Moisture Desorption Isotherms for Fresh and Osmotically Treated Mangoes

Pheeraya Chottanon and Singhanant Phoungchandang
Department of Food Technology, Faculty of Technology, Graduate School,
Khon-Kaen University, Khon-Kaen 40001, Thailand

Abstract: Desorption isotherms of fresh and osmotically treated mangoes have been measured at 25, 35 and 45°C by the static method using a Novasina manometer. A non-linear regression program was used to fit three moisture sorption isotherm models, Modified-Halsey, Modified-Henderson and Modified-Oswin to the experimental data. The Modified-Henderson and the Modified-Oswin models gave the best fit for moisture desorption isotherms for fresh and osmotically treated mangoes, respectively. The osmotic pretreatment affected the graphical form of the desorption isotherms because of biopolymer binding at low $a_w$ values and dissolution of sucrose at high $a_w$ values.

Key words: Mango, desorption isotherm, osmotic pretreatment, sorption isotherm model, Novasina manometer

INTRODUCTION

Mango, Magnifera indica L., is a very popular tropical fruit with people in many countries. It is highly perishable because of enzymatic reaction. Therefore, efficient processing and storage of mango are required to retain quality and ensure a high price. Air drying has been widely used to reduce moisture content for preservation and lower transport costs. However, water removal leads to a serious decrease in the nutritive and sensorial values. Osmotic dehydration is one method that can reduce moisture content of raw materials before applying a drying process. Osmotic dehydration is defined as the partial removal of water from food by immersing it in hypertonic solutions such as sucrose, glucose, fructose, corn syrup, glycerol, mannitol, etc. Improving the quality of preserved food products, providing the required moisture and solute ranges of raw materials to further processing, minimization of thermal stress and reduction of energy input over conventional drying are some of the advantages reported for osmotic dehydration on a conventional stabilization process.

Knowledge of moisture sorption isotherms is required for the efficient processing and storage of food. This is especially so when a drying process is used to obtain appropriate moisture content levels. The moisture sorption isotherm shows in a graphical form the variation in water activity ($a_w$) with change in moisture content of a sample at a specified temperature. For food system, the value of water activity is the same as the relative humidity of the surrounding atmosphere in equilibrium (ERH). Water activity better describes food spoilage than moisture content. Not only product stability but process design and control may also be predicted from moisture sorption isotherms especially the prediction of Equilibrium Moisture Content (EMC) which is used as one of the input parameters in drying models. Two basic methods to determine moisture sorption isotherms are the manometric and gravimetric methods. The manometric method records the ERH of a known constant moisture content by using a manometer such as a Novasina manometer. Moisture sorption isotherm models, both theoretical models such as BET, QAB and Halsey and empirical models such as Chung Pforst, Oswin and Henderson have been developed to describe the relationship between EMC and $a_w$ of tested materials. However, there is a form of sorption isotherm specific to each complex mixture, such as foods, so empirical models have been used to better fit specific foods. The three empirically modified models of Modified-Henderson, Modified-Halsey, and Modified-Oswin (Table 1) have been found to be the most commonly used models. The Modified-Henderson model has been developed as a standard model by the American Society of Agricultural Engineers (ASAE) for the description of cereals and oil seeds. The Modified-Halsey model has been reported to be the best fit for prunes and soya beans and the Modified-Oswin model has been shown to describe the equilibrium moisture content and water activity data for bananas. The effect of osmotic pretreatment of mangoes has not, so far, been distinctly verified on the graphical form of moisture sorption isotherms or moisture sorption isotherm models.

Corresponding Author: Pheeraya Chottanon, Department of Food Technology,
Faculty of Technology, Graduate School, Khon-Kaen University, Khon-Kaen 40001, Thailand
Tel: 066 043 362132 Fax: 066 362131 E-mail: Pheeraya2514@hotmail.com
Table 1: The moisture sorption equations

<table>
<thead>
<tr>
<th>Model</th>
<th>Mathematic expression</th>
<th>ERH= f(EMC,T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified-Halsey (MHAM)</td>
<td>$EMC = \left(\frac{-\ln ERH}{exp(C + kT)}\right)^{\frac{1}{n}}$</td>
<td>$ERH = \exp\left[-\exp(kT + C)EMC^{-n}\right]$</td>
</tr>
<tr>
<td>Modified-Henderson (MHM)</td>
<td>$EMC = \left(\frac{-\ln(1 - ERH)}{k(T + C)}\right)^{\frac{1}{n}}$</td>
<td>$ERH = 1 - \exp(-k(T + C)EMC^{n})$</td>
</tr>
<tr>
<td>Modified-Oswwin (MOM)</td>
<td>$EMC = (C + kT)\left(\frac{ERH}{1 - ERH}\right)^{\frac{1}{n}}$</td>
<td>$ERH = 1\left[\left(\frac{C + kT}{EMC}\right)^{n} + 1\right]$</td>
</tr>
</tbody>
</table>

RH is equilibrium relative humidity (decimal); EMC is equilibrium moisture content (%d.b.); T is temperature (°C). C, k and n are constants.

The objectives of this study were to establish the equilibrium moisture content and equilibrium relative humidity for fresh and osmotically treated mangoes. Other objectives include the evaluation of the effect of osmotic pretreatment on the graphical form of moisture sorption isotherms and ability of three commonly used moisture sorption isotherm models to fit the experimental data.

MATERIALS AND METHODS

Mango and sucrose solution: Chockanant mangoes and sucrose were purchased from a local market. Mangoes, yellow and firm, 13% soluble solid (ATAGO refractometer) were peeled, deseeded and sliced into 5 mm thick pieces by using a slicer. Moisture content of mango slices was determined by using the standard method[9]. Sucrose solution was prepared at 103°C[6] to achieve the complete dissolution. The solution concentration was controlled at 63% (w/w), following the previous study of osmotic dehydration of mango slices in sucrose solution[10]. This concentration gave the high water removal and low solute gain of osmotically treated mango slices.

Moisture desorption isotherm procedure: Mango slices were osmectically soaked in sucrose solution at 35°C for 2 h to remove a large amount of water[11]. The ratio of mango slices to sucrose solution was 1:6[9]. After the osmotic treatment, the slices were lightly rinsed with water to remove excess sugar solution, drained and then placed on a pre-weighted drying tray in order to proceed to the drying process. The fresh (FM) and osmotically treated (OM) mango slices were dried by using a tray drier (Armfield limited) at 60°C to obtain eight different levels of moisture content. The dried slices were cut manually into 2x2 mm pieces and 3-5 g samples were measured for equilibrium relative humidity at 25, 35 and 45°C by using a Novasina manometer (TH2/TRD-33/35) which is specially designed for temperature controlled measurement of water activity or relative humidity at equilibrium state. The temperature of the measurement chamber is regulated to a set point by a controller with accuracy to 0.2°C and its range is 0-50°C. The relative humidity converted from the humidity signal by a transmitter ranges from 0-100%.

Data analysis procedure: Experiments were performed in triplicate and the average values were reported. The data were fitted to three moisture desorption isotherm models (Table 1) including Modified-Henderson (MHM), Modified-Halsey (MHAM) and Modified-Oswwin (MOM). The model parameters were processed by non-linear regression techniques using SPSS 9.0 for Windows, which minimized the sum of squares of deviation in a series of iteration. All desorption isotherm models are three parameter equations which can be solved explicitly for equilibrium moisture content as a function of equilibrium relative humidity and temperature (EMC= f(ERH,T)) or for equilibrium relative humidity as a function of equilibrium moisture content and temperature (ERH= f(EMC,T)). The non-linear regression procedure required that initial parameter estimates be chosen to the true values. The goodness of fit of tested models was evaluated using the coefficient of determination ($R^2$) and standard error of estimate ($E_0$) as follows:

$$R^2 = \frac{\sum(Y' - \bar{Y}')^2}{\sum(Y - \bar{Y})^2}$$

$$E_0 = \sqrt{\frac{\sum(Y - \bar{Y}')}{d_f}}$$

Where, $Y$ is the experimental value, $Y'$ is the calculated value by model, $\bar{Y}$ is the mean of experimental value and $d_f$ is the degree of freedom on the regression model. The higher the value of $R^2$ and the lower the value of $E_0$ were chosen as the criteria for goodness of fit.
RESULTS

Moisture desorption isotherms of fresh and osmotically treated mangoes: The average value of moisture content of fresh and osmotically treated mangoes, used in this experiment was 86.33 and 70.84%, respectively. The average value of soluble solid of fresh and osmotically treated mangoes was 13 and 20.26%, respectively. The desorption isotherm data for fresh and osmotically treated mangoes shifted by temperature. Figure 1 shows the desorption isotherms of fresh and osmotically treated mangoes at three temperatures. The desorption isotherms were not sigmoid but were in agreement with the reported shape for high sugar foodstuffs. It can be seen that all isotherms were similar in shape, showing a gradually increasing sorption pattern, which is characteristic of fruits that have significant sugar content. At low water activities, the products contained a relatively small amount of water. When \( a_w \) increased, the sorption increased considerably. A similar behavior has been reported by other authors for different fruits.

Modelling of desorption isotherms of fresh and osmotically treated mangoes: Table 2 shows the predicted parameters and models with \( ERH = f(EMC,T) \) in which the moisture content of samples was taken as the independent variable. The criteria to select the best model used in this research were the coefficient of determination \( (R^2) \) and standard error of estimate \( (E_r) \). The higher the value of \( R^2 \) and the lower the values of \( E_r \) were chosen as the criteria for goodness of fit. From these criteria indices, all models could be used for ERH prediction of fresh and osmotically treated mangoes because the \( R^2 \) values were greater than 0.945. The Modified-Henderson and the Modified-Oswin models were each considered to be the best model for fresh and osmotically treated mangoes respectively due to the highest \( R^2 \) values and the lowest \( E_r \). Likewise, Table 3 shows the predicted parameters and models with \( EMC = f(ERH,T) \) in which equilibrium relative.

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![Fig. 1: Comparison between experimental (symbol) and predicted (continuous line) desorption isotherms for fresh above and osmotically treated below mangoes. Temperatures (●) 25°C, (▲) 35°C and (●) 45 °C](image1)

![Fig. 2: The surface plot of equilibrium moisture content values as a function of \( a_w \) and temperature predicted by the Modified-Henderson equation (EMC=f(ERH,T)) for fresh mangoes above and the Modified-Oswin equation (EMC=f(ERH,T)) for osmotically treated mangoes below](image2)
Table 2: Predicted parameters and comparison criteria for ERH=ERH(T) for fresh and osmotically treated mangoes

<table>
<thead>
<tr>
<th>Parameter and criteria</th>
<th>Fresh mangoes</th>
<th>Osmotically treated mangoes</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0.00035</td>
<td>-0.0064</td>
</tr>
<tr>
<td></td>
<td>-0.0064</td>
<td>-0.00011</td>
</tr>
<tr>
<td></td>
<td>-0.0039</td>
<td>-0.0583</td>
</tr>
<tr>
<td>C</td>
<td>138.3668</td>
<td>2.6307</td>
</tr>
<tr>
<td></td>
<td>2.6307</td>
<td>-14707.52</td>
</tr>
<tr>
<td></td>
<td>1.6872</td>
<td>15.7074</td>
</tr>
<tr>
<td>n</td>
<td>0.8349</td>
<td>0.9898</td>
</tr>
<tr>
<td></td>
<td>0.9898</td>
<td>0.5573</td>
</tr>
<tr>
<td></td>
<td>0.7428</td>
<td>0.9190</td>
</tr>
<tr>
<td>R²</td>
<td>0.978</td>
<td>0.946</td>
</tr>
<tr>
<td></td>
<td>0.946</td>
<td>0.977</td>
</tr>
<tr>
<td></td>
<td>0.979</td>
<td>0.981</td>
</tr>
<tr>
<td>Eₗ₀</td>
<td>0.0344</td>
<td>0.0543</td>
</tr>
<tr>
<td></td>
<td>0.0543</td>
<td>0.0202</td>
</tr>
<tr>
<td></td>
<td>0.0193</td>
<td>0.0183</td>
</tr>
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</table>

Table 3: Predicted parameters and comparison criteria for EMC=ERH(T) for fresh and osmotically treated mangoes

<table>
<thead>
<tr>
<th>Parameter and criteria</th>
<th>Fresh mangoes</th>
<th>Osmotically treated mangoes</th>
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</thead>
<tbody>
<tr>
<td>K</td>
<td>0.00915</td>
<td>-0.0080</td>
</tr>
<tr>
<td></td>
<td>-0.0086</td>
<td>-0.0012</td>
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<tr>
<td></td>
<td>-0.1187</td>
<td>-0.1871</td>
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<tr>
<td>C</td>
<td>188.4800</td>
<td>5.4047</td>
</tr>
<tr>
<td></td>
<td>24.9182</td>
<td>134.39</td>
</tr>
<tr>
<td></td>
<td>2.4069</td>
<td>21.1843</td>
</tr>
<tr>
<td>n</td>
<td>1.0099</td>
<td>1.7805</td>
</tr>
<tr>
<td></td>
<td>1.9973</td>
<td>0.5000</td>
</tr>
<tr>
<td></td>
<td>0.8598</td>
<td>0.9902</td>
</tr>
<tr>
<td>R²</td>
<td>0.998</td>
<td>0.946</td>
</tr>
<tr>
<td></td>
<td>0.981</td>
<td>0.976</td>
</tr>
<tr>
<td></td>
<td>0.992</td>
<td></td>
</tr>
<tr>
<td>Eₗ₀</td>
<td>3.5159</td>
<td>6.8006</td>
</tr>
<tr>
<td></td>
<td>5.7999</td>
<td>3.5083</td>
</tr>
<tr>
<td></td>
<td>3.9877</td>
<td>3.4196</td>
</tr>
</tbody>
</table>

Fig. 3: Comparison of desorption isotherms of fresh (continuous line) and osmotically treated mangoes (dotted line) at 25°C predicted by Modified-Henderson equation (EMC=ERH(T))

humidity of samples was taken as the independent variable. The Modified-Henderson and the Modified-Oswin models were also each considered to be the best model for fresh and osmotically treated mangoes, respectively. Both models could adequately present equilibrium moisture content values in the wide range of water activity and temperature as shown in the surface plot of equilibrium moisture content values as a function of aₜ and temperature for fresh mangoes and osmotically treated mangoes (Fig. 2). Conventionally, equilibrium moisture content values were found to increase with decrease in temperature at constant water activity and to increase with increase in water activity when temperature was kept constant. These satisfactory results would be useful for the drying kinetics and food storage when they are used in a drying model fitting and use as the appropriate moisture content at the lower limit (aₜ, 0.6) of available water for microbial growth during storage.

Effect of osmotic pretreatment on a graphical form of desorption isotherms of mangoes: Figure 3 shows that the osmotic pretreatment affected the graphical form of the desorption isotherms. At aₜ, value below 0.67, the moisture content of osmotically treated mangoes was lower than those of the fresh ones at corresponding values of aₜ which is in agreement with moisture sorption affected by sucrose pretreatment of apple and papaya[29] and plantain[23].

DISCUSSION

All desorption isotherms of fresh and osmotically treated mangoes shown in Figure 1 were similar in shape, showing a gradually increasing sorption pattern. At low water activities, the products contained a relatively small amount of water especially for osmotically treated mangoes. When aₜ increased, the sorption increased considerably. At low aₜ, the sorption might be mainly a superficial phenomenon due to the biopolymers and crystalline sugars, whereas at high aₜ, the increase in sorption might be mainly due to the dissolution of sugar[21]. For the model fitting, the Modified-Henderson and Modified-Oswin models were the best model for fresh and osmotically treated mangoes, respectively (Table 2 and 3). These models are empirically modified models which have been reported to be the most versatile models for many foods because of the use of a third parameter. The parameters estimated from the models with EMC=ERH(T) were not the same as the corresponding parameters estimated from the models with ERH=EMC(T). The observed result was similar with several reports[12,13,36]. They noted that the models with EMC=ERH(T) were obtained by logarithmic transformation of the models with ERH=EMC(T) and in the non-linear regression analysis, the error were assumed to be normally and independently distributed. This caused distortions in the models, thereby causing the corresponding model constants to take on different least-square values.

Figure 3 reveals the effect of osmotic pretreatment on the graphical form of moisture sorption of mangoes. At aₜ, value between 0.6 and 0.7 the isotherms of the fresh and the osmotically treated mangoes were crossed over and the moisture content of osmotically treated mangoes was higher than that of fresh mangoes. It may be noted that for the values of aₜ, greater than 0.67, the osmotically treated mangoes contain a higher water content than the fresh ones. This might suggest that the osmotically treated mangoes need more water to dissolve the extra
sugar at high water activity. The effect on quality was that
the osmotically treated mangoes hold more water while
still preserved. The additional moisture brings about a
more palatable product compared with conventional dried
mangoes.

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