

Characterization and Sorption Isotherms of Mexican Mango (*Mangifera Indica L.*) Ataulfo Variety with Ultrasound Pretreatment

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ABSTRACT

The ripening stage of mango after harvesting was characterized by physicochemical tests, in order to establish certain standards that serve as a reference for the selection of these fruits. Besides, a technique was implemented in order to obtain complete sorption isotherms with and without ultrasound (40 kHz/20min) pretreatment at 65°C. For the physicochemical, characterizations were settled five maturity stages, from the physiological maturity to the commercial maturity. As expected, the weight, size, Chroma and soluble solids increase as the ripening stage progresses; in contrast the acidity, firmness and moisture decrease. Moisture data on a dry basis (g water/g dry solid) and water activity, on the average of three replicates for each sample (stage 3) in different a_w micro-environments, were analyzed to obtain sorption isotherm complete curves and adjusted to a GAB equation.

Keywords: Mango, Ultrasound, Sorption isotherm, GAB model.

INTRODUCTION

Mango (*Mangifera indica L.*) is considered one of the three or four finest tropical fruits. It belongs to the Anacardiaceae family and is described as the most appreciated fruit in the tropics for their economic value. In Mexico, the Ataulfo variety is native to the region of Soconusco, Chiapas, whose government was given the designation of origin by the Mexican Institute of Industrial Property in 1963.

The mango shelf life depends on the state of maturity in which were harvested, immature fruit ripening shows erratic behavior, *ie*, not fully develop its flavor and aroma, which leads to the rejection of the product. Attempts have been made to set a standard of maturity in the mango, based on the specific gravity and firmness [1, 2, 3], but the inconsistencies between mango varieties have limited its use as a criterion for predicting the maturity. Determinations of chemical and physiological maturity, involve laborious laboratory techniques, and most consumers determined this maturity by the firmness of the surface, gloss, flavor, etc., so very subjective. However, the "measure" of maturity is of utmost importance to harvest fruit for optimal post-harvest quality. For example, mature fruit is considered when the total soluble solid reaches 18° Brix.

The food stability depends on the free water content. Natural foods contain between 60 to 95% moisture, so evaluate this content is useful to determine the product composition, to select the raw materials for an industrial transformation and to facilitate their process, to prolong the shelf life and/or to maintain the product texture and consistency.

Like other fruits and vegetables, the mango has a short shelf life because of its high moisture content

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($\approx 84\%$). However, the moisture content, by itself, is not always the best parameter to express the water effect in the deterioration reaction rates, so that the water activity (a_w) term is used [4]:

$$a_w = \frac{P_v}{P_{v0}} \quad (1)$$

This relationship between the food water vapor pressure (P_v) and the vapor pressure of pure water (P_{v0}) represents the fraction of total moisture content of a product that is free; it means, available for deterioration reactions. Therefore, it is an indicator for the food lifetime prediction. Sorption isotherms graphically relate the equilibrium moisture content of a product with the water activity, at a constant temperature. They are constructed with thermodynamic equilibrium values, when the a_w is equal to the relative humidity surrounding the product. They are important for food process design and analysis (drying, blending and packaging), to predict food stability changes and also to choice of packaging material [5]. The theoretical intervals are generally not possible, are obtained experimentally. [6].

With respect to food processing technology, the development of non-thermal processing methods has attracted attention in the food industry. Examples of non-thermal processing technologies include high pressure processing (HPP), pulsed electric and magnetic fields [7] and ultrasound-assisted technologies for modifying or improving products process [8, 9]. The advantage of using ultrasound is that the process can be performed at room temperature, and heating is not necessary, reducing the likelihood of degradation of the food. Ultrasonic treatment not incorporates fruit soluble solids when using distilled water as the liquid medium [10, 11]. Depending on the frequency used and the applied wavelength range, one can observe a number of physical, chemical and biochemical changes, which allows a variety of applications. Studies of osmotic dehydration, ultrasound and ultrasound assisted osmotic dehydration, have shown that different fruits respond differently to the application of these pretreatments before drying [12-15], for example, reduces diffusion boundary layer and increases the convective mass transfer in the food.

MATERIALS AND METHODS

The Ataulfo Mangoes (*Mangifera indica L.*) were purchased in the local market and kept in controlled conditions of temperature and relative humidity (14 °C and 90% RH). Testing of the mangoes was as follows: The firmness and soluble solids were measured according to the NMX-FF-058-SCFI-2006 [16], titratable acidity and moisture by the methods 942.15 and 934.06 of the AOAC [17], respectively. Evaluation of color through digital images (SONY cyber-shot, DSC-P32) processed with Adobe Photoshop CS [18] on the scale CIE $L^*a^* b^*$ (Comision Internationale l'Eclairage), calculating the hue angle ($^{\circ}$ Hue) and chromaticity:

$$^{\circ} Hue = \tan^{-1} \left(\frac{b^*}{a^*} \right) \quad (2)$$

$$C = \sqrt{(a^*)^2 + (b^*)^2} \quad (3)$$

Further, weight, size and sphericity were determined [19]. Image acquisition was performed on a system consisting of a digital camera mounted on a tripod, in which the lens was 30 cm and 90° with respect to the fruit, which was placed on a black surface for no reflecting light; the lamp was at 45° on the target [20].

Experimental data histograms and the correlation between variables were made in order to settle five

ripening stages. After selecting the appropriate maturity, mangoes were washed, peeled and cut into 1 cm³ sample cubes.

Proximity Equilibrium Cells (PEC) were adapted to performing isopiestic method [21], where the moisture content of the sample is determined until the equilibrium vapor pressure of certain salts is identical to the reference pressure sample vapor at equilibrium [22]. PEC is shown in Figure 1; plastic boxes with a perforated base and a stainless steel mesh were implemented as the sample container. Both vessels were introduced into the PEC and finally placing the system in the incubator chamber.

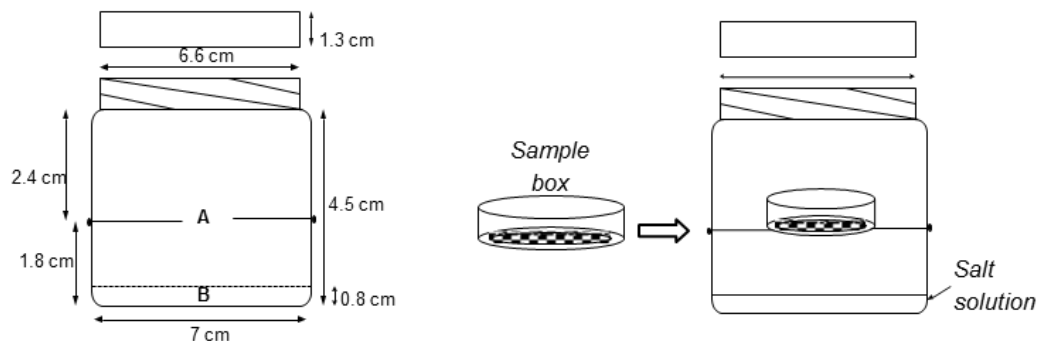


Figure 1. Adapted Proximity Equilibrium Cells (PEC) with sample box.

As seen in Figure 2, incubator chamber was also constructed from half inch pine wood with a one inch insulating coating (polystyrene foam); an asbestos block with a heating element was placed in the base, connected to a thermostat for temperature control. To achieve temperature homogeneity within the chamber was placed a high resistance fan on the top. As PEC's support was placed a stainless steel mesh at 16.5 cm height.

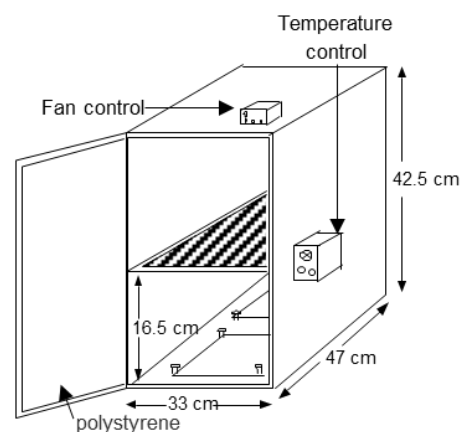


Figure 2. Constructed incubator chamber

For sorption isotherms, the samples were dehydrated in a convection oven (100 °C/1 h), and the moisture was determined before and after contact with the saturated solutions of reference salts with known a_w (Table 1). The selected saturated solution was deposited and tempered with 24 hours in the incubator chamber to produce the microenvironment inside the PEC (65°C). After that, sample boxes were introduced into the cell, until equilibrium was reached. The samples moisture determination was followed by the AOAC 934.06 method [17]. a_w was measured, using a hygrometer (Aqua-Lab, Decagon Devices), at equilibrium with microenvironment generated by salt solutions, which was determined when the weight difference (OHAUS analytical scale) respect of testing time was less than 1% of the sample.

Table 1. Water activity of saturated solutions

Salt	a_w 65 °C
Lithium chloride	0.110
Magnesium chloride	0.293
Potassium carbonate	0.432
Magnesium Nitrate	0.440
Sodium chloride	0.745
Potassium Chloride	0.803
Potassium Sulphate	0.950

Greenspan, 1977

Moisture data on a dry basis (g water / g dry solid) and a_w , on the average of three replicates for each sample in the different micro-environments, were analyzed by confidence intervals for the mean ($\alpha=0.05$) to obtain sorption isotherms. The obtained curves were adjusted by GAB model (Guggenheim, Anderson and de Boer), which describes the isotherm behavior until $a_w = 0.9$:

$$\frac{M}{M_0} = \frac{Cka_w}{(1 - ka_w)(1 - ka_w + Cka_w)} \quad (4)$$

C and k are constants related to the interaction energies between the first and the most distant molecule adsorbed on individual sites of sorption [23]. The adjustment was performed by rearranging the equation in a polynomial second degree:

$$\frac{a_w}{M} = \alpha \cdot a_w^2 + \beta \cdot a_w + \gamma \quad (5)$$

considering: $\alpha = \frac{k}{M_0} \left(\frac{1}{C} - 1 \right)$, $\beta = \frac{1}{M_0} \left(1 - \frac{2}{C} \right)$ and $\gamma = \frac{1}{M_0 Ck}$

The α , β and γ values were calculated by least squares analysis of determinants [24] to obtain the constants, where C = Guggenheim constant, associated to the energy of sorption of the first layer on the first sites, M_0 = moisture content on the dry basis, corresponding to the primary sites saturation for a water molecule (monolayer in BET theory [25]) and k = correction factor of molecules properties in multilayers. The constants values were corroborated obtaining the experimental error:

$$\% \text{ Error} = \sqrt{\frac{\sum (a_{we} - a_{wc})^2}{N}} \quad (6)$$

where N is the number of experimental points, a_{we} is the average of the experimental water activity, and a_{wc} is the calculated water activity.

The samples subjected to pretreatment, were placed in Erlenmeyer flasks with distilled water 4:1 (water: fruit) in an ultrasonic bath (Cole Parmer, IL, USA.) at 40 kHz for 20 min; after 5 min on absorbent paper, each sample weight was determined in APX 200 analytical balance (Denver Instruments, Göttingen Germany).

RESULTS AND DISCUSSION

Table 2 shows the experimental results for the mangoes classification average in five stages of maturity, with the state 1 representing physiological maturity to state 5 that corresponds to the so-called commercial maturity. From this table, we can get the values from which you can select the raw material for a given transformation process, according to the required characteristics of the raw material or for fresh consumption.

Table 2. Mango Ataulfo classification of maturity in 5 states

Ripening stage	Weight (g)	Size (mm)	Sphericity	Color •Hue Croma		Firmness (N)	•Bx	Acidity *	Moisture %
1	225	80	0.64	67.94	49.59	88.58	11.3	0.47	89.05
2	247	81	0.66	57.15	49.72	75.18	12.5	0.45	88.37
3	256	82	0.66	38.97	51.83	70.79	13.1	0.41	86.99
4	276	83	0.72	37.56	55.07	68.27	14.8	0.36	84.62
5	295	85	0.64	32.70	60.80	65.00	16.6	0.25	83.66

*g malic acid/100g

The fruit size and its sphericity and weight, increase gradually as they mature. Similarly, the development of desirable characteristics in fruit ripening is favored, as is the case of color and sweetness, are reflected in the increased chroma, °Bx and also in decreased firmness and acidity with storage time.

Loss of firmness can be attributed to changes in the polymers, such as pectin from the cell wall during ripening. Hue values (°Hue) obtained, indicate the color change of the mangoes surface, green to yellow color characteristic of the mature fruit.

Figure 3 shows the sorption isotherms obtained for selected fresh fruits in the maturity stage 3 for the experiment. It can be seen having a sigmoidal shape, the type III as classified by Braunauer et al. [26], as most of the food, where the material has the same affinity for water and for itself, so that once a molecule has been adsorbed it also acts as a free site for another molecule is adsorbed, thereby increasing the range of the monolayer.

Dry fruits contain a high percentage of sugars (monosaccharides), which give the characteristic shape of the adsorption isotherms, with low moisture contents at low water activities and sustained increase of moisture in high-water activity, due to the dissolution of fruit sugars [27].

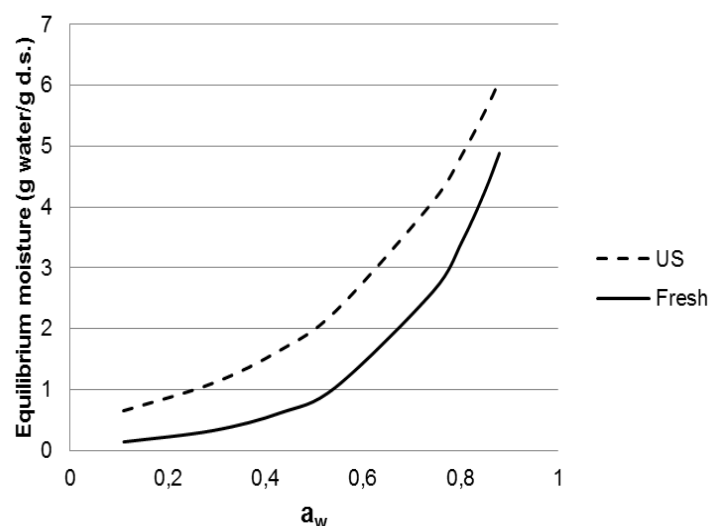


Figure 3. Sorption Isotherm for mango Ataulfo at 65°C

The value of the constants fit GAB equation, are shown in Table 3. The monolayer (M_0) moisture value increases with sonication, it represents the extent of the water molecules by the effect of ultrasound with the consequent increase of active sites for adsorption, *ie*, the strongly adsorbed water and immobilized on such sites. This implies that it requires more energy to move the water molecules with increasing moisture content. Increasing the parameter C with respect to sonication, indicates a higher binding energy of the monolayer high humidity, this can be interpreted as the adsorption process is strongly localized since water molecules sorbed stay longer in the first layer, and it is no longer available to act as a solvent or reagent [28]. Higher values of the correction factor K for the properties of molecules in multilayer correspond to the mangoes without ultrasonic pretreatment, which have lower values of the monolayer.

Table 3. GAB equation constants

Constants	Fresh Mango	US Mango
<i>K</i>	1.047±0.01	0.937±0.004
<i>Mo</i>	0.549±0.05	1.212±0.008
<i>C</i>	2.057±0.55	6.905±0.10

This phenomenon may happen because the ultrasound produces a series of effects when it travels across a medium that can affect mass and heat transfer; can generate the growth and collapse of bubbles inside liquids (cavitation), the heating of the medium, the microstirring at interfaces and several structural effects such as the “sponge effect” or the generation of micro channels inside the fruit structure [29]. In addition, solvent and solute molecules present within the cavitation bubbles are decomposed under the extreme conditions of temperature and pressure during its collapse and generate several highly reactive radicals. For example, if the sonicated medium is water, H• and •OH radicals are generated [30]. The relative effect of ultrasound depends on the transfer resistance affected. In treatments with a solid immersed in a fluid, ultrasound could accelerate the internal transport making the entry of fluids in the solid matrix and/or their exit easier and also facilitating the exchanges between the solid surface and the surrounding fluid [31, 32]. Besides cavitation, another phenomenon may happen during the application of ultrasound. Bloated cells due to the broadening of the microscopic channels offers lower resistance for water flow within the fruit sample and may explain further increase in mass transfer of water [10]. It is also possible that the H• generated had formed new hydrogen bonds, due to plasticizer molecules (water) that fill up voids between the fruit matrix molecules lowering the free volume [33] and increasing the binding energy.

Other components of the fruit, have no influence on the adsorption of moisture, since the breaking of bonds between these with sonication leave more active sites for water molecules, so that they have larger values of the monolayer but stronger bonds.

CONCLUSIONS

From the Ataulfo mango moisture isotherms obtained can be known the values of equilibrium moisture, if the water activity required during the transformation process that wants to apply, design or control is known (or vice versa).

The isotherms shape is high-sugar food characteristic, which adsorb relatively low moisture at low water activities, and adsorbing more at major activities.

The slight sigmoidal shape in the first part of the isotherm for the dry mango, is caused by the water sorption in polymers, and the moisture increasing at higher water activities due to the sugars sorption. The method used to dry the sample before sorption has great influence on the formation of porous structure and in the way the product adsorbed or desorbed water.

The use of ultrasound as a pretreatment in the conditions applied in this study makes it use an interesting methodology complementary to food processes involving heat and/or mass transfer.

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