Moisture sorption equilibrium and thermodynamic properties of palm kernel

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A b s t r a c t. Equilibrium relative humidity – moisture content data for palm kernel at five different temperatures (40, 50, 60, 70, and 80°C) and moisture content values ranging from 8.6 to 19.1% (dry basis) were determined using the vapour pressure manometric method. A non-linear least squares regression programme was used to evaluate four moisture sorption models. The models were compared using the standard error of estimate, the mean relative percent deviation, the fraction-explained variation, and residual plots. Modified Henderson model was found to be the best model for predicting both the equilibrium moisture content and equilibrium relative humidity of palm kernel. The experimental data and the model that best predicted the equilibrium relative humidity were used to determine the thermodynamic characteristics of palm kernel. The heat of vapourization of moisture in the kernel decreased with increase in moisture content and approached the latent heat of pure water at a moisture content between 28 and 32% dry basis. The spreading pressure increased with increase in relative humidity and was not significantly affected by temperature. Net integral enthalpy decreased with increase in moisture content and became asymptotic in trend as the moisture content of 24% (db) was attained. Net integral entropy had positive values in the moisture range from 8.6 to 15% (db) and negative values from the moisture content of 15.3% (db) till 20% (db) was approached.

K e y w o r d s: palm kernel, equilibrium moisture content, thermodynamic properties

INTRODUCTION

Palm kernel is a source of oil that is of significant importance to the industrial development of Nigeria. It is obtained by cracking the palm nut, which is a by – product of palm oil expression from oil palm fruits. The kernel contains about 49% oil which is similar to coconut oil and is used in the manufacture of soaps, toiletries, surface active ingredients, bakery coatings, whipped creams and sugar confectionery. The efficient processing and storage of palm kernel requires that the moisture content be reduced to appropriate levels by drying. The proper modelling and optimisation of the drying process require the knowledge of equilibrium relative humidity – moisture content relationships at different temperatures, the energy requirement, as well as the state and mode of moisture sorbed within the product.

The methods used for the determination of equilibrium moisture sorption isotherms of agricultural products can be classified into those in which the material is brought into equilibrium with air of fixed temperature and relative humidity and the moisture content of the material is measured (Equilibrium Moisture Content (EMC) or gravimetric method), and those in which air is brought into equilibrium with the material at a fixed temperature and moisture content and the relative humidity of the air determined (Equilibrium Relative Humidity (ERH) method). Rao and Pfost (1978) determined the equilibrium moisture sorption isotherms of some 20 agricultural products and concluded that the Equilibrium Relative Humidity methods are simpler and faster. The most commonly used ERH methods are the dew point method and the vapour pressure manometric (VPM) methods. The dew point method has been used to obtain the equilibrium moisture sorption isotherms of rapeseed (Sokhansanj *et al.*, 1986) and wheat flour (Henderson and Pixton, 1982). The VPM method has been used to obtain the equilibrium moisture isotherms of apples (Singh and Lund, 1984), dry milk (Sood and Heldman, 1974), and sesame seed (Ajibola and Dairo, 1998). Labuza *et al.* (1976) observed that the VPM method is one of the best methods of determining the sorption isotherms of food and agricultural materials as it measures directly the vapour pressure exerted by the

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moisture in the kernels of previously evacuated jar. Devices and procedures that are based on this method have been described by Labuza (1976).

Several theoretical, semi-theoretical and empirical models have been proposed and used by investigators for fitting the equilibrium moisture content data. Chirife and Iglesias (1978) reviewed some of these models and discussed 23 commonly used equations for fitting the sorption isotherms of food, while van den Berg and Bruin (1981) presented a more comprehensive list. Most of these models have been tested and their constants evaluated for the sorption data of many agricultural and food products. The sorption data of palm kernel, however, appear to be unavailable.

Thermodynamics has been reported as one of the three approaches used to understand the properties of water in food and to calculate the energy requirements of heat and mass transfer in biological systems (Rizvi and Benado, 1984). Others are the structural approach, which describes the mechanism of hydrogen bonding and the molecular positioning obtained using spectroscopic techniques, and the dynamic approach, which involves the analysis of the motion of water molecules and their contribution to the hydrodynamic properties of the system. The applications of structural and dynamic approaches are limited in biological systems application due to limited information on the theory of the behaviour of water associated with solid biological materials (Rizvi and Benado, 1984). The properties determine the end point to which food must be dehydrated in order to achieve a stable product with optimal moisture content, and yield a figure for the theoretical minimum amount of energy required to remove a given quantity of water from food. They also provide an insight into the microstructure associated with food and a basis for the theoretical interpretation of physical phenomena occurring at the food-water interface (Rizvi, 1986).

Thermodynamic functions are readily calculated from moisture sorption isotherms and this enables the thermodynamic approach to allow the interpretation of experimental results in accordance with the statement of the theory (Iglesias *et al.*, 1976). These functions include free energy, heat of vapourization (differential heat of sorption), integral enthalpy and integral entropy. Fish (1958) studied the thermodynamics of water in potato starch gel and noted that starch at very high moisture content is thermodynamically similar to pure water. Iglesias *et al.* (1976) studied the thermodynamics of water vapour sorption by sugar beet root and advanced hypotheses which were mainly concerned with configurational modification of the adsorbents during the course of sorption, to explain the values and trends observed. Viollaz and Rovedo (1999) determined the equilibrium moisture sorption isotherms of starch and gluten and proposed a new method of calculating the isosteric heat (differential heat of sorption) at different temperatures. Fasina and Sokhansanj (1993), Fasina *et al.*

(1997), Fasina *et al.* (1999), Aviara *et al.* (2002) and Aviara and Ajibola (2002), respectively, calculated the thermo-dynamic functions of moisture sorption in alfalfa pellets, winged bean seed and gari, sesame seed, and melon seed and cassava, from their moisture sorption isotherms.

The main aim of this study was to establish the experimental equilibrium relative humidity – equilibrium moisture content data for palm kernel at different temperatures. Other objectives include the evaluation of the ability of four of the commonly used EMC-ERH models to fit the data obtained, and the determination of the thermodynamic functions of the product using the moisture sorption isotherms.

MATERIALS AND METHODS

The palm kernel used in this study was purchased from the local market at Ile-Ife, Nigeria. The bulk quantity of kernels was cleaned and milled in a hammer mill. The moisture content of the milled kernels was determined by oven – drying at 130°C for 6 h, as recommended by Young *et al.* (1982) for oilseeds with high oil contents. Samples of the product were conditioned to different moisture levels by the addition of calculated amounts of water. They were stored in clearly labelled cellophane bags and kept in a refrigerator for about 7 days. Before use, the samples were brought out of the refrigerator and stored for at least 2 h in the laboratory to enable them to acquire the room temperature. A fraction of the samples was set aside for moisture content determination. The EMC-ERH data was obtained using the vapour pressure manometric (VPM) method.

Figure 1 shows the VPM apparatus consisting of a Dymak MK1 vacuum pump (Charles Auston Pumps Ltd.) (A), a Budenburg vacuum/pressure gauge (Broadhealth, Manchester) (B), a Gallenkamp WF-455 compenstat water bath (C), a Gilmont G-1500-A micromanometer (Cole-Palmer Instrument Company) (D), two 25/40 top quickfit flasks (E, F), two mercury thermometers (G, H), rubber tubings and 2- and 3-way stopcocks. The water bath has a temperature range of between 20 to 100°C in 5°C divisions, while the micromanometer has a range of 0 to 5 mm in 0.05 mm divisions with sensitivity of 0.0125 mm. The manometer oil with specific gravity determined as 0.82 was obtained from Cole-Palmer, while $CaCl_2$ was used as the desiccant as suggested by Nunes *et al.* (1985).

The procedure suggested by Lewicki *et al.* (1978) was used for the determination of equilibrium relative humidity of palm kernel. Thirty grams of palm kernel meal were put into the sample flask with an equal amount of desiccant placed in the desiccant flask. The two flasks were sealed into the system apparatus. They were put into the water bath and the sample flask was allowed to equilibrate with the water temperature. The whole system was then evacuated excluding the sample flask. After the evacuation, the stopcock above the desiccant flask (V3) was closed and the stopcock
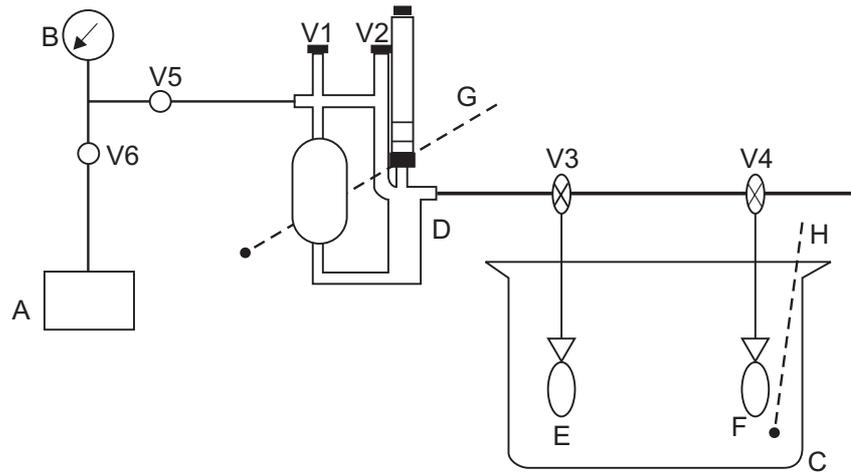
Fig. 1. Schematic diagram of the VPM apparatus: A – vacuum pump, B – vacuum gauge, C – water bath, D – micromanometer, E – desiccant flask, F – sample, G,H – thermometers, V1 to V6 – stop cocks.

over the sample flask (V4) was opened to connect the sample with the evacuated air space. The system was again evacuated for between 60 and 90 s. After the evacuation, the stopcock across the manometer (V5) was closed causing the level of the oil in the micromanometer to respond to the vapour pressure exerted by the sample. When the oil level reached a steady value, the difference was recorded as H_1. After equilibration, the stopcock over the sample was closed and the desiccant stopcock was opened such that the system was connected with the desiccant flask. The desiccant then absorbed the moisture in the air space, and this caused a change in the height of the manometric oil. After the oil has reached a constant height, the reading of the micromanometer was recorded as H_2.

The sample was thereafter removed from the system and the moisture content was determined using the standard oven method of drying at 130°C for 6 h. The apparatus excluding the sample flask was then evacuated for the next equilibrium relative humidity determination. The above procedure was followed at five temperature levels of the water bath (40, 50, 60, 70, and 80°C) and different moisture levels of the palm kernel meal between 8 and 20% (dry basis). Two replications were performed at each test condition. The equilibrium relative humidity was calculated from Eq. (1) given by Lewicki *et al.* (1978):

$$\frac{RH}{100} \approx \frac{(H_1 - H_2)\left(\dfrac{273 + T_S}{273 + T_0}\right)}{P_S}, \tag{1}$$

where: RH is the equilibrium relative humidity (%), H_1 is the micromanometer reading with the sample flask connected to the system (mm of manometric oil), H_2 is the micromanometer reading with the desiccant flask connected to the system (mm of manometric oil), T_s is the temperature of the water bath taken as the temperature of the sample (°C), T_0 is the temperature of the environment surrounding the

micromanometer (°C) and P_S is the saturated water vapour pressure at the sample temperature (mm of manometric oil).

Analysis of data

Moisture sorption isotherms

The experimental EMC-ERH data were fitted to four commonly used moisture sorption isotherm models, namely the Modified Henderson (Thompson, 1972), Modified Chung-Pfost (Pfost *et al.*, 1976), Modified Halsey (Iglesias and Chirife, 1976a) and Modified Oswin (Chen, 1988) models. All of them are three parameter models that can be solved explicitly for the equilibrium relative humidity as a function of temperature and moisture content, or for the equilibrium moisture content as a function of temperature and relative humidity.

The Modified Henderson ERH and EMC models are:

$$RH \approx 1 - \exp\left[-A(T + B)M^C\right], \tag{2}$$

$$M \approx \left[\frac{-\ln(1 - RH)}{A(T + B)}\right]^{1/C}. \tag{3}$$

The Modified Chung-Pfost ERH and EMC models are:

$$RH \approx \exp\left[\left(\frac{-A}{T + B}\right)\exp(-CM)\right], \tag{4}$$

$$M \approx \left(\frac{-1}{C}\right)\ln\left[\left(\frac{-(T + B)}{A}\right)\ln(RH)\right], \tag{5}$$

The Modified Halsey ERH and EMC models are:

$$RH \approx \exp\left[-\exp(A + BT)M^{-C}\right], \tag{6}$$

$$M \approx \left[\frac{-\ln(RH)}{\exp(A + BT)}\right]^{1/C}. \tag{7}$$

The Modified Oswin ERH and EMC models are:

$$RH \approx \frac{1}{\left[\dfrac{(A+BT)}{M} \right]^{C} + 1}, \qquad (8)$$

$$M \approx (A+BT) \left[\frac{RH}{1-RH} \right]^{1/C}, \qquad (9)$$

where: M – equilibrium moisture content (% dry basis); RH – equilibrium relative humidity (decimal); T – temperature (°C); A, B, C – constants of the models.

The NLIN procedure (SAS, 1986), a non-linear regression analysis procedure that minimizes the sum of squares of deviations in a series of iterative steps, was used to fit the four moisture sorption isotherm models to the moisture sorption data. The procedure requires that the initial parameter estimates be chosen close to the true values. These estimates were obtained by linearization of the models through logarithmic transformation and application of linear regression analysis using the REG procedure (SAS, 1986). Model parameters were estimated for the models first by taking the equilibrium relative humidity (ERH) to be the dependent variable and secondly by taking the equilibrium moisture content (EMC) as the dependent variable. The goodness of fit of each of the models was evaluated using an estimate of the residual mean square (standard error) calculated by the procedure, mean relative percent error, fraction explained variation and residual plots.

Several authors have used these parameters to evaluate the fitting ability of EMC-ERH equations. Ajibola (1986a, 1989) and Ajibola *et al*. (2003) used the standard error of estimate to evaluate different models. Boquet *et al*. (1979) used the mean relative percent deviation to compare the fitting ability of different models, Pappas and Rao (1987) used the fraction-explained variation to compare the fitting ability of several models, while Chen and Morey (1989) and Mazza and Jayas (1991) used the standard error of estimate, mean relative percent deviation and residual plots to evaluate the fitting ability of models.

The mean relative percent deviation (P) is defined as:

$$P \approx \frac{100}{N} \sum \left(\frac{Y - Y'}{Y} \right). \qquad (10)$$

The standard error of estimate (*SEE*) is defined as:

$$SEE \approx \sqrt{\frac{\sum (Y - Y')^2}{df}}. \qquad (11)$$

The fraction – explained variation (*FEV*) is defined as:

$$FEV \approx \frac{SSM}{TSS}, \qquad (12)$$

where: Y – the measured value, Y' – the value predicted by the model, N – the number of data points, df – degrees of freedom on regression model, SSM – sum of square due to model, TSS – total sum of squares.

The residual plots were plots of residuals (the differences between measured and predicted values of ERH or EMC) against the predicted values. A model was considered acceptable if the residuals were uniformly scattered around the horizontal value of zero showing no systematic tendencies towards a clear pattern. A model is considered better than another if it has a lower standard error, lower mean relative percent deviation and higher fraction explained variation.

Heat of vapourization

The heat of vapourization of moisture (L) in palm kernel was estimated by applying the Clausius-Clapeyron equation to the sorption isotherms. This, after some mathematical manipulations (Aviara and Ajibola, 2000) yielded the expression:

$$\ln (P_0) \approx \frac{L}{h_{fg}} (P_S) + C_1, \qquad (13)$$

where: P_0 – actual water vapour pressure in the material (Pa), P_S – saturated water vapour pressure (Pa), L – heat of vapourization of moisture in the product (J kg^{-1}), h_{fg} – latent heat of vapourization of free water (J kg^{-1}), and C_1 – constant.

The saturation vapour pressure at different temperatures was obtained from Rogers and Mayhew (1981) and the vapour pressure of moisture in the material was obtained from the equation:

$$P_0 \approx P_S (ERH). \qquad (14)$$

The values of ERH were obtained from the moisture sorption isotherm model, which gave the best fit for the palm kernel ERH. A plot of $\ln (P_0)$ versus $\ln (P_S)$ yielded the ratio of the heat of vapourization of moisture in the material to the latent heat of saturated vapour from the slope of the straight line obtained.

The non-linear regression procedure in SPSS 9.0 for Windows was used to fit the Gallaher (1951) model to the data obtained and to relate the latent heat ratio to the material moisture content. The Gallaher model is stated as follows:

$$\frac{L}{h_{fg}} \approx 1 + a \exp (-bM), \qquad (15)$$

where: a and b are constants and M – moisture content in decimal, dry basis.

The values of coefficients a and b were determined and the values of L/h_{fg} computed and plotted against moisture content.

Net integral enthalpy and entropy

The integral enthalpy of sorption and desorption of water in food products provides an indication of the binding strength of water molecules to the solid and has some bearing on the energy balance of drying and freezing operations (Gal, 1975). The equation for calculating net integral enthalpy was derived from the first law of thermodynamics following the procedure reported by Rizvi (1986), as:

$$\left.\frac{d(\ln[R])}{d\left(\frac{1}{T}\right)}\right|\phi \approx \frac{-Q_{in}}{R}, \qquad (16)$$

where: Q_{in} – net integral enthalpy (J kg^{-1}), R – gas constant of water vapour (0.462 kJ kg^{-1}), ϕ – spreading pressure (J m^{-2}).

The spreading pressure, also known as surface potential and which is the surface excess free energy, was estimated using an analytical procedure similar to the ones described by Iglesias *et al*. (1976) and Fasina *et al*. (1999), from the relationship:

$$\phi \approx \frac{KT}{A_m}\int_0^{a_w}\frac{\theta}{RH}d(RH), \qquad (17)$$

where the moisture ratio:

$$\theta \approx \frac{M}{M_m}, \qquad (18)$$

K – Boltzmann constant (1.380 x 10^{-23} J kg^{-1}), A_m – area of water molecule (1.06 x 10^{-19} m^2 (Mazza, 1980)), M_m – monolayer moisture content (% dry basis).

The monolayer moisture content was obtained by applying the BET equation (Brunauer *et al*., 1938) to the experimental data on equilibrium moisture relationships of palm kernel. The BET equation is stated as:

$$\frac{RH}{M(1-RH)} \approx \frac{1}{M_m C_2} + \frac{(C_2-1)(RH)}{M_m C_2}, \qquad (19)$$

where C_2 is a constant.

A plot of $RH/(1 – RH)M$ vs. RH yielded a straight line with slope and intercept on the Y-axis from which M_m was calculated.

The spreading pressure calculated using Eq. (17) was found to be indeterminate at the $RH = 0$, therefore, the lower limit employed was $RH = 0.05$. The computed values of spreading pressure were adjusted by adding the values corresponding to the interval $RH = 0$ to $RH = 0.05$, which was calculated by assuming that a linear relationship (Henry's law) exists between RH and θ within this relative humidity range. For the interval of $RH = 0$ to $RH = 0.05$, Eq. (17) becomes:

$$\phi \approx \frac{KT\theta}{A_m}. \qquad (20)$$

A plot of $\ln(RH)$ versus $1/T$ at constant spreading pressure yielded the net integral enthalpy from the slope of the straight line obtained. The values of net integral enthalpy were then plotted against moisture content.

Integral entropy describes the degree of disorder, randomness of motion and other statistical approach related to water sorption by food products (Mazza and Le Maguer, 1978). It was determined using the integral enthalpy in the following equation:

$$S_{in} \approx \frac{-Q_{in}}{T} - R \ln(RH)_{gm}, \qquad (21)$$

where: S_{in} – net integral entropy (J kg^{-1}K^{-1}), and $(RH)_{gm}$ – the geometric mean relative humidity obtained at constant spreading pressure. The values of the net integral entropy obtained were then plotted against the moisture content.

RESULTS AND DISCUSSION

The moisture content of palm kernel measured after each equilibrium relative humidity determination was observed to be lower than the moisture content before the determination. The difference is believed to be due to loss of moisture that accompanied the evacuation process during equilibrium relative humidity determination. A similar observation was made by Labuza (1976) and Lewicki *et al*. (1978). The moisture content after evacuation was always considered to be in equilibrium with the measured relative humidity. The experimental values of equilibrium relative humidity for palm kernel at different conditions considered were taken each as the average of two readings and are presented in Table 1. These were used to estimate the parameters in both the ERH and EMC models.

Table 2 shows the parameter estimates for the ERH models in which the ERH is taken as the dependent variable. Table 3 shows the parameter estimates for the EMC models in which the EMC is taken as the dependent variable. The different analyses provide flexibility in that the user can select the model and associated parameter values that best suit the particular application. The tables also show the parameters used in comparing the models, namely the standard error of estimate, the mean relative percent error, the fraction-explained variation and the nature of the residual plots. An examination of the tables indicates that the parameter estimates obtained with the ERH models were not the same as the corresponding parameter estimates obtained with the EMC models. These differences have also been noted for other crops by Duggal *et al*. (1982), Ajibola (1986a, 1986b, 1986c, 1989), Ajibola and Adams (1986), Ajibola and Dairo (1998), and Ajibola *et al*. (2003). The

T a b l e 1. Observed ERH/EMC data for palm kernel

Temperature (°C)	ERH (% db)	EMC (% db)	Temperature (°C)	ERH (% db)	EMC (% db)
40	13.1	11.7	60	33.1	13.8
40	20.3	13.2	60	51.2	18.1
40	31.5	15.8	70	9.4	8.9
40	47.4	18.5	70	10.7	9.1
50	10.8	10.1	70	18.7	10.2
50	15.5	11.7	70	27.2	12.4
50	27.2	14.8	70	42.4	14.5
50	41.7	17.2	80	8.7	8.6
50	53.4	19.1	80	10.4	8.9
60	10.3	9.6	80	15.6	9.1
60	12.6	9.8	80	24.9	10.3
60	19.1	11.3	80	32.3	12.1

T a b l e 2. Estimated parameters and comparison criteria for equilibrium relative humidity models of data for palm kernel

Parameter*	Modified Henderson	Modified Chung-Pfost	Modified Halsey	Modified Oswin
A	1.82E – 6	1.23E3	6.30	22.32
B	35.1	78.7	– 9.72E – 3	– 9.2E – 2
C	2.92	0.15	– 2.15	0.26
SEE	4.63	5.07	6.22	4.9
FEV	0.984	0.981	0.971	0.982
P	14.8	14.8	14.6	11.48
Residual plot	Random	Random	Random	Random

*A, B, C – regression constants, *SEE* – standard errors of estimation, *FEV* – fraction explained variation, *P* – mean relative percent deviation.

T a b l e 3. Estimated parameters and comparison criteria for equilibrium moisture content models of data for palm kernel

Parameter	Modified Henderson	Modified Chung-Pfost	Modified Halsey	Modified Oswin
A	8.2E – 7	1.9E3	9.9	20.02
B	65.5	86.9	– 1.42E – 2	– 6.76E – 2
C	3.12	0.18	– 3.46	0.21
SEE	1.06	1.27	1.78	1.30
FEV	0.995	0.993	0.985	0.992
P	6.3	6.6	10.6	6.8
Residual plot	Random	Random	Patterned	Patterned

Explanations as in Table 2.

EMC models were obtained by logarithmic transformations of the ERH models and in the non-linear regression analysis, the errors were assumed to be normally and independently distributed. This caused some distortions in the models, thereby causing the corresponding model constants to take on different least square values.

Using the residual plot criterion, all the models were found acceptable in predicting equilibrium relative humidity, but only the Modified Henderson and Modified Chung-Pfost models were found acceptable in predicting equilibrium moisture content. The Modified Henderson model was found to be the best equation for predicting the equilibrium relative humidity as it gave the lowest standard error of estimate of ERH, an acceptable mean relative percent deviation. and the highest fraction explained variation. The Modified Henderson model, therefore, became the equation with which the ERH values were determined for use in thermodynamic analysis. In terms of ERH, the Modified Henderson model for palm kernel can be stated as:

$$RH \approx 1 - \exp[-1.82\,10^{-6}\,(T+35.1)M^{2.92}].\quad(22)$$

From Table 3, of the two models found acceptable, the lower standard error of estimate of EMC, the lower mean relative percent deviation and the higher fraction explained variation were obtained by using the Modified Henderson model. It was noted that though the model is the best one to predict temperature dependency in the moisture sorption isotherms of palm kernel, it is only applicable in the low relative humidity range.

The plots of $\ln(P_o)$ versus $\ln(P_s)$ for palm kernel at various moisture levels are presented in Fig. 2. The ratio of the heat of vapourization of water in palm kernel to the latent heat of vapourization of saturated water was obtained from the slope of the straight line at each moisture content. The values of the coefficients 'a' and 'b' obtained in Eq. (15) were 0.5335 and 9.64 with standard errors of 0.019 and 0.386, respectively. The standard error of estimate for L/h_{fg} was 0.008.

For the ratio of the heat of vapourization of moisture in palm kernel to the latent heat of free water, Eq. (15) can be expressed as:

$$\frac{L}{h_{fg}} \approx 1 + 0.5335\exp(-9.64M).\quad(23)$$

The effect of moisture content on L/h_{fg} is shown in Fig. 3. From this figure, it can be seen that L decreased with increase in moisture content. This confirms the fact that at higher moisture levels, the strength of water binding decreases. However, L approached h_{fg} at the moisture content between 28 and 32% dry basis. Iglesias and Chirife (1976b) explained that the moisture level at which the heat of sorption approaches the heat of vapourization of water can be an indication of the point at which water exists in free form in the food product and Aviara *et al.* (2002) denoted this point as the free water point. However, it may be noted that the presence of dissolved soluble components can cause the actual point to be masked.
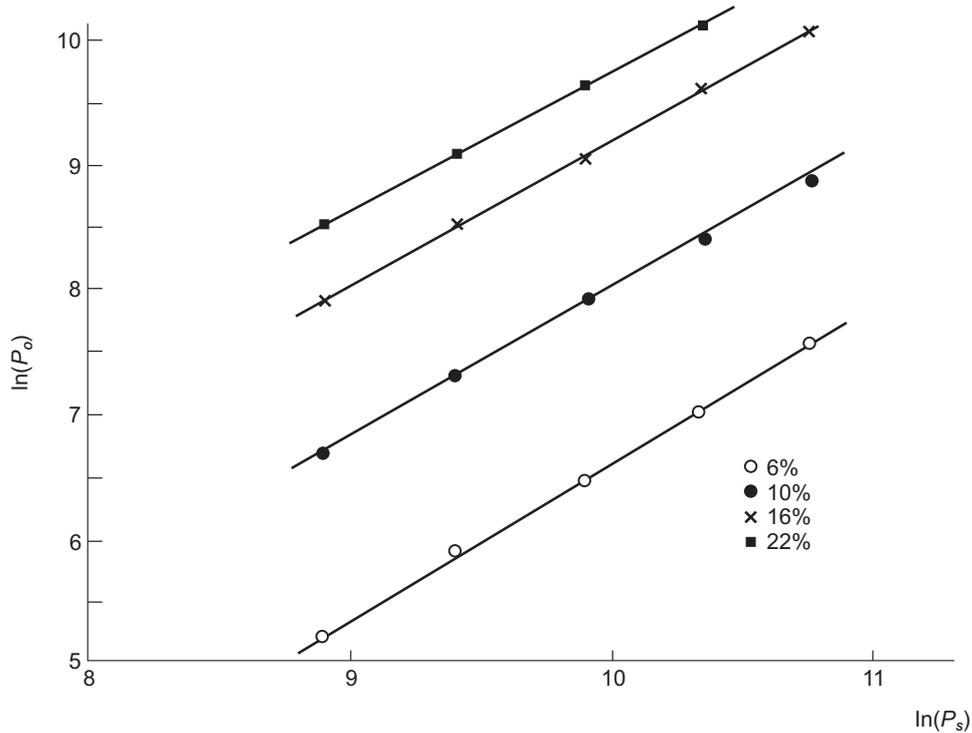

Fig. 2. Relationships between $\ln(P_o)$ and $\ln(P_s)$ for palm kernel at 6, 10, 16, and 22% moisture contents.

Equations in the form of Eq. (15) have been used by many researchers to relate the heat of vapourization of moisture in agricultural products to their moisture content (Cenkowski *et al.*, 1992; Fasina and Sokhansanj, 1993; Yang and Cenkowski, 1993; Fasina *et al.*, 1999; Aviara and Ajibola, 2002; Aviara *et al.*, 2002; Ajibola *et al.*, 2003).

The values of monolayer moisture content of palm kernel obtained from Eq. (19) at the temperatures of 40, 50, 60, 70 and 80°C were 10.3, 10.2, 10.1 and 10% dry basis, respectively. These show that the mono-layer moisture content decreased only slightly with increase in temperature. There was also little effect of temperature on
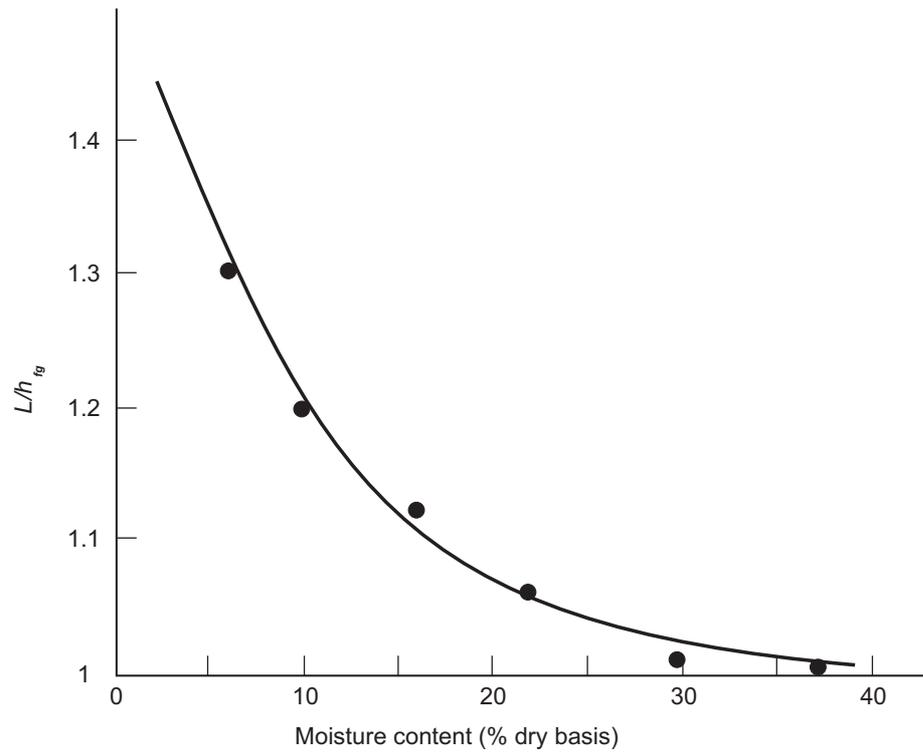
Fig. 3. Effect of moisture content on the heat of vapourization of moisture in palm kernel.
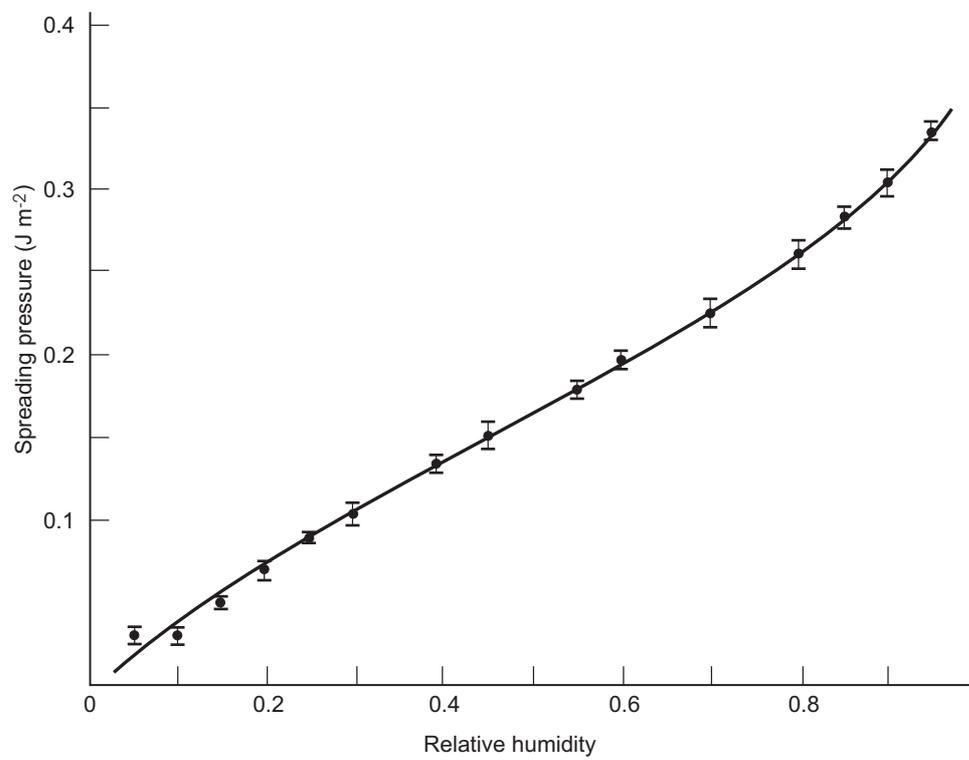
Fig. 4. Average spreading pressure isotherm of palm kernel in the temperature range 40 to 80°C.

the values of the spreading pressure obtained using Eqs (17) and (20). Consequently, the spreading pressure values between the temperatures of 40 and 80°C were averaged at any given relative humidity and the values obtained were used in further analysis. Figure 4 shows the spreading pressure isotherm of palm kernel obtained using the average pressures.

The variation of net integral enthalpy with moisture content is shown in Fig. 5. Net integral enthalpy of palm kernel was observed to decrease with increase in moisture content. The trend became asymptotic as the moisture content of about 25% (dry basis) was attained.

The variation of net integral entropy with moisture content is shown in Fig. 6. Net integral entropy was positive
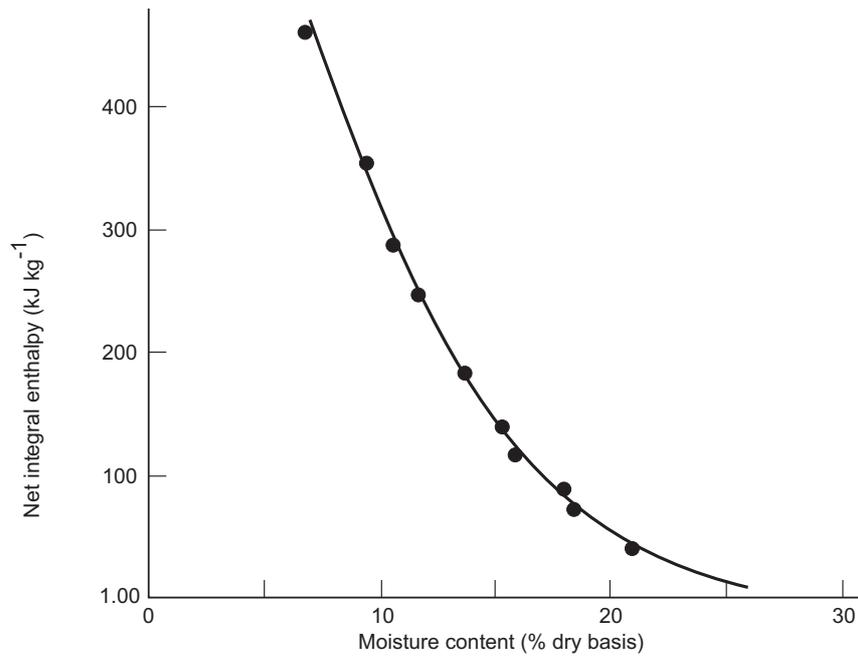

Fig. 5. Net integral enthalpy of palm kernel as a function of moisture content.
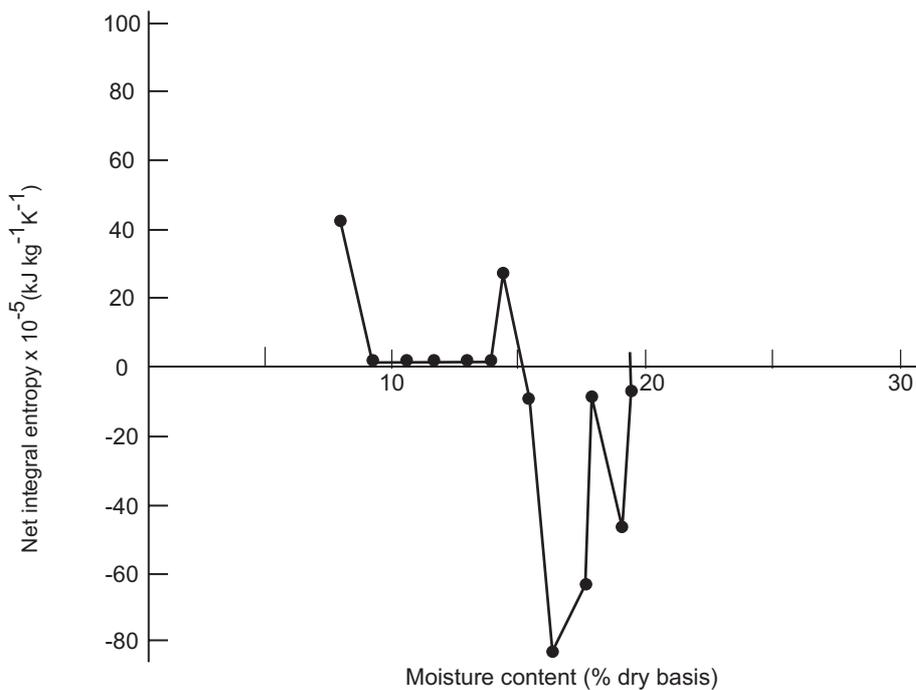

Fig. 6. Net integral entropy of palm kernel as a function of moisture content.

in value and decreased with increase in moisture content till the moisture level of about 9.5% (dry basis) was reached. It remained constant within the moisture range from 9.5 to 14% (dry basis), and became negative in value from the moisture content of 15.3% (dry basis) till 20% (dry basis) was approached. The decrease of entropy in the low water activity range has been thought to be due to lateral interaction in the adsorbed film caused by restrictive effect (loss of rotational freedom) of the adsorbed water molecules as available sites become saturated, and structural alteration of the adsorbing food towards increased crystallinity (Kapsalis, 1987). The increase in entropy after a point indicates that newly bound water molecules were held less strongly and that they possess more degree of freedom as a result of gradual opening and swelling of the polymeric constituents. Rizvi and Benado (1984) explained the phenomenon by postulating that in foods, there tend to be two entropic contributions upon moisture sorption, namely, loss of entropy from localization of water and increase in entropy due to incipient solution formation, that is structural transformations in food arising from solubilization and swelling. The trend of entropy could be used for the qualitative explanation of irreversibility in a drying process. Entropy creation could be an indication of irreversible consumption of energy, while lowering of entropy could be due to the entrapment of water in microcapillaries and matrix collapse.

CONCLUSIONS

1. The equilibrium moisture content of palm kernel determined using the vapour pressure manometric method increased with increase in equilibrium relative humidity and decreased with increase in temperature.

2. All the models tested, namely Modified Henderson, Modified Chung-Pfost, Modified Halsey and Modified Oswin models were found acceptable for predicting the equilibrium relative humidity (ERH) of palm kernel. However, the Modified Henderson model, which gave the lowest standard error of estimate, an acceptable mean relative percent deviation and the highest fraction explained variation, was considered to be the best model for predicting the ERH of palm kernel.

3. The Modified Henderson and Modified Chung-Pfost were found acceptable for the prediction of the equilibrium moisture content (EMC). However, the Modified Henderson, which gave the lower standard error of estimate, lower mean relative percent deviation and higher fraction explained variation, was considered the best model for predicting the EMC of palm kernel, though the temperature dependence of the isotherms of the product can only be predicted more accurately at the low relative humidity range.

4. The heat of vapourization of moisture in palm kernel decreased with increase in moisture content and approached the latent heat of vapourization of pure water at a moisture content between 28 and 32% (dry basis).

5. The mono-layer moisture content of palm kernel and the spreading pressure of moisture in the product were not significantly affected by temperature.

6. The net integral enthalpy decreased with increase in moisture content and the trend became asymptotic as the moisture content of 25% (dry basis) was attained, while the net integral entropy was positive in value in the moisture range of 8.6 to 15% (dry basis) and negative in value from 15.3% till the moisture content of 20% (dry basis) was approached.

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