

FUNDAMENTAL PRINCIPLES OF DRYING

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1. INTRODUCTION

The separation operation of drying converts a solid, semi-solid or liquid feedstock into a solid product by evaporation of the liquid into a vapor phase via application of heat. In the special case of freeze drying, which takes place below the triple point of the liquid being removed, drying occurs by sublimation of the solid phase directly into the vapor phase. This definition thus excludes conversion of a liquid phase into a concentrated liquid phase (evaporation), mechanical dewatering operations such as filtration, centrifugation, sedimentation, supercritical extraction of water from gels to produce extremely high porosity aerogels (extraction) or so-called drying of liquids and gases by use of molecular sieves (adsorption). Phase change and production of a solid phase as end product are essential features of the drying process. Drying is an essential operation in the chemical, agricultural, biotechnology, food, polymer, ceramics, pharmaceutical, pulp and paper, mineral processing, and wood processing industries.

Drying is perhaps the oldest, most common and most diverse of chemical engineering unit operations. Over four hundred types of dryers have been reported in the literature while over one hundred distinct types are commonly available. It competes with distillation as the most energy-intensive unit operation due to the high latent heat of vaporization and the inherent inefficiency of using hot air as the (most common) drying medium. Various studies report national energy consumption for industrial drying operations ranging from 10-15% for USA, Canada, France, and UK to 20-25% for Denmark and Germany. The latter figures have been obtained recently based on mandatory energy audit data supplied by industry and hence are more reliable.

Energy consumption in drying ranges from a low value of under five percent for the chemical process industries to thirty five percent for the papermaking operations. In the USA, for example, capital expenditures for dryers are estimated to be in the order of only \$800 million per annum. Thus, the major costs for dryers are in their operation rather than in their initial investment costs.

Drying of various feedstocks is needed for one or several of the following reasons: need for easy-to-handle free-flowing solids, preservation and storage, reduction in cost of transportation, achieving desired quality of product, etc. In many processes, improper drying may lead to irreversible damage to product quality and hence a non-salable product.

Before proceeding to the basic principles, it is useful to note the following unique features of drying which make it a fascinating and challenging area for R&D:

- Product size may range from microns to tens of centimeters (in thickness or depth)
- Product porosity may range from zero to 99.9 percent
- Drying times range from 0.25 sec (drying of tissue paper) to five months (for certain hardwood species)
- Production capacities may range from 0.10 kg/h to 100 t/h
- Product speeds range from zero (stationary) to 2000 m/s (tissue paper)
- Drying temperatures range from below the triple point to above the critical point of the liquid
- Operating pressure may range from fraction of a millibar to 25 atmospheres
- Heat may be transferred continuously or intermittently by convection, conduction, radiation or electromagnetic fields

Clearly, no single design procedure that can apply to all or even several of the dryer variants is possible. It is therefore essential to revert to the fundamentals of heat, mass and momentum transfer coupled with a knowledge of the material properties (quality) when attempting design of a dryer or analysis of an existing dryer. Mathematically speaking, all processes involved, even in the simplest dryer, are highly nonlinear and hence scale-up of dryers is generally very difficult. Experimentation at laboratory and pilot scales coupled with field experience and know-how is essential to the development of a new dryer application. Dryer vendors are necessarily specialized and normally offer only a narrow range of drying equipment. The buyer must therefore be reasonably conversant with the basic knowledge of the wide assortment of dryers and be able to come up with an informal preliminary selection before going to the vendors with notable exceptions. In general, several different dryers may be able to handle a given application.

2. BASIC PRINCIPLES AND TERMINOLOGY

Drying is a complex operation involving transient transfer of heat and mass along with several rate processes, such as physical or chemical transformations, which, in turn,

may cause changes in product quality as well as the mechanisms of heat and mass transfer. Physical changes that may occur include: shrinkage, puffing, crystallization, glass transitions. In some cases, desirable or undesirable chemical or biochemical reactions may occur leading to changes in color, texture, odor or other properties of the solid product. In the manufacture of catalysts, for example, drying conditions can yield significant differences in the activity of the catalyst by changing the internal surface area.

Drying occurs by effecting vaporization of the liquid by supplying heat to the wet feedstock. As noted earlier, heat may be supplied by convection (direct dryers), by conduction (contact or indirect dryers), radiation or volumetrically by placing the wet material in a microwave or radio frequency electromagnetic field. Over 85 percent of industrial dryers are of the convective type with hot air or direct combustion gases as the drying medium. Over 99 percent of the applications involve removal of water. All modes except the dielectric (microwave and radio frequency) supply heat at the boundaries of the drying object so that the heat must diffuse into the solid primarily by conduction. The liquid must travel to the boundary of the material before it is transported away by the carrier gas (or by application of vacuum for non-convective dryers).

Transport of moisture within the solid may occur by any one or more of the following mechanisms of mass transfer:

- Liquid diffusion, if the wet solid is at a temperature below the boiling point of the liquid
- Vapor diffusion, if the liquid vaporizes within material
- Knudsen diffusion, if drying takes place at very low temperatures and pressures, e.g., in freeze drying
- Surface diffusion (possible although not proven)
- Hydrostatic pressure differences, when internal vaporization rates exceed the rate of vapor transport through the solid to the surroundings
- Combinations of the above mechanisms

Note that since the physical structure of the drying solid is subject to change during drying the mechanisms of moisture transfer may also change with elapsed time of drying.

2.1 Thermodynamic Properties of Air-Water Mixtures and Moist Solids

2.1.1 Psychrometry

As noted earlier, a majority of dryers are of direct (or convective) type. In other words, hot air is used both to supply the heat for evaporation and to carry away the evaporated moisture from the product. Notable exceptions are freeze and vacuum dryers, which are used almost exclusively for drying heat-sensitive products because they tend to be significantly more expensive than dryers operate near to atmospheric pressure. Another exception is the emerging technology of superheated steam drying (Mujumdar, 1995). In certain cases, such as the drum drying of pasty foods, some or all of the heat is supplied indirectly by conduction.

Drying with heated air implies humidification and cooling of the air in a well-insulated (adiabatic) dryer. Thus, hygrothermal properties of humid air are required for the design calculations of such dryers. Table 1 summarizes the essential thermodynamic and transport properties of the air-water system. In Table 2, a listing of brief definitions of various terms encountered in drying and psychrometry is given. It also includes several terms not explicitly discussed in the text.

Table 1 Thermodynamic and transport properties of air-water system (Mujumdar, 1995; Pakowski et al., 1991)

Property	Expression
P_v	$P_v = 100 \exp[27.0214 - (6887 / T_{abs}) - 5.32 \ln(T_{abs} / 273.16)]$
Y	$Y = 0.622 RH P_v / (P - RH P_v)$
c_{pg}	$c_{pg} = 1.00926 \times 10^3 - 4.0403 \times 10^{-2} T + 6.1759 \times 10^{-4} T^2 - 4.097 \times 10^{-7} T^3$
k_g	$k_g = 2.425 \times 10^{-2} - 7.889 \times 10^{-5} T - 1.790 \times 10^{-8} T^2 - 8.570 \times 10^{-12} T^3$
ρ_g	$\rho_g = PM_g / (RT_{abs})$
μ_g	$\mu_g = 1.691 \times 10^{-5} + 4.984 \times 10^{-8} T - 3.187 \times 10^{-11} T^2 + 1.319 \times 10^{-14} T^3$
c_{pv}	$c_{pv} = 1.883 - 1.6737 \times 10^{-4} T + 8.4386 \times 10^{-7} T^2 - 2.6966 \times 10^{-10} T^3$
c_{pw}	$c_{pw} = 2.8223 + 1.1828 \times 10^{-2} T - 3.5043 \times 10^{-5} T^2 + 3.601 \times 10^{-8} T^3$

Figure 1 is a psychrometric chart for the air-water system. It shows the relationship between the temperature (abscissa) and absolute humidity (ordinate, in kg water per kg dry air) of humid air at one atmosphere absolute pressure over 0° to 130° C. Line representing percent humidity and adiabatic saturation are drawn according to the thermodynamic definitions of these terms. Equations for the adiabatic saturation and wet-bulb temperature lines on the chart are as follows (Geankoplis, 1993):

$$\frac{Y - Y_{as}}{T - T_{as}} = - \frac{c_s}{\lambda_{as}} = - \frac{1.005 + 1.88Y}{\lambda_{as}} \quad (1)$$

and

$$\frac{Y - Y_{wb}}{T - T_{wb}} = - \frac{h / M_{air} k_y}{\lambda_{wb}} \quad (2)$$

The ratio $(h/M_{air}k_y)$, the psychrometric ratio, lies between 0.96 - 1.005 for air-water vapor mixtures; thus it is nearly equal to the value of humid heat c_s . If the effect of humidity is neglected, the adiabatic saturation and wet-bulb temperatures (T_{as} and T_{wb} , respectively) are almost equal for the air-water system. Note, however, that T_{as} and T_w are conceptually quite different. The adiabatic saturation temperature is a gas temperature and a thermodynamic entity while the wet-bulb temperature is a heat and mass transfer rate-based entity and refers to the temperature of the liquid phase. Under constant drying conditions, the surface of the drying material attains the wet-bulb temperature if heat transfer is by pure convection. The wet-bulb temperature is independent of surface geometry as a result of the analogy between heat and mass transfer.

Table 2 Definitions of commonly encountered terms in psychrometry and drying

Term/symbol	Meaning
Adiabatic saturation temperature, T_{as}	Equilibrium gas temperature reached by unsaturated gas and vaporizing liquid under adiabatic conditions. (Note: For air/water system only, it is equal to the wet bulb temperature (T_{wb}))
Bound moisture	Liquid physically and/or chemically bound to solid matrix so as to exert a vapor pressure lower than that of pure liquid at the same temperature
Constant rate drying period	Under constant drying conditions, drying period when evaporation rate per unit drying area is constant (when surface moisture is removed)
Dew point	Temperature at which a given unsaturated air-vapor mixture becomes saturated
Dry bulb temperature	Temperature measured by a (dry) thermometer immersed in vapor-gas mixture
Equilibrium moisture content, X^*	At a given temperature and pressure, the moisture content of moist solid in equilibrium with the gas-vapor mixture (zero for non-hygroscopic solids)
Critical moisture content, X_c	Moisture content at which the drying rate first begins to drop (under constant drying conditions)
Falling rate period	Drying period (under constant drying conditions) during which the rate falls continuously in time
Free moisture, X_f $X_f = X - X^*$	Moisture content in excess of the equilibrium moisture content (hence free to be removed) at given air humidity and temperature
Humid heat	Heat required to raise the temperature of unit mass of dry air and its associated vapor through one degree ($J\ kg^{-1}\ K^{-1}$ or $Btu\ lb^{-1}\ ^\circ F^{-1}$)
Humidity, absolute	Mass of water vapor per unit mass of dry gas ($kg\ kg^{-1}$ or $lb\ lb^{-1}$)
Humidity, relative	Ratio of partial pressure of water vapor in gas-vapor mixture to equilibrium vapor pressure at the same temperature
Unbound moisture	Moisture in solid which exerts vapor pressure equal to that of pure liquid at the same temperature
Water activity, a_w	Ratio of vapor pressure exerted by water in solid to that of pure water at the same temperature
Wet bulb tempera-	Liquid temperature attained when large amounts of air-vapor

ture, T_{wb}

mixture is contacted with the surface. In purely convective drying, drying surface reaches T_{wb} during the constant rate period

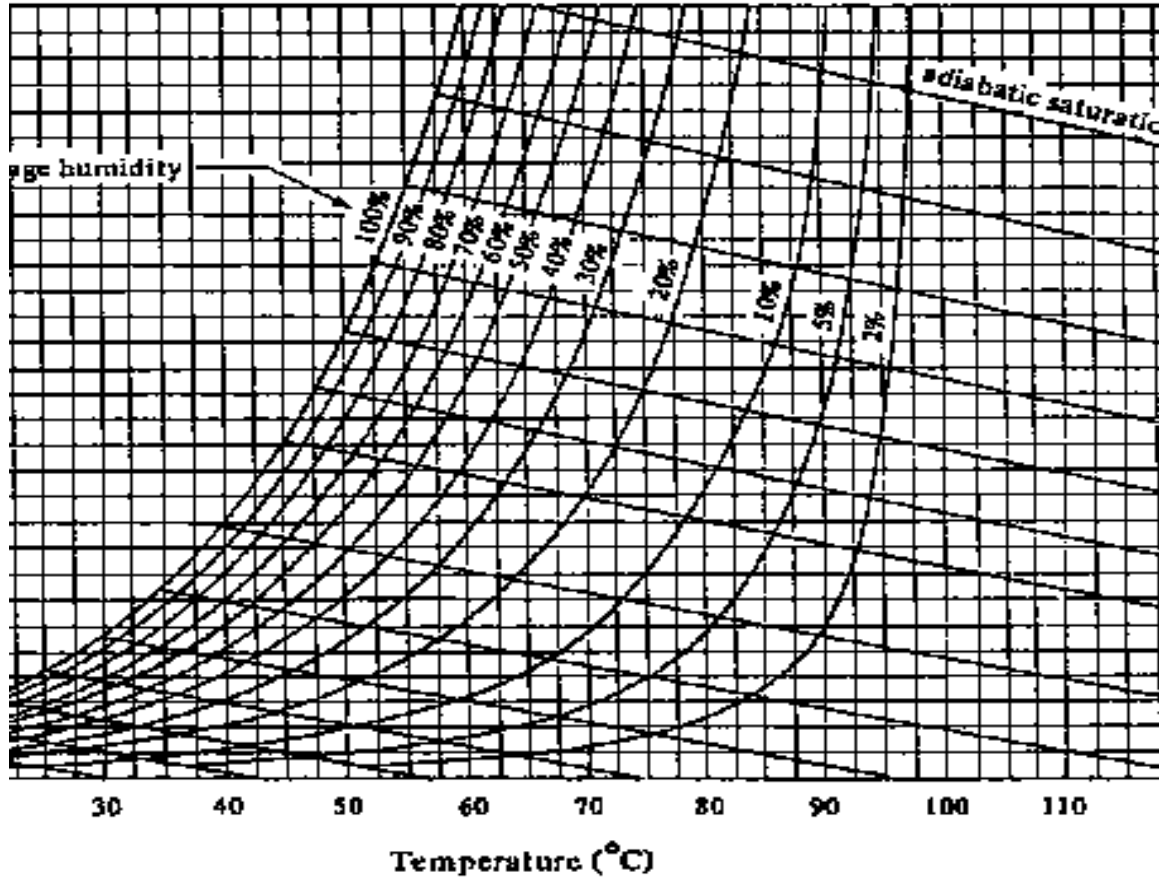


Figure 1 Psychrometric chart for the air-water system

Most handbooks of engineering provide more detailed psychrometric charts including additional information and extended temperature ranges. Mujumdar (1995) includes numerous psychrometric charts for several gas-organic vapor systems as well.

2.1.2 Equilibrium Moisture Content

The moisture content of a wet solid in equilibrium with air of given humidity and temperature is termed the equilibrium moisture content (EMC). A plot of EMC at a given temperature versus the relative humidity is termed sorption isotherm. An isotherm obtained by exposing the solid to air of increasing humidity gives the adsorption isotherm. That obtained by exposing the solid to air of decreasing humidity is known as the desorption isotherm. Clearly, the latter is of interest in drying as the moisture content of the solids progressively decreases. Most drying materials display “hysteresis” in that the two isotherms are not identical.

Figure 2 shows the general shape of the typical sorption isotherms. They are characterized by three distinct zones, A, B and C, which are indicative of different water binding mechanisms at individual sites on the solid matrix. In region A, water is tightly bound to the sites and is unavailable for reaction. In this region, there is essentially monolayer adsorption of water vapor and no distinction exists between the adsorption and desorption isotherms. In region B, the water is more loosely bound. The vapor pressure depression below the equilibrium vapor pressure of water at the same temperature is due to its confinement in smaller capillaries. Water in region C is even more loosely held in larger capillaries. It is available for reactions and as a solvent.

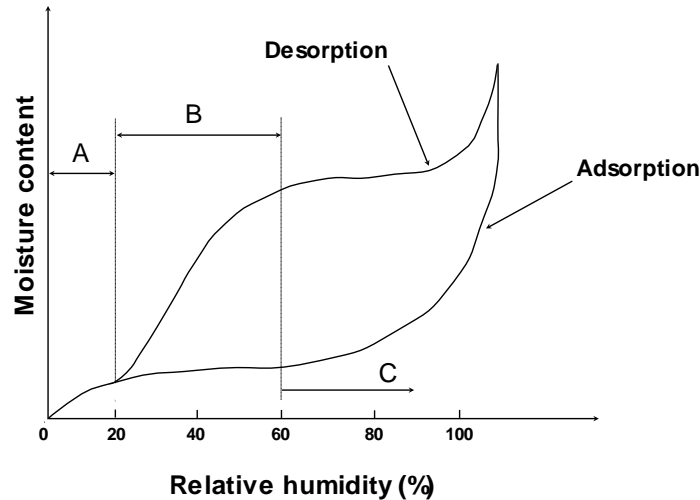


Figure 2 Typical sorption isotherms

Numerous hypotheses have been proposed to explain the hysteresis. The reader is referred elsewhere (Bruin and Luyben, 1980; Fortes and Okos, 1980; Bruin, 1988) for more information on the topic.

Figure 3 shows schematically the shapes of the equilibrium moisture curves for various types of solids. Figure 4 shows the various types of moisture defined in Table 2. Desorption isotherms are also dependent on external pressure. However, in all practical cases of interest, this effect may be neglected.

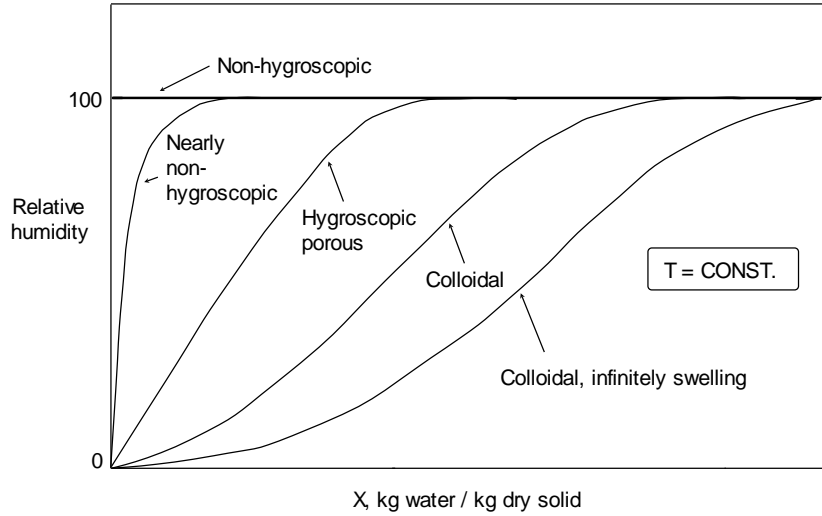


Figure 3 Equilibrium moisture content curves for various types of solids

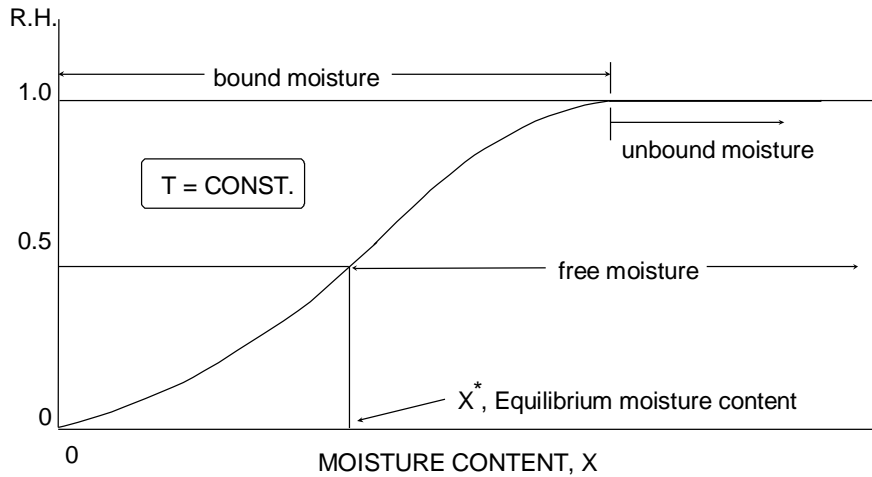


Figure 4 Various types of moisture content

According to Keey (1978), the temperature dependence of the equilibrium moisture content can be correlated by:

$$\left[\frac{\Delta X^*}{\Delta T} \right]_{\Psi = \text{constant}} = -\alpha X^* \quad (3)$$

where X^* is the dry-basis equilibrium moisture content, T is the temperature and Ψ is the relative humidity of air. The parameter α ranges from 0.005 to 0.01 K^{-1} . This correlation may be used to estimate the temperature dependence of X^* if no data are available.

For hygroscopic solids, the enthalpy of the attached moisture is less than that of pure liquid by an amount equal to the binding energy, which is also termed the enthalpy of

wetting, ΔH_w (Keey, 1978). It includes the heat of sorption, hydration and solution and may be estimated from the following equation:

$$\left. \frac{d(\ln \Psi)}{d(1/T)} \right|_{X=\text{constant}} = -\frac{\Delta H_w}{R_g T} \quad (4)$$

A plot of $\ln(\Psi)$ against $1/T$ is linear with a slope of $\Delta H_w/R_g$ where R_g is the universal gas constant ($R_g = 8.314 \times 10^3 \text{ kg kgmol}^{-1} \text{ K}^{-1}$). Note that the total heat required to evaporate bound water is the sum of the latent heat of vaporization and the heat of wetting; the latter is a function of the moisture content X . The heat of wetting is zero for unbound water and increases with decreasing X . Since ΔH_w is responsible for lowering the vapor pressure of bound water, at the same relative humidity, ΔH_w is almost the same for all materials (Keey, 1978).

For most materials, the moisture binding energy is positive; generally it is a monotonically decreasing function of the moisture content, with a value of zero for unbound moisture. For hydrophobic food materials (e.g., peanut oil, starches at lower temperatures) the binding energy can, however, be negative.

In general, water sorption data must be determined experimentally. Some 80 correlations, ranging from those based on theory to those that are purely empirical, have appeared in the literature. Two of the most extensive compilations are due to Wolf et al. (1985) and Iglesias and Chirife (1982). Aside from temperature, the physical structure as well as composition of the material also affect water sorption. The pore structure and size as well as physical and/or chemical transformations during drying can cause significant variations in the moisture binding ability of the solid.

2.1.3 Water Activity

In drying of some materials, which require careful hygienic attention, e.g., food, the availability of water for growth of microorganisms, germination of spores, and participation in several types of chemical reaction becomes an important issue. This availability, which depends on relative pressure, or water activity, a_w , is defined as the ratio of the partial pressure, p , of water over the wet solid system to the equilibrium vapor pressure, p_w , of water at the same temperature. Thus, a_w , which is also equal to the relative humidity of the surrounding humid air, is defined as:

$$a_w = \frac{p}{p_w} \quad (5)$$

Different shapes of the X versus a_w curves are observed, depending on the type of material (e.g., high, medium or low hygroscopicity solids).

Table 3 lists the measured minimum a_w values for microbial growth or spore germination. If a_w is reduced below these values by dehydration or by adding water-binding agents like sugars, glycerol, or salt, microbial growth is inhibited. Such additives should not affect the flavor, taste, or other quality criteria, however. Since the amounts of soluble additives needed to depress a_w even by 0.1 is quite large, dehydration becomes particularly attractive for high moisture foods as a way to reduce a_w . Figure 5 shows schematically the

water activity versus moisture content curve for different types of food. Rockland and Beuchat (1987) provide an extensive compilation of results on water activity and its applications.

Table 3 Minimum water activity, a_w , for microbial growth and spore germination (adapted from Brockmann, 1973)

Micro-organism	Water activity
Organisms producing slime on meat	0.98
<i>Pseudomonas</i> , <i>Bacillus cereus</i> spores	0.97
<i>B. subtilis</i> , <i>C. botulinum</i> spores	0.95
<i>C. botulinum</i> , <i>Salmonella</i>	0.93
Most bacteria	0.91
Most yeast	0.88
<i>Aspergillus niger</i>	0.85
Most molds	0.80
Halophilic bacteria	0.75
Xerophilic fungi	0.65
Osmophilic yeast	0.62

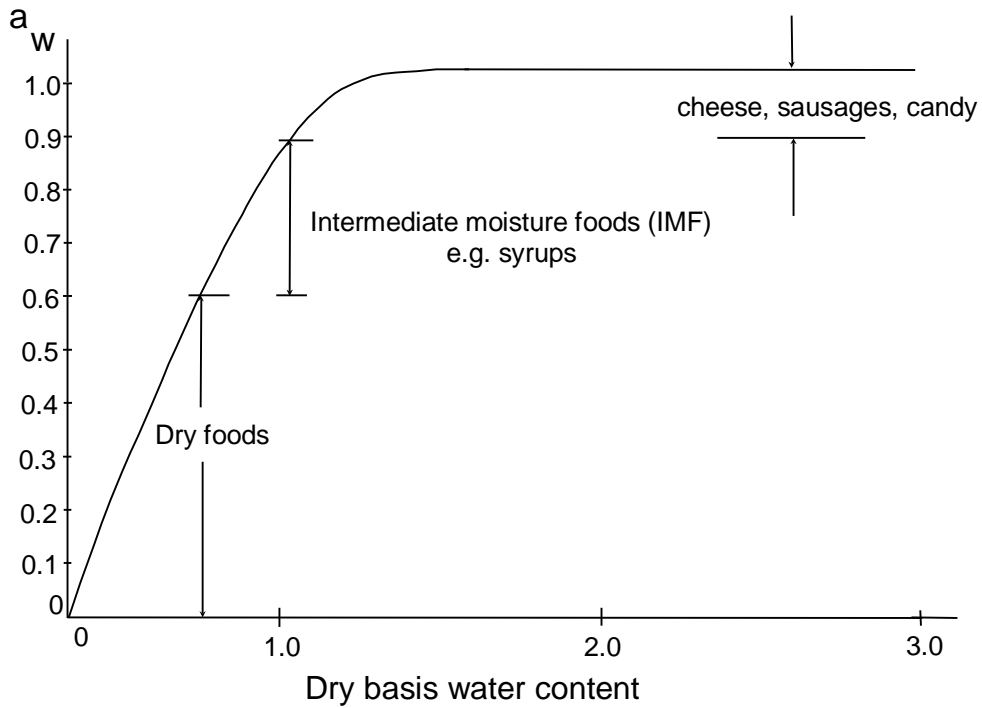


Figure 5 Water activity versus moisture content plot for different types of food

Figure 6 shows the general nature of the deterioration reaction rates as a function of a_w for food systems. Aside from microbial damage, which typically occurs for $a_w > 0.70$, oxidation, non-enzymatic browning (Maillard reactions) and enzymatic reactions can occur even at very low a_w levels during drying. Laboratory or pilot testing is essential to ascertain that no damage occurs in the selected drying process since this cannot, in general, be predicted.

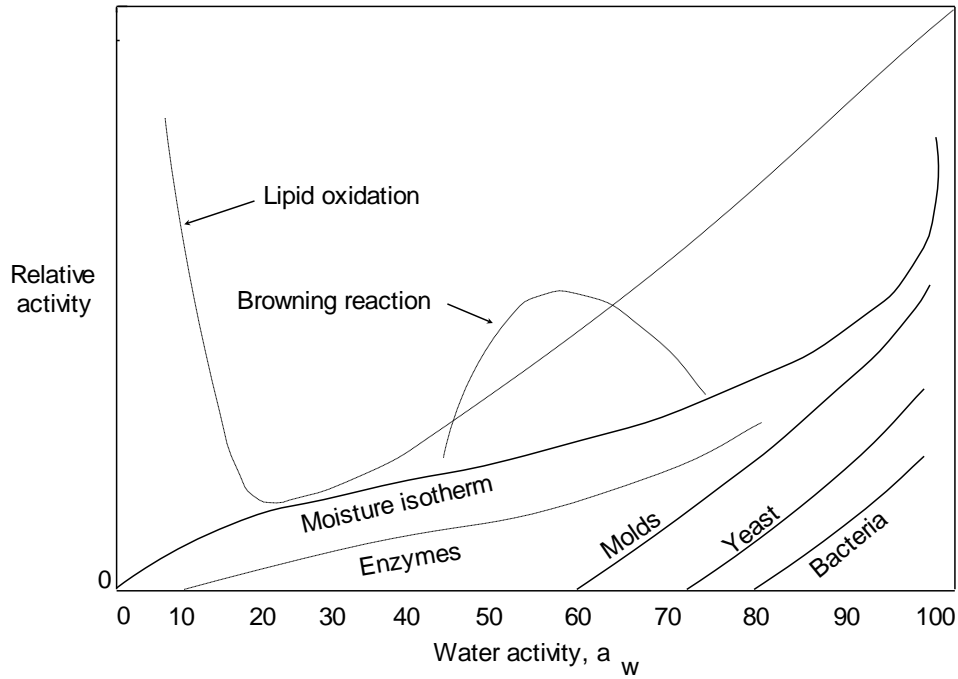


Figure 6 Deterioration rates as a function of water activity for food systems

2.2 Drying Kinetics

Consider the drying of a wet solid under fixed drying conditions. In the most general cases, after an initial period of adjustment, the dry-basis moisture content, X , decreases linearly with time, t , following the start of the evaporation. This is followed by a non-linear decrease in X with t until, after a very long time, the solid reaches its equilibrium moisture content, X^* and drying stops. In terms of free moisture content, defined as:

$$X_f = (X - X^*) \tag{6}$$

the drying rate drop to zero at $X_f = 0$.

By convention, the drying rate, N , is defined as:

$$N = -\frac{M_s}{A} \frac{dX}{dt} \text{ or } -\frac{M_s}{A} \frac{dX_f}{dt} \tag{7}$$

under constant drying conditions. Here, N ($\text{kg m}^{-2} \text{h}^{-1}$) is the rate of water evaporation, A is the evaporation area (may be different from heat transfer area) and M_s is the mass of bone dry solid. If A is not known, then the drying rate may be expressed in kg water evaporated per hour.

A plot of N versus X (or X_f) is the so-called drying rate curve. This curve must always be obtained under constant drying conditions. Note that, in actual dryers, the drying material is generally exposed to varying drying conditions (e.g., different relative gas-solid velocities, different gas temperatures and humidities, different flow orientations). Thus, it is necessary to develop a methodology in order to interpolate or extrapolate limited drying rate data over a range of operating conditions.

Figure 7 shows a typical “textbook” drying rate curve displaying an initial constant rate period where $N = N_c = \text{constant}$. The constant rate period is governed fully by the rates of external heat and mass transfer since a film of free water is always available at the evaporating surface. This drying period is nearly independent of the material being dried. Many foods and agricultural products, however, do not display the constant rate period at all since internal heat and mass transfer rates determine the rate at which water becomes available at the exposed evaporating surface.

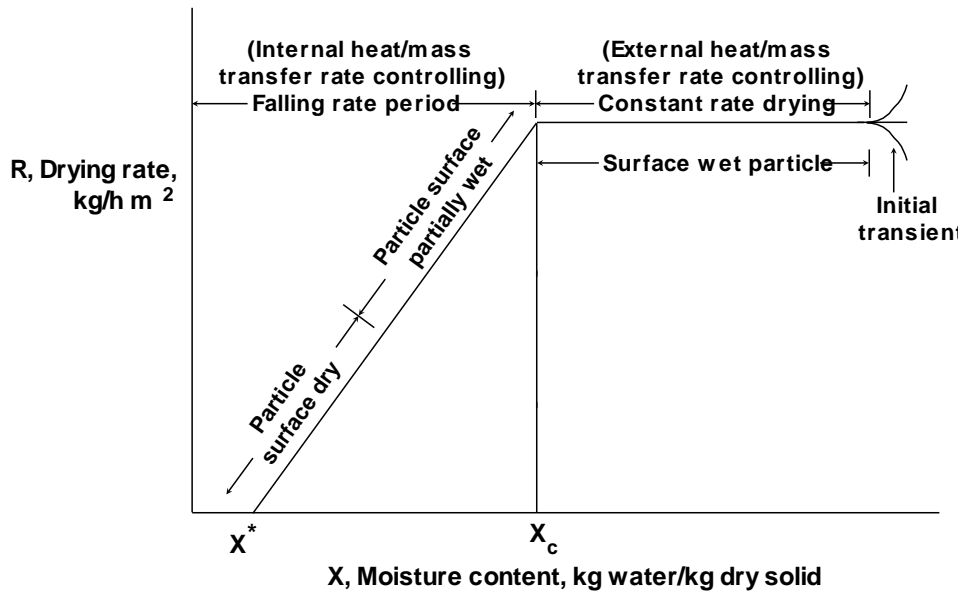


Figure 7 Typical textbook batch drying rate curve under constant drying conditions

At the so-called critical moisture content, X_c , N begins to fall with further decrease in X since water cannot migrate at the rate N_c to the surface due to internal transport limitations. The mechanism underlying this phenomenon depends on both the material and drying conditions. The drying surface becomes first partially unsaturated and then fully unsaturated until it reaches the equilibrium moisture content X^* . Detailed discussions of drying rate curves are given by Keey (1991), Mujumdar and Menon (1995). Approximate critical moisture content values for some selected materials are given in Table 4.

Note that a material may display more than one critical moisture contents at which the drying rate curve shows a sharp change of shape. This is generally associated with changes in the underlying mechanisms of drying due to structural or chemical changes. It is

also important to note that X_c is not solely a material property. It depends on the drying rate under otherwise similar conditions. It must be determined experimentally.

Table 4 Approximate critical moisture contents for various materials

Material	Critical moisture content (kg water/kg dry solid)
Salt crystals, rock salt, sand, wool	0.05-0.10
Brick clay, kaolin, crushed sand	0.10-0.20
Pigments, paper, soil, worsted wool fabric	0.20-0.40
Several foods, copper carbonate, sludges	0.40-0.80
Chrome leather, vegetables, fruits, gelatin, gels	> 0.80

It is easy to see that N_c can be calculated using empirical or analytical techniques to estimate the external heat/mass transfer rates (Keey, 1978; Geankoplis, 1993). Thus,

$$N_c = \frac{\sum q}{\lambda_s} \quad (8)$$

where $\sum q$ represents the sum of heat fluxes due to convection, conduction and/or radiation and λ_s is the latent heat of vaporization at the solid temperature. In the case of purely convective drying, the drying surface is always saturated with water in the constant rate period and thus the liquid film attains the wet-bulb temperature. The wet-bulb temperature is independent of the geometry of the drying object due to the analogy between heat and mass transfer.

The drying rate in the falling rate period(s) is a function of X (or X_f) and must be determined experimentally for a given material being dried in a given type of dryer.

If the drying rate curve (N versus X) is known, the total drying time required to reduce the solid moisture content from X_1 to X_2 can be simply calculated by:

$$t_d = - \int_{X_1}^{X_2} \frac{M_s}{A} \frac{dX}{N} \quad (9)$$

Table 5 lists expressions for the drying time for constant rate, linear falling rates and a falling rate controlled by liquid diffusion of water in a thin slab. The subscripts c and f refer to the constant and falling rate periods, respectively. The total drying time is, of course, a sum of drying times in two succeeding periods. Different analytical expressions are obtained for the drying times t_f depending on the functional form of N or the model used to describe the falling rate, e.g., liquid diffusion, capillarity, evaporation-condensation. For some solids, a receding front model (wherein the evaporating surface recedes into the drying solid) yields a good agreement with experimental observations. The principal goal of all

falling rate drying models is to allow reliable extrapolation of drying kinetic data over various operating conditions and product geometries.

Table 5 Drying times for various drying rate models (Mujumdar, 1997)

Model	Drying time
Kinetic model, $N = -\frac{M_s}{A} \frac{dX}{dt}$	$t_d =$ Drying time to reach final moisture content X_2 from initial moisture content X_1
$N = N(X)$ (General)	$t_d = \frac{M_s}{A} \int_{X_2}^{X_1} \frac{dX}{N}$
$N = N_c$ (Constant rate period)	$t_c = -\frac{M_s (X_2 - X_1)}{A N_c}$
$N = aX + b$ (Falling rate period)	$t_f = \frac{M_s (X_1 - X_2)}{A (N_1 - N_2)} \ln \frac{N_1}{N_2}$
$N = Ax$ $X^* \leq X_2 \leq X_c$	$t_f = \frac{M_s X_c}{AN_c} \ln \frac{X_c}{X_2}$
Liquid diffusion model $D_L =$ constant, $X_2 = X_c$ Slab; one-dimensional diffusion, evaporating surface at X^*	$t_f = \frac{4a^2}{\pi D_L} \ln \frac{8X_1}{\pi^2 X_2}$ $X =$ average free moisture content $a =$ half-thickness of slab

The expression for t_f in Table 5 using the liquid diffusion model (Fick's second law of diffusion form applied to diffusion in solids with no real fundamental basis) is obtained by solving analytically the following partial differential equation:

$$\frac{\partial X_f}{\partial t} = D_L \frac{\partial^2 X_f}{\partial x^2} \quad (10)$$

subject to the following initial and boundary conditions:

$$\begin{aligned} X_f &= X_i, \text{ everywhere in the slab at } t = 0 \\ X_f &= 0, \text{ at } x = a \text{ (top, evaporating surface), and} \\ \frac{\partial X_f}{\partial x} &= 0, \text{ at } x = 0 \text{ (bottom, non-evaporating surface)} \end{aligned} \quad (11)$$

The model assumes one-dimensional liquid diffusion with constant effective diffusivity, D_L , and no heat (Soret) effects. X_2 is the average free moisture content at $t = t_f$ obtained by integrating the analytical solution $X_f(x, t_f)$ over the thickness of the slab, a . The expression in Table 5 is applicable only for long drying times since it is obtained by retaining only the first term in the infinite series solution of the partial differential equation.

The moisture diffusivity in solids is a function of both temperature and moisture content. For strongly shrinking materials the mathematical model used to define D_L must account for the changes in diffusion path as well. The temperature dependence of diffusivity is adequately described by the Arrhenius equation as follows:

$$D_L = D_{L0} \exp[-E_a / R_g T_{abs}] \quad (12)$$

where D_L is the diffusivity, E_a is the activation energy and T_{abs} is the absolute temperature. Okos et al. (1992) have given an extensive compilation of D_L and E_a values for various food materials. Zogzas et al. (1996) provide methods of moisture diffusivity measurement and an extensive bibliography on the topic. Approximate ranges of effective moisture diffusivity for some selected materials are given in Table 6.

It should be noted that D_L is not a true material property and care should be taken in applying effective diffusivity correlations obtained with simple geometric shapes (e.g., slab, cylinder or sphere) to the more complex shapes actually encountered in practice as this may lead to incorrect calculated results (Gong et al., 1997).

In addition to being dependent on geometric shapes, diffusivity depends as well on the drying conditions. At very high activity levels, no differences might be observed but at lower activity levels, the diffusivities may differ by an order-of-magnitude due to the inherently different physical structure of the dried product. Thus, the effective diffusivity is regarded as a lumped property that does not really distinguish between the transport of water by liquid or vapor diffusion, capillary or hydrodynamic flow due to pressure gradients set up in the material during drying. Further, the diffusivity values will show marked variations if the material undergoes glass transition during the drying process.

Table 6 Approximate ranges of effective moisture diffusivity in some materials (Zogzas et al. (1996), Marinos-Kouris and Marouris (1995) and other sources)

Material	Moisture content (kg/kg, d.b.)	Temperature (°C)	Diffusivity (m ² /s)
Alfalfa stems	3.70	26	2.6×10^{-10} - 2.6×10^{-9}
Animal feed	0.01 - 0.15	25	1.8×10^{-11} - 2.8×10^{-9}
Apple	0.10 - 1.50	30 - 70	1.0×10^{-11} - 3.3×10^{-9}
Asbestos cement	0.10 - 0.60	20	2.0×10^{-9} - 5.0×10^{-9}
Banana	0.01 - 3.50	20 - 40	3.0×10^{-13} - 2.1×10^{-10}
Biscuit	0.10 - 0.60	20 - 100	8.6×10^{-10} - 9.4×10^{-8}
Carrot	0.01 - 5.00	30 - 70	1.2×10^{-9} - 5.9×10^{-9}
Clay brick	0.20	25	1.3×10^{-8} - 1.4×10^{-8}
Egg liquid	-	85 - 105	1.0×10^{-11} - 1.5×10^{-11}
Fish muscles	0.05 - 0.30	30	8.1×10^{-11} - 3.4×10^{-10}
Glass wool	0.10 - 1.80	20	2.0×10^{-9} - 1.5×10^{-8}
Glucose	0.08 - 1.50	30 - 70	4.5×10^{-12} - 6.5×10^{-10}
Kaolin clay	< 0.50	45	1.5×10^{-8} - 1.5×10^{-7}

Muffin	0.10 - 0.95	20 - 100	$8.5 \times 10^{-10} - 1.6 \times 10^{-7}$
Paper - thickness	~ 0.50	20	5×10^{-11}
direction			
Paper - in-plane	~0.50	20	1×10^{-6}
direction			
Pepperoni	0.16	12	$4.7 \times 10^{-11} - 5.7 \times 10^{-11}$
Raisins	0.15 - 2.40	60	$5.0 \times 10^{-11} - 2.5 \times 10^{-10}$
Rice	0.10 - 0.25	30 - 50	$3.8 \times 10^{-8} - 2.5 \times 10^{-7}$
Sea sand	0.07 - 0.13	60	$2.5 \times 10^{-8} - 2.5 \times 10^{-6}$
Soybeans	0.07	30	$7.5 \times 10^{-13} - 5.4 \times 10^{-12}$
Silica gel	-	25	$3.0 \times 10^{-6} - 5.6 \times 10^{-6}$
Starch gel	0.20 - 3.00	30 - 50	$1.0 \times 10^{-10} - 1.2 \times 10^{-9}$
Tobacco leaf	-	30 - 50	$3.2 \times 10^{-11} - 8.1 \times 10^{-11}$
Wheat	0.12 - 0.30	21 - 80	$6.9 \times 10^{-12} - 2.8 \times 10^{-10}$
Wood, soft	-	40 - 90	$5.0 \times 10^{-10} - 2.5 \times 10^{-9}$
Wood, yellow poplar	1.00	100 - 150	$1.0 \times 10^{-8} - 2.5 \times 10^{-8}$

Keey (1978) and Geankopolis (1993), among others, have provided analytical expressions for liquid diffusion and capillarity models of falling rate drying. Table 7 gives solution of the one-dimensional transient partial differential equations for cartesian, cylindrical and spherical coordinate systems. These results can be utilized to estimate the diffusivity from the falling rate drying data or to estimate the drying rate and drying time if the diffusivity value is known.

It is noteworthy that the diffusivity, D_L , is a strong function of X_f as well as temperature and must be determined experimentally. Thus, the liquid diffusion model should be regarded purely as an empirical representation drying in the falling rate period. More advanced models are, of course, available but their widespread use in the design of dryers is hampered by the need for extensive empirical information required to solve the governing equations. Turner and Mujumdar (1997) provide a wide assortment of mathematical models of drying and dryers, and also discuss the application of various techniques for the numerical solution of the complex governing equations.

One simple approach to interpolating a given falling rate curve over a relatively narrow range of operating conditions is that first proposed by van Meel (1958). It is found that the plot of normalized drying rate $\nu = N/N_c$ versus normalized free moisture content $\eta = (X - X^*)/(X_c - X^*)$ was nearly independent of the drying conditions. This plot, called the characteristic drying rate curve, is illustrated in Figure 8. Thus, if the constant rate-drying rate, N_c , can be estimated and the equilibrium moisture content data are available, then the falling rate curve can be estimated using this highly simplified approach. Extrapolation over wide ranges is not recommended, however.

Waananen et al. (1993) have provided an extensive bibliography of over 200 references dealing with models for drying of porous solids. Such models are useful to describe drying processes for the purposes of engineering design, analysis and optimization. A mathematical description of the process is based on the physical mechanisms of internal heat and mass transfer that control the process resistances, as well as the structural and thermodynamic assumptions made to formulate the model. In the constant rate period, the

overall drying rate is determined solely by the heat and mass transfer conditions external to the material being dried, such as the temperature, gas velocity, total pressure and partial pressure of the vapor. In the falling rate period, the rates of internal heat and mass transfer determine the drying rate. Modeling of drying becomes complicated by the fact that more than one mechanism may contribute to the total mass transfer rate and the contributions from different mechanisms may even change during the drying process.

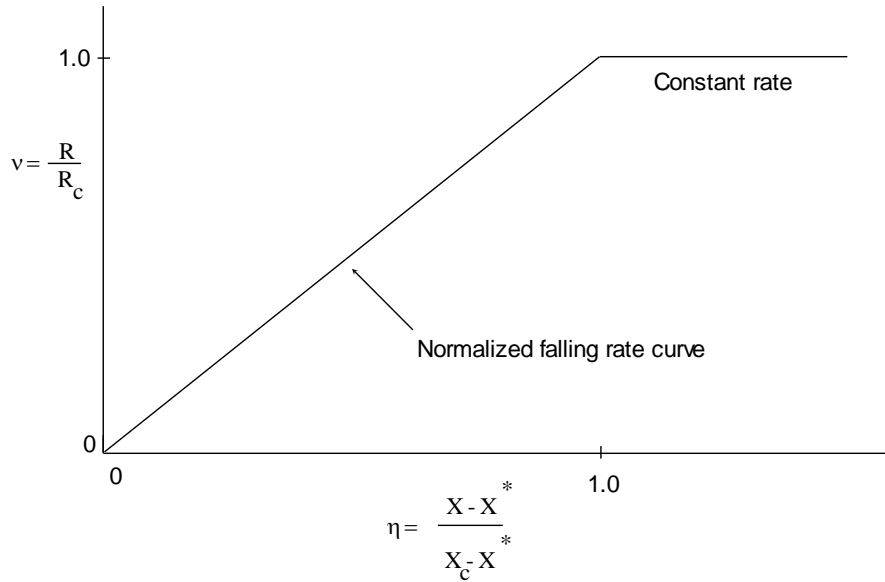


Figure 8 Characteristic drying rate curve

Table 7 Solution to Fick's second law for some simple geometries (Pakowski and Mujumdar, 1995)

Geometry	Boundary conditions	Dimensionless average free M.C.
Flat plate of thickness $2b$	$t = 0; -b < z < b; X = X_0$	$X = \frac{8}{\pi^2}$
	$t > 0; z = \pm b; X = X^*$	$\sum_{n=1}^{\infty} \frac{1}{(2n-1)} \exp\left[-(2n-1)^2 \frac{\pi^2}{4b} \left(\frac{D_L t}{b}\right)\right]$
Infinitely long cylinder of radius R	$t = 0; 0 < r < R; X = X_0$	$X = 4 \sum_{n=1}^{\infty} \frac{1}{R^2 \alpha_n^2} \exp(-D_L \alpha_n^2 t)$
	$t > 0; r = R; X = X^*$	
Sphere of radius R	$t = 0; 0 < r < R; X = X_0$	$X = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[\frac{-n^2 \pi^2}{R} \left(\frac{D_L t}{R}\right)\right]$
	$t > 0; r = R; X = X^*$	

where α_n are positive roots of the equation $J_0(R\alpha_n) = 0$

Diffusional mass transfer of the liquid phase, as discussed earlier, is the most commonly assumed mechanism of moisture transfer used in modeling drying that takes place at temperatures below the boiling point of the liquid under locally applied pressure. At higher temperatures, the pore pressure may rise substantially and cause a hydrodynamically driven flow of vapor, which, in turn, may cause a pressure driven flow of liquid in the porous material.

For solids with continuous pores, a surface tension driven flow (capillary flow) may occur as a result of capillary forces caused by the interfacial tension between the water and the solid. In the simplest model, a modified form of the Poiseuille flow can be used in conjunction with the capillary force equation to estimate the rate of drying. Geankoplis (1993) has shown that such a model predicts the drying rate in the falling rate period to be proportional to the free moisture content in the solid. At low solid moisture contents, however, the diffusion model may be more appropriate.

The moisture flux due to capillarity can be expressed in terms of the product of a liquid conductivity parameter and moisture gradient. In this case, the governing equation has, in fact, the same form as the diffusion equation.

For certain materials and under conditions such as those encountered in freeze drying, a “receding-front” model involving a moving boundary between “dry” and “wet” zones often describes the mechanism of drying much more realistically than does the simple liquid diffusion or capillarity model. Examination of the freeze drying of a thin slab indicates that the rate of drying is dependent on the rate of heat transfer to the “dry-wet” interface and the mass transfer resistance offered by the porous dry layer to permeation of the vapor which sublimates from the interface. Because of the low pressures encountered in freeze drying, Knudsen diffusion may be significant. Liapis and Marchello (1984) have discussed models of freeze drying involving both unbound and bound moisture.

When drying materials under intense drying conditions, diffusion or capillarity models generally do not apply. If evaporation can occur within the material there is a danger of the so-called “vapor-lock” that occurring within the capillary structure causing breaks in liquid-filled capillaries. This phenomenon can cause departure from the classical drying curve, e.g., no constant rate drying may appear under intense drying conditions but may do so under milder drying conditions (Zaharchuk, 1993).

CLOSING REMARKS

An attempt is made here to provide a concise overview of the fundamental principles and terminology used in the drying literature. Advanced models and calculation procedures for drying and dryers of various types can be found in the literature cited. It must be noted that the models and estimation methods given here are necessarily simplistic and caution must be exercised in applying them in practice. Almost without exception design and scale-up of most dryers must be preceded with appropriate laboratory and/or pilot scale experimentation. Although no mention is made here about quality considerations, it is important to recognize that drying involves both heat and mass transfer processes but also material science. Drying affects product quality in a decisive manner and hence must be an essential part of any dryer calculation and specification.

NOMENCLATURE

A	evaporation area, m^2
a_w	water activity, -
c_p	specific heat, $J\ kg^{-1}\ K^{-1}$
c_s	humid heat, $J\ kg^{-1}\ K^{-1}$
D_L	effective diffusivity, $m^2\ s^{-1}$
D_{L0}	effective diffusivity at reference temperature, $m^2\ s^{-1}$
E_a	activation energy, J
ΔH_w	enthalpy of wetting, $J\ kg^{-1}$
h	convective heat transfer coefficient, $W\ m^{-2}\ K^{-1}$
k_g	thermal conductivity, $W\ m^{-1}\ K^{-1}$
k_y	convective mass transfer coefficient, $kg\ mol\ s^{-1}\ m^{-2}\ mol\ frac^{-1}$
M_{air}	molar mass of air, $kg\ mol^{-1}$
M_s	mass of bone dry solid, kg
N	drying rate, $kg\ m^{-2}\ h^{-1}$
P_v	vapor pressure of pure water, Pa
p	partial pressure, Pa
p_w	equilibrium vapor pressure of water, Pa
RH	relative humidity, decimal fraction, -
R_g	universal gas constant, $8.314\ J\ mol^{-1}\ K^{-1}$
T	temperature, $^{\circ}C$
T_{abs}	absolute temperature, K
T_{wb}	wet-bulb temperature, $^{\circ}C$
t	time, s (or h)
X	total moisture content, kg water/kg dry solid, -
X_c	critical moisture content, kg water/kg dry solid, -
X_f	free moisture content, kg water/kg dry solid, -
X^*	equilibrium moisture content, kg water/kg dry solid, -
Y	absolute air humidity, kg water vapor/kg dry air

Greek letters

η	normalized drying rate, -
λ_s	latent heat of vaporization, $J\ kg^{-1}$
μ_g	dynamic viscosity, $kg\ m^{-1}\ s^{-1}$
ν	normalized drying rate, -
ρ_g	density, $kg\ m^{-3}$

Subscripts

c	constant rate period
f	falling rate period
g	gas
s	solid

<i>v</i>	vapor
<i>w</i>	water
<i>wb</i>	wet-bulb

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