

DETERMINATION OF THE ISOSTERIC HEAT TO PLANTAIN PULP (*musa paradisiaca*) BY SORPTION ISOTHERMS

DETERMINACIÓN DEL CALOR ISOSTÉRICO PARA PULPA DE PLÁTANO (*musa paradisiaca*) POR ISOTERMAS DE SORCIÓN

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ABSTRACT: For sorptional data to be useful in simulation and design of storage and drying systems, they must be represented by equations valid in the conditions usually found in industrial practice. Using the modified Chung–Pfof model and fitted by desorption the net and total isosteric heat of plantain pulp was evaluated. The net isosteric heat decreased with increasing moisture content ranging from 1670 kJ/kg (5%.d.b) to 215 kJ/kg (26%.d.b) where the better goodness of fit was presented by polynomial and power-law models.

KEYWORDS: Physical properties, moisture content, isosteric heat.

RESUMEN: Las isotermas de sorción para ser usadas en la simulación y diseño de procesos de secado y almacenamiento de alimentos deben ser representadas por modelos válidos dentro de las condiciones encontradas en la práctica industrial. Usando el modelo de Chung–Pfof y ajustado por desorción el calor isostérico neto y total para pulpa de plátano fueron determinados. El calor neto isotérico neto decreció con el contenido de humedad del producto variando desde 1670 kJ/kg (5%.d.b) a 215 kJ/kg (26%.d.b) donde esta variación fue representada por el modelo potencial y polinomial.

PALABRAS CLAVE Propiedades físicas, contenido de humedad, calor isostérico.

1. INTRODUCTION

The plantain is a species of the genus *Musa* and is generally used for cooking, in contrast to the soft, sweet banana (which is sometimes called the dessert banana). Plantains tend to be firmer and lower in sugar content than dessert bananas and are used either when green or under-ripe

(and therefore starchy) or overripe (and therefore sweet). Plantains are a staple food in the tropical regions of the world, treated in much the same way as potatoes and with a similar neutral flavour and texture when unripe. In Colombia the plantain under-ripe is called as “plátano

verde” and its pulp is used extensively by its high culinary quality and industrial processing as flour. The “plátano” is one of the products more important at domestic marketing, since it participates with the 6,8% of the agricultural production occupying the fifth place after the coffee, flowers, banana and sugarcane. This product is fundamental in the Colombians diet with a consumption by person of 61,9 kg/year.

The sorption isosteric heat (also called latent heat of vaporization, desorption–vaporization) in foodstuffs is of practical interest in drying operations, handling, storage and processing (Mulet *et al.*, 2002; Ashraful *et al.*, 2007; Yan *et al.*, 2008). The value of latent heat of vaporization is neither constant nor equal to the heat of pure water evaporation (Tolaba *et al.*, 2004). It is a function of temperature and moisture content, that is, the value is varied throughout the drying process (Rucklod *et al.*, 2003). A simple model including moisture content and temperature term is very useful to compute the latent heat of vaporization (Kaya and Kahyaoglu, 2005).

The net isosteric heat is defined as the total heat of sorption in the food minus the heat of vaporization of water, at the system temperature (Tsami, 1990). The total isosteric heat of sorption is the total heat supply for drying of a material. As a differential molar quantity, isosteric heat of sorption determines the temperature dependence of water activity of a biological material. The heat of vaporization of sorbed water may increase to values well above the vaporization of pure water as food is dehydrated to low moisture levels (Rizvi, 2005). The extent of material moisture content at which the isosteric heat of sorption approaches the latent heat of vaporization of water is often considered as an indication of the amount of “bound water” existing in the food (Kiranoudis *et al.*, 1993). Conventionally, is a positive quantity when heat is evolved during adsorption, and negative when heat is absorbed during desorption. The heat of adsorption is a measure of the energy released on sorption, and the heat of desorption the energy requirement to break the intermolecular forces between the molecules of water vapour and the surface of adsorbent. Thus, the heat of sorption

is considered as indicative of the intermolecular attractive forces between the sorption sites and water vapour (Rizvi, 2005).

The application of thermodynamic principles to sorption isotherm data has been used to obtain more information about the properties of water, food microstructure, and physical phenomena on the food surfaces, and sorption kinetic parameters (McMinn and Magee, 2003). The net isosteric heat of sorption is used as thermodynamic function for analysis of sorption isotherms. The net isosteric heat of sorption or differential enthalpy shows the energy requirement for removing moisture from food material (water–solid binding strength) has a practical use in complete drying calculations and modeling of energy (Rizvi, 2005). The net integral enthalpy or net equilibrium heat of sorption indicates the binding strength of water molecules to food particles and could be a measure of the food–water affinity (Aviara *et al.*, 2004).

Two methods are available for measurement of the differential heat of sorption. The first is direct calorimetric measurement of the heat evolved, and the second is application of the Clausius-Clayperon equation on the isosteric equilibrium pressures at different temperatures (the ‘isosteric’ heat of sorption). Sorption calorimetry is difficult because of the technique needed for precise measurement of the small quantities of heat evolved. For this reason, calorimetrically measured heats of sorption are much less common than those calculated from the sorption isotherm, however, they offer a higher degree of accuracy when determined with care (Al-Muhtaseb *et al.*, 2002).

Moisture sorption isotherms describe the relationship between the equilibrium moisture content and the water activity at constant temperatures and pressures (Kaleemullah and Kailappan, 2004). For food materials these isotherms give information about the sorption mechanism and the interaction of food biopolymers with water. The moisture sorption isotherms are extremely important in modelling the drying process, in design and optimisation of drying equipment, in predicting shelf-life

stability, in calculating moisture changes which may occur during storage and in selecting appropriate packaging material (Gabas et al., 2000; Kaymak-Ertekin and Gedik, 2004)

The objective of this study was to determine the thermodynamic function of isosteric heat in relation to moisture sorption in plantain pulp using a sorption model.

2. MATERIALS AND METHODS

Isotherm models

In this study the isosteric heat of plantain pulp was determined through the sorption isotherm method. Two A_w models incorporating temperature terms have been evaluated for sorption data (Ciro *et al.*, in press). The modified Chung–Pfof model fitted by desorption was adopted in this study to compute the q_{st} (the net isosteric heat) and Q_{st} (total heat of sorption) values. The fitted model is:

$$M_E = 0,452 - 0,09747 \ln[-(T + 4,7138) \ln(A_w)] \quad (1)$$

The model cited above presented the best goodness of fit (Ciro *et al.*, in press) and was fitted to $25^\circ\text{C} \leq T \leq 50^\circ\text{C}$, activity water of $0,4 \leq A_w \leq 0,8$ and equilibrium moisture content of $5\% \text{ d.b.} \leq M_E \leq 26\% \text{ d.b.}$

Net isosteric heat of sorption

The Clausius–Clapeyron equation

The net isosteric heat of sorption (q_{st}) is obtained by subtraction of heat of water vaporization from total heat of sorption (Q_{st}). The q_{st} could be determined from experimental data using Clausius–Clapeyron equation in the form (Aguerre *et al.*, 1988; Rizvi, 2005; Chen, 2006; Perez-Alonso *et al.*, 2006; Vulloud *et al.*, 2006; Samapundo *et al.*, 2007):

$$\left. \frac{\partial(\ln(A_w))}{\partial\left(\frac{1}{T_k}\right)} \right|_{M=\text{constant}} = - \left[\frac{Q_{st} - \lambda}{R} \right] = - \frac{q_{st}}{R} \quad (2)$$

Integrating Eq. (2), assuming that the net isosteric heat of sorption (q_{st}) is temperature independent gives the following equation:

$$\ln(A_w) \Big|_{M=\text{constant}} = - \frac{q_{st}}{R} \left[\frac{1}{T_k} \right] + K \quad (3)$$

Where:

q_{st} = $Q_{st} - \lambda$ (kJ/kg)

K = Integration constant

A_w = Water activity (decimal)

λ = Latent heat of vaporization of pure water (kJ/kg)

R = Gas constant (0,4618 kJ/kg K)

T_k = Temperature (K)

M = Moisture content (% dry basis)

The heat to vaporization of pure water (λ) can be calculated by:

$$\lambda = R [6887 - 5,31 * T_k] \quad (4)$$

In this study, the isosteric heat of sorption was determined from the slope after plotting $\ln(A_w)$ versus $1/T_k$ at constant moisture content. This approach assumes that isosteric heat of sorption does not change with temperature.

The Othmer equation

The relationship between P_{vs} (saturated water vapor pressure) and the P_v (vapor pressure of water in food products) was given by Othmer (1940) as:

$$\ln P_v = \ln P_{vs} * \left[\frac{Q_{st}}{\lambda} \right] + Z \quad (5)$$

where λ is the heat of evaporation for pure water in kJ/kg, Q_{st} total heat of sorption isosteric or latent heat of vaporization of food products in kJ/kg (Brooker *et al.*, 1992); P_v is the vapor

pressure in food stuffs in kPa; and P_{vs} is the saturate vapor pressure in kPa. This model considers that the Q_{st}/λ value is independent of temperature. From the linear regression analysis technique, the slope, Q_{st} , can be found from $\ln(P_v)$ and $\ln(P_{vs})$ data.

In the equation (5), the saturation vapor pressure was determined using the Tetens equation (Weiss, 1977):

$$P_{vs} = 0,61078 * 10^{\left[\frac{7,5T}{237,3+T} \right]} \quad (6)$$

The vapor pressure in the food was calculated as:

$$P_v = ERH * P_{vs} \quad (7)$$

To equilibrium conditions the equilibrium relative humidity (ERH) is equal to water activity (A_w) (Jayendra et al., 2005; Ashraful et al., 2007)

Fitting Models

Several researchers reported the isosteric heat of sorption as an empirical function of moisture content (Tsami et al., 1990; Wang and Brennan, 1991; Sopade and Ajisegiri, 1994; Oztekin and Soysal, 2000; Hossain et al., 2001; Kaya and Kahyaoglu, 2005; Chen, 2006; Ashraful et al., 2007; Iguaz and Virseda, 2007). The isosteric heat of sorption of plantain pulp as a function of equilibrium moisture content (M_E) in the following forms were considered:

$$q_{st} = a * EXP \left[\frac{M_E}{b} \right] \quad (8)$$

$$q_{st} = -a M_E^3 + b M_E^2 - c M_E + d \quad (9)$$

$$q_{st} = \frac{a M_E^b}{c + M_E^d} \quad (10)$$

In the equation (8), “ b ” indicates the changes in binding energy with changes in water content, and “ a ” is the isosteric heat of sorption for the strongest bound water molecule (Rahman et al., 2002).

The accuracy of fit was evaluated by calculating the root mean square percent error (RMS) (Lievonen and Roos, 2002):

$$RMS = \sqrt{\frac{1}{N} \left[\sum_1^N \left(\frac{U_{exp} - U_p}{U_{exp}} \right)^2 \right]} * 100 \quad (11)$$

U_{exp} and U_p are the values of isosteric heat observed and predicted, respectively.

3. RESULTS AND DISCUSSION

Isosteric heat of sorption

Values of the heat of sorption at a specific moisture content provides an indication of the state of the sorbed water and hence, a measure of the physical, chemical and microbiological stability of the food material under given storage conditions. In addition, the variation in heat of sorption with moisture content provides valuable data for energy consumption calculations and subsequent design of drying equipment, and knowledge of the extent of the water–solid versus water–water interactions (McMinn and Magee, 2003). The net isosteric heats of sorption values with respect to moisture content are represented in Fig. 1. The curve shows that the heat of desorption decreased with increase in moisture content, initially rapidly up to 15 g moisture/100 g dry solids and later slowly, as observed in many other food systems (Sawhney et al., 1991; Tsami, 1991; Rahman et al., 2002; Delgado and Sun, 2002b; Tolaba et al., 2004; Yazdani et al., 2006; Sapamundo et al., 2007; Ashraful et al., 2007; García-Pérez et al., 2008). The decrease in the isosteric heat with the increase in sorbed water content may be attributed to the fact that sorption initially occurs on the most active sites such as hydrophilic polar groups giving rise to the greatest interaction energy. With increase in the moisture content, as these sites become occupied, sorption occurs on the less active sites viz., peptide bonds or hydrophobic hydration sites resulting in lower

heats of sorption (Delgado and Sun, 2002b; Jayendra et al., 2005).

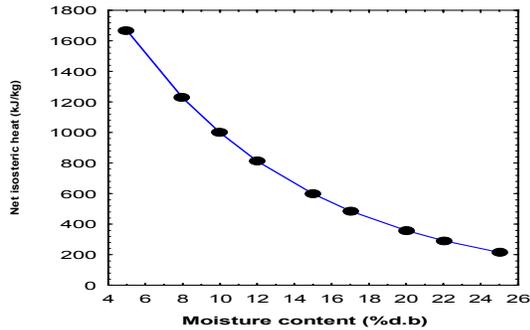


Figure 1. Net isosteric heat as a function of equilibrium moisture content (equation 3) de contenido de humedad (ecuación 3)

The ratio of latent heat of vaporization as a function of moisture content calculated by *Othmer equation* can be observed in Fig. 2. The ratio of (Q_{st}/λ) at low moisture contents is high, indicating that the heat of sorption is nearly twice the heat of vaporization of pure water (λ). This initial heat may result probably from the chemisorption on polar groups (Simal et al., 2007). The value of (Q_{st}/λ) was higher than one at every moisture contents but tending to one as the moisture content increased. The results of the Fig. 1 shown that during a drying process of plantain pulp the energy requirements are very high.

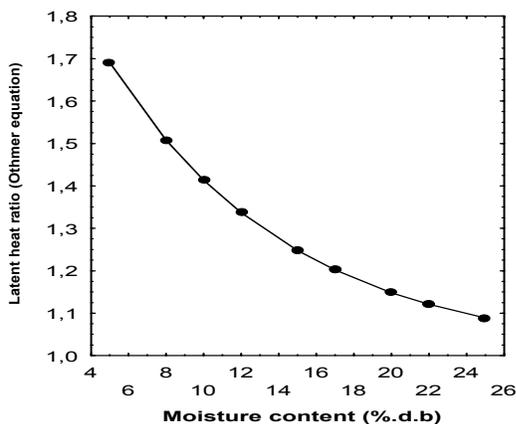


Figure 2. Latent heat of vaporization using Othmer's equation

The analysis statistical (ANOVA with $P=0,05$) did not found differences to the total isosteric heat calculated by *Clausius–Clapeyron* and *Othmer* equation. The total isosteric heats of desorption of plantain pulp are presented in Table 1. It is evident a marked increases in isosteric heat at the lower moisture contents. The evaporation of water from pulp requires energy to overcome the heat of evaporation of pure water (2408,4 kJ/kg). The values were calculated to 25°C using the Eq. 2 and 5.

Table 1. Total isosteric heat as a function of moisture content to plantain pulp

Moisture content (%d.b)	Equation 2	Equation 5
5	4077,01	4071,62
8	3634,93	3631,13
10	3407,40	3404,26
12	3222,08	3219,53
15	3006,51	3004,71
17	2895,54	2893,92
20	2766,49	2765,31
22	2700,06	2699,08
25	2622,79	2622,01

Fitting Models

The calculation of isosteric heat variation with moisture content was done using the power model (Eq.8), polynomial model (Eq.9) and non-linear model (Eq.10) and plotted in Fig. 3. The agreement was excellent for the desorption curve ($R^2 \cong 1$). The parameters and the standard error of estimate of the parameters for fitting the Eq. (8), (9) and (10) are shown in Table 2. The results of Table 2 suggesting that polynomial and power model considered in this study can be used to predict the net isosteric heat of plantain pulp with excellent approximation.

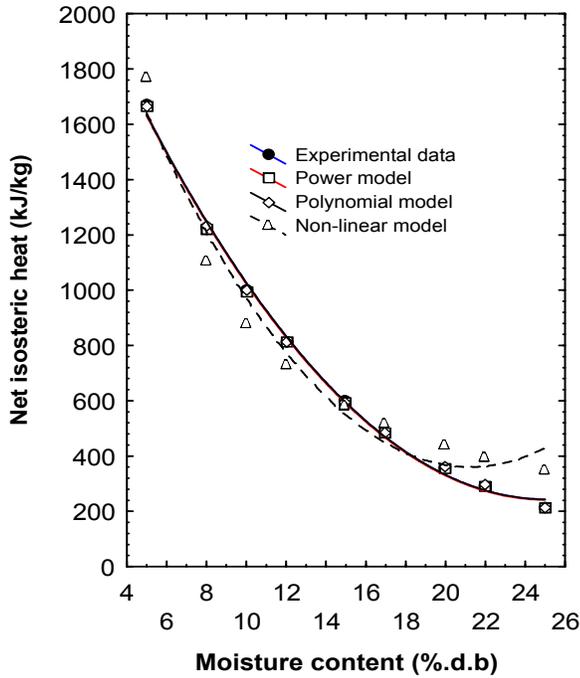


Figure 3. Fitted models to net isosteric heat according to moisture content

Table 2. Estimated parameters for the different models

Parameter	Eq.8	Eq.9	Eq.10
<i>a</i>	2787	0,1155	24,51
<i>b</i>	0,103	8,6425	-1,0
<i>c</i>	NA	2,4249	-0,99
<i>d</i>	NA	2677	0
<i>R</i> ²	1	1	0,97
<i>RMS</i>	0,006	0,006	0,28

4. CONCLUSION

The net and total isosteric heat of sorption by desorption of plantain pulp increased with decreasing moisture content. The net isosteric heat was found to be a polynomial and power function of equilibrium moisture content. This set of equations will be useful in the simulation of drying and storage of plantain pulp.

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