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Moisture Sorption Isotherms and Isotherm Model Performance Evaluation for Food and Agricultural Products

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Abstract

Moisture sorption characteristics of agricultural and food products play important roles in such technological processes as drying, handling, packaging, storage, mixing, freeze-drying and other processes that require the prediction of food stability, shelf life, glass transition and estimation of drying time and texture and prevention of deteriorative reactions. They are useful in the computation of thermodynamic energies of moisture in the products. An understanding of moisture sorption phenomena in products, moisture sorption isotherm (MSI) determination techniques and moisture sorption isotherm model evaluation procedures would be useful in the development or selection, modeling and controlling as well as optimization of appropriate processes to make for enhanced efficiency. The phenomena addressed in this chapter are equilibrium moisture content (EMC)-water activity (a_w) relationships and MSI types, temperature influence on isotherms and occurrence of moisture sorption hysteresis. MSI measurement techniques highlighted are the gravimetric, vapor pressure manometric (VPM), hygrometric and inverse gas chromatographic and the use of AquaLab equipment. Commonly used moisture sorption isotherm models (BET, GAB, modified GAB, Hailwood-Horrobin, modified Hailwood-Horrobin, modified Halsey, modified Henderson, modified Chung-Pfost and modified Oswin) were selected, and their evaluation procedures using moisture sorption data were outlined. Static gravimetric technique involving the use of saturated salt solution appears to be the most widely used and recommended method of determining the EMC of agricultural and food products. Most of the MSI models can be fitted to moisture sorption data thorough linearization by logarithmic transformation, while others can be solved using such expression as second-order polynomial. Model goodness of fit can be determined using standard (SE) error of estimate, coefficient of determination (R^2), mean relative percentage deviation (P) and fraction explained variation (FEV). The acceptance of a model depends on the nature of its residual plots. A model is considered acceptable if the residual plots show uniform scatter around the horizontal value of zero showing no systemic tendency towards a clear pattern. A model is better than another model if it has lower SE, lower P, higher R^2 and higher FEV. Although it appears as if a generalized MSI model is yet to exist, it is recommended that the Ngoddy-Bakker-Arkema (NBA) model should be given thorough going and extensive testing on the MSI of different categories of food as it could prove true to its generalized model posture due to the fundamental nature of its derivation.

Keywords: adsorption, desorption, equilibrium moisture isotherm, moisture sorption isotherm models, moisture sorption isotherm hysteresis

1. Introduction

A fundamental characteristic of biological materials, which influence virtually every aspect of handling, storage, manufacturing and consumption of food products [1], including every aspect of the dehydration process and storage stability of the dried products [2], is their basic hygroscopicity. By this, it is meant that when biological materials are exposed to water vapor of a definite pressure, sorption of the water vapor by the product will occur. This chapter discusses the phenomena at play, their technological applications, factors that influence the characteristics, measurement techniques, models that are commonly used to predict them and models' predictive performance evaluation procedures.

2. Sorption phenomena in biological materials

Biological materials at constant moisture content and temperature display characteristic vapor pressure and would tend to approach equilibrium with the temperature and vapor pressure of the surrounding gaseous atmosphere. To attain this equilibrium, the material either gains moisture from the environment or loses moisture to the environment depending on whether the vapor pressure of the surrounding is higher or lower than its vapor pressure [3]. The former process is called adsorption and the latter desorption. If the conditions of the surrounding are not changed for a sufficiently long period of time (theoretically for infinitely long time), the temperature at which the vapor pressure of the material and its surrounding is the same is established. At equilibrium, no further change in moisture content of the product occurs, and the moisture content of the material at that point is called equilibrium moisture content (EMC), while the relative humidity is known as equilibrium relative humidity. Water activity (a_w) is another term used to denote the ERH in decimal unit. The definition of water activity is based on the concept of thermodynamics and refers to the availability of moisture in biomaterials for physical, chemical and biological changes [4, 5], and it is a property of the material.

2.1 Moisture sorption isotherm

When equilibrium is attained, the moisture content is termed adsorption EMC or desorption EMC depending on whether the equilibrium was reached thorough the adsorption or desorption process. The EMC obtained thorough the desorption process usually lies above the one obtained thorough the adsorption process in the isotherm plots and leads to formation of the hysteresis loop (MSI) when graphically expressed [6]. Brunauer et al. [7] classified moisture sorption isotherms into five general types (**Figure 1**). The type I is the Langmuir, while the type II is the sigmoid or S-shaped isotherm. The type III is known as the Flory-Huggins isotherm and is usually influence by the presence of solvent or plasticizer such as glycerol above the glass transition temperature, and type IV is due to the presence of swellable hydrophilic solid that influence the moisture sorption process until a maximum site hydration is reached, while the type V is the BET multilayer adsorption isotherm. Moisture sorption isotherms of most foods are nonlinear, generally sigmoidal in shape, and of the type II classification [1, 6].

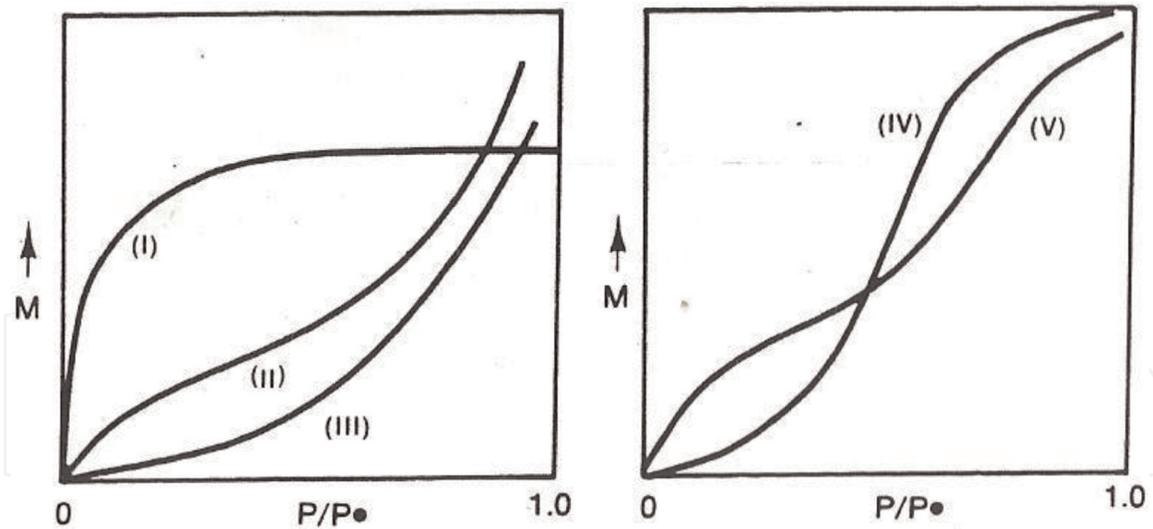


Figure 1.
Types of moisture sorption isotherm for food. Source: Rizvi [6].

2.2 Applications of moisture sorption isotherm

In drying operation, it is the removal of water which is important, and hence the desorption equilibrium moisture relationship is required to determine the lowest attainable moisture content at the process temperature and relative humidity [8]. Labuza and Hyman [9] applied the changing of water activity of food ingredients and effective diffusivity to control moisture migration in multidomain foods, when temperature changes occur. The moisture sorption isotherms of food and agricultural products are therefore of special interest in the design of storage and preservation processes such as packaging, drying, mixing, freeze-drying and other processes that require the prediction of food stability, shelf life and glass transition and estimation of drying time [10], texture and deteriorative reactions in agricultural and food products. The precise determination of equilibrium moisture contents of dehydrated foods provides valuable information for the accurate computation of thermodynamic energies from existing theories [1].

2.3 Factors influencing moisture sorption characteristics

The adsorption and desorption characteristics of agricultural and food products are affected by numerous factors [11], and these include composition, origin, postharvest history and methodology of measurement. In general, polymers sorb more water than sugars and other soluble components at lower water activities [12]. However, the soluble components sorb more water above certain water activity. The MSIs for the same material from different sources usually differ and are comparable only with qualification. The type of treatments given to the product may change the polar and other groups that bind water, along with changes in the capillary and other configurations of the food structure [13]. Greig [14] showed that the denaturation of native cottage cheese whey had no effect on the sorption isotherm at low water activities but significantly increased sorption at high water activities. Yu et al. [15] studied the moisture sorption characteristics of freeze-dried, osmo-dried, osmo-freeze-dried and osmo-air-dried cherries and blue berries and found that the EMC of osmo-air-dried cherries was generally higher than that of the osmo-freeze-dried and freeze-dried cherries at the lower temperature of 10°C, but at higher temperatures of 25 and 40°C, the difference was not significant. Similar result was reported for blue berries. San Jose et al. [16] showed that the drying

method (freeze- and spray-drying) of lactose-hydrolyzed milk did not affect the adsorption isotherms but had profound effect on the desorption isotherms. Tsami et al. [17] investigated the effect of drying method on the sorption characteristics of model fruit powder and reported that freeze-dried gel adsorbed more vapor at 25°C than microwave-dried gel, which had a higher sorption capacity than vacuum- and conventionally dried product. Mittal and Usborne [18] determined the moisture sorption isotherms of meat emulsions and showed that their EMC was affected by the fat-protein ratio. Mazza [19] reported that at 40°C and in the monolayer region of the isotherm, the EMC of precooked dehydrated pea was higher than that of raw pea but that at water activities above 0.5, the sorption capacity of precooked pea was lower than that of raw pea. Aviara [20] noted that chemical modification (cross-linking and hydroxypropylation) of cassava, maize and sorghum starches had profound influence on their moisture adsorption and desorption characteristics. While cross-linking lowered the sorptive capacity of the starches, hydroxypropylation enhanced the ability of the starches to sorb or desorb moisture. Palou et al. [21] studied the moisture sorption characteristics of three cookies and two corn snacks whose main composition difference was in fat and total carbohydrate and found the EMC difference at 5% level of significance. Igbeka et al. [22], Ajibola and Adams [23] and Gevaudan et al. [24] studied the moisture sorption characteristics of cassava and presented data that were fitted by different moisture sorption isotherm models. The variance in EMC may be due to the source of the material, product's postharvest and sorption history and varietal differences, methodology of measurement, temperature range and limitations imposed by model selection.

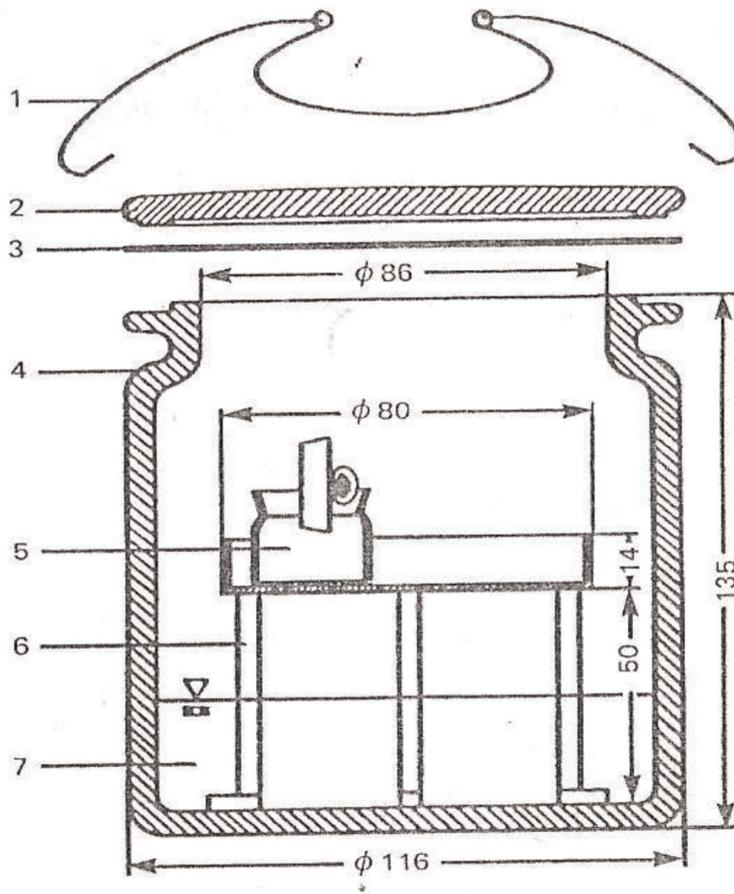
3. Moisture sorption isotherm measurement techniques

Several methods of determining the moisture sorption isotherm of agricultural and food products have been employed by investigators [25]. Gal [26–28] carried out a thorough review of the methods and pointed out that the basic techniques include the gravimetric, hygrometric, vapor pressure manometric and inverse gas chromatography and special method involving the use of AquaLab.

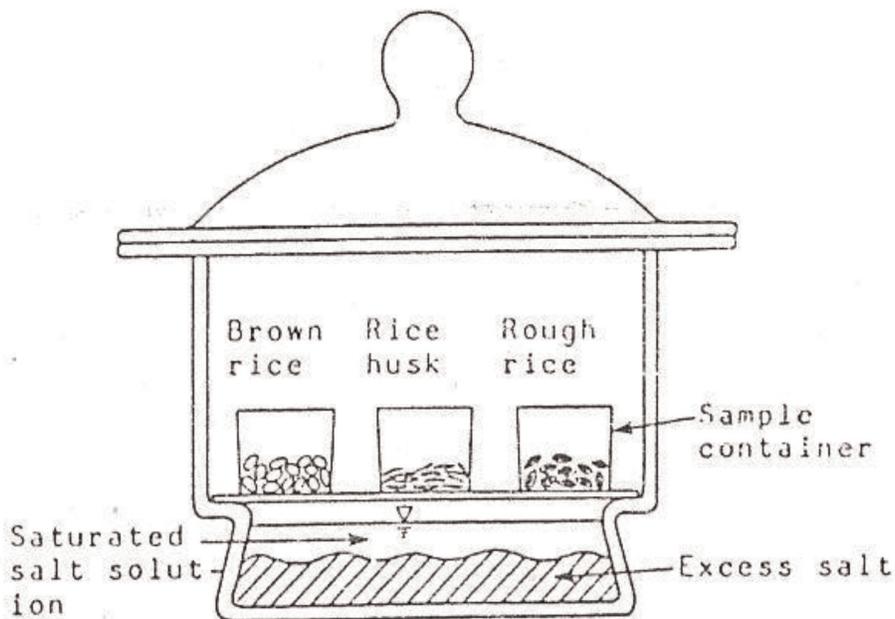
3.1 Gravimetric method

There are two common gravimetric methods of determining the EMC of agricultural and food products at different temperatures and water activities. One of these methods is the static gravimetric method which involves the placement of the product in an atmosphere with which it then comes into equilibrium (weight loss or gain stops) without mechanical agitation of the air or product. For this method, several weeks may be required for the product to come into equilibrium, and because of the long period of time, mold usually develops on high and intermediate moisture foods at water activities above 0.8. For data obtained at water activities above 0.8 to be reliable, mold growth must be prevented during equilibration. At the point of equilibration, the moisture content is then determined as the EMC. The second one is the dynamic method in which the atmosphere surrounding the product or the product itself is mechanically moved. The dynamic method is quicker but presents the problem of design and instrumentation. The static method has been used extensively and reported to be preferable for obtaining complete sorption isotherms [27]. It has also been recommended as the standard method of determining the moisture sorption isotherms of agricultural and food products [29]. It involves the placement of small sample (10–25 g) of agricultural and food material in vacuum desiccators containing different concentrations of sulfuric acid

(**Figure 2a**) to maintain the relative humidity (water activity) of the surrounding air at different values from 0 to 100% (0.00–1.00) or saturated solution (**Figure 2b**) of different salts to achieve different values of relative humidity at a specified temperature. Usually a thermostatically controlled water bath or oven



(a)



(b)

Figure 2.
 (a) Desiccator containing concentrated sulfuric acid: (1) locking clamp, (2) lid, (3) rubber seal ring, (4) desiccator barrel, (5) sample basket or can, (6) sample basket mounting stand and (7) concentrated sulfuric acid. Source: Spiess and Wolf [29]. (b) Desiccator containing saturated salt solution employed by Kameoka et al. [32] in determining the EMC of brown and rough rice and hull.

(Figure 3) is used to obtain the desired temperature. The water activity of sulfuric acid at different concentrations and temperatures is presented in Table 1, and that of saturated solutions of different salts at various temperatures are presented in Table 2.

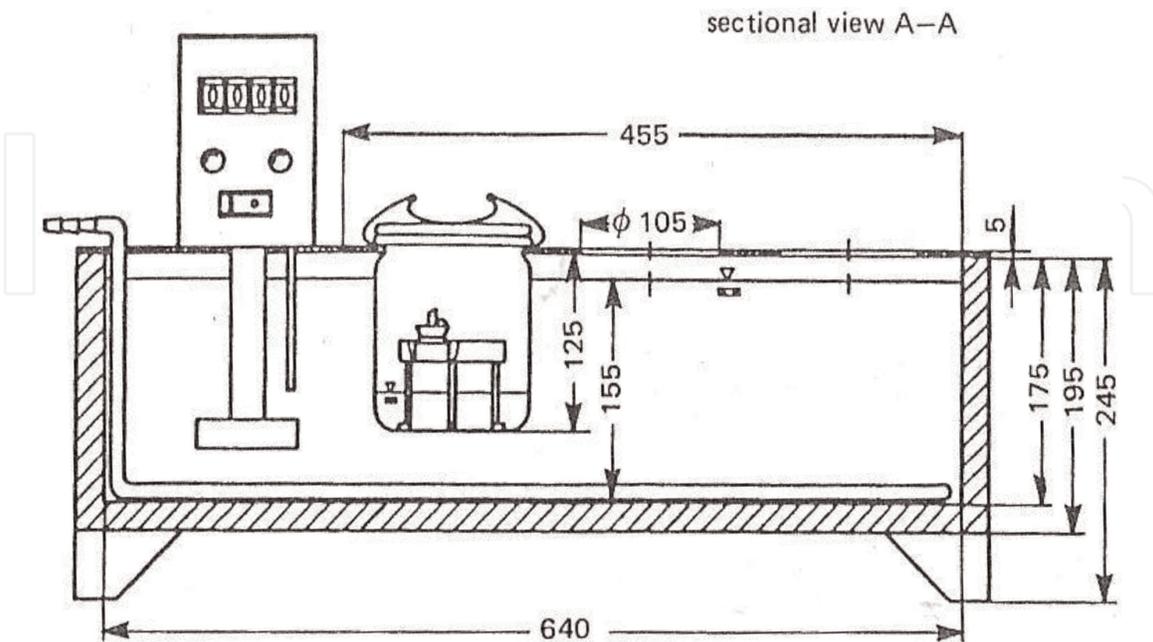


Figure 3. Thermostatically controlled water bath or oven for moisture sorption isotherm determination. Source: Spiess and Wolf [29].

Percent H ₂ SO ₄	Density at 25°C (g/cm ³)	Temperature (°C)						
		5	10	20	25	30	40	50
5.00	1.0300	0.9803	0.9804	0.9806	0.9807	0.9808	0.9811	0.9814
10.00	1.0640	0.9554	0.9554	0.9558	0.9562	0.9562	0.9565	0.9570
15.00	1.0994	0.9227	0.9230	0.9237	0.9241	0.9245	0.9253	0.9261
20.00	1.1365	0.8771	0.8779	0.8796	0.8802	0.8814	0.8831	0.8848
25.00	1.1750	0.8165	0.8183	0.8218	0.8218	0.8252	0.8285	0.8317
30.00	1.2150	0.7396	0.7429	0.7491	0.7509	0.7549	0.7604	0.7655
35.00	1.2563	0.6464	0.6514	0.6607	0.6651	0.6693	0.6773	0.6846
40.00	1.2991	0.5417	0.5480	0.5599	0.5656	0.5711	0.5816	0.5914
45.00	1.3437	0.4319	0.4389	0.4524	0.4589	0.4653	0.4775	0.4891
50.00	1.3911	0.3238	0.3307	0.3442	0.3509	0.3574	0.3702	0.3827
55.00	1.4412	0.2255	0.2317	0.2440	0.2502	0.2563	0.2685	0.2807
60.00	1.4940	0.1420	0.1471	0.1573	0.1625	0.1677	0.1781	0.1887
65.00	1.5490	0.0785	0.0821	0.0895	0.0933	0.0972	0.1052	0.1135
70.00	1.6059	0.0355	0.0377	0.0422	0.0445	0.0470	0.0521	0.0575
75.00	1.6644	0.0131	0.0142	0.0165	0.0177	0.0190	0.0218	0.0249
80.00	1.7221	0.0035	0.0039	0.0048	0.0053	0.0059	0.0071	0.0085

Source: Rizvi [6], Bell and Labuza [56].

Table 1. Water activity of sulfuric acid solution at different concentrations and temperatures.

Salt	Temperature (°C)								
	20	25	30	35	40	45	50	60	70
Sodium hydroxide	0.09	0.08	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Lithium chloride	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
Potassium acetate	0.23	0.22	0.22	—	—	—	—	—	—
Calcium chloride	—	—	—	0.22	0.22	0.22	0.21	0.21	0.20
Magnesium chloride	0.33	0.33	0.32	0.32	0.32	0.32	0.31	0.31	0.30
Potassium carbonate	0.43	0.43	0.43	—	—	—	—	—	—
Magnesium nitrate	0.54	0.53	0.51	0.499	0.48	0.47	0.45	0.45	0.44
Manganese chloride	—	—	—	—	0.51	0.5	0.5	0.5	0.5
Sodium bromide	0.59	0.58	0.56	0.55	—	—	—	—	—
Sodium nitrite	—	—	—	—	0.61	0.61	0.6	0.6	0.6
Sodium chloride	0.75	0.75	0.75	0.75	0.75	0.74	0.74	0.74	0.75
Potassium chloride	0.85	0.84	0.84	0.83	0.82	0.82	0.81	0.8	0.8
Barium chloride	—	—	—	—	—	0.89	0.89	0.88	0.88
Potassium nitrate	0.95	0.93	0.92	0.91	0.89	—	—	—	—
Potassium sulfate	0.97	0.97	0.97	0.97	0.96	0.96	0.96	0.95	0.94

Source: Rizvi [6], Bell and Labuza [56].

Table 2.
Water activity of saturated salt solutions at different temperatures.

Acids are not used extensively because of the danger involved in its handling and the changes that can occur in its composition—it is susceptible to dilution or increase in concentration with time due to the release or absorption of water by the product—thereby effecting a change in the air-water activity. Acids also easily corrode and release fume that can be toxic in the food material. Saturated salts are safer to use, and constant humidity can be maintained by leaving excess salt in the solution. That way, the solution is made to remain saturated throughout the duration of the experiment in spite of the release or absorption of water by the product. The use of saturated salt solution, however, requires many salts in order to go through the relative humidity (water activity) range of 0–100% (0.00–1.00), whereas only one acid could be used for the same purpose.

The static gravimetric method involving the use of saturated salt solutions was applied successfully to the determination of MSIs of Jerusalem artichoke [30]; uncooked meat emulsions [18]; ground and short-time roasted coffee [31]; rice [32]; pigeon pea type-17 [33]; cassava [23]; plantain, winged bean seed and gari [34–36]; freeze-dried, osmo-freeze-dried and osmo-air-dried cherries and blue berries [15]; vetch seeds [37]; lupine [38]; high oleic sunflower seeds and kernels [39]; quinoa grains [40]; soya bean [41]; red chillies [42]; chickpea flour [43]; black gram nuggets [44]; sorghum malt [45]; IR-8 rice variety [46]; native and chemically modified starches [20]; and castor seeds [47]. Young [48], Oyelade et al. [49, 50], Al-Muhtaseb et al. [51], Bello [52] and Afkawa [53] applied the static gravimetric method involving the use of different concentrations of sulfuric acid in determining the MSIs of Virginia-type peanuts, maize flour, yam flour, potato, high amylopectin and high amylose starch powders, groundnut and neem seeds and shea nut and desert date kernels, respectively. Bosin and Easthouse [54] suggested the dynamic

gravimetric method, and Igbeka et al. [22], Roman et al. [25] and Rahman and Al-Belushi [55] utilized it in establishing the MSIs of cassava and potato, apple and freeze-dried garlic powder, respectively.

3.2 Hygrometric method

Electric hygrometers are widely used for obtaining the MSIs of agricultural and food products. There are quite a lot of commercially available and specially designed hygrometers that are in use. The instrument (**Figure 4**) consists basically of a sensor, sample chamber and potentiometer. The sensor could use a hygroscopic chemical such as lithium chloride or an ion-exchange resin such as sulfonated polysterne; the conductivity of which changes according to the water activity above the sample. The sensor could be a humidity sensor which is based on capacitance changes in a thin film capacitor. Electric hygrometers give rapid, relatively precise results and are easy to operate. The main problems involved with the use of hygrometers are:

- i. Evaluation of the equilibration time between the sample and sensor
- ii. Proper temperature control
- iii. Need for recalibration for some instrument

Crapiste and Rostein [57], Fasina and Sokhansanj [58], Tsami et al. [17] and Arslan and Togrul [59] employed the hygrometric method in studying the moisture sorption behavior of potatoes, alfalfa pellets, model fruit powders and crushed chillies, respectively.

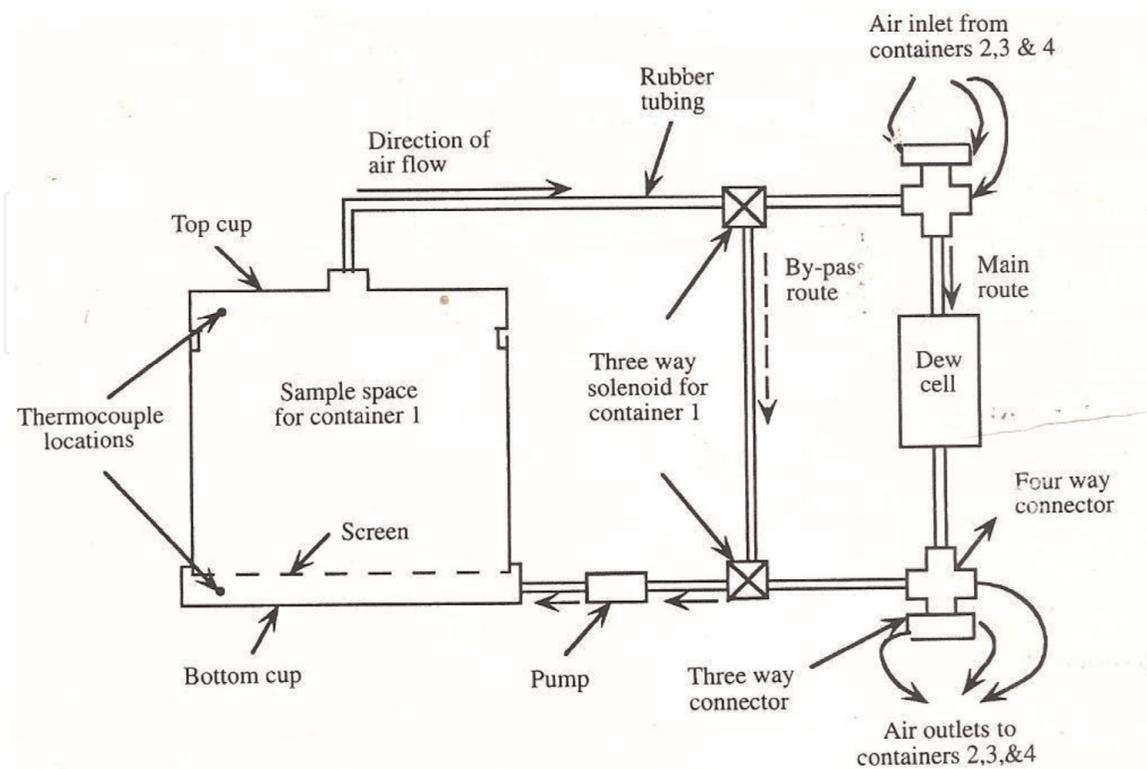


Figure 4. Diagram of moisture sorption isotherm apparatus utilizing the hygrometer. Source: Fasina and Sokhansanj [58].

3.3 Vapor pressure manometric (VPM) method

The vapor pressure manometric method involves bringing air to equilibrium with the agricultural or food product at a fixed temperature and moisture content and the relative humidity of the air measured as the equilibrium relative humidity (ERH). In this method, the vapor pressure exerted by the moisture in the product is directly measured. As a result, it is taken as one of the best methods of determining the MSI of food [60]. The equilibrium relative humidity is then obtained from the ratio of the vapor pressure in the sample to that of pure water at the same temperature. A schematic diagram of the apparatus and simplified diagram of the system set-up is shown in **Figures 5** and **6**, respectively. The procedure for determining the ERH of agricultural and food products using the method is as follows:

- i. The prepared sample and VPM system are allowed to reach the desired temperature.
- ii. About 10–50 g of sample is put in the sample flask, and an equal amount of desiccant (CaSO_4 , CaCl_2) is placed in the desiccant flask and sealed on to the apparatus using high vacuum grease.
- iii. Keeping the sample flask isolated, the system is evacuated to less than 200 μmHg (Rizvi, 1986). The cold strap should be filled with nitrogen prior to evacuation of the system to trap any moisture reaching the vacuum pump.
- iv. The space in the sample flask is then connected to the evacuated air space by opening the stopcock over the sample V_4 (**Figure 6**), and the system is again evacuated for 1 min.

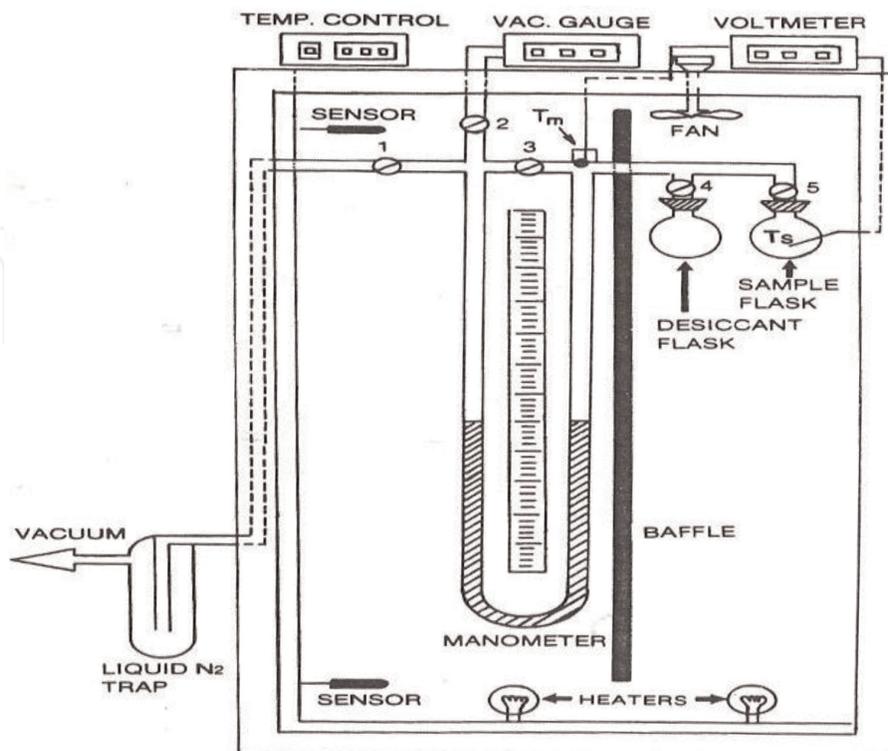


Figure 5. Schematic diagram of vapor pressure manometric apparatus. Source: Rizvi [6].

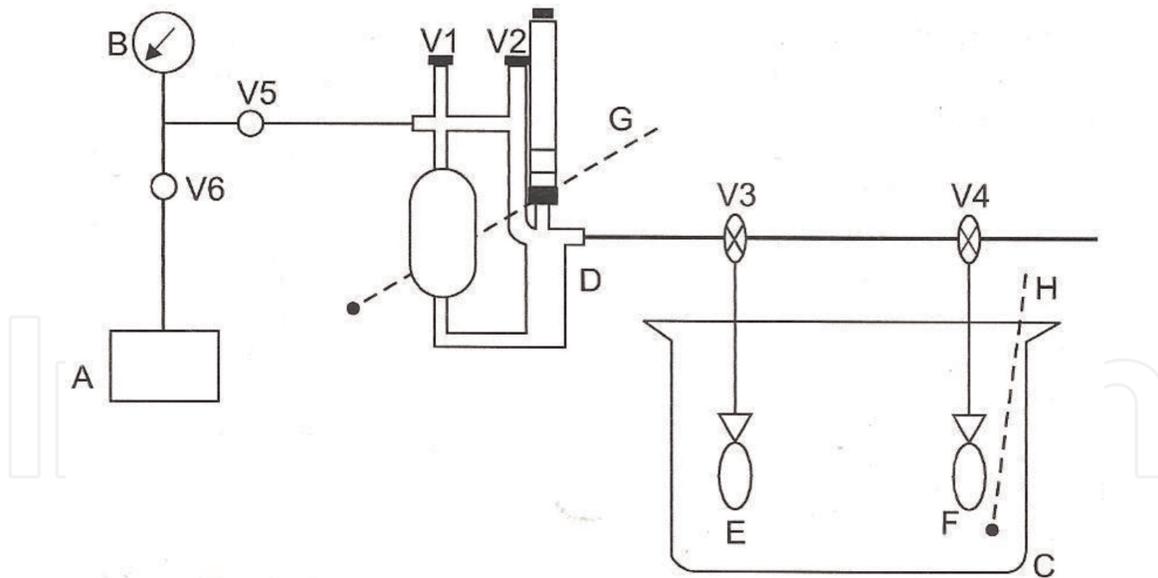


Figure 6.

Schematic diagram of vapor pressure manometric system set-up. Source: Ajibola et al. [65].

- v. The stopcock across the manometer V_5 is closed causing the oil in the micromanometer to respond to the vapor pressure exerted by the sample. When the oil level reaches a steady value, the difference is recorded as H_1 .
- vi. The stopcock over the sample is then closed, and the desiccant stopcock is opened to connect the system with the desiccant, causing a change in the height of the manometric oil. After the oil reaches a constant height, the micromanometer reading is recorded as H_2 .
- vii. The sample is removed from the system, and the moisture content is determined using a standard method.
- viii. With the data obtained, the equilibrium relative humidity is calculated using Eq. (1):

$$ERH = \frac{(H_1 - H_2) \left(\frac{T_s}{T_o} \right)}{P_s} \quad (1)$$

where ERH is the equilibrium relative humidity (%), H_1 is the micromanometer reading with sample flask connected to the system (mm of manometric oil), H_2 is the micromanometer reading with desiccant flask connected to the system (mm of manometric oil), T_s is the temperature of the environment surrounding the water bath taken as the temperature of sample (K), T_o is the temperature of the environment surrounding the micromanometer (K) and P_s is the saturated vapor pressure at sample temperature (mm of manometric oil).

The VPM method is rapid and precise but requires the use of vacuum pump, an accurate manometer and closed glass tube system. Proper temperature control is critical to this method, and volatile constituents other than water may contribute to the pressure exerted by the food.

The VPM method has been used to obtain the MSI of cereal grains and rape [61], dry milk [62], sesame seed [63], cowpea [64] and palm kernels [65].

3.4 Inverse gas chromatography

The inverse gas chromatography (IGC) is a rapid and effective system for studying the thermodynamic properties of a solid taken as the stationary phase in relation to a mobile gas phase containing selected solutes such as water. It is particularly suitable for the study of the lower region of water activity and for products with very low equilibrium moisture contents [66, 67]. With IGC the sorbed solute is injected into the carrier gas stream, and its linear transport is retarded owing to interaction with the product under study, which constitutes the stationary phase. Moisture sorption isotherms are then determined using the chromatographic data obtained and the following equations, which relate chromatograph operating parameters and peak data to the sorption isotherm:

$$a = \frac{m_a I_{ads}}{m I_{pic}} \quad (2)$$

and

$$p = \frac{m_a h R T}{I_{pic} W} \quad (3)$$

where a is the uptake of sorbed water (g/g stationary phase), m_a is the mass of water injected (g), m is the mass of stationary phase (g) and I_{ads}/I_{pic} is the ratio of the areas $(A + B)/B$ calculated from the chromatogram (**Figure 7**), p is the partial pressure (atm), h is the peak height (detector units), R is the gas constant ($82.0567 \text{ cm}^3 \text{ atm mole}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), W is the flow rate of carrier gas (cm^3/min) and I_{pic} is the area B in **Figure 7**.

It has been used successfully to determine the MSIs of homogeneous solid food ingredients like sucrose, glucose and starch [68] and complex heterogeneous foods like bakery products [69], wheat flour [66] and wheat and soy flour [70].

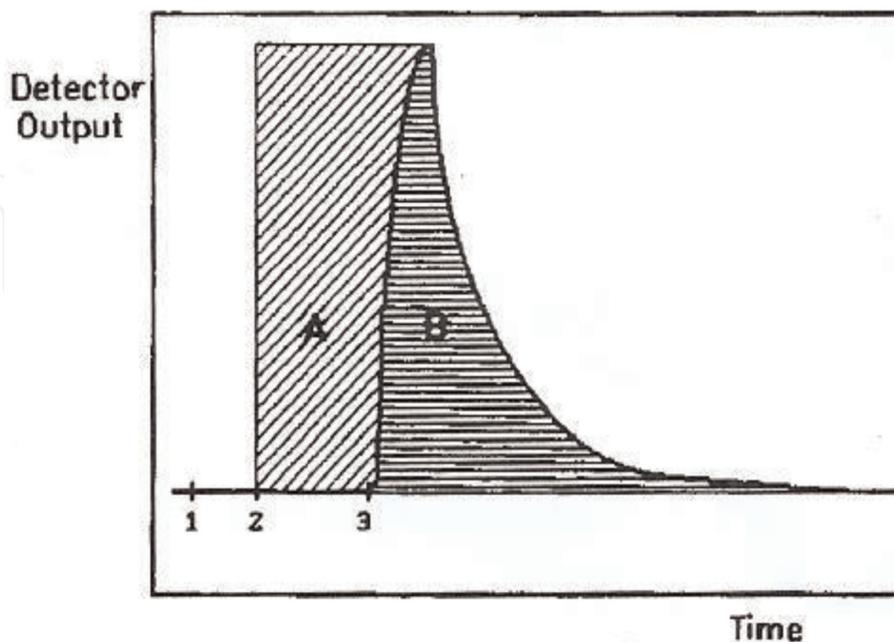


Figure 7. Typical gas chromatogram obtained by IGC: 1 = point of injection; 2 = point of emergence of unadsorbed peak (air); 3 = point of emergence of probe peak (water), I_{pic} = area B; and I_{ads} = area A + B. Source: Manuel Sa and Sereno [67].

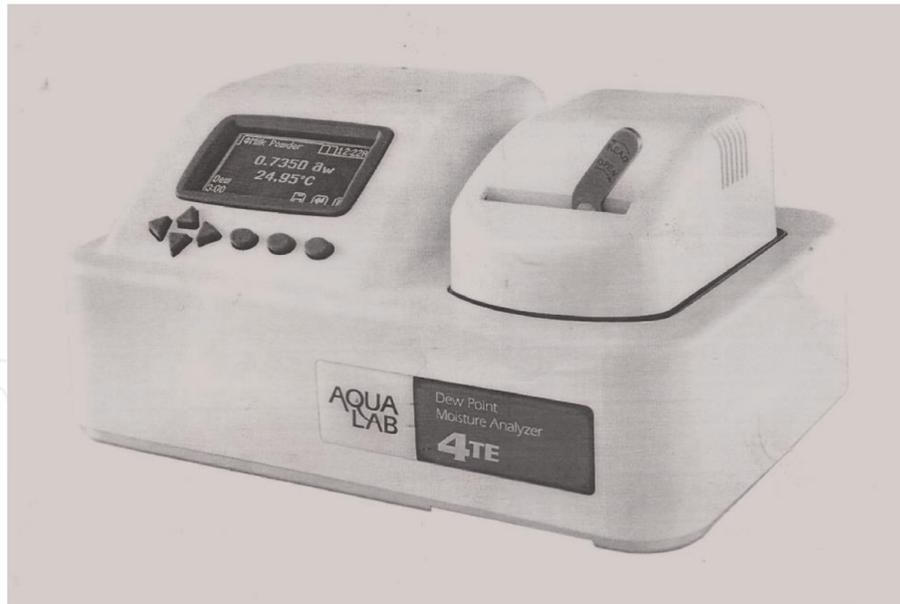


Figure 8. 4TE model AquaLab moisture content—water activity measuring instrument. Source: METER Group, Inc. [71].

3.5 AquaLab instrument

AquaLab is the fastest, most accurate and most reliable instrument available for measuring water activity, giving readings in 5 min or less [71]. It is easy to use and provides accurate and timely results. Its readings are reliable, providing $\pm 0.003 a_w$ accuracy. The instrument is easy to clean and checking calibration is simple. The photograph of 4TE model of the equipment is shown in **Figure 8**.

4. Influence of temperature on moisture sorption isotherms

Temperature affects the mobility of water molecules and the dynamic equilibrium between the vapor and the adsorbed gases [13]. If water activity is kept constant, an increase in temperature causes a decrease in the amount of sorbed water [20] (**Figure 9**). This indicates that the food becomes less hygroscopic. Iglesias and Chirife [72] pointed out that increase of temperature represents a condition unfavorable to water sorption.

An exception to this rule is shown by certain sugars and other low molecular weight food constituents, which become more hygroscopic at higher temperature because they dissolve in water. Temperature shifts can have an important practical effect on the chemical and microbiological reactivity related to quality deterioration of a food in a closed container [73]. An increase of temperature at constant moisture content causes increase in water activity (**Figure 10**). This increases the rate of reactions and leads to deterioration [74–76]. Weisser [31] studied the effect of temperature on the sorption isotherms of roasted coffee and reported that the product showed consistent separation of the isotherms at different temperatures. However, not all foods exhibit such consistency. In the work reported by Saravacos et al. [12], crossing over occurred at high water activity ($a_w = 0.78$) in the 20 and 30°C adsorption isotherms of sultana raisins and 5, 20 and 45°C adsorption and desorption isotherms of Chilean papaya shown in **Figure 11** [77]. Such crossing over has earlier been observed by Saravacos and Stinchfield [78] on model systems of starch-glucose, Audu et al. [79] on sugars, Weisser et al. [80] on sugar and alcohols

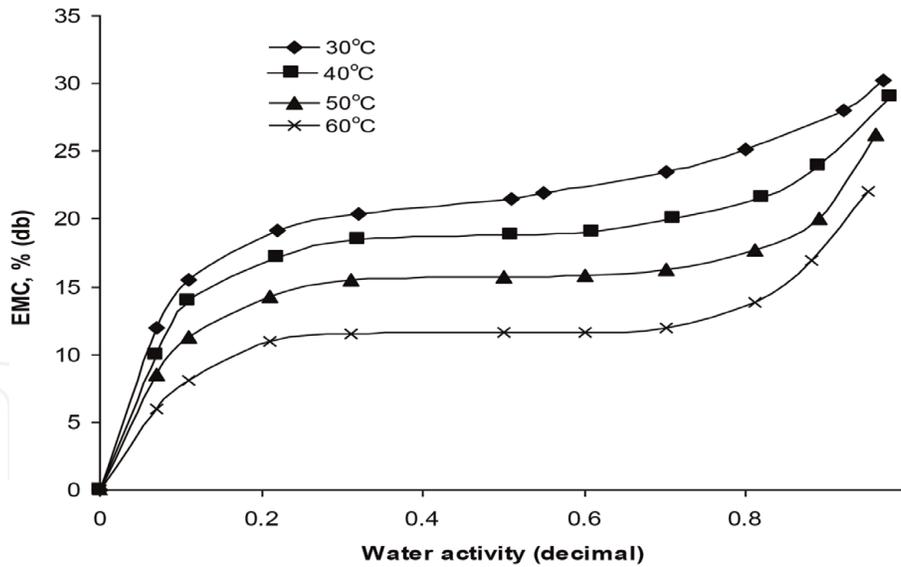


Figure 9.
 Adsorption EMC of hydroxypropylated cassava starch showing variation of MSI with temperature. Source: Aviara [20].

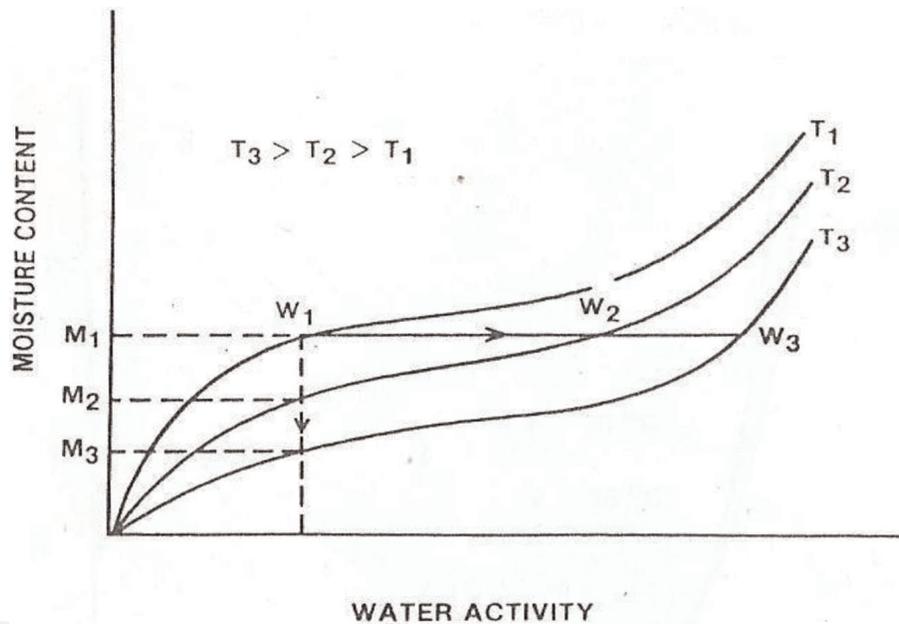


Figure 10.
 Changes in water activity at constant moisture content and in moisture content at constant water activity with changes in temperature. Source: Rizvi [6].

and Silverman et al. [81] on 20 and 37°C isotherms of precooked bacon. These substances contain large amounts of low molecular weight constituents in a mixture of high molecular weight biopolymers. At lower water activity values, the sorption of water is due mainly to the biopolymers, and an increase of temperature has the normal effect of lowering the isotherms [13]. As water activity is raised beyond the intermediate region, moisture begins to be sorbed primarily by the sugars and other low molecular constituents leading to the swinging up of the isotherm. Dissolution, which is favored by higher temperature, offsets the opposite effect of temperature on higher molecular weight constituents. The net result is an increase of moisture content (crossing over) of the isotherms. This has bearing on the sign and magnitude of the binding energy [13]. The binding energy of sultana raisin decreased as the temperature increased from 22 to 32°C in the low moisture region [12], but the effect of temperature showed a crossing over of the lines at higher moisture

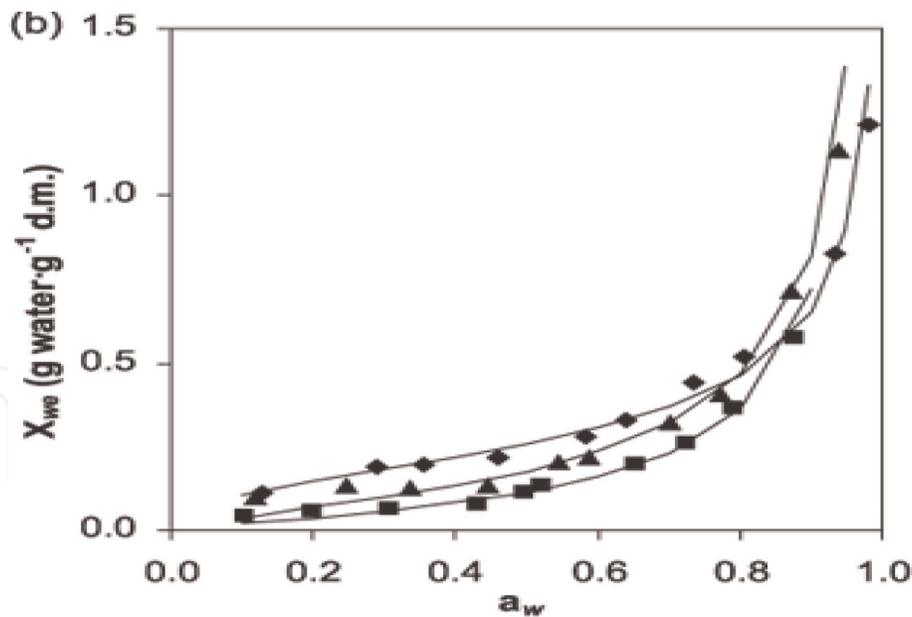


Figure 11. Moisture desorption isotherms of Chilean papaya showing isotherm crossing at higher water activities with increase in temperature. Source: Vega-Galvez et al. [84].

contents due to the endothermic dissolution of fruit sugars. Iglesias and Chirife [82] studied the equilibrium moisture contents of air-dried beef and found that the higher the drying temperature, the lower the sorption capacity of the dried beef. Similar results were reported for cookies and corn snacks [21] and apples [25]. Temperature changes also have effects on the water activity of saturated salt solutions, which are used in the determination of sorption isotherms. Labuza et al. [83] used experimental data and thermodynamic analysis to demonstrate that water activity of saturated salt solutions should decrease with increase in temperature.

5. Moisture sorption hysteresis

A product which attains its moisture equilibrium with the surrounding by losing moisture at a given temperature is said to have reached the desorption EMC. When the relatively dry material absorbs moisture from a high humidity environment at the same temperature, it will eventually reach the adsorption EMC. The isotherm plots may indicate a significant difference at certain water activities and temperatures between desorption and adsorption EMC values, with the desorption values being higher than the adsorption counterpart. This difference is called moisture sorption hysteresis [13, 45]. A typical hysteresis loop presented in **Figure 12** could occur within the region of monolayer moisture but could begin at a higher water activity and extend down to zero water activity, depending on its class according to Kapsalis [13] classification.

Moisture sorption hysteresis has important theoretical and practical implications in foods. These include the general aspects of the irreversibility of moisture sorption process and the question of validity of thermodynamic parameters derived from a particular arm of the isotherm. Moisture sorption hysteresis has effect on chemical and microbiological deterioration of low and intermediate moisture foods.

5.1 Hysteresis classification

The hysteresis phenomenon in agricultural and food products varies in magnitude, shape and extent, depending on the type of food and temperature [13]. Hysteresis size or magnitude is depicted by the area enclosed by the loop, while the

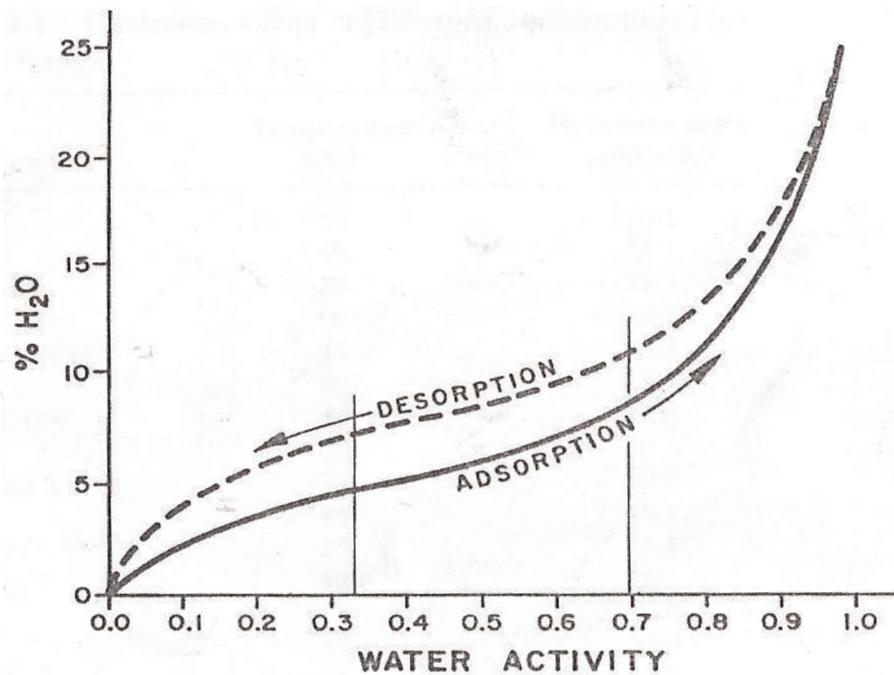


Figure 12.
Moisture sorption hysteresis loop. Source: Kapsalis [13].

span or extent is denoted by the water activity range covered. Kapsalis [13] grouped moisture sorption hysteresis into three general types as follows:

Type I hysteresis: This type of hysteresis is normally pronounced mainly in the lower moisture content region, below the first inflection point of the isotherm. Although the total hysteresis may be large, no occurrence is normally observed above the 0.65 water activity or in the intermediate moisture range. The type I hysteresis is normally exhibited by high-sugar and high-pectin foods, exemplified by air-dried apple.

Type II: In this type, moderate hysteresis begins at high water activity, in the capillary condensation region, and extends over the rest of the isotherm to zero water activity. In both desorption and adsorption arms, the isotherm's sigmoidal shape is retained. This type of hysteresis is normally exhibited by high-protein foods exemplified by freeze-dried pork.

Type III: In this type, large hysteresis loop occurs with a maximum at about 0.70 water activity, which is within the capillary condensation region. This type of hysteresis normally occurs in starchy foods such as freeze-dried rice.

5.2 Effect of temperature on hysteresis

Increasing temperature decreases the total hysteresis and limits the span of the loop along the isotherm [84]. Iglesias and Chirife [85] studied the effect of temperature on the magnitude of moisture sorption hysteresis of foods and reported that increasing temperature decreased or eliminated hysteresis for some foods, while for others, the total hysteresis size remained constant, or even increased. In the case where the hysteresis loop decreased, it did so more appreciably at high temperatures. The effect of temperature was found to be more pronounced on the desorption isotherms than the adsorption isotherms.

5.3 Theories of moisture sorption hysteresis

Several theories have been proposed to explain hysteresis phenomena in agricultural and food products. The most prominent of the theories are the ink bottle

theory, the incomplete wetting theory, the open-pore theory, the shrinkage theory and the capillary condensation-swelling fatigue theory.

Ink bottle theory: This theory assumes that an agricultural and food product is a porous body having capillaries consisting of narrow, small-diameter necks with large bodies resembling ink bottles (**Figure 13**). It explains hysteresis on the basis of difference in the radii of the porous sorbent. During desorption, the small radii of necks control the emptying of the capillaries and result in a lowering of the relative humidity above the product; whereas during adsorption, the large area for the bodies needs to be filled, thus requiring higher relative humidity. The explanation can be better understood using the Kelvin equation which states that

$$\ln\left(\frac{P}{P_o}\right) = \frac{-2\sigma V \cos\theta}{RT r_m} \quad (4)$$

where P is the vapor pressure of liquid over the curved meniscus (Pa), P_o is the saturation vapor pressure (Pa) at temperature T (K), σ is the surface tension (N/m), θ is the angle of contact (in complete wetting, θ is 0 and $\cos\theta = 1$), V is the molar volume of liquid (m^3/mol) and r_m is the mean radius of curvature of meniscus.

For desorption, by substituting r_1 in **Figure 13** for r_m in Eq. (4) with $\cos\theta = 1$ (complete wetting), Eq. (4) becomes transformed into Eq. (5):

$$P_d = P_o \exp\left(\frac{-2\sigma V}{RT r_1}\right) \quad (5)$$

In adsorption with condensation first taking place in the large diameter cavity, Eq. (4) becomes

$$P_a = P_o \exp\left(\frac{-2\sigma V}{RT r_2}\right) \quad (6)$$

From the above, it follows that for a given amount of water sorbed, the pressure will be higher during adsorption than during desorption.

Incomplete wetting theory: This theory is also dependent on capillary condensation based on Eq. (4), but it notes that due to the presence of impurities, the contact

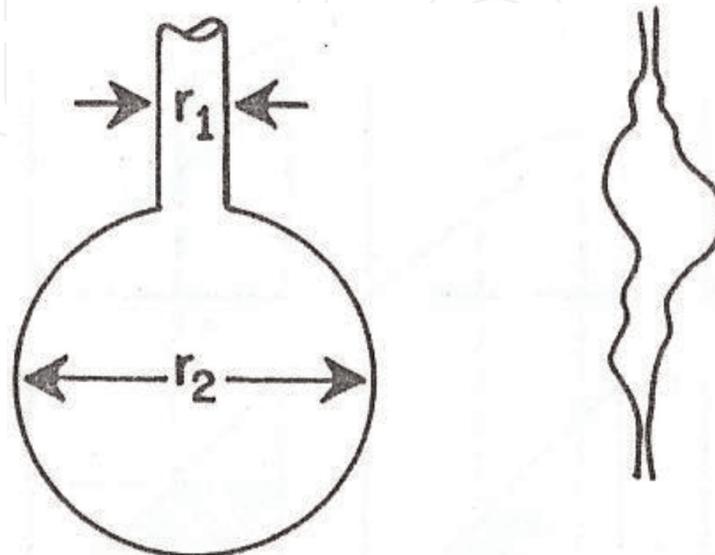


Figure 13.

Ink bottle neck theory of moisture sorption hysteresis (left, schematic representation and, right, actual pore).
Source: Kapsalis [13].

angle of the receding film upon desorption is smaller than that of the advancing film upon adsorption. Therefore, condensation along the adsorption branch of the isotherm will be at a higher vapor pressure resulting in open hysteresis as illustrated in **Figure 14**. However, in foods the most common type of hysteresis is the closed-end, retracable loop showing that this theory is limited in its application to foods.

Open-pore theory: this theory extends the ink bottle theory by including considerations of multilayer adsorption. It is based on the difference in vapor pressure between adsorption P_a and desorption P_d as affected by the shape of the meniscus. During adsorption, the meniscus is considered cylindrical and the Cohan equation (not presented here) applies, whereas during desorption, the shape is considered to

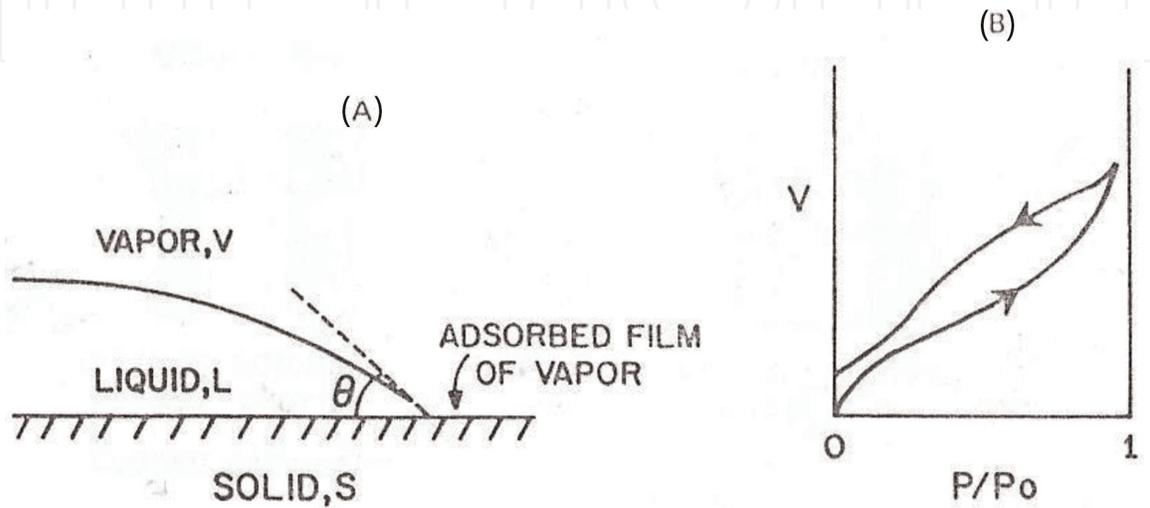


Figure 14. Incomplete wetting theory of hysteresis (A) contact angle and (B) open hysteresis. Source: Kapsalis [13].

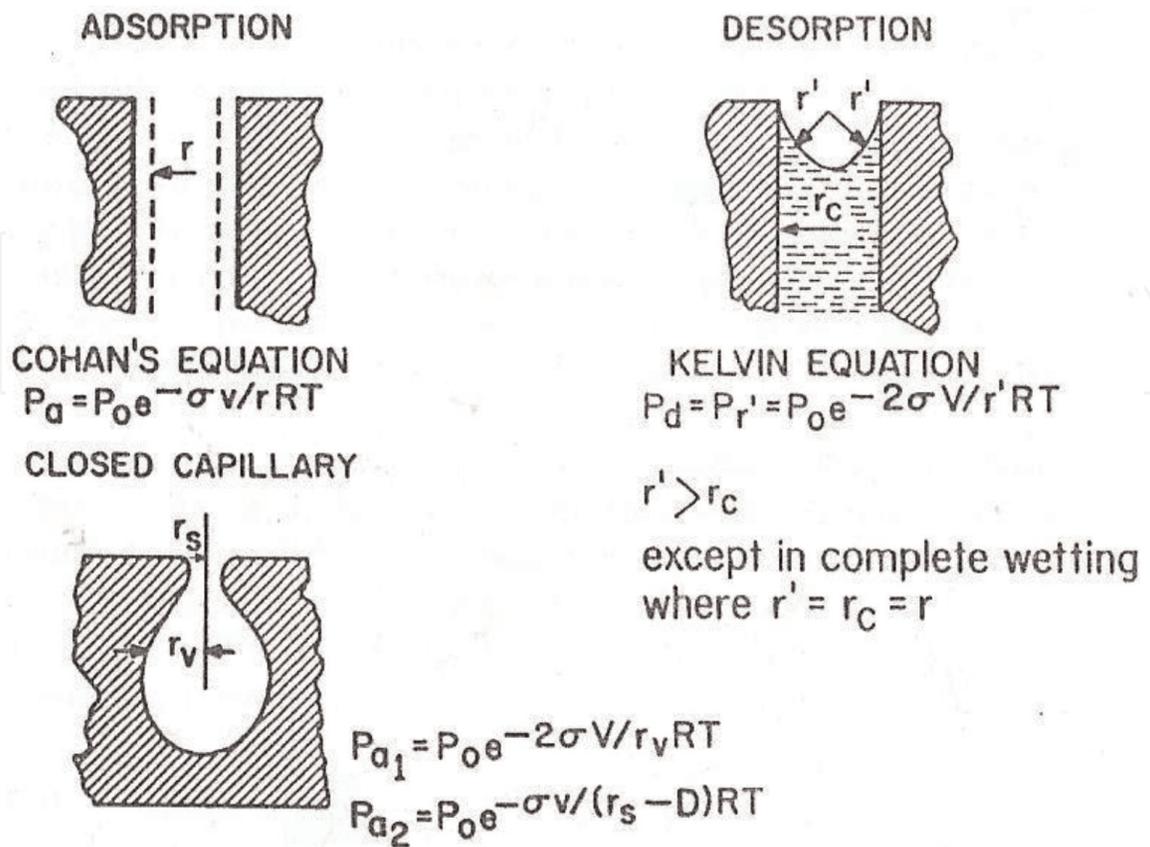


Figure 15. Open-pore theory of hysteresis. Source: Kapsalis [13].

be hemispherical in which the Kelvin equation is applied. The open-pore theory is illustrated in **Figure 15**.

Shrinkage theory: This states that while agricultural and food product is drying out, the force of attraction causes water-holding spaces to shrink (molecular shrinkage). This permanent shrinkage reduces the water-binding polar sites and water-holding capacity of the material; hence less amount of water is absorbed during the adsorption process.

Capillary condensation and swelling fatigue theory: In this theory proposed by Ngoddy-Bakker-Arkema [86], the sorption hysteresis is considered linked with condensation and evaporation in irregular voids (capillary condensation) and influence of adsorbed water molecules on such physical properties of agricultural and food products as strength, elasticity, rigidity, swelling and evolution of heat (swelling fatigue). The above combination was simulated by adopting the Cohan theory of capillary condensation with modifications and combining it with the ink bottle theory in the first approximation. The theory presented expressions for calculating the desorption isotherms of biomaterials from corresponding adsorption isotherm using bulk moduli determined as a function of moisture content.

6. Moisture sorption isotherm models

Equations for fitting the moisture sorption isotherms are of special importance in many aspects of crop and food preservation by drying. These include the prediction of the drying times, shelf life of the dried product in a packaging material and the equilibrium conditions after mixing products with varying water activities [87]. Others are the analytical determination of control for undesirable chemical and enzymatic reactions [88] and control of moisture migration in multidomain foods [9]. Moisture sorption isotherm models, therefore, not only constitute an essential part of the overall theory of drying but also provide information directly useful in the accurate and optimum design of drying equipment [1]. They are needed in the evaluation of the thermodynamic functions related to moisture sorption in biological materials [89].

Several theoretical, semi-theoretical and empirical models have been proposed and used by investigators to fit the equilibrium moisture content data of food and agricultural products. Chirife and Iglesias [87] reviewed part of the isotherm equations and presented a discussion of 23 common models, while Van den Berg and Bruin [5] presented a more comprehensive list. Ngoddy-Bakker-Arkema [1] developed a generalized moisture sorption isotherm model for biological materials based primarily on the BET and capillary condensation theories and indirectly on Polanyi's potential theory. This model appears to possess very high versatility but needs to be modified to reduce the number of parameters and incorporate the temperature term. A thorough going and extensive testing of the model on various categories of food is also necessary to confirm its versatility and prove the generalized posture. Ferro Fontan et al. [2] and Chirife et al. [90] presented a new model, which Iglesias and Chirife [91] compared with the GAB model and reported to be an alternative. Chen [92] derived a new moisture sorption isotherm model from a reaction engineering approach. The Brunauer-Emmett-Teller (BET) [87] and Guggenheim-Anderson-de Boer (GAB) [56, 91, 93] models have been used for estimating the monolayer moisture content of agricultural and food products. Boquet et al. [94] noted that the Hailwood and Horrobin model has a remarkably good ability to fit the experimental data for most food types. A test of the model on moisture sorption data of native cassava and sorghum starches [95] showed that it has good predictive

performance with R^2 ranging from 0.92 to 0.99. It, however, lacked the temperature term and was modified to incorporate the term. Other commonly used models include modified Henderson, modified Chung-Pfost, modified Halsey and modified Oswin and the GAB. The modified Henderson [96] and modified Chung-Pfost [97] models have been adopted as the standard equations by the American Society of Agricultural and Biological Engineers (ASABE) for describing the EMC- a_w data for cereals and oil seeds [98]. The modified Halsey [85] has been reported as the best model for predicting the EMC- a_w relationships of several tropical crops [99] and alongside with the modified Oswin [100] has been shown to describe the EMC- a_w data of many seed satisfactorily [101, 102]. The Guggenheim-Anderson-de Boer (GAB) model has been recognized as the most satisfactory theoretical isotherm Equation [103–106] and has been recommended as the standard model for use in food laboratories in Europe [105] (1985) and the USA [107]. The GAB does not incorporate a temperature term; therefore, the determination of the effect of temperature on isotherms using the model usually involves the evaluation of up to six constants. Jayas and Mazza [108], however, developed a modified form of the GAB, which incorporates the temperature term. The MSI models considered in this study were selected from the above list and presented as follows:

1. Brunauer-Emmett-Teller (BET) model

$$M = \frac{M_m C a_w}{(1 - a_w)[1 + (C - 1)a_w]} \quad (7)$$

2. Guggenheim-Anderson-de Boer (GAB) model

$$M = \frac{CKM_m a_w}{(1 - Ka_w)[1 - Ka_w + CKa_w]} \quad (8)$$

3. Modified GAB model

$$M = \frac{AB\left(\frac{C}{T}\right)a_w}{(1 - Ba_w)\left[1 - Ba_w + \frac{C}{T}Ba_w\right]} \quad (9)$$

4. Hailwood-Horrobin model

$$M = \left(\frac{A}{a_w} + B - Ca_w\right)^{-1} \quad (10)$$

5. Modified Hailwood-Horrobin model

$$M = \left(T\left(\frac{A}{a_w} + B\right) - \frac{C}{T^n}a_w\right)^{-1} \quad (11)$$

6. Modified Chung-Pfost model

$$M = \frac{-1}{C} \text{Ln} \left[-\frac{(T + B)}{A} \text{Lna}_w \right] \quad (12)$$

7. Modified Halsey model

$$M = \left[\frac{-\text{Lna}_w}{\exp(A + BT)} \right]^{-1/c} \quad (13)$$

8. Modified Henderson model

$$M = \left[\frac{-\text{Ln}(1 - a_w)}{A(T + B)} \right]^{1/c} \quad (14)$$

9. Modified Oswin model

$$M = (A + BT) \left[\frac{a_w}{1 - a_w} \right]^{1/c} \quad (15)$$

10. Ngoddy-Bakker-Arkema model

$$M = \frac{\rho\varepsilon}{\eta} \left\{ 3.2^\eta \left[\left(\left(\frac{1.75}{\text{Ln}\left(\frac{P_o + P_m}{P + P_m}\right)} \right)^{\frac{1}{2}} + \frac{\sigma V}{R_g T \text{Ln}\left(\frac{P_o + P_m}{P + P_m}\right)} \right)^\eta - \left(\left(\frac{1.75}{\text{Ln}\left(\frac{P_o + P_m}{P_m}\right)} \right)^{\frac{1}{2}} + \frac{\sigma V}{R_g T \text{Ln}\left(\frac{P_o + P_m}{P_m}\right)} \right)^\eta \right] \right\} \quad (16)$$

where M is the moisture content, (db); M_m is monolayer moisture content, (db); a_w is water activity; T is absolute temperature, (K); A , B , C and k are constants; η is primary characteristic parameter of pore structure; ε is secondary characteristic parameter of pore structure; σ is surface tension of sorbate in bulk liquid form, (N/m); R_g is universal gas constant; V is molal volume of sorbate in its bulk liquid condition, (m³/mol); P_m is vapor pressure corresponding to monolayer, (N/m²); P_o is saturated vapor pressure, (N/m²); and P is vapor pressure at the condition under which the study is carried out, (N/m²).

7. Isotherm model predictive performance evaluation

Sun and Byrne [109], Sun [110] and Sun [111] evaluated the predictive performance of the moisture sorption isotherm models that have been reported for fitting the EMC and ERH data of rapeseed, rice, other grains and oilseeds and selected the models that gave the best fits.

Coefficient of terms in the moisture sorption isotherm equations is usually determined using nonlinear regression procedure, and the predictive performance of an equation on sorption data is evaluated using such goodness of fit parameters as standard error of estimate (estimate of the residual mean square), residual sum of square, coefficient of determination, mean relative percent error, fraction explained variation and residual plots. Several investigators used these parameters to evaluate the fitting ability of EMC- a_w equations. For instance, Ajibola [35–37], Ajibola and Adams [34], Ajibola [112], Gevaudan et al. [24], Talib et al. [8], Pezzutti and Crapiste [113], Tsami et al. [17] and Ajibola et al. [64] used the standard error of estimate, and Young [48] and Jayas et al. [114] used the residual sum of squares to compare the fitting ability of different models. Boquet et al. [94], Chirife et al. [90], Weisser [31], Saravacos et al. [12], Pollio et al. [115], Iglesias and Chirife [91] and Khalloufi et al. [10] used the mean relative percent deviation (MRE), while Shepherd and Bhardwaj [33], Demertzis et al. [116], Diamante and Munro [117] and Sopade et al. [118] employed coefficient of determination in evaluating the fitting ability of several models. Pappas and Rao [119] used the fraction explained

variation, Chen [92] used both coefficient of determination and mean relative percent error and Sun [110] and Sun [111] employed the residual sum of squares, standard error of estimate and mean relative percent error in comparing moisture sorption isotherm models for food. Other combinations of parameters that have been used include standard error of estimate and mean relative percent error [120], coefficient of determination and residual sum of squares [18] and standard error of estimate, mean relative percent deviation and residual plots [15, 41, 65, 101, 102]. A model is considered acceptable for predictive purpose, if the residuals are uniformly scattered around the horizontal value of zero showing no systematic tendency towards a clear pattern [41, 45, 64, 65]. A model is considered better than another if it has lower standard error of estimate and mean relative percent deviation and higher fraction explained variation and coefficient of determination.

Menkov [37] reported that of five moisture sorption isotherm models fitted to the experimental data on the EMC of vetch seeds, the modified Oswin model proved the best for describing the adsorption and desorption branches. Aviara et al. [41] and Oyelade [121] reported that the modified Oswin model gave the best fit to the EMC of soya bean and lafun, respectively. Santalla and Mascheroni [39] in a similar study on the EMC of sunflower seeds and kernels reported that the GAB model gave the best fit to the experimental data. Other crops whose moisture sorption isotherms have recently been studied include quinoa grains [40], crushed chillies [59], amaranth grains [122] and black gram nuggets [44].

7.1 Model parameter evaluation procedures

The procedure followed in evaluating a moisture sorption isotherm model depends on the nature of the model. For the selected models (Eqs. (7)–(16)), the procedures are as follows:

- a. BET model: the BET model (Eq. (7)) can be linearized thorough algebraic manipulations to yield Eq. (17):

$$\frac{a_w}{M(1-a_w)} = \frac{1}{M_m C} + \left(\frac{C-1}{M_m C}\right)a_w \quad (17)$$

A plot of $\frac{a_w}{M(1-a_w)}$ against a_w within the water activity range of 0.01–0.5 at each temperature yields a straight line with the slope as $\left(\frac{C-1}{M_m C}\right)$ and intercept on the y-axis as $\frac{1}{M_m C}$, and from these, the values of M_m and C can be obtained and used as the starting values in nonlinear regression. The nonlinear regression analysis procedure minimizes the sum of deviation in the evaluation of a model using a series of iterative steps. The procedure could require that initial parameter estimates be chosen close to the true values.

- b. GAB model: the GAB model (Eq. (8)) can be transformed to a quadratic form by algebraic manipulation to yield Eq. (18):

$$\frac{a_w}{M} = Aa_w^2 + Ba_w + C \quad (18)$$

Eq. (18) can be solved by plotting $\frac{a_w}{M}$ against a_w at each temperature and fitting a polynomial of the second order to the plots. This will yield the following functions from Eq. (8):

$$A = \frac{k}{M_m} \left(\frac{1}{C} - 1 \right), B = \frac{1}{M_m} \left(1 - \frac{2}{C} \right), C = \frac{1}{M_m C k} \quad (19)$$

The values of M_m , C and k obtained at each temperature are then used as the initial values of the parameters in the nonlinear regression procedure of Eq. (8) to evaluate the model.

- c. Modified GAB model: the modified GAB model (Eq. (9)) like the original GAB model can be transformed to a quadratic form by algebraic manipulation to yield Eq. (20):

$$\frac{a_w}{M} = X a_w^2 + Y a_w + Z \quad (20)$$

Plotting $\frac{a_w}{M}$ against a_w and fitting a polynomial of the second order to the plot yield the following functions from Eq. (9):

$$X = \frac{B}{A} \left(\frac{T}{C} - 1 \right), Y = \frac{1}{A} \left(1 - \frac{2T}{C} \right), Z = \frac{1}{ABC} \quad (21)$$

The average values of A , B and C are obtained and used as initial parameter estimates in the nonlinear regression analysis to evaluate the model.

- d. Hailwood-Horrobin model: The Hailwood-Horrobin model (Eq. (10)) is mathematically similar to the GAB and can after algebraic manipulations be represented in the form

$$\frac{a_w}{M} = C a_w^2 + B a_w + A \quad (22)$$

Plotting $\frac{a_w}{M}$ against a_w and fitting a polynomial of the second order to the plot at each temperature yield the values of C , B and A for use as initial parameter estimates in the nonlinear regression procedure for the model evaluation.

- e. Modified Hailwood-Horrobin model: this model (Eq. 11) also has mathematical similarity with the GAB. It can be transformed algebraically to yield Eq. (23):

$$\frac{a_w}{M} = \lambda a_w^2 + \mu a_w + \varphi \quad (23)$$

Plotting $\frac{a_w}{M}$ against a_w and fitting a polynomial of the second order to the plot yield the following functions from Eq. (11):

$$\lambda = \frac{C}{T^n}, \mu = BT \text{ and } \varphi = TA \quad (24)$$

The average values of A , B and C are obtained and used as initial parameter estimates in the nonlinear regression analysis to evaluate the model.

- f. Modified Chung-Pfost model: the modified Chung-Pfost model (Eq. (12)) is transformed by algebraic manipulations to yield Eq. (25):

$$a_w = \exp \left[\left(\frac{-A}{(T+B)} \right) \exp(-CM) \right] \quad (25)$$

Linearizing Eq. (25) by logarithmic transformation is carried out as follows:

$$\ln(a_w) = \frac{-A}{(T+B)} \exp(-CM) \quad (26)$$

$$-\ln(a_w) = \frac{A}{(T+B)} \exp(-CM) \quad (27)$$

$$\ln[-\ln(a_w)] = \ln\left[\frac{A}{(T+B)}\right] - CM \quad (28)$$

A plot of $\ln[-\ln(a_w)]$ against M at each temperature yields a straight line with slope as $-C$ and intercept on the y-axis as $\ln\left[\frac{A}{(T+B)}\right]$.

With the expression for the slope, further algebraic manipulation is carried out as follows in order to solve for the temperature-related parameters of the model:

$$\exp(b) = \frac{A}{(T+B)}, \text{ implying that } T+B = \frac{A}{\exp(b)} = A \exp(-b) \quad (29)$$

From the above, $T = A \exp(-b) - B$.

A plot of T against $\exp(-b)$ yields a straight line with A as slope and intercept on the y-axis as $-B$.

In the nonlinear regression procedure, the avC as C and A and B are used as the initial parameter estimates in the equation.

g. Modified Halsey model: the modified Halsey model (Eq. (13)) can be transformed by algebraic manipulations to yield Eq. (30):

$$a_w = \exp[-\exp(A+BT)M^{-C}] \quad (30)$$

Linearizing Eq. (30) by logarithmic transformation yields

$$\ln(a_w) = -\exp(A+BT)M^{-C} \quad (31)$$

$$-\ln(a_w) = \exp(A+BT)M^{-C} \quad (32)$$

So

$$\ln[-\ln(a_w)] = (A+BT) - C \ln M \quad (33)$$

A plot of $\ln[-\ln(a_w)]$ against $\ln M$ at each temperature yields a straight line with slope as $-C$ and intercept on the y-axis as $A+BT$. Using the intercept on y-axis for different temperature plots of the above, the values of the intercepts are then plotted against temperature to yield another straight line with slope as B and intercept on y-axis as A . In the nonlinear regression analysis, the avC as C and A and B values are used as the starting values in parameter estimates for the model.

h. Modified Henderson model: the modified Henderson model (Eq. (14)) is transformed to yield Eq. (34):

$$a_w = 1 - \exp[-A(T+B)M^C] \quad (34)$$

Eq. (34) is linearized by logarithmic transformation as follows:

$$1 - a_w = \exp[-A(T + B)M^C] \quad (35)$$

$$\ln(1 - a_w) = -A(T + B)M^C \quad (36)$$

$$-\ln(1 - a_w) = A(T + B)M^C \quad (37)$$

$$\ln[-\ln(1 - a_w)] = \ln[A(B + T)] + C \ln M \quad (38)$$

A plot of $\ln[-\ln(1 - a_w)]$ against $\ln M$ at each temperature yields a straight line with slope $a_1 = C$ and intercept on the y-axis $b_1 = \ln[A(B + T)]$. To solve for the temperature-related parameters, intercept on the y-axis is used.

$$\text{Therefore, } \exp(b_1) = A(T + B) = AT + AB. \quad (39)$$

A plot of $\exp(b_1)$ against T yields a straight line with slope a_2 as A and intercept on y-axis b_2 as AB . In the nonlinear regression procedure, $\ln C$ and A and B are used as initial parameter estimates for the model.

- i. Modified Oswin model: the modified Oswin model (Eq. (15)) can be manipulated algebraically to yield Eq. (40):

$$a_w = \frac{1}{\left[\frac{(A+BT)}{M}\right]^C + 1} \quad (40)$$

$$\frac{1}{a_w} = \left[\frac{(A + BT)}{M}\right]^C + 1 \text{ and } \frac{1}{a_w} - 1 = \left[\frac{(A + BT)}{M}\right]^C \quad (41)$$

Linearizing Eq. (41) by logarithmic transformation yields

$$C \ln(A + BT) - C \ln M = \ln\left(\frac{1 - a_w}{a_w}\right) \quad (42)$$

A plot of $\ln\left(\frac{1-a_w}{a_w}\right)$ against $\ln M$ at each temperature yields a straight line with slope as $-C$ and intercept on the y-axis as $C \ln(A + BT)$.

The expression for intercept on the y-axis is solved further to evaluate the temperature-related parameters of the model and yield Eq. (43),

$$\exp(b/c) = (A + BT) \quad (43)$$

A plot of $\exp(b/c)$ against T yields a straight line with slope as A and intercept on the y-axis as B . In the nonlinear regression procedure, $\ln C$ as C and A and B are used as the initial parameter estimates in the model evaluation.

- j. Ngoddy-Bakker-Arkema model: the Ngoddy-Bakker-Arkema model, which has been postulated to be a generalized model, has the following parameters (unknowns): σ , V , P_m , ρ , ε and η .

Evaluating the model requires a lot of care. The starting values of parameters for application in the nonlinear regression procedure can be obtained as follows:

σ , V , ρ and P_0 can be obtained at different temperatures from the steam table P can be calculated using the expression $P = a_w$, ε can be taken as having a typical value of 0.1 though its value can be less, P_m is the monolayer value of P and η can be assumed to lie between -1 and $+1$ in the form of $-1 \leq \eta \leq +1$ with 0.1 as a typical starting value.

7.2. Moisture sorption isotherm model predictive indicators

After values of model constants have been determined using the nonlinear regression analysis, the suitability of a model for predictive purpose or its goodness of fit is determined using the following indices:

a. Residual plots: these are plots of residuals (difference between measured and predicted values of the EMC) against the measured values.

b. Standard error of estimate given as

$$SE = \left[\frac{\sum (Y - Y')^2}{df} \right]^{1/2} \quad (44)$$

c. Mean relative percent deviation given as

$$MRE = \frac{100}{N} \sum \left| \frac{Y - Y'}{Y} \right| \quad (45)$$

d. Fraction explained variation given as

$$FEV = \frac{SSM}{SST} \quad (46)$$

e. Residual sum of squares (RSS) given as

$$RSS = \frac{\sum (Y - Y')^2}{N} \quad (47)$$

f. Coefficient of determination, R^2 .

where Y is the measured EMC value, Y' is the EMC value predicted by the model, N is the number of data points, df is the degree of freedom, SSM is the sum of squares due to the model and SST is the total sum of squares.

8. Conclusions

Moisture sorption phenomena govern several technological processes (drying, storage, mixing and packaging to mention a few) involving agricultural and food products. Moisture sorption isotherms of these products are generally of the type II, sigmoidal in shape and temperature dependent. The isotherms can be determined using the static or dynamic gravimetric, vapor pressure manometric, hygrometric and inverse gas chromatographic methods. Desorption isotherm path could differ from that of adsorption leading to moisture sorption hysteresis.

Commonly used moisture sorption isotherm models include the BET, GAB, modified GAB, Hailwood-Horrobin, modified Hailwood-Horrobin, modified Chung-Pfost, modified Halsey, modified Henderson and modified Oswin models. Ngoddy-Bakker-Arkema model which was proposed as a generalized model was considered. While some of the models can be evaluated by fitting polynomial functions of the second order to them and applying nonlinear regression procedure, others can be solved thorough linearization by logarithmic transformation and nonlinear regression. For the Ngoddy-Bakker-Arkema model, the initial parameter

estimates for use in nonlinear regression have to be obtained from the steam table. A model is considered acceptable for predictive purpose, if the residuals are uniformly scattered around the horizontal value of zero showing no systematic tendency towards a clear pattern. Model goodness of fit is determined using standard error of estimate, mean relative percent deviation, fraction explained variation, coefficient of determination and residual sum of squares.

Conflict of interest

This chapter has no conflict of interest.

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