FOOD DEHYDRATION

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Contents

Summary

Drying is a widely used method of food preservation. In this article, aspects of this wide but still developing field are presented. Relationships between the state of water and dried food stability, moisture migration mechanisms, drying kinetics, as well as traditional and novel drying techniques, are addressed.

1. Introduction

Drying is a unit operation where moisture is eliminated from a solid, suspension, or liquid solution, resulting in a solid product. It is one of the most important processes in food production and preservation. The main objectives of drying are as follows:

- Extended shelf life of product (inhibition of microbial growth and minimization of deterioration reactions, such as lipid oxidation and enzymatic and non-enzymatic browning, by reduction in water activity) (see *Colligative Properties, Kinetics of Chemical Reactions in Foods)*.

- Ease of handling (reduction in weight and volume, storage, and transportation costs) (see *Food Plant Design*).
- Improved additional processing (greater energy conservation and improved mixing, milling, or segregation) (see *Food Processing*).

This operation has been in use since ancient times. Throughout history, humans have known that the removal of water increases the shelf life of perishable products. Today, dehydration has widespread application in the food industry, with a large variety of conventional dehydrated foods being available. In spite of the large quantity of experimental and theoretical research performed in the field, an in-depth understanding of the drying phenomenon is not yet available because of its great complexity. Water removal is usually performed via evaporation, vaporization, or sublimation by means of a simultaneous (and often coupled and multiphase) heat, mass and momentum transfer process, within the food itself, and between the food and the drying medium. In addition, associated chemical reaction phenomena occur, such as Maillard browning of amino acids/reducing sugars, sugar caramelization, protein denaturation/degradation, and pyrolysis of the various organic constituents, as well as loss of volatile compounds, gelatinization of starch, and modification of food material structure and ultrastructure, changing the characteristics of the raw material to different degrees.

2. Basic Concepts Associated with Drying

2.1. State of Water in Foods

2.1.1. Water Activity and Molecular Mobility

Water is the most abundant substance on earth and one of the most important components in foods ($\cong$ 50 to 80 percent w/w in meats, $\cong$ 80 to 95 percent w/w in fruit, and $\cong$ 74 to 95 percent w/w in vegetables), influencing quality attributes and shelf stability.

Studies on the state of water in foods have a long history. Before the concept of water activity (a_w) was developed, the moisture content in food was thought to be the critical parameter controlling microbial growth and chemical reactions. In the late 1950s, a British microbiologist named Scott suggested that it was the "availability" of water, not the moisture content alone, which governed the deterioration of foods. Scott proposed that the water activity parameter was a better and more reliable means of measuring the "availability" of water. The term "availability" of water is a measure of how "freely" water molecules participate in reactions or how easily water molecules diffuse to the reaction sites to participate in reactions. Since then, many food scientists and industries have used the a_w concept as a primary guideline for safety and quality control (see *Colligative Properties Hurdle Technology*).

Briefly, the concept of "activity", assuming solution ideality and thermodynamic equilibrium, states that a_w is equal to f/f_0, where f is the fugacity of water in the system (i.e., the escaping tendency of water from solution) and f_0 is the fugacity of pure water. At low pressures, the difference between f/f_0 and p_w/p_{w0} is less than 1 percent and results in the equality, $a_w = p_w/p_{w0}$.

In recent years, however, questions related to the meaningfulness of a_w have been asked by many researchers: a_w is defined under equilibrium conditions, that is, the measured partial vapor pressure above the food system is presumed to be the same as that of the water within the food. This assumption is valid for infinite dilute systems, where diffusion rates of water molecules are high compared to the time scale of thermodynamic measurement. But most intermediate moisture and dried food systems are non-equilibrium systems. Conversely, they may be in a state of thermodynamic instability ("pseudo" stability), and often this unstable state is maintained during processing and storage, lasting longer than the product's shelf life. Another defect in the a_w concept is that it does not take into account the effect *per se* of solute-solute and solute-water interactions, which have profound influence on the kinetics of food reactions (see *Kinetics of Chemical Reactions in Foods*). Many foods having the same a_w differ significantly in perishability. Thus, a_w alone is not a reliable indicator of food stability, at least for certain foods.

As a partial solution to these problems, in the late 1980s, Levine and Slade introduced the polymer science approach to food science, in which molecular mobility is considered key to product stability. In this sense, a material stored below the glass transition temperature (T_g) would be physically, chemically, and biologically stable, while at temperatures stored above T_g it would not. The glass transition is a change in the physical state of amorphous material, from a solid glassy state to a supercooled viscous liquid or rubbery state. In a glassy state, the viscosity is extremely high ($>10^{12}$ Pa s), the small molecules lose their translational mobility, and the molecular motions are restricted to vibrations and short-range rotational motions, behaving practically like solid liquids in the material. This second-order transition results in a dramatic drop in viscosity and also a dramatic increase in molecular mobility.

Today, many researchers argue that this molecular mobility concept is a broadening and an extension of the a_w approach, and that food stability must be predicted by both thermodynamic and mobility concepts. The concept of a_w enables the prediction of microbial activity and of chemical reactions controlled by chemical reactivity, while the concept of molecular mobility is useful for predicting virtually all physical properties and also all chemical reactions limited by diffusion.

Waters ability to engage in three-dimensional hydrogen bonding is thought to be the most important characteristic of water, which is responsible for its unusual physical properties and functionality. Heat capacity, melting and boiling points, heat during phase transitions (sublimation, fusion, and vaporization), surface tension, permittivity, and thermal conductivity are much higher than in many liquids, indicating the additional energy needed to break intermolecular hydrogen bonds. Liquid water has a structure that causes the orientation and mobility of a given water molecule to be affected by its neighbors. Moreover, water behaves differently in different environments, showing that water molecules are "bound" to other substances to varied degrees. Water interacts with other molecules through several types of water-solute interactions: dipole-ion (i.e., water-free ion, and water-charged group on organic molecule); dipole-dipole (i.e., water-NH, water-CO, and water-OH); hydrophobic hydration (i.e., water-alkyl group), and hydrophobic interaction.

A very simplified model of water interactions in heterogeneous environments (e.g., foods) was proposed in the early 1960s with Ling's induction theory. This supposes that the fixed charges on the macromolecules of the biological system and their associated counter ions constrain much of the cellular water to form a matrix of polarized multi-layers with restricted motion, as compared to pure water. The formation of such multi-layers is discussed next.

Hydrophilic groups on macromolecules (i.e., –NH, -OH) may form hydrogen bonds with nearby water molecules, which, due to polarization caused by hydrogen bonding, will be more inclined to form hydrogen bonds with water molecules in the next layer, and so on. Such "ordered" water differs significantly from pure water. At first, a dry macromolecule absorbs water slowly, and a monolayer of water molecules forms through localized adsorption of polar water molecules on to the polar sorption sites of the rigid macromolecule. This monolayer of water molecules is almost immobilized, behaving in many respects like part of the solid or like the water in the ice. Additional water layers are attached to the monolayer when more water is taken up by the macromolecules, forming multi-layers of water molecules, a phenomenon often regarded as "hydration". The binding force exerted by the polar groups of the macromolecule on the surrounding water molecules decreases with distance from the macromolecule. Thus, the water layers far from the macromolecule will have the highest mobility, essentially similar to that of pure water (traditionally called "free" water), while the monolayer and probably together with the next few layers will have the lowest mobility (traditionally called "bound" water). Unfortunately, no clear point of distinction between "free" and "bound" water exists and, also, it is not yet known if there is a mobility continuum. This lack of elucidation of the nature of water layers has led to the proposal of various terms for referencing the states and mobility of water in biopolymers, such as "bound", "unfreezable", "icelike", "hydration", "free", etc., many of which are derived from the method used in their experimental determination. In this sense, it is important to note that quantitative estimations of mobility of water vary widely, depending on the technique and interpretation of results.

2.1.2. Moisture Sorption Isotherms

The sorption isotherm of a food material is a curve obtained by plotting the moisture content (usually expressed as mass water per unit mass of dry material) in equilibrium with the water activity of the vapor space surrounding the material, or the percent of equilibrium relative humidity in the environment at constant temperature (Figure 1). According to the adsorption isotherm classification of Brunauer, Emmett, and Teller made in 1938, and based on the Van der Waals adsorption of gases on various solid substrates, food materials usually present Type II isotherms (manifested by a nonlinear, sigmoidal curve) or Type III behavior (manifested by a concave shape), this last characteristic pertaining to foods rich in soluble components.

A phenomenon commonly observed in heterogeneous food materials is the occurrence of moisture sorption hysteresis. A displacement exists between the adsorption and desorption isotherms, the desorption path lying above the adsorption one. Thus, more moisture is retained in the desorption process as compared to adsorption at a given a_w (Figure 1b). Hysteresis is present to some degree in almost every food, with the

magnitude, shape, and extent of the loop dependent on the nature and state of food components, the rate of desorption, and temperature. A decreased hysteresis is generally observed as temperature increases. Capillary condensation phenomena, ink bottle neck theory as related to large diameter pores with narrow passages, swelling phenomena, and non-equilibrium states are some of the theories suggested for the hysteresis effect, but a conclusive elucidation of this phenomenon is lacking.

For better interpretation, the generalized moisture isotherm in Figure 1a may be divided into three regions. In region I, water is tightly bound to the polar sites of food material via water-solid interactions (water-ion, dipole-dipole, hydrophobic interactions). Thus, it is most strongly sorbed, least mobile, and unfreezable at –40ºC. It cannot act as a plastic, it is unavailable for chemical and microbial reactions, and has an enthalpy of vaporization greater than that of pure water. In boundary regions I and II, water is considered to form a monolayer over each accessible highly polar group of dry food (the so-called "BET monolayer"). As will be discussed later, this water content is associated with the greatest chemical stability of dried foods. Region II corresponds to the adsorption of additional layers over the monolayer, mainly by hydrogen bonding to neighboring water molecules and solute molecules. This water is less firmly bonded than the first layer, slightly less mobile than bulk water, and available to dissolve solutes, accelerating the rate of many reactions. However, most of it is unfreezable at –40ºC. This water has a plasticizing action on glassy solutes, lowering their glass transition temperature and swelling the solid matrix. Water at the beginning of region III is enough to complete a monolayer hydration shell for the macromolecules. As water content increases, molecular mobility and reaction rates significantly increase, and viscosity decreases. Water is freezable, available for chemical reactions and micro-organism growth, and glass-rubber transitions in the glassy regions may occur. This water exhibits properties comparable to those of free water. Basically, it is held in the voids, crevices, and pores of the material by physical forces related to surface tension. In high moisture foods, water in region III, or "free" water constitutes more than 95 percent of the total water content, while water in regions I and II or "bound" water accounts for less than 5 percent of the total water content.

For a given a_w, the amount of water adsorbed usually decreases as temperature increases. This isotherm shift is attributed to the change in water binding, dissociation of water, and/or the physical state of water. In foods with high solute content (e.g., fruit or ham), an inversion of the temperature effect is produced at a_w values > 0.7, due to an increase in solubility of the solutes in water. Information related to the energetics of the system and drying requirements can be obtained through knowledge of the temperature dependence of the sorption isotherm, using the well-known Clausius-Clapeyron equation:

$$\ln \frac{a_{w2}}{a_{w1}} = \frac{Q+L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2} \right) \tag{1}$$

where Q is the excess heat of sorption (a measure of the moisture binding energy), L is the latent heat of vaporization for water, and a_{w1} and a_{w2} are the water activities at temperatures T_1 and T_2, respectively, at a fixed moisture content. The Q value can be

determined from a plot of ln a_w versus $1/T$ at different moisture contents. The binding energy of the water within the product weakens progressively as the moisture content rises and the Q value is higher at lower moisture contents. Temperature dependence of Q is more important as moisture content decreases.
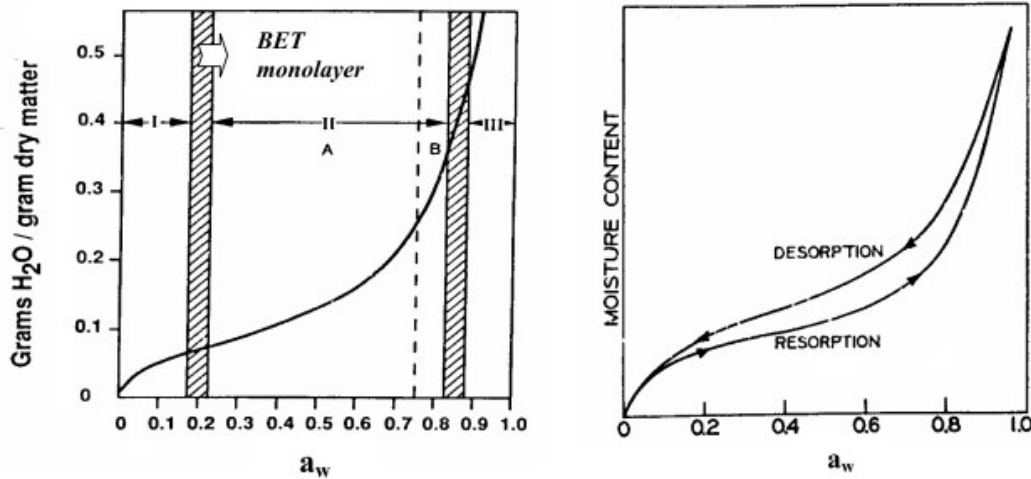

Figure 1. a) Typical schematic moisture sorption isotherm showing the different zones according to the properties of associated water; b) Hysteresis effect on moisture sorption isotherms.
(From: Fennema O.R. (1996). Water and ice. In *Food Chemistry.* 3rd (ed. O.R. Fennema), 17-94. New York, USA: Marcel Dekker, Inc.).

A mathematical description of the a_w-water content equilibrium relationship is useful in drying process design, formulation of ingredient mixtures, packaging requirement specifications, and determination of water content values to assure chemical and microbiological stability. Such description has often resulted from fitting empirical and theoretical adsorption models to experimental data. More than seventy models with different degrees of fundamental validity have been reported for mathematical interpretation of moisture sorption isotherms. Some of the most widely used models for foods are listed in Table 1.

It is unlikely that any equation could ever be devised to describe the whole sorption curve from 0 to 100 percent relative humidity, since the shape of the curve is governed by distinct phenomena in the three regions, which determine the binding energy of the water within the product. In fact, moisture sorption isotherms represent the integrated hygroscopic properties of numerous constituents, with different ones being dominant over various parts of the curve.

The BET formula is one of the most widely used models to characterize the monolayer of water. The constant is related to the net heat of sorption. The theory supposes, among others, that the binding energy of the monolayer is the same for all the water molecules and, on the other layers, is equal to that of pure water. Although the theoretical assumptions are incorrect for heterogeneous food surface interactions, for practical purposes, this equation has been found to be very useful in determining the optimum

moisture content for storage chemical stability. The equation was later modified to consider the maximum number of layers that the capillary could hold.

The Halsey equation was devised for physical adsorption of non-uniform surfaces, assuming the binding energy varied inversely with the distance from the surfaces. It has been used to describe the water sorption properties of a variety of foods and food components with reasonable success. The Iglesias and Chirife equation is applied to foods with high sugar content, in which the monolayer is completed at very low moisture content. The equation proposed by Chung and Pfost is based on the consideration of polymolecular adsorbed films of vapor on polar sorbents by dipole propagation, assuming a direct relationship between moisture content and free energy change for sorption. The empirical Henderson's equation is widely used for fitting sorption isotherms to foods.

The Oswin model is based on a series expansion for sigmoid-shaped curves, and has thus been applied to type II isotherms. A three-parameter equation based on steady-state drying for systems in which diffusion is the main moisture transport mechanism was developed by Chen and was successfully applied to cereal grains.

The GAB equation, also a three-parameter model, is now recognized as the most versatile sorption model and has been recommended as such by the European COST 90 Project. It involves a modification of the BET model, which takes into account the energies of interaction between the first and distant sorbed molecules at the individual sorption sites. Their constants involve the molar sorption enthalpies of the monolayer, the multilayers, and the bulk liquid. The main advantages are a) it has a theoretical basis; b) it is a relatively simple mathematical form with only three parameters; c) the parameters have physical meaning, and d) it takes into account the effect of temperature on isotherms.

Author	Equation	Application range
Brunauer, Emmett & Teller (BET)	$\dfrac{a_{\mathrm{w}}}{(1-a_{\mathrm{w}})M} = \dfrac{1}{M_{\mathrm{M}}C} + \dfrac{C-1}{M_{\mathrm{M}}C}\,a_{\mathrm{w}}$	$0.05 < a_{\mathrm{w}} < 0.45$
Brunauer, Emmett & Teller	$M = \left[\dfrac{M_{\mathrm{M}}C\,a_{\mathrm{w}}}{1-a_{\mathrm{w}}}\right]\left[\dfrac{1-(n+1)(a_{\mathrm{w}})^{n}+n(a_{\mathrm{w}})^{n+1}}{1-(C-1)\,a_{\mathrm{w}}-C(a_{\mathrm{w}})^{n+1}}\right]$	up to a_{w} 0.80
Halsey	$a_{\mathrm{w}} = \exp(-A/RT\theta^{r})\qquad \theta = M/M_{\mathrm{M}}$	$0.1 < a_{\mathrm{w}} < 0.8$
Henderson	$\ln(1-a_{\mathrm{w}}) = -CTM^{n}$	--
Chung & Pfost	$\ln a_{\mathrm{w}} = -\dfrac{C_{1}}{RT}\exp(-C_{2}\,M)$	$0.2 < a_{\mathrm{w}} < 0.70\text{-}0.90$
Oswin	$M = C\left(\dfrac{a_{\mathrm{w}}}{1-a_{\mathrm{w}}}\right)^{n}$	up to a_{w} 0.95
Chen	$a_{\mathrm{w}} = \exp\left[C_{1}-C_{2}\exp(-C_{3}\,M)\right]$	--

| Iglesias – Chirife | $\ln\left[M + (M^2 + M_{0.5})^{1/2}\right] = C_1\,a_w + C_2$ $M_{0.5} = M$ at a_w 0.5 | -- |
| Guggenheim – Anderson – de Boer (GAB) | $\dfrac{M}{M_M} = \dfrac{C\,K\,a_w}{(1 - K\,a_w)(1 - K\,a_w + C\,K\,a_w)}$ | $0 < a_w < 0.9$ |

Table 1. Mathematical description of food isotherms: selected models.

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Biographical Sketches

Pascual Viollaz received his degree in Chemical Engineer from the Chemical Engineering Faculty of Santa Fe, Argentina, and a degree in Petroleum Engineer from the Engineering Faculty of Buenos Aires, Argentina. He also conducted specialized studies in Process Control. He has published more than 60 papers on drying of solids and sorption. He is now full professor in the Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires.

Stella M. Alzamora received her B.S. in Industrial Chemistry and her Ph.D. in Chemistry from the University of Buenos Aires (UBA), Argentina, where she is now Professor of Food Technology and Director of the Master in Science and Technology of the Industrialization of Foods. She is responsible for the Food Technology Programme of UBA and is Principal Researcher of the National Council of Scientific and Technical Research. She was Head of the Industry Department in the Exact and Natural Sciences School (UBA) from 1991-1999. In 1993, she received the Konex Award, granted to 100 personalities of Science and Technology. Her research areas include innovative technologies for food preservation (mainly fruits) based on the hurdle effect, microbiological and physicochemical stability, quantitative microbiology and structural changes in vegetable tissues, and their relationship with mechanical properties. She is Visiting Professor at the University of the Americas, Puebla, Mexico; and is Vice President of ALACCTA (Asociación Latinoamericana y del CARIBE de Ciencia y Tecnología de Alimentos) 2000-2002. She has presented more than 150 research papers at national and international meetings, and has published more than 75 scientific works in international journals and 17 chapters in books; in addition, she has edited 4 books. She is part of the editorial board of various journals and a Research Proposals referee for the national councils of Argentina, Chile, and Uruguay. She has advised various universities in Argentina on Food Science and Engineering educational curricula.