Pa) external ambient through a 20 μm orifice, an isothermal dehydration process can be triggered by means of a turbomolecular pump. In these conditions the driving force sucking water molecules out of the cell is the drop of water partial pressure, p_W, across the orifice. Since $(p_W)_{ext}$ in the external ambient is always at least two-order of magnitude lower than $(p_W)_{int}$ within the cell, it can be easily shown that the loss rate dm/dt is proportional to $(p_W)_{int}$, namely, $(dm_W)/(dt)=K(p_W)_{int}$, where K is constant for a given gas escaping from a Knudsen orifice of given geometrical sizes and at a given temperature. The ratio between DTG curves obtained, at the same temperature and with the same Knudsen cell, from the sample of a given material and a sample of pure water gives the trend of the relative humidity (RH) of the material considered [2]. When saturated salt solutions are examined, this ratio can be referred to as the relevant water activity, a_W. Figure 2 reports a sketch of a Knudsen cell and the expressions that allow evaluation of RH and/or a_W as well as the calibration straight line obtained by examining various saturated salt solutions.

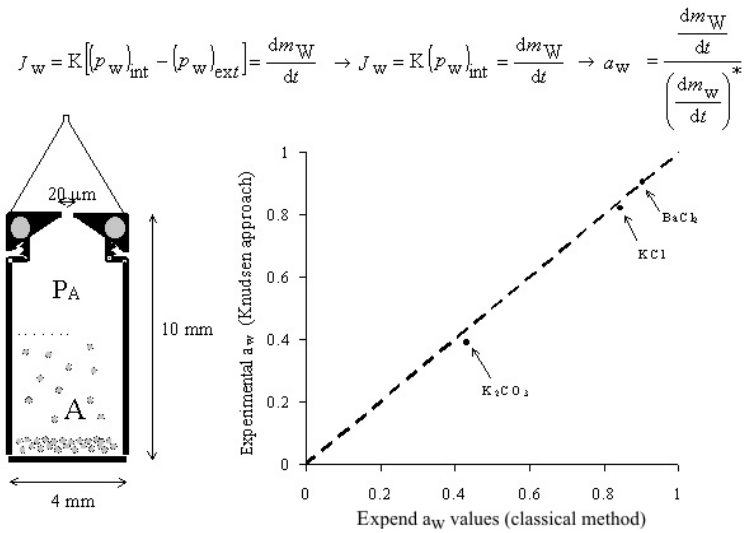

Fig. 2 Expressions of the mass flux J_i through a Knudsen orifice that lead to the relationship between thermodynamic activity of the volatile 'i' and the ratio of the mass loss rates recorded from the sample considered and the relevant pure liquid. Schematic view of the Knudsen cell that replaces the standard pan of a thermobalance. The insert reports the standardization of the water activity data obtained from saturated salt solutions [2]

In this paper we report the case of wheat flour dough, chosen as an example of complex system, where a number of phases are present because of the thermodynamic incompatibility between flour proteins and polysaccharides. The experimental data reported have been collected in the last five years and in the course of some investigations which are still in progress. The details about the relevant materials and methods can be found in the authors' papers quoted in the References section of this paper.

The case of wheat flour dough

A wheat flour dough is a heterogeneous system [3] where several aqueous phases coexist being separated by inter-phase regions across which water can move because of chemical potential gradients, resulting in the modification of the local compliance to chemical and biochemical activities.

In spite of previous heat and/or mechanical stresses, high-*RH* water micropoaches can be preserved for long periods at ambient and sub-ambient temperatures within high viscosity media, like very concentrated solutions, gels and protein networks in flour doughs and baked foods, and allow some residual activity of enzymes and/or microorganisms [4].

Since the physical properties of each dough phase directly depend on its moisture content, the control of water displacements during various steps of preparation, like mixing, proofing, freezing and baking (as well as in bread staling), is of utmost importance.

When water is mixed with flour, the hydrophilic components adsorb the moisture either physically or chemically. The water soluble compounds, like salts, simple sugars, amino-acids and globular proteins form a homogeneous aqueous solution wetting the starch granules. The initial gluten aggregates (from gliadins and glutenins) and the non-starch polysaccharides, like arabinoxylans and arabinogalactans, are thermodynamically incompatible with each other and with globular proteins [5], and therefore tend to form separated and disperse aqueous phases. At this stage the dough is a complex water-in-water (W/W) dispersion [4] with starch granules and insoluble fibers as dispersed 'solids'. Once starch undergoes gelatinization, incompatibility appears between amylose and amylopectin [6]. At microscopic level water molecules indeed occupy rather different states, ranging between being tightly bound to substrates and practically free as an imbibing agent.

The *RH* of a macroscopic dough sample equilibrated with suitable saturated salt solutions is larger than 99.99% [7]. This does not mean that *RH* has the same large value throughout the sample: at microscopic level water molecules indeed occupy rather different states, ranging between being tightly bound to substrates and practically free as an imbibing agent. The latter condition however prevails in exchanges with the vapor phase and is therefore responsible for the large relative humidity (RH) experimental value [7]. In the course of a dehydration process $(p_W)_{int}$ decreases and the water loss rate tends to vanish. The TG and the DTG traces allow evaluation of the residual moisture content and the relevant loss rate, respectively, in any moment of the process (Fig. 3). When these quantities are plotted *vs*. each other, the isothermal dehydration curve is directly obtained. The experiment lasts a few hours (depending on the size of the Knudsen orifice).

Water partition is governed by the gradients of chemical potential across the inter-phase region which is basically formed by the aqueous solution of low molecular mass solutes. Solvent migration across phases occurs via membrane less osmosis [5] and attainment of a true equilibrium is hindered by the inter-phase viscosity. Surfactants and hydrophobic compounds are concentrated within the inter-phase regions [8].

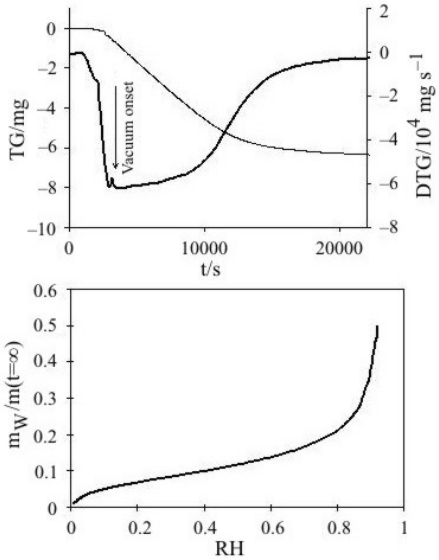

Fig. 3 Isothermal DTG record in Knudsen regimen from a wheat flour dough (upper). Desorption isotherm (lower). m_W=water mass and $m(t=\infty)$=sample mass at the end of the run were obtained by properly scaling the TG record, while *RH*=relative humidity was the ratio between the DTG record of the dough and the constant level of the DTG record of pure water at the same temperature

Nevertheless the proportions of these populations of water molecules can change with mixing and during the rest after mixing [1]. These changes are rather slow (min or h) and prove that a steady partition of water between different dough phases is not as immediate as one could expect from the molecular mobility determined with a spectroscopic approach, like NMR relaxometry, which reveals local motions [9]. The picture that comes out is therefore that of water molecules restlessly flipping from one state to the other being practically affected only by short range driving forces.

It must be emphasized that the fraction of water engaged in the gluten meshes plays a major role in determining the structure and the physical properties of the dough that is being mixed.

Figure 4 reports the DTG record of the dehydration of a wheat flour dough. This trace can be deconvoluted in two main gaussian components, each relevant to a fraction of the dough moisture content. One fraction is released well above 100°C and therefore has to be referred to as structural water, in the sense that it is an element of the structure of the substrate. In the case of wheat flour dough, structural water is mainly linked to the gluten component [1]. The relevant DTG peak is relatively narrow and accounts for about 15% of the overall moisture content of the dough. Its T_{vap} is affected by the stress experienced by the dough before the experimental run and by the overall moisture content of the sample. The rest of the dough moisture is instead released below 100°C according to a simple diffusion law [1], just as expected for im-

bibing water: no detectable effect is produced by the gelatinization of starch that takes place in this temperature range.

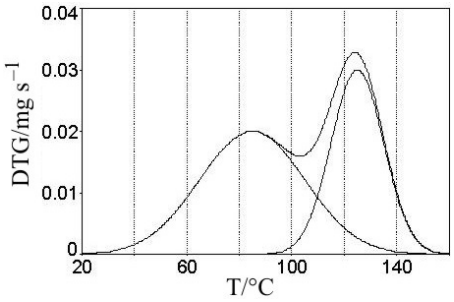

Fig. 4 Deconvolution of the DTG trace from a sample of wheat flour dough into a couple of gaussian components

It is worth noting that at the beginning of the thermogravimetry run, the dough is a suspension of superficially hydrated starch granules within the meshes of a very loosen gluten network, while at the end of the run it is very similar to the bread crumb. The release of water that takes place in the course of the TG run strongly depends on the starting conditions of the system, while no important effects come from the changes of the system structure. In other words, any treatment, like mixing and kneading at room temperature, that can affect water partition within the dough before the experimental run, produces modifications of the DTG trace, namely, amount of water in each fraction and relevant T_{vap}, while no effects come from starch gelatinization and gluten reticulation. The starting situation indeed governs starch gelatinization and gluten reticulation and the rate of water loss in the course of the TG run [1]. A two-hour rest at room temperature is enough for an overmixed dough to re-establish the original water partition and therefore to re-obtain the DTG trace of a non-stressed dough [1].

Proofing is the preparation step during which a disperse gas phase is produced because of the leavening action of yeast and/or suitable chemicals. The air incorporated during dough mixing forms bubbles that act as nucleation sites for bubble growth during proofing: without these sites the CO_2 produced by the yeast would be largely lost to atmosphere resulting in a low loaf volume. The main factors governing the blowing of gas bubbles [10] are gas pressure, which is primarily related to water vaporization, and medium viscosity that, at this stage, is related to the gluten ripening attained in mixing.

The gas bubbles are indeed lined by an aqueous layer that hosts gas/liquid and liquid/liquid surfactants, like globular proteins (flour albumins and globulins) and polar lipids [11]. The CO_2 produced by the yeast cells is dissolved in the liquid phase from where it migrates into the bubbles thus contributing to the overall internal pressure.

The external border of the bubbles is a gluten film meshwork hosting starch granules. Taking into account that the increase of the bubble size is a result of the competition between gas pressure and compliance of the surrounding matrix, the gluten film becomes thinner, while this is not necessarily the case for the inter-phase aqueous film. Some water diffuses from neighboring regions toward the bubble, since some moisture vaporizes

into the bubble. At the same time the stress produced by the bubble expansion squeezes the imbibing water from the surrounding matrix. Because of the overall extension of the inter-phase regions, the surfactant/water mass ratio decreases and, as a consequence, the surface tension of the lining aqueous film increases. Bubbles closer to the surface of the dough loaf may pop out, whereas the bulk dough elastic stress counterbalance the gas pressure within the bubbles. Laplace principle allows to predict that small bubbles disappear whereas the larger ones expand.

Rupture of the bubbles reduces the overall extension of the inter-phase regions and therefore contributes to restore the previous water/surfactant mass ratio. At the same time the leavening effects drop down and the stiffness of the bubble walls increases because of the starch gelatinization and (later on) gluten reticulation [11].

The early stages of baking see the continuation of the leavening process (oven spring) but the picture changes on trespassing the threshold of the starch gelatinization: coalescence and rupture of many internal bubbles take place and inter-communicating cavities (precursors of the crumb alveoli) are formed.

The structure of the systems changes into that of an open sponge which allows an easy vaporization to the external atmosphere [11]. Because of this process starch gelatinization and, to some extent, gluten reticulation cannot attain exhaustion [12].

Structural water remains adsorbed onto dough polymers (mainly gluten) and can be only partially delivered at the loaf surface where the crust is being formed at a temperature above 100°C [1]; the water loss from the loaf bulk, whose temperature never attains 100°C, is instead reduced in spite of the crumb-to-crust concentration gradients [13].

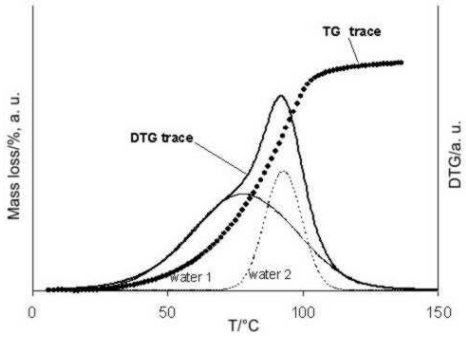

Fig. 5 TG and DTG records of a sample of freshly baked bread crumb. The latter can be deconvoluted into a couple of gaussian components

Figure 5 shows the DTG record of a sample of freshly baked bread crumb. Again two peaks can be recognized after mathematical deconvolution of the trace [14].

The relevant water fractions change during the bread ageing (Fig. 6) in sealed bags. This means that during the early phases of ageing the more mobile fraction (water 1) is displaced toward sites where it is more tightly fixed thus increasing the fraction of the other fraction (water 2). Further ageing produces modifications of the crumb structure that releases some water which migrates toward the crust of the bread loaf (the declining trend of the overall moisture content reported in Fig. 6).

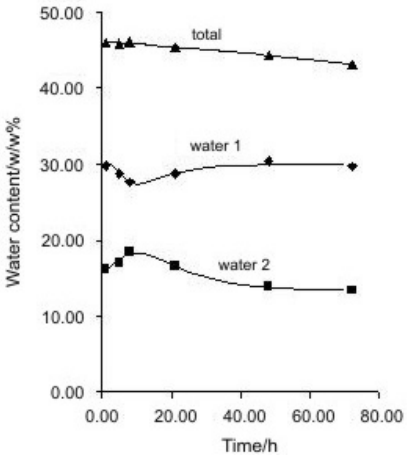

Fig. 6 Evolution of the water fractions and total water in bread crumb during ageing at room temperature (modified after [14]). The total water loss in the crumb is related to the migration of water from the crumb to the crust of the loaf

What has to be noticed is that in this case the T_{vap} of the second DTG peak is shifted toward higher temperatures with increasing ageing. When the crumb is stored at 28°C, the DTG records is the one reported in Fig. 7: the shape of the high T peak and the relevant T_{vap} (above 175°C) suggest that this dehydration step may actually correspond to some structure breaking event. More detailed information about this behavior are given elsewhere [15].

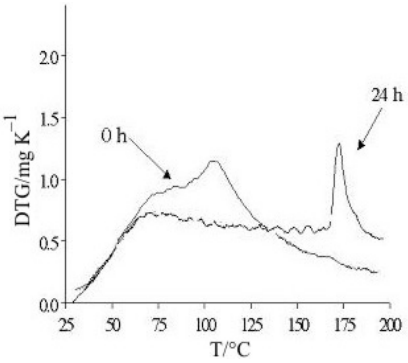

Fig. 7 Change of T_{vap} of the high-T component of water loss with bread ageing

Water activity of bread crumb decreases with aging. Nevertheless an early increase followed by a plateau trend has been observed during the early hours of storage [14]. These findings suggest that some process, like amylose crystallization and/or adjustment of the long range structure, may produce some 'free' water that migrates toward the crust [13]. The overall process produces a detectable reduction of the crumb moisture with increase of the water content in the crust even when the bread loaf is sealed in water impermeable bags.

The water loss is accompanied by crumb firming and together with the amylopectin retrogradation contributes to increase the crumb harshness of the stale bread. It is therefore clear that any ingredient that can act as a water supplier will reduce the rate of the process [16]. Side effects on the sensorial properties of the product, like crust color and crumb taste, can appear in some cases, being often related to the previous process of structure formation.

Freezing is accompanied by formation of ice crystals, the size of which depends on the cooling rate and on the viscosity of the aqueous phase where they are formed. The early ice embryos behave as seeds where further water molecules can adhere moving from close regions; this process produces strains, which are spread over a large range within the dough structure, and consequent damages that can be related to the increased viscosity and/or stiffness of the medium depleted of the liquid phase.

Water molecules migrate toward the ice embryos leaving the original liquid phases which become more concentrated and more viscous. This process ceases when no further displacement of water molecules is allowed, namely when the temperature of a given phase approaches the 'local' glass transition threshold. This means that some phases which attain this condition first can no longer sustain the growth of ice crystals, while others, where water molecules can be still easily displaced, can sustain the progress of freezing and/or spread moisture toward the formers which therefore delay their final hardening. When the medium viscosity does not allow such migration, a multiple glass transition signal can be seen in the DSC record (on heating). A similar situation is observed for a frozen sucrose aqueous solution: on reheating, two close glass transition signals appear in the DSC trace [17], one of which disappears on annealing the sample or after a few heating-cooling cycles in the relevant temperature range. Eventually a single glass transition is detected the temperature of which is T_g', corresponding to the highest freeze concentration of the system [18].

It comes out that, aside from some ice crystals separated from the less viscous aqueous phases, the rest of the system undergoes a 'coordinated' progress toward the glassy state. The phases hosting some residual liquid water would eventually vitrify almost simultaneously, namely at the same subzero temperature, as long as they attain practically the same viscosity level at which ice growth is hindered. Figure 8 sketches the overall freezing process.

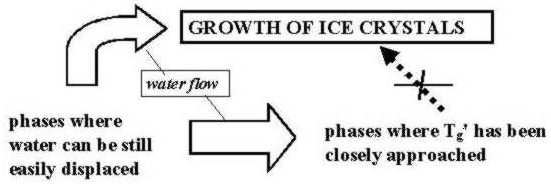

Fig. 8 Schematic representation of water displacements in freezing dough. Within poorly viscous phases where water mobility is still large, water molecules move toward the ice growth front; from these phase water can also migrate toward neighboring aqueous phases with a higher T_g', where, because of a larger viscosity, the production of ice crystals is hindered

The solute concentrations (in % mass/mass units) of these phases can however be rather far apart, since the viscosity of a given phase mainly depends on temperature and the chemical nature of the solutes (e.g., low or large molecular mass). As an example, a diluted aqueous solution of a polymer can be as viscous as a concentrate aqueous solution of simple sugars at the same temperature [18, 19].

Conclusions

A relatively simple technique like TG allows an easy check of the partition of water in a flour dough, when the relevant signals are mathematically treated so as to split them in various components. A fraction of the moisture content behaves like pure water as far as its vaporization is limited only by the diffusion from the core to the surface of the sample. This fraction is responsible for the large value of the relative humidity, *RH*, of a freshly prepared dough.

Another main fraction (about 15% of the overall moisture content) can be removed from the sample only at a much higher temperature: it has been recognized this fraction is related to the gluten meshwork of the dough. Mechanical treatments, like kneading, can affect this partition, reducing the amount of water trapped by the gluten; the starting distribution is however recovered if the dough is let at rest for a couple of hours at room temperature. This means that water is indeed mobile, no matter the fraction concerned, although differences should be expected between fractions.

Similar results can be obtained from samples of bread crumb and allow to follow up changes of the water partition in the course of bread ageing.

The evaluation of *RH* is again achievable by means of TG when the standard cells are replaced with Knudsen cells. This Knudsen variant of TG indeed allows to directly draw the whole desorption isotherm from a single experimental run.

These experimental evidences support the reliability of the use of thermogravimetry in food science investigations. At the same time they also confirm the necessity to couple the correct management of the experimental conditions with a comprehensive knowledge of the systems considered.

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