Subject: Food Technology

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Paper No. : 04 Unit Operations in Food Processing

Module : 15 Drying 1: Theory of drying

Development Team

Principal Investigator	Prof. (Mrs.) Vijaya Khader, Ph.D Former Dean, Acharya N G Ranga Agricultural University
Paper Coordinator	Er. Dibyakanta Seth Asst. Professor, Tezpur University, Assam
Content Writer	Er. Prakash Nayak CIT, Kokrajhar, Assam
Content Reviewer	Prof. (Mrs.) Vijaya Khader, Ph.D Former Dean, Acharya N G Ranga Agricultural University Dr. MC Varadaraj , Chief Scientist CSIR-CFTRI, Mysore

Food Technology

Unit Operations in Food Processing

Drying 1: Theory of drying

Description of Module	
Subject Name	Food Technology
Paper Name	04 Unit Operations in Food Processing
Module Name/Title	Drying 1: Theory of drying
Module Id	FT/UOFP/15
Pre-requisites	Basic of Heat Transfer & mass transfer
Objectives	To understand mechanism of drying, heat and mass transfer during drying and to study the EMC and their uses in agricultural processing.
Keywords	Heat Transfer, Mass Transfer, Dryer Efficiencies & EMC
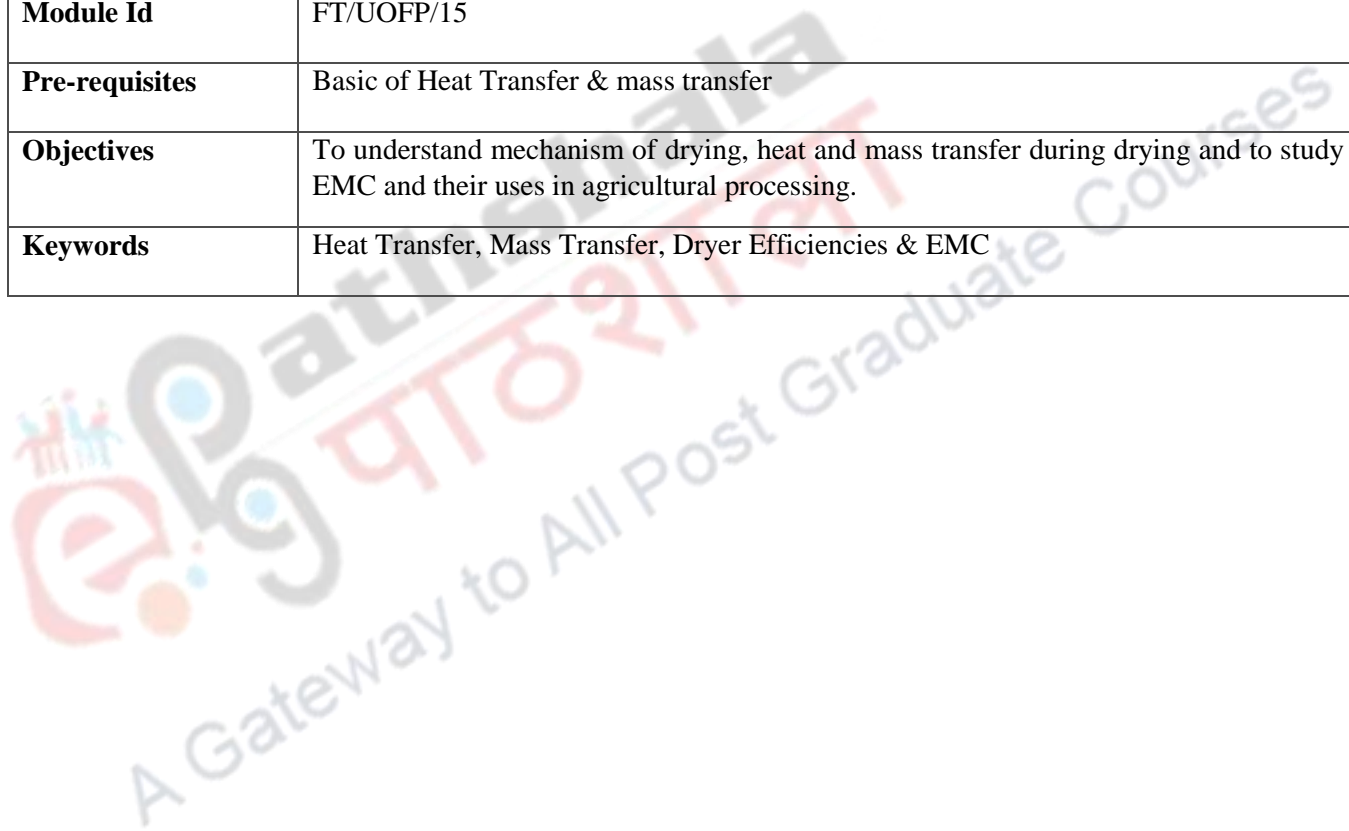
16.1 Introduction

Drying is one of the oldest methods of preserving food. Primitive societies practiced the drying of meat and fish in the sun long before recorded history. Today the drying of foods is still important as a method of preservation. Dried foods can be stored for long periods without deterioration occurring. The principal reasons for this are that the microorganisms which cause food spoilage and decay are unable to grow and multiply in the absence of sufficient water and many of the enzymes which promote undesired changes in the chemical composition of the food cannot function without water.

Preservation is the principal reason for drying, but drying can also occur in conjunction with other processing. For example in the baking of bread, application of heat expands gases, changes the structure of the protein and starch and dries the loaf. Losses of moisture may also occur when they are not desired, for example during curing of cheese and in the fresh or frozen storage of meat, and in innumerable other moist food products during holding in air. (Detailed discussed in module 16)

Drying of foods implies the removal of water from the foodstuff. In most cases, drying is accomplished by vaporizing the water that is contained in the food, and to do this the latent heat of vaporization must be supplied. There are, thus, two important process-controlling factors that enter into the unit operation of drying:

(a) Transfer of heat to provide the necessary latent heat of vaporization,

(b) Movement of water or water vapour through the food material and then away from it to effect separation of water from foodstuff.

Drying processes fall into three categories:

Air and contact drying under atmospheric pressure: In air and contact drying, heat is transferred through the foodstuff either from heated air or from heated surfaces and the water vapour is removed with the air.

Vacuum drying: In vacuum drying, advantage is taken of the fact that evaporation of water occurs more readily at lower pressures than at higher ones. Heat transfer in vacuum drying is generally by conduction, sometimes by radiation.

Freeze Drying: In freeze drying, the water vapour is sublimed off frozen food. The food structure is better maintained under these conditions. Suitable temperatures and pressures must be established in the dryer to ensure that sublimation occurs

16.2 THEORY OF DRYING PHASE DIAGRAM

Pure water can exist in three states, solid, liquid and vapour. The state in which it is at any time depends on the temperature and pressure conditions and it is possible to illustrate this on a phase diagram, as in Fig 15.1
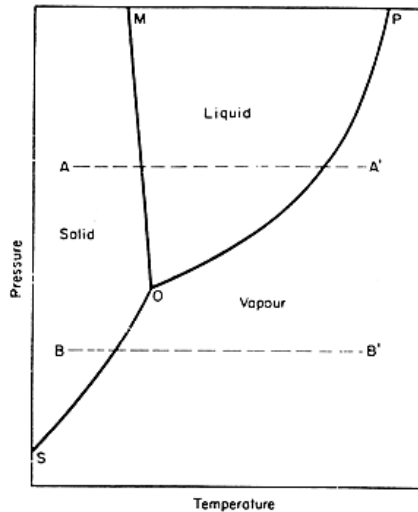
Figure 15.1 Phase diagram for water

If we choose any condition of temperature and pressure and find the corresponding point on the diagram, this point will lie, in general, in one of the three labelled regions, solid, liquid, or gas. This will give the state of the water under the chosen conditions.

Under certain conditions, two states may exist side by side, and such conditions are found only along the lines of the diagram. Under one condition, all three states may exist together; this condition arises at what is called the triple point, indicated by point O on the diagram. For water it occurs at 0.0098°C and 0.64 kPa (4.8 mm of mercury) pressure.

If heat is applied to water in any state at constant pressure, the temperature rises and the condition moves horizontally across the diagram, and as it crosses the boundaries a change of state will occur. For example, starting from condition A on the diagram adding heat warms the ice, then melts it, then warms the water and finally evaporates the water to condition A'. Starting from condition B, situated below the triple point, when heat is added, the ice warms and then sublimes without passing through any liquid state.

5

Liquid and vapour coexist in equilibrium only under the conditions along the line OP. This line is called the vapour pressure/temperature line. The vapour pressure is the measure of the tendency of molecules to escape as a gas from the liquid. The vapour pressure/temperature curve for water is shown in Fig. 15.2, which is just an enlargement for water of the curve OP of Fig. 15.1.
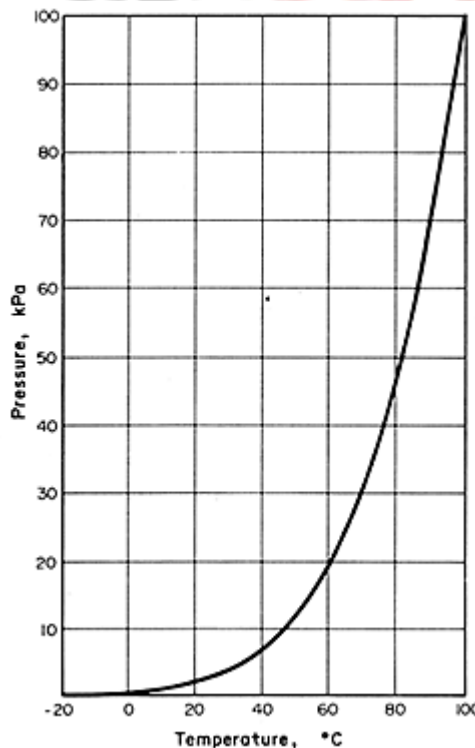
Figure 15.2. Vapour pressure/temperature curve for water

Boiling occurs when the vapour pressure of the water is equal to the total pressure on the water surface. The boiling point at atmospheric pressure is of course 100°C. At pressures above or below atmospheric, water boils at the corresponding temperatures above or below 100°C, as shown in Fig. 15.2 for temperatures below 100°C.

15. 3 Latent Heat of Sublimation

Sublimation is a physical process in which a solid directly converts into a gaseous (vapor) state without going through a liquid state. The latent heat of sublimation at a particular temperature is the amount of heat required to convert a unit mass of solid into gas. For example, when ice sublimates into vapor, the amount of heat required at 0°C is estimated equal to 2,838 kJ/kg, which is the latent heat of sublimation of ice at 0°C. In the crystal growth of ice and snow in atmosphere, this process plays a dominant role. This process is opposite to the process of deposition.

15.4 Latent Heat of Vaporization

The enthalpy of vaporization, (symbol ΔH_{vap}) also known as the (latent) heat of vaporization or heat of evaporation, is the enthalpy change required to transform a given quantity of a substance from a liquid into a gas at a given pressure(often atmospheric pressure as in STP).

It is often measured at the normal boiling point of a substance; although tabulated values are usually corrected to 298 K, the correction is often smaller than the uncertainty in the measured value.

The heat of vaporization is temperature-dependent, though a constant heat of vaporization can be assumed for small temperature ranges and for reduced temperature $T_r<<1.0$. The heat of vaporization diminishes with increasing temperature and it vanishes completely at the critical temperature ($T_r=1$) because above the critical temperature the liquid and vapor phases no longer exist, since the substance is a supercritical fluid.

15.5 Heat Requirements for Vaporization

The energy, which must be supplied to vaporize the water at any temperature, depends upon this temperature. The quantity of energy required per kg of water is called the latent heat of vaporization, if it is from a liquid, or latent heat of sublimation if it is from a solid. The heat energy required to vaporize water under any given set of conditions can be calculated from the latent heats given in the steam table, as steam and water vapour are the same thing.

Example 15.1

A food containing 80% water is to be dried at 100°C down to moisture content of 10%. If the initial temperature of the food is 21°C, calculate the quantity of heat energy required per unit weight of the original material, for drying under atmospheric pressure. The latent heat of vaporization of water at 100°C and at standard atmospheric pressure is 2257 kJ kg^{-1}. The specific heat capacity of the food is 3.8 kJ kg^{-1} °C^{-1} and of water is 4.186 kJ kg^{-1} °C^{-1}. Find also the energy requirement/kg water removed.

Solution:

Calculating for 1 kg food

Initial moisture = 80%

800 g moisture are associated with 200 g dry matter.

Final moisture = 10 %,

100 g moisture are associated with 900 g dry matter,

Therefore (100 x 200)/900 g = 22.2 g moisture are associated with 200 g dry matter.

1kg of original matter must lose (800 - 22) g moisture = 778 g = 0.778 kg moisture.

Heat energy required for 1kg original material

= heat energy to raise temperature to 100°C + latent heat

to remove water

= (100 - 21) x 3.8 + 0.778 x 2257

= 300.2 + 1755.9

= 2056 kJ.

Energy/kg water removed, as 2056 kJ are required to remove 0.778 kg of water,

= 2056/0.778

= 2643 kJ

Steam is often used to supply heat to air or to surfaces used for drying. In condensing, steam gives up its latent heat of vaporization; in drying, the substance being dried must take up latent heat of vaporization to convert its liquid into vapour, so it might be reasoned that 1 kg of steam condensing will produce 1 kg vapour. This is not exactly true, as the steam and the food will in general be under different pressures with the food at the lower

pressure. Latent heats of vaporization are slightly higher at lower pressures, as shown in Table 15.1. In practice, there are also heat losses and sensible heat changes which may require to be considered.

TABLE 15.1

LATENT HEAT AND SATURATION TEMPERATURE OF WATER

Absolute pressure (kPa)	Latent heat of vaporization (kJ kg^{-1})	Saturation temperature (°C)
1	2485	7
2	2460	18
5	2424	33
10	2393	46
20	2358	60
50	2305	81

100	2258	99.6
101.35 (1 atm)	2257	100
110	2251	102
120	2244	105
200	2202	120
500	2109	152

Example 15.2 (Heat Energy in Vacuum drying)

Using the same material as in Example 15.1, if vacuum drying is to be carried out at 60°C under the corresponding saturation pressure of 20 kPa abs. (or a vacuum of 81.4 kPa), calculate the heat energy required to remove the moisture per unit weight of raw material.

Solution:

Heat energy required per kg raw material

= heat energy to raise temperature to 60°C + latent heat of vaporization at 20 kPa abs.

= (60 - 21) x 3.8 + 0.778 x 2358

= 148.2 + 1834.5

= 1983 kJ.

In freeze drying the latent heat of sublimation must be supplied. Pressure has little effect on the latent heat of sublimation, which can be taken as 2838 kJ kg^{-1}

Example 15.3 (Heat Energy in Freeze drying)

If the foodstuff in the two previous examples were to be freeze dried at 0°C, how much energy would be required per kg of raw material, starting from frozen food at 0°C?

Solution:

Heat energy required per kilogram of raw material= latent heat of sublimation

$$= 0.778 \times 2838$$
$$= \underline{2208 \text{ kJ}}.$$

15.6 Heat Transfer in Drying

We have been discussing the heat energy requirements for the drying process. The rates of drying are generally determined by the rates at which heat energy can be transferred to the water or to the ice in order to provide the latent heats, though under some circumstances the rate of mass transfer (removal of the water) can be limiting. All three of the mechanisms by which heat is transferred - conduction, radiation and convection - may enter into drying. The relative importance of the mechanisms varies from one drying process to another and very often one mode of heat transfer predominates to such an extent that it governs the overall process.

As an example, in air drying the rate of heat transfer is given by:

$q = h_sA(T_a - T_s)$

where q is the heat transfer rate in J s^{-1}, h_s is the surface heat-transfer coefficient J m^{-2} s^{-1} °C^{-1}, A is the area through which heat flow is taking place, m^2, T_a is the air temperature and T_s is the temperature of the surface which is drying, °C.

To take another example, in a roller dryer where moist material is spread over the surface of a heated drum, heat transfer occurs by conduction from the drum to the foodstuff, so that the equation is

$q = UA(T_i - T_s)$

Where U is the overall heat-transfer coefficient, T_i is the drum temperature (usually very close to that of the steam), T_s is the surface temperature of the food (boiling point of water or slightly above) and A is the area of drying surface on the drum.

The value of U can be estimated from the conductivity of the drum material and of the layer of foodstuff. Values of U have been quoted as high as 1800 J m^{-2} s^{-1} °C^{-1} under very good conditions and down to about 60 J m^{-2} s^{-1} °C^{-1} under poor conditions.

In cases where substantial quantities of heat are transferred by radiation, it should be remembered that the surface temperature of the food may be higher than the air temperature. Estimates of surface temperature can be made using the relationships developed for radiant heat transfer although the actual effect of combined radiation and evaporative cooling is complex. Convection coefficients also can be estimated using the standard equations.

13

For freeze drying, energy must be transferred to the surface at which sublimation occurs. However, it must be supplied at such a rate as not to increase the temperature at the drying surface above the freezing point. In many applications of freeze drying, the heat transfer occurs mainly by conduction.

As drying proceeds, the character of the heat transfer situation changes. Dry material begins to occupy the surface layers and conduction must take place through these dry surface layers which are poor heat conductors so that heat is transferred to the drying region progressively more slowly

15.7 Mass Transfer in Drying

In heat transfer, heat energy is transferred under the driving force provided by a temperature difference, and the rate of heat transfer is proportional to the potential (temperature) difference and to the properties of the transfer system characterized by the heat-transfer coefficient. In the same way, mass is transferred under the driving force provided by a partial pressure or concentration difference. The rate of mass transfer is proportional to the potential (pressure or concentration) difference and to the properties of the transfer system characterized by a mass-transfer coefficient.

Writing these symbolically, analogous to $q = UA \, \square T$, we have

$$dw/dt = k'_g \, A \square Y$$

Where *w* is the mass being transferred kg s^{-1}, *A* is the area through which the transfer is taking place, k'_g is the mass-transfer coefficient in this case in units of kg m^{-2} s^{-1}, and *Y* is the humidity difference in kg kg^{-1}.

Limitations:

Unfortunately the application of mass-transfer equation is not as straightforward as heat transfer, one reason being because the movement pattern of moisture changes as drying proceeds. Initially, the mass (moisture) is transferred from the surface of the material and later, to an increasing extent, from deeper within the food to the surface and thence to the air. So the first stage is to determine the relationships between the moist surface and the ambient air and then to consider the diffusion through the food. In studying the surface/air relationships, it is necessary to consider mass and heat transfer simultaneously. Air for drying is usually heated and it is also a major heat-transfer medium. Therefore it is necessary to look carefully into the relationships between air and the moisture it contains.

15.8 Equilibrium Moisture Content

It is important to understand that there are limits to the amount of water which can be removed from a food material under any given conditions. The moisture content of wet material in equilibrium with air of given humidity and temperature is termed the equilibrium moisture content (EMC). The equilibrium moisture content of solid varies with the direction from which equilibrium is approached. When product losing moisture and attains EMC with surrounding, then the desorption isotherm is obtained. But if product gains moisture from the surrounding, and attains EMC, the adsorption isotherm is obtained. The characteristic hysteresis is produced by differences in adsorption and desorption of curve.
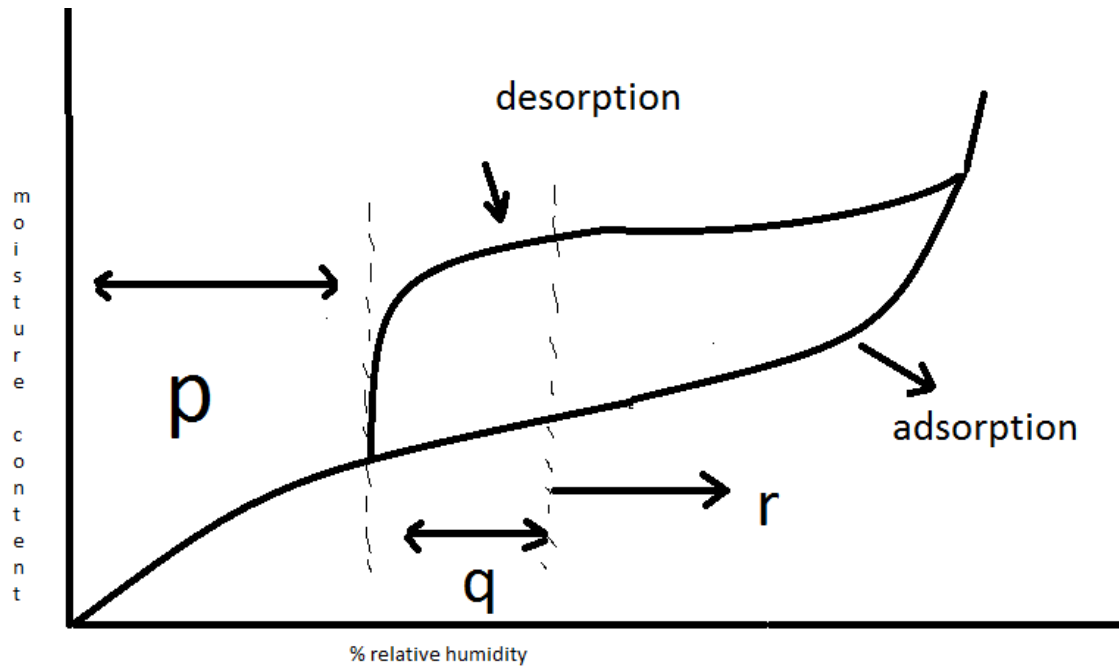
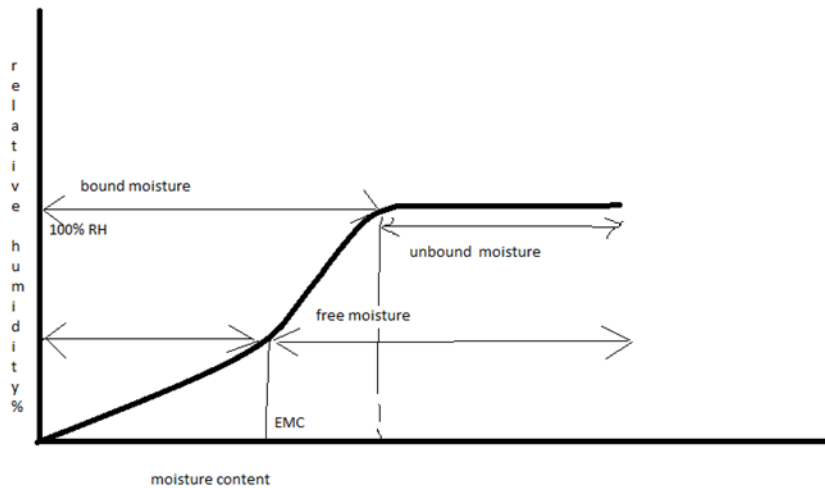Fig. 15. 3.   Adsorption-desorption isotherm

Fig.15.4 Relationship between moisture content and surrounding humidity

A plot of EMC at given temperature versus the relative humidity is termed sorption isotherm. Figure 15.3 shows two typical sorption isotherms. They are characterized by three distinct zones, which are discussed as below:

i. *Zone P*: In zone P, the water is bound very strongly to sites and is unavailable for reaction. This moisture is referred to as monolayer moisture and it is strongly bound by adsorption forces. As shown in figure, it is observed that there is no distinction exists between the adsorption and desorption isotherm.

ii. *Zone Q*: In zone Q represents a transition zone. The water is bound in multiple layers; it is less strongly bound.

iii. *Zone R*: Water in zone R is even more loosely held. Water acts as a solvent and it can serve to mobilize the reactants.

Figure 15.4 which represents plot % RH against the moisture content of food is different way of presenting the same information. The figure indicates three distinct moisture of product, which are defined as below:

1. *Bound Moisture*: Bound moisture in a solid is determined from intersection of the equilibrium moisture content of the material with the 100% humidity line. The bound water exerts a vapour pressure lower than that of pure liquid at the same temperature. Substances containing bound water are called hygroscopic materials.

2. *Unbound Moisture*: If a material contains more water than indicated by interaction with 100% humidity line, then this excessive moisture content is

called unbound moisture and is held primarily in voids of the solid. It exerts a vapour pressure as high as that of ordinary water at the same temperature.

3. *Free Moisture*: It is the moisture content of a material that can be removed by drying under the given temperature and humidity. It may include both bound and unbound moisture. Free moisture content obtained from the total average moisture content minus the equilibrium moisture content for the prevailing conditions of drying

15.8.1 EMC Models

For determination of EMC of agricultural and food products many theoretical and experimental models have been proposed.

Some of EMC Models are listed as below:

a) Kelvin Equation

b) Harkin- Jura Equation

c) Chung- Pfost Equation

d) Henderson's Equation

e) Langmuir Model

f) BET Model

g) GAB Model

a) Kelvin Equation: In the year 1871 Kelvin proposed this model of moisture absorption for solid material. For evolving this model, the phenomenon of capillary condensation in pores of solid materials was considered.

$$\ln(P_v/P_{vs}) = 2\sigma V\cos\alpha/rRT_a$$

P_v= vapour pressure of food material

P_{vs}=saturated vapour pressure

σ=moisture surface tension

α=angle between moisture and capillary wall

V=volume of moisture

R=universal gas constant

r=radius of cylindrical capillary

T_a=absolute temperature

Limitations:

The utility of above equation for grain EMC determination is limited in condition of relative humidity more than 95% when the action capillary condensation takes place.

b) Harkin- Jura Equation: This model is based on the theory of existence of a potential field above surfaces. The equation is as under

$$\ln(P_v/P_{vs}) = d - e/V^2$$

d and e are product constant depend upon temperature

Limitation:

Harkins- Jura equations does not predict satisfactorily accurate EMC value when the relative humidity is more than 30%.

c) Chung-Pfost Equation: Chung-Pfost has proposed this equation for determination of EMC on the basis of potential field theory.

$$\ln(P_v/P_{vs}) = -(A/RT) \exp(-BM)$$

A and B are product constant

M= moisture content

T= temperature at Kelvin

Limitation:

The above equation provides fairly accurate EMC value between 20% to 90% relative humidity.

d) <u>Henderson's Equation</u>: This EMC equation is very much popular to fit the empirical data. This equation has the following form:

$1-rh = \exp(-CTM^n)$

rh= relative humidity in decimal

C and n are product constant

M= EMC (%dry basis).

Example 15.4

Calculate the EMC of brinjal seed at rh=10%, T=50^{0}C using Henderson' equation?

Solution:

Given data: rh=0.1; T=50^{0}C or 323k; C=6.5*10^{-6}; n=1.8

Therefore,

$1-rh = \exp(-CTM^n)$

$1-0.1 = \exp(-6.5*10^{-6}*323*M^{1.8})$

$\ln 0.9 = -6.5*10^{-6}*323*M^{1.8})$

EMC of brinjal seed is 8.7886.

e) <u>Langmuir Model:</u>

The Langmuir adsorption model is the most common model used to quantify the amount of adsorbate adsorbed on an adsorbent as a function of partial pressure or concentration at a given temperature. It considers adsorption of an ideal gas onto an idealized surface. The gas is presumed to bind at a series of distinct sites on the surface of the solid and the adsorption process is treated as a reaction where a gas molecule A_g reacts with an empty site, S, to yield an adsorbed complex A_{ad}

$$A_g \; + \; S \; \rightleftharpoons \; A_{ad}$$

Basic assumptions of the model

Inherent within this model, the following assumptions are valid specifically for the simplest case: the adsorption of a single adsorbate onto a series of equivalent sites on the surface of the solid.

1. The surface containing the adsorbing sites is perfectly flat plane with no corrugations (assume the surface is homogeneous)
2. The adsorbing gas adsorbs into an immobile state.
3. All sites are equivalent.
4. Each site can hold at most one molecule of A (mono-layer coverage only).

22

5. There are no interactions between adsorbate molecules on adjacent sites.

Equation Derivation

The Langmuir equation is derived starting from the equilibrium between empty surface sites (S^*), particles (P) and filled particle sites (SP)
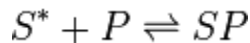
$$S^* + P \rightleftharpoons SP$$

The equilibrium constant K is thus given by the equation:

$$K = \frac{[SP]}{[S^*][P]}$$

Because the number of filled surface sites (SP) is proportional to θ, the number of unfilled sites (S^*) is proportional to 1-θ, and the number of particles is proportional to the gas pressure or concentration (p), the equation can be rewritten as:

$$\alpha = \frac{\theta}{(1-\theta)p}$$

Where α is a constant

Rearranging this as follows:

$$\theta = \alpha(1-\theta)p$$
$$\theta = p\alpha - p\theta\alpha$$
$$\theta + p\theta\alpha = p\alpha$$
$$\theta(1 + p\alpha) = p\alpha$$

Leads to Langmuir equation:

$$\theta = \frac{\alpha \cdot p}{1 + \alpha \cdot p}$$

f) <u>Brunauer–Emmett–Teller (BET) Model</u>:

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting *BET equation* is

$$\frac{1}{v\left[(p_0/p) - 1\right]} = \frac{c - 1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c}, \qquad (1)$$

Where p and p_0 are the equilibrium and the saturation pressure of adsorbents at the temperature of adsorption, v is the adsorbed gas quantity (for example, in volume units), and v_m is the monolayer adsorbed gas quantity. c is the *BET constant*,

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right), \qquad (2)$$

Where E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction.
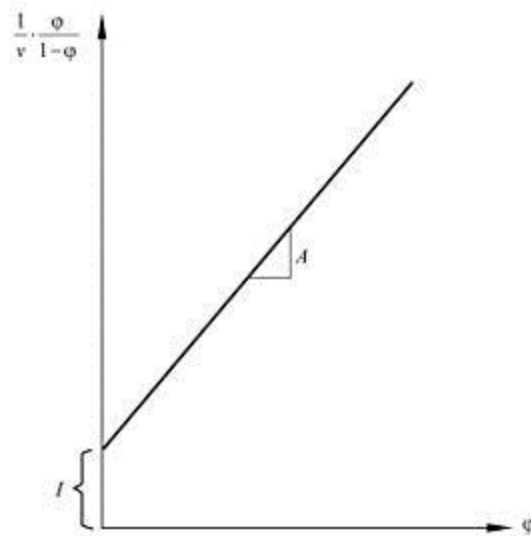
Fig 15. 5 BET plot

Equation (1) is an adsorption isotherm and can be plotted as a straight line with $1/v[(p_0/p) - 1]$ on the y-axis and $\phi = p/p_0$ on the x-axis according to experimental results. This plot is called a *BET plot*. The linear relationship of this equation is maintained only in the range of $0.05 < p/p_0 < 0.35$. The value of the slope A and the y-intercept I of the line are used to calculate the monolayer adsorbed gas quantity v_m and the BET constant c. The following equations can be used:

$$v_m = \frac{1}{A + I} \qquad (3)$$

$$c = 1 + \frac{A}{I}. \qquad (4)$$

25

The BET method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. The total surface area S_{total} and the specific sueface area S_{BET} are given by

$$S_{total} = \frac{(v_m N s)}{V}, \qquad (5)$$

$$S_{BET} = \frac{S_{total}}{a}, \qquad (6)$$

where v_m is in units of volume which are also the units of the molar volume of the adsorbate gas, N is Avogadro's number, s the adsorption cross section of the adsorbing species, V the molar volume of the adsorbate gas, and a the mass of the solid sample or adsorbent

g) Gab Model: This equation has a similar form of BET, but has an extra constant, K. BET is actually a special case of GAB, with K = 1. The GAB equation was used to model water adsorption of these shale samples as follows:

$$m = CKa_{Wm}/(1-Ka_w)(1-Ka_w+KCa_W) \qquad (1)$$

Where m is the amount of sorbate adsorbed by 1g of sorbant at sorbate activity aw, M is the monolayer moisture content. C and K are GAB constants and are related to monolayer and multilayer properties. The assumption of the GAB model over the BET (Brunauer, Emmett and Teller) formulation stating that the sorption state of the sorbate molecules in the layers beyond the first is the same, but different to the pure liquid state, demands the

introduction of the additional constant K. C and K are related to the temperature effect being expressed by equation

2 and 3:

$$C = C° \exp(\Delta h_c / RT) \qquad (2)$$

$$K = K° \exp(\Delta h_k / RT) \qquad (3)$$

Where Δhc is the specific bonding enthalpy of water monolayer (J/kg), Δhk is the mean specific bonding enthalpy of the water multilayer (J/kg), R is the universal gas constant (J/kg/K), T is the absolute temperature (K), Δhs, mono is the specific sorption enthalpy of water monolayer (J/kg), $\Delta hvap$ is the specific vaporization enthalpy of water (J/kg), Δhs, multi is the mean specific sorption enthalpy of the water multilayer (J/kg), C° and K° are adjustable parameters accounting for temperature effect.

$$\Delta h_K = \Delta h_{S,multi} - \Delta h_{vap}$$
$$\Delta h_c = \Delta h_{S,mono} - \Delta h_{vap}$$

The GAB equation can be rearranged to polynomial expression:

$$a_w/m = K/M°(1/C-1)a_w^2 + ((C-2)/(C+M°))a_w + 1/C*K*M° \qquad (4)$$

The modified GAB equation replaces C with C/T, where T is the temperature in ^0C. This enables isotherms to be estimated for any temperature, based on data measured at one temperature.

However, the accuracy of this is approximate only, as it assumes all materials are affected by temperature identically.

Application of GAB Model:

The present investigation deals with analyzing the validity of GAB model for isotherms of different food products. The model was found satisfactory for different food products with different shapes of isotherms under widely varying conditions (temperature: 4–140C; moisture %D.B.: 2–71; activity: 0.059–0.99). The present study covered a wide range of food products from green vegetables, fruits, cereals and nuts to casein, pectin and protein. Food products with complex molecular structure and high sugar contents were also included. A nonlinear regression method was applied to evaluate the six parameters of the GAB model. The Guggenheim constant, factor for multilayer molecules and the monolayer moisture were assumed to follow an Arrhenius type relationship with temperature variation. The values of net isosteric heat of sorption obtained by GAB model and Claudius Chaperon equation were compatible.

Food Technology

Unit Operations in Food Processing

Drying 1: Theory of drying