Isosteric Heats of Water Vapor Sorption in Two Castor Varieties

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Abstract

Equilibrium moisture content-water activity data for two varieties of castor (GSS and WBS) at temperatures 30, 40, 50, 60 and 70°C and water activity range of 0.07-0.98 were determined using the static gravimetric method. A non-linear regression programme was used to fit four sorption isotherm models (modified Halsey, modified Henderson, modified Oswin and modified Guggenheim-Anderson-de Boer (GAB)) to the experimental data. These models were then compared using standard error of estimate and randomness of residuals. The sorption isosteric heats were determined by the application of Clausius-Clapeyron equation. The modified Oswin and modified Halsey proved the best for predicting equilibrium moisture content of castor with standard error of estimate of 0.238 and 0.242 for GSS and WBS respectively. The isosteric heats decreased exponentially with increase in moisture content and approached the latent heat of pure water at a free water point of between 13 and 16% moisture content (d.b). The difference in isosteric heats of both varieties was not significant.

Keywords: Castor; Isosteric heat; Water Activity; Equilibrium Moisture Content

Introduction

Castor (Ricinus communis L) is an under-exploited tropical crop. The products derivable from it range from synthetic resins and fibres, lubricants, embalming fluids, soap manufacture, opal wax in polishes, cosmetics and brake fluids [1]. The leaves have insecticidal properties, while the stalks are a source of pulp and cellulose [2]. The seeds are ovoid, compressed dorsally, tick-like shining, pale grey (hereafter referred to as Grey Small Size, GSS) predominant in the north-eastern part of Nigeria, or yellowish white and big size (hereafter known as White Big Size, WBS) common in the eastern part of Nigeria.

Drying operations are involved after harvest in the processing of this crop as reported in earlier studies [3-5]. The design of more efficient drying systems and storage systems for crops require knowledge of energy requirements, state and mode of moisture sorption within them [6]. This could be achieved by stating the correct mathematical models to estimate the heat and mass transfer mechanisms. It is also essential to determine the energy required to remove moisture from agricultural crops (isosteric sorption heat) to complete the drying simulation model [7].

Isosteric heat of sorption (KJ.mol⁻¹) defined as the heat of sorption at constant specific volume hence a measure of moisture-solid site binding strength [8]. It is the total energy required to transfer water molecules from vapor state to a solid surface and vice-versa, as well as a measure of work done by a system to accomplish adsorption or desorption process. It is therefore used as an indicator of the state of adsorbed water by solid particles [6]. Isosteric heat is useful in predicting drying models, calculating energy consumption during the drying or wetting of agricultural materials, the design of drying equipment and describing any heat and mass transfer related processes [6,9-11].

The most widely used method for evaluation of isosteric heat is the application of the Clausius-Clapeyron equation which relates water activity and temperature at constant moisture content [12,13]. The other methods of estimation of sorption isosteric heat are calorimetric technique and Riedel equation [7,14,15]. It is noted that there is a good agreement between the isosteric sorption heats obtained by the calorimetric techniques and the Clausius-Clapeyron equation [15,16]. Several authors have reported and studied the isosteric heats of agricultural products [6,7,15-21].

The purpose of the present work is to examine the application of Clausius-Clapeyron equation to sorption isotherms of two varieties of castor and to compare the calculated isosteric sorption heats using the adsorption isotherms. This is with a view to providing information useful in the drying process of the less explored castor varieties. Whole castor seeds are extremely poisonous they however become fit for human consumption when properly processed.

Materials and Methods

Sample preparation

Two castor varieties namely GSS and WBS obtained from castor farms in Borno and Anambra States, Nigeria, were used in this study. Triplicate samples, each weighing 10 g were used to determine the moisture content of whole seeds using the oven drying method as recommended in the ASABE standard. This involved drying in an oven at 103 ± 2 °C until constant weight was obtained [24]. The initial moisture contents were found to be 4.80 and 5.24 ± 0.2% (db) respectively for the two varieties. The bulk quantity of seeds was cleaned and divided into two portions. One portion was prepared for use in determining the desorption equilibrium moisture content by rewetting it to a higher moisture content. A calculated amount of water was added to this portion and the grains were then sealed in polyethylene bags and stored for 24 hours. This enabled the moisture content to be raised to stable and uniform levels of 17.00 and 18.00% (db) for GSS and WBS respectively. The polyethylene bags were marked and transferred into...
a refrigerator at 4°C and when needed for experiments, the grains were allowed to equilibrate in the ambient condition for six hours. The other portion was prepared for use for experiments on adsorption. The sample was dried at 80°C for two days to obtain a lower moisture content of about 3.23 and 3.95% (db) GSS and WBS respectively. The seeds from this portion were also sealed in marked polyethylene bags and kept in a refrigerator. They were equally allowed to equilibrate in the ambient conditions for six hours, when needed for experiments.

**Equilibrium moisture content-equilibrium relative humidity determination**

The desorption equilibrium moisture contents (EMC) of the two castor varieties were determined at temperatures of 40, 50, 60 and 70°C over a water activity (a_w) range of 0.07-0.98 using the static gravimetric method. This method involves the use of saturated salt solutions to maintain constant relative humidity (r.h.) in enclosed still moist air at a certain temperature to obtain the complete sorption isotherms. The triplicate samples of GSS and WBS weighing about 15 g were put into specimen baskets and placed inside glass desiccators. Saturated solutions of salts as used by Brooker et al. [25] and Rizvi [12] were used to maintain constant relative humidity levels in the desiccators [26,27]. Excess salt was maintained in each solution.

The samples were placed in an open flat container and arranged in each desiccator bottle so that they will not be in contact with the salt solution. The desiccators containing the salt solutions and castor seed samples were marked and placed inside temperature-controlled Gallenkamp DV 400 ovens (Weiss Gallenkamp, UK) which were set at 30, 40, 50, 60 and 70°C. The oven temperatures were monitored to within ±1.0°C to maintain constant temperature for each setting. The samples were weighed daily using an analytical balance (Mettler PC2200 DeltaRange, Mettler-Toledo Inc., USA) with an accuracy of 0.001 g. Equilibrium was considered to have been attained when three identical consecutive measurements were obtained. This took between 7 and 12 days.

The dry matter content was then determined by oven drying the sample at 103 ± 2°C until constant weight was attained [24]. The EMC was calculated on a dry basis from the weight change and dry matter content of about 3.23 and 3.95% (db) GSS and WBS respectively. The seed samples were marked and placed inside temperature-controlled Gallenkamp DV 400 ovens (Weiss Gallenkamp, UK) which were set at 30, 40, 50, 60 and 70°C. The oven temperatures were monitored to within ± 1.0°C to maintain constant temperature for each setting. The samples were weighed daily using an analytical balance (Mettler PC2200 DeltaRange, Mettler-Toledo Inc., USA) with an accuracy of 0.001 g. Equilibrium was considered to have been attained when three identical consecutive measurements were obtained. This took between 7 and 12 days.

The dry matter content was then determined by oven drying the sample at 103 ± 2°C until constant weight was attained [24]. The EMC was calculated on a dry basis from the weight change and dry matter content, and the average values at each temperature and water activity were determined. At higher water activity above 0.85, microbial growth may occur in sample and may ruin it. Two methods are often used to maintain constant relative humidity (r.h.) in enclosed still moist air at a certain temperature to obtain the complete sorption isotherms.

**Analysis of data**

The experimental EMC-a_w data of GSS and WBS castor seeds were fitted to four moisture sorption isotherm models namely the Modified Halsey [19,28], Modified Henderson [29,30], Modified Oswin model [31,32] and the GAB model [33,34] as modified by Jayas and Mazza [35]. These models are:

The Modified Halsey a_w model

\[ a_w = \exp\left(-\exp\left[(A + BT)M^C\right]\right) \]  

(1)

The Modified Henderson a_w model

\[ a_w = \exp\left(-A(T + B)M^C\right) \]  

(2)

The Modified Oswin a_w model

\[ \frac{1}{a_w} = \left[\frac{A + BT}{M}\right]^{1} + 1 \]  

(3)

The Modified GAB a_w model

\[ 2 + \frac{C}{(A + BT)} - \left[\frac{2 + C}{(A + BT)} - 1\right]^{1} \]  

(4)

Symbols are defined in Notation section.

**Model fitting**

The desorption and adsorption equilibrium moisture content data of castor seeds were fitted to moisture sorption models using the non-linear regression procedure in SPSS 16.0 for Windows, which minimizes the sum of squares of deviations between experiment and theory in a series of iterative steps. All the models are three parameter equations, which can be solved explicitly for a_w as a function of temperature and moisture content. The non-linear regression procedure required that initial parameter estimates be chosen close to the true values. The initial parameter estimates were obtained by linearization of the models through logarithmic transformation and application of linear regression analysis, or solving a quadratic form of the equation in the case of modified GAB model. The least-squares estimates or coefficients of the terms were used as the coefficients of the terms of the sorption models tested for the initial parameter estimates in the non-linear regression procedure. Model parameters were estimated by taking the water activity (a_w) to be the dependent variable.

**Heat of vaporization**

Igathinathane et al. [8] have reported the procedure for calculating isosteric sorption heat. The Clausius-Clapeyron equation as applied to vapor from free water is given by [11,12,36]:

\[ \frac{1}{R} \frac{\partial P_r}{P_r} = \frac{\partial T}{RT^2} \]  

(5)

If in Equation (5), the P_r is replaced by the actual vapor pressure (P_p) in the material and the right hand side of the equation remains the same for both vapor from free water and vapor from moisture in material [6], then the following equation can be obtained:

\[ \frac{1}{R} \frac{\partial P_r}{P_r} = \frac{1}{T} \frac{\partial T}{P_p} \]  

(6)

Integrating Equation (6) at constant moisture content yields

\[ \ln(P_r) = \frac{L}{R} \ln(P_p) + c_1 \]  

(7)

Where c_1 is a constant. The saturation vapor pressure (P_p) at different temperatures can be obtained from Rogers and Mayhew [1981] and subsequently, vapor pressure in the material determined as:

\[ P_r = a_w P_p \]  

(8)

The values of a_w were obtained from the moisture sorption isotherm models which best describes the equilibrium moisture relations of GSS and WBS castor varieties respectively.

The slope of the logarithmic plot of P_r against P_p gives the ratio of heat of vaporization of moisture in a material to the latent heat of saturated vapor. The non-linear regression procedure in SPSS 16.0 for Windows was used to fit the Gallaher (1951) model (Equation 9) to the data obtained and to relate the latent heat ratio to the material moisture...
Other researchers too have used this equation to relate the free energy or latent heat of vaporization of agricultural crops to moisture content [6,11,37]. The model can be stated thus:

\[ \frac{L}{h_{fg}} = 1 + a \exp(-bM) \]  

(9)

The values of coefficients 'a' and 'b' were obtained through the process of logarithmic transformation and non-linear regression and the values of \( L/h_{fg} \) were computed and plotted against moisture content.

Results and Discussion

Equilibrium moisture content and water activity relationships

The experimental values of equilibrium moisture content-water activity at different temperatures are as presented in table 1. It was observed that the moisture content of castor seeds measured after each emc-a\(_w\) determination was lower than the moisture content before the determination. Ajibola [27] observed same and opined that this difference could be due to loss of moisture that accompanied the evacuation process.

EMC increased with increase in a\(_w\) and were lower at higher temperatures in both castor seed varieties. Similar trends for many seeds have been reported in the literature [28,38-42]. At low water activity values, the equilibrium moisture contents for both crop varieties were higher at low temperatures. These results are in agreement with the general characteristics of food isotherms, and the theory of physical adsorption which predicts that the quantity of sorbed water at a given water activity increases as the temperature decreases [43,44].

The experimental values of EMC-a\(_w\) for castor seeds at the different temperatures considered were taken as the average of two readings for each. These were used to estimate the best a\(_w\) model. The EMC models were obtained by logarithmic transformations of the a\(_w\) models and in the non-linear regression analysis, the errors were assumed to be normally and independently distributed. The Modified Oswin and Modified Halsey were found to be the best a\(_w\) models for GSS and WBS castor respectively with Standard Error of Estimate (SEE) of 0.238 and 0.242 (Table 2) and the residual plots showed high degree of randomness (The random plot for GSS adsorption and WBS desorption are presented in Figures 1a and 1b. The modified Henderson model which has been published for many agricultural seeds did not fit well. These two models (Modified Oswin and Modified Halsey), therefore, became the models with which the a\(_w\) values as presented in Equations (1) and (3) were determined for use in the analysis of isosteric heats and are represented as:

\[ a_w = \frac{1}{\left[ \left( \frac{4.809 - 0.1187}{M} \right)^{0.435} + 1 \right]} \]  

(10)

Parameter and Criteria

<table>
<thead>
<tr>
<th>GSS</th>
<th>WBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified Oswin</td>
<td>Modified Halsey</td>
</tr>
<tr>
<td>A</td>
<td>44.809</td>
</tr>
<tr>
<td>B</td>
<td>0.118</td>
</tr>
<tr>
<td>C</td>
<td>10.457</td>
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<tr>
<td>R²</td>
<td>0.943</td>
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<tr>
<td>SEE</td>
<td>0.238</td>
</tr>
</tbody>
</table>

Residual plot

Table 1: Desorption and adsorption equilibrium moisture contents of castor seed.

Table 2: Estimated parameters for water activity models of castor seeds (adsorption).
The log plots of the vapour pressures (actual, ln(P_0) and saturated, ln(P_s)) for both castor varieties at various moisture levels are presented in figures 2 and 3 as discussed in Equation (7). The natural log of actual vapor pressure ln (P_0) increased linearly with increase in the natural log of saturated water vapor pressure ln (P_s) and moisture content in both cases. Other authors reported similar findings for winged bean seed and gari [6], unripe and ripe plantain [23], melon seed and cassava [45], cowpea and plantain. Therefore the relationship existing between ln (P_0) and ln (P_s) at the four moisture contents 4, 8, 12 and 16% d.b. respectively can be expressed by the regression equations (Equations 12-19 with their corresponding R^2 as indicated):

\[
\begin{align*}
\text{GSS:} \\
\ln(P_0) &= 4.6706 \ln(P_s) - 39.57 \quad (R^2 = 0.99) \\
\ln(P_0) &= 1.7499 \ln(P_s) - 7.50 \quad (R^2 = 0.96) \\
\ln(P_0) &= 1.0235 \ln(P_s) - 0.23 \quad (R^2 = 0.99) \\
\ln(P_0) &= 1.0010 \ln(P_s) - 0.01 \quad (R^2 = 1.00)
\end{align*}
\]

\[
\begin{align*}
\text{WBS:} \\
\ln(P_0) &= 1.0004 \ln(P_s) - 1.01 \quad (R^2 = 1.00) \\
\ln(P_0) &= 0.7749 \ln(P_s) - 1.36 \quad (R^2 = 0.97)
\end{align*}
\]

The ratios of heat of vaporization of saturated water at each of the moisture content were obtained from the slopes of the plots in figure 2 and 3. Using non-linear regression procedure (SPSS 16.0 for windows), Equation (9) was used to relate L to material moisture content. The values of the coefficients 'a' and 'b' in Equation (9) presented in Equations (20 and 21) were 19.173 and 41.298 for GSS and 70.916 and 102.994 for WBS castor seeds. The standard errors of estimate for \( L/h_g \) were 0.650 and 0.702 for GSS and WBS castor respectively. The ratios of the heat of vaporization of moisture in the castor seed varieties to the latent heat of free water in Equation (9) are then obtained as:

\[
\begin{align*}
\text{GSS:} \\
\frac{L}{h_g} &= 1 + 19.173 \exp(-41.29M) \\
\text{WBS:} \\
\frac{L}{h_g} &= 1 + 70.916 \exp(-102.94M)
\end{align*}
\]

The effect of moisture content on \( L/h_g \) is shown in figure 4. The figure shows that \( L \) decreased with increasing moisture content in both castor varieties. This confirms the fact that at higher moisture levels, the strength of water binding decreases. The heat of sorption of both GSS and WBS castor varieties approached that of pure water at moisture contents of 16% and 10% respectively.

\[
\begin{align*}
\text{GSS:} \\
\ln(P_0) &= 1.0187 \ln(P_s) - 0.19 \quad (R^2 = 0.99) \\
\ln(P_0) &= 1.0010 \ln(P_s) - 0.01 \quad (R^2 = 1.00)
\end{align*}
\]

\[
\begin{align*}
\text{WBS:} \\
\ln(P_0) &= 1.0004 \ln(P_s) - 1.01 \quad (R^2 = 1.00) \\
\ln(P_0) &= 0.7749 \ln(P_s) - 1.36 \quad (R^2 = 0.97)
\end{align*}
\]
(contents of between 13 and 16% dry basis. Fasina and Sokhansanj [46], explained that beyond this moisture range, water existing in the seeds may not be in a bound form but existing as mono or multi-layer. There was no significant difference between the isosteric sorption heat of both castor varieties. Iglesias and Chirife [19], explained that the level of moisture content at which the heat of sorption approaches the heat of vaporization of water can be a sign of water existing in free form in a food product and Aviara et al. [37], denoted this point as the free moisture contents of between 13 and 16% dry basis. Fasina and Sokhansanj [46], explained that beyond this moisture range, water existing in the seeds may not be in a bound form but existing as mono or multi-layer. There was no significant difference between the isosteric sorption heat of both castor varieties. Iglesias and Chirife [19], explained that the level of moisture content at which the heat of sorption approaches the heat of vaporization of water can be a sign of water existing in free form in a food product and Aviara et al. [37], denoted this point as the free water point, explaining further that the presence of dissolved soluble components can cause the actual point to be masked.

Conclusions

1. The equilibrium moisture content of GSS and WBS castor varieties determined using the static gravimetric method increased with increase in aw but decreased with increasing temperature.

2. The Modified Oswin and the Modified Halsey which gave the least standard error of estimate and randomness of residuals proved the best aw models for predicting adsorption aw of GSS and WBS castor seeds respectively.

3. For both varieties of castor seeds isosteric heats decreased exponentially with increase in moisture content and approached the latent heat of vaporization of pure water at a moisture content between 13 and 16% (dry basis), an energy equivalent to that for free water may be adequate to dislodge moisture from castor seeds. There was no significant difference between the isosteric heats of the castor varieties.

Nomenclature

aw: water activity (mass fraction)
A, B, C: constants of sorption models
T: absolute temperature (K)
emc: equilibrium moisture content (% dry basis)
Pa: actual water vapor pressure (Pa)
P: saturated water vapor pressure (Pa)
R: gas constant for water vapor (0.462kJ/kg K)
h: latent heat of vaporization of free water in material (J/kg water)
L: heat of vaporization of moisture in the product (J/kg water)

a, b, c: constants

M: moisture content in decimal, dry basis

References


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