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Sorption behaviour of papayas as affected by compositional and structural alterations from osmotic pretreatment and drying



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ABSTRACT

Moisture sorption dynamics and isotherms of fresh, osmotically-pretreated and dried papayas at temperatures of 30, 50 and 70 °C and water activity in the range of 0.113–0.907 were investigated. Chemical composition as well as volume, density, porosity and microstructure of the fruits were analysed. Results showed that the time required to reach equilibrium moisture content was mainly dependent on temperature, water activity level and processing method. The difference in moisture sorption characteristics between fresh, pretreated and dried papayas was attributed to (i) changes in the contents of sugars after osmotic dehydration and (ii) structural modifications caused by drying, which were corroborated by examination of micrographs. The differences in sorption behaviour of the pretreated and dried papayas, whereas the untreated, fresh samples were better predicted by the modified Oswin equation. Further indication that osmotic pretreatment and drying influenced the interaction between the sorption sites and water molecules was imparted by the values of isosteric heat of sorption (Q_{st}) for fresh and dried papayas at different temperatures.

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1. Introduction

The most common preservation method for papayas and other tropical fruits in Thailand is convective drying in fixed-bed- (Nagle et al., 2010), cabinet- (Precoppe et al., 2011), solar tunnel- (Janjai et al., 2009a) or solar greenhouse-dryers (Janjai et al., 2009b). Osmotic dehydration is frequently carried out as a pretreatment before convective drying, which involves immersion of cut fruit pieces in 30-70 °Brix sugar solution at an operational pH of 4.0 and temperature ranges between 30-60 °C. The process is typically applied on fruits such as pineapple, mango, papaya and lychee in order to enhance taste and maintain structural characteristics during drying (Riva et al., 2005). After pretreatment and drying, the papayas are packed in hygienic polyethylene bags or used as an ingredient in various confectionaries. For optimum processing and packaging, knowledge of the equilibrium relationship between relative humidity and moisture content of papayas is required to avoid quality deterioration. In addition, moisture sorption data can provide a theoretical interpretation for the interaction between water vapor and the chemical constituents of the material.

Food composition (Kingsly and Ileleji, 2009) and drying method can play a major role on the form of moisture sorption isotherms. More specifically, Djendoubi Mrad et al. (2012) found that desorption isotherms of osmo-dehydrated apricots were affected by the sugar composition and concentration due to the biopolymer binding at low a_w values and the dissolution of sucrose at high a_w values. Sugars may occur in different phases, i.e. in crystalline phase, amorphous phase and solution, each of them showing specific sorption behaviour. The ability of sugar to bind water is based on the ratio between crystallized and dissolved forms. Any change in this ratio during processing affects the amount of water that the material can bind. The different types of sugar (glucose, fructose and sucrose) found in food usually show various degrees of affinity to water. Moreover, sugar solubility increases at higher temperatures and certain amounts of crystalline sugar are converted into sugar solutions. Yu et al. (2008) stated that the presence of large quantities of crystalline sugar, i.e. glucose in dry fruits, caused an intersection of sorption isotherms at certain temperatures. In another study reported by Acevedo et al. (2008), the moisture adsorption properties of apple were altered due to the structural modifications caused by drying. In addition, rearrangements of structure with subsequent changes in volume, density and porosity can also be induced during osmotic dehydration



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(Nieto et al., 2013). Al-Muhtaseb et al. (2004) noticed that the hysteresis effect between desorption and adsorption isotherms depends on compositional and structural changes caused by processing methods. The observation was in agreement with an additional study by Alam and Singh (2011). They reported that the hysteresis effect was observed prominently for un-osmosed and salt-osmosed samples in comparison to sugar-osmosed samples. With hysteresis, the equilibrium moisture content in desorption phase is higher than that in adsorption phase. The magnitude of difference in each product varies with the level of relative humidity and temperature applied.

Normally, the shape of sorption isotherms can be divided into three zones corresponding to monolayer strongly bound water, less rigidly and capillary adsorbed water (linear region) and solvent or free water. Mathlouthi (2001) mentioned that the homogeneous soluble sugar adopts an asymptotic shape of isotherm when relative humidity tends toward 100%, whereas heterogeneous matter, such as foods, display a sigmoid curve. To account for the behaviour of sugar-rich fruits, several theoretical and empirical sorption models can be retrieved from the literature, however the selection of the appropriate equation depends on the complexity of fruit structure and composition as well as the affinity of the constituents for water (Mathlouthi and Rogé, 2003). For instance, the Guggenheim, Anderson and de Boer (GAB) model was used to fit the experimental sorption data of various tropical fruits like banana, mango and pineapple (Talla et al., 2005). Apart from the GAB model, the modified Oswin equation proved as the best threeparameter model to describe the sorption isotherms within the range of 30-50 °C for lychee (Janjai et al., 2010), mango (Janjai et al., 2007) and longan (Janjai et al., 2006). Noshad et al. (2012) proposed the Peleg model as best fitting for both treated and untreated quince, while the Halsey equation predicted the sorption isotherms of grapes, apricots and apples adequately (Kaymak-Ertekin and Gedik, 2004). However, it is worth noting that the influence of temperature was not incorporated in the equations of some works mentioned above. Furthermore, Moreira et al. (2009) developed a generalized model for the prediction of moisture sorption isotherms of several fruits based on the composition of the main components such as sugar, salt, protein, fibre and starch

Although the application of osmotic dehydration has been intensively studied in many fruits, its effect on sorption isotherm properties of fresh and dried papayas still remains undocumented. Consequently, the objectives of this study were to (a) investigate the effect of osmotic pretreatment on physicochemical and microstructure attributes of fresh and dried papayas, (b) determine the impact of sugar composition and structural changes on sorption isotherm characteristics at different temperatures, (c) fit the experimental sorption data using suitable three-parameter models for sugar-rich products and (d) calculate the isosteric heat of sorption at different temperatures by the best-fitting sorption model based on the Clausius–Clapeyron theory.

2. Materials and methods

2.1. Raw material

Fresh papayas (*Carica papaya* cv. Pluk Mai Lie) were imported from Thailand by a company in Germany and selected in order to obtain samples with similar shape (elongated club), mass $(1.0 \pm 0.2 \text{ kg/fruit})$ and ripening stage $(70 \pm 10\% \text{ of yellowness})$ skin). The fruits were refrigerated at a temperature of $10 \pm 1 \degree$ C for not more than 5 days. Prior to moisture sorption experiments, papaya samples were divided into three different groups. A batch of untreated, fresh samples was used for the determination of desorption isotherms. Meanwhile, a second batch of samples was subjected to osmotic treatment and a third batch of osmoticallypretreated fruits was dried by convection for determination of sorption isotherms.

2.2. Processing

2.2.1. Osmotic pretreatment

Samples were osmotically-pretreated according to the procedure described in a previous study by Udomkun et al. (2014). Fruits were hand peeled and cut into a cuboid shape $(20 \times 30 \times 20 \text{ mm})$ using a stainless steel cutter designed for this study. Cubes were rinsed with tap water and then immersed in 25 g L⁻¹ calcium lactate solution for 1 h at controlled temperature $(20 \pm 2 \,^{\circ}\text{C})$. Subsequently, samples were blanched at $60 \pm 2 \,^{\circ}\text{C}$ for 1 min and then soaked in sucrose solution at a starting temperature of $60 \pm 2 \,^{\circ}\text{C}$ for 1 h before allowing to stand at room temperature for 6 h. The osmotic solution was prepared by mixing 99.9% refined sucrose with water to give a concentration of 30 °Brix and then pH was adjusted to 4.0 using citric acid. The osmotic solution to fruit ratio was maintained at 1:1 (gravimetric basis). After removal from the solution, the samples were rinsed with water, drained and finally blotted with absorbent paper to remove the surface water.

2.2.2. Convective drying

Pretreated samples (600–650 g) were evenly spread on a round stainless steel tray (diameter of 240 mm) and dried by air convection in a through-flow laboratory dryer. A detailed description of the experimental system has been given by Argyropoulos et al. (2011a, 2011b). The drying experiments were carried out at a temperature of 70 °C, constant specific humidity of 10 g kg⁻¹ dry air and air velocity of 0.5 m s⁻¹ until constant mass of the samples was achieved corresponding to a moisture content of 13.5 ± 0.05% wet basis (w.b.) with a water activity ranging between 0.5 ± 0.05.

2.3. Sorption characteristics

The equilibrium moisture content of fresh, pretreated and dried papaya samples was determined at different values of water activity (a_w) and temperature using the static gravimetric method (Spiess and Wolf, 1987). Each glass jar contained a specific saturated salt solution to develop a wide range of a_w between 0.113 and 0.907 at 30, 50 and 70 °C as shown in Table 1. A Petri dish containing thymol was also placed in the glass jars with a_w higher than 0.6 to avoid mould growth in the samples. About 2 g of papaya was placed in the sample holder. Then, all glass jars were placed in a climate temperature system (CTS) chamber (C-20/1000, Clima Temperature. The samples were taken out and periodically

Table 1

Values of water activity (a_w) created using different saturated salt solutions at 30, 50 and 70 °C (Arabhosseini et al., 2005; Greenspan, 1977; Young, 1967).

Salt solution	Water activity $a_w(-)$		
	30 °C	50 °C	70 °C
LiCl ₂	0.113	0.112	0.108
CH₃COOK	0.216	0.189	0.162
MgCl ₂	0.324	0.305	0.278
K ₂ CO ₃	0.432	0.427	0.416
$Mg(NO_3)_2$	0.514	0.464	0.451
NaBr	0.560	0.509	0.497
NaCl	0.751	0.744	0.751
KCl	0.836	0.812	0.780
KNO ₃	0.907	0.848	0.791

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