Sorption and Thermal Properties of Rice, Potato Starch, and Oat Flakes

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Abstract


A precise design of the equipment for thermal sterilisation of rice, potato starch, and oat flakes by dry heat requires the knowledge of the relevant values of physical properties of these products. Water activity and enthalpy are presented as functions of temperature and humidity. Water activity was measured as a function of the moisture content and temperature in the desorption process that reproduces the real conditions existing during dry heat processing in the pilot rotating steriliser equipment. The heat of evaporation can be predicted from these data as a function of the moisture content of these products. DSC (differential scanning calorimetry) method was used for measuring the enthalpy of these products as a function of temperature during desorption of moist products starting from various levels of the moisture content. The total energy $E_c$ necessary for heating the product and evaporation of the given amount of water can be calculated.

Keywords: moisture content; humidity; water activity; enthalpy; evaporation; heat; bound water

Rice, potato starch, and oat flakes are products which can contain pathogenic microorganisms, namely moulds and Bacillus cereus, a typical microorganism occurring in cereals (Houška et al. 2007). Moulds can be the source of very dangerous metabolites, namely aflatoxins and similar substances with mutagenic and carcinogenic effects.

For the decontamination, it is possible to apply a dry heat process using rotating steriliser equipment. For the design of the heating and homogenising equipment, it is necessary to know the specific heat or enthalpy of the products as functions of the temperature and moisture content.

Thermal properties of foods can often be predicted from the composition of the foods by software such as COSTHERM (Miles & Morley 1997), however, the evaporation of water during the drying of products poses a problem due to the dynamically changing water content and the changing energy of water binding. The evaporation heat can be regarded as the evaporation of pure water only to some lower level of the water content (humidity) e.g. Kaleemullah and Kailappan (2005). These authors dealt with the red pepper drying process and the prediction of sorption isotherms of that substance, Kaleemullah and Kailappan (2004). A similar procedure was used for predicting the heat of sorption of sunflower seeds by Giner and Gely (2005), for mushrooms by Shivhare et al. (2004) and quinoa grains by Tolaba et al. (2004). Fontan et al. (1982) investigated the validity for food of the physical model (isotherm equation) originally developed by other authors for polymers. The importance

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of the multi-temperature fitting procedure in the
description of water sorption on foodstuffs was
pointed out by Furmaniak et al. (2007a, b). The
applicability of the Generalised D’Arcy and WATT
(GDW) model to the description of water vapour
sorption on pineapple and other foodstuffs was
presented by Furmaniak et al. (2007a, b).

Below a certain limit of the water content, the
heat of water evaporation from the product is
much greater than the standard latent heat of
water evaporation. It is determined by the degree
of water binding in the material that is in turn
related to the water activity.

The aim of this paper was to determine the heat
of water evaporation from the products as a func-
tion of the moisture content, and to predict the
total enthalpy as a function of the temperature
and water content. This dependence enables to
calculate the total energy necessary for the heating
of the product from the initial temperature \( T_i \)
to the final temperature \( T_f \) and during the simulta-
neous change of the moisture content from \( x_{w1} \) to
\( x_{w2} \) (Landfeld et al. 2008).

**MATERIAL AND METHODS**

**Product sample.** All samples of the products
used were bought at a supermarket: rice – peeled
(longseed) BASK, originated Italy, harvest 2006;
potato starch – Solamyl, potato originated in the
Czech Republic, harvest 2006; oat flakes – origi-
nated in the Czech Republic, harvest 2006.

**Pre-preparing of the product sample.** The
original size of the rice and oat flakes particles
was not suitable for the measurement by DSC
differential scanning calorimetry) method (small
size of the pans). Therefore, the rice and oat flakes
were milled using the mill appliance P-14 (Fritsch,
Germany) by which fine powder was prepared
(particles dimension being smaller than or equal
to 0.5 mm – given by the dimension of holes in
the sieve). There occurred a certain reduction of
the moisture content of the samples caused by
heating in the mill appliance.

**Prediction of heat of water evaporation from
the product sample.** The method for predicting
the heat of evaporation was adopted from the paper by
also specified this method as generally applicable to
the prediction of sorption isosteric heat of water in
different foods. The prediction procedure is based
on the Clausius-Clapeyron equation:

\[
\frac{dp_{vs}}{dT} = \frac{L}{(V_v + v_f) \times T}
\]

At the standard temperature and pressure, the
specific volume of the liquid can be omitted in
comparison with the specific volume of vapour.
If we assume that the vapour behaves as the ideal
gas, the following relation can be derived:

\[
\ln(p_v) = \frac{L_w}{L} \times \ln(p_{vs}) + C
\]

The water vapour pressure over the product was
calculated for each moisture content level from
the relation:

\[
p_v = \text{ERH} \times p_{vs}
\]

ERH (equilibrium relative humidity expressed
as a fraction between 0 and 1, under the equilib-
rium conditions equivalent to the water activity
frequently designated as \( a_w \)).

Ten samples of the products were prepared. The
hot air sterilisation chamber HS62A (Chirana,
Czech Republic) was used for drying the prod-
ucts. The water activity meter AWVD (Rotronic,
Switzerland) was used for the measurement of
equilibrium relative humidity of each sample at
the temperatures of 20, 30, and 40°C. The accuracy
of the appliance used was for humidity \( \pm 1.5\% \) at
23°C, for temperature \( \pm 0.2\°C \), the reproducibili-
ity for humidity was \( < 0.1\% \); the calibration was made
with the use of 35% and 80% calibration solutions.
Using the tabulated data for pure water, see e.g.
Šesták et al. (1993), the corresponding equilibrium
water vapour pressure for the given temperature
was predicted. Using Equation (3), the actual va-
pour pressure \( p_v \) over the given product sample
at the given temperature was calculated.

The dependence of \( \ln p_v = f (\ln p_{vs}) \) was plotted
and linear regression was applied by means of the
theoretical Equation (2). The ratio of \( L_v / L \) was pre-
dicted as the linear regression constant at \( \ln(p_{vs}) \)
valid for the given moisture content of the product.
This expression represents the ratio of the heat of
water evaporation from the product sample of
the given moisture content and the evaporation heat
of pure water. This ratio was plotted in a graph
and the dependence of the ratio on the moisture
content was found by the non-linear regression
software DataFit (Oakdale Engineering, USA).
The dependence \( L_v / L(x_w) \) was integrated and the
relation was calculated for total energy neces-
sary for the evaporation of water bound in the product. The input parameters are here only the temperature and initial and final moisture contents of the product. A similar equation was derived by Kaleemullah and Kailappan 2005.

**Prediction of enthalpy of product sample (without evaporation).** The initial products moisture contents were with potato starch – 15.86%, rice – 8.01%, and oat flakes – 7.2%, respectively. Samples with different moisture contents were prepared from these products. The products were placed into a hot air steriliser HS62A (Chirana, Czech Republic) and the respective samples were taken during drying. The samples were prepared with the moisture contents according to Table 1. These samples were used for the measurement of enthalpy in a differential scanning calorimeter DSC Diamond (Perkin Elmer, USA). The sample pan had a volume of 40 µl (diameter 7.5 mm, material aluminium). An empty pan was used as the reference sample.

Table 1. Equilibrium relative humidity ERH values and partial water vapour pressures as a function of temperature and moisture content (wet base) of potato starch, the rice and the oat flakes

<table>
<thead>
<tr>
<th>Powder moisture content (% wet basis)</th>
<th>Equilibrium relative humidity of water vapour above powder ERH (–)</th>
<th>Partial pressure of water vapour $P_v$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>30°C</td>
<td>40°C</td>
</tr>
<tr>
<td><strong>Potato starch</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.86</td>
<td>0.516</td>
<td>0.533</td>
</tr>
<tr>
<td>13.58</td>
<td>0.400</td>
<td>0.422</td>
</tr>
<tr>
<td>11.58</td>
<td>0.268</td>
<td>0.318</td>
</tr>
<tr>
<td>9.51</td>
<td>0.185</td>
<td>0.218</td>
</tr>
<tr>
<td>7.66</td>
<td>0.125</td>
<td>0.152</td>
</tr>
<tr>
<td>5.80</td>
<td>0.075</td>
<td>0.086</td>
</tr>
<tr>
<td>3.72</td>
<td>0.035</td>
<td>0.042</td>
</tr>
<tr>
<td>1.55</td>
<td>0.010</td>
<td>0.015</td>
</tr>
<tr>
<td>1.16</td>
<td>0.007</td>
<td>0.008</td>
</tr>
<tr>
<td>0.72</td>
<td>0.005</td>
<td>0.008</td>
</tr>
<tr>
<td><strong>Rice</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.01</td>
<td>0.238</td>
<td>0.259</td>
</tr>
<tr>
<td>6.72</td>
<td>0.137</td>
<td>0.165</td>
</tr>
<tr>
<td>5.92</td>
<td>0.096</td>
<td>0.118</td>
</tr>
<tr>
<td>5.09</td>
<td>0.065</td>
<td>0.089</td>
</tr>
<tr>
<td>3.79</td>
<td>0.047</td>
<td>0.047</td>
</tr>
<tr>
<td>2.62</td>
<td>0.025</td>
<td>0.031</td>
</tr>
<tr>
<td>1.50</td>
<td>0.012</td>
<td>0.017</td>
</tr>
<tr>
<td>1.37</td>
<td>0.009</td>
<td>0.015</td>
</tr>
<tr>
<td>1.02</td>
<td>0.006</td>
<td>0.011</td>
</tr>
<tr>
<td><strong>Oat flakes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.20</td>
<td>0.282</td>
<td>0.318</td>
</tr>
<tr>
<td>5.82</td>
<td>0.240</td>
<td>0.29</td>
</tr>
<tr>
<td>4.77</td>
<td>0.170</td>
<td>0.212</td>
</tr>
<tr>
<td>3.46</td>
<td>0.107</td>
<td>0.153</td>
</tr>
<tr>
<td>2.47</td>
<td>0.066</td>
<td>0.100</td>
</tr>
<tr>
<td>1.17</td>
<td>0.040</td>
<td>0.048</td>
</tr>
<tr>
<td>0.63</td>
<td>0.025</td>
<td>0.034</td>
</tr>
</tbody>
</table>
Indium was used as the calibration material. The scanned range of temperature was 5–130°C. The heating rate was chosen to be 10°C/min. The samples were weighed also after the scan to check that no significant loss of mass had occurred during the DSC measurements. The measured enthalpy as a function of temperature for the samples with different moisture contents was processed using the regression procedure provided by the software DataFit (Oakdale Engineering, USA), and the final dependence of enthalpy as a function of temperature and humidity was predicted. Each sample of the given moisture content was measured in five replications.

The derived function was used for the calculation of the energy necessary for changing the temperature of the powder in such situations where the water evaporation from powder is negligible. This function can be combined with the heat of evaporation for the calculation of the total energy necessary for changing the temperature and moisture content of the product at the same time (Landfeld et al. 2008).

RESULTS AND DISCUSSION

Heat of evaporation

The experimental equilibrium relative humidity values and partial pressures $p_v$ are given in Table 1 as a function of the temperature and moisture content of the samples.

The data for $p_v$ were correlated with the corresponding values of the saturated water vapour pressure $p_{vs}$ for the given water content of the sample by linear Equation (2) and the values of the ratio $L_w/L$ were determined. The values of this ratio were plotted as a function of the product moisture content of product (Figure 1).

It is apparent from these figures that the heat of evaporation increases as the moisture content of the product decreases. Non-linear regression procedure was used and the mathematical dependences of $L_w/L$ ration. The moisture content of the product was predicted (Table 2).

Using the procedure of Kaleemullah and Kallappan (2005) and calculating the total evaporation

![Figure 1. Ratio $L_w/L$ as a function of moisture content for potato starch powder (A), rice (B) and oat flakes (C)](image-url)
heat necessary for the evaporation of water from the mass \( m_w \) of the product (changing the water content from \( x_w^1 \) to \( x_w^2 \)), the relation (Table 3), is obtained. The procedure considers the change of the evaporation heat with the decrease of the water content, the respective equations are given in Table 2. Evaporation heat of pure water \( L \) has to be put in as a function of temperature.

Enthalpy

The enthalpy of the products as derived from the measurements using the differential scanning calorimeter is plotted in Figures 2–4. The individual curves represent the dependencies of enthalpy as a function of temperature for the individual moisture contents. We tested various equations representing the dependence of enthalpy on the temperature and water content. General shape of equation for enthalpy \( H = f(T, x_w) \):

\[
H = a + b \times T + c \times T^2 + d \times x_w + e \times x_w^2 + f \times T \times x_w
\]

It should be kept in mind that this equation applies to the condition of negligible evaporation of water (for closed DSC pans). The numerical values of the parameters for the enthalpy equation are given in Table 4. The enthalpy of oat flakes exhibited a weak dependence on the moisture content (parameters \( d, e, f \) are equal zero).

The total energy \( E_c \) necessary for the heating of the product and evaporation of the given amount of water is given by the relation (5)

\[
E_c = m_w \left( H_2 - H_1 \right) + L_{w(x_w^1 \rightarrow x_w^2)}
\]

where:
- \( H_1 \) – enthalpy at initial state
- \( H_2 \) – enthalpy in the final state of the product

CONCLUSIONS

The water activity expressed as equilibrium relative humidity was measured as a function of
Table 3. Total evaporation heat necessary for the evaporation of water from the mass \( m_w \) of the product

<table>
<thead>
<tr>
<th>Product</th>
<th>( L_{w(x_{w1} \to x_{w2})} = f(m_w, L, x_w) )</th>
<th>Validity ( x_w ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice</td>
<td>( -\frac{m_w \cdot L}{100} \left[ x_w - 6.1657 \cdot \exp(-0.141 \cdot x_w) \right]^{x_{w2}} - \frac{m_w \cdot L}{100} \left[ x_w - 6.4283 \cdot \exp(-0.096 \cdot x_w) \right]^{x_{w1}} )</td>
<td>1.02–8.01</td>
</tr>
<tr>
<td>Potato starch</td>
<td>( -\frac{m_w \cdot L}{100} \left[ x_w - 3.5594 \cdot \exp(-0.227 \cdot x_w) \right]^{x_{w2}} )</td>
<td>0.72–15.86</td>
</tr>
<tr>
<td>Oat flakes</td>
<td>( -\frac{m_w \cdot L}{100} \left[ x_w - 3.5594 \cdot \exp(-0.227 \cdot x_w) \right]^{x_{w1}} )</td>
<td>0.63–7.2</td>
</tr>
</tbody>
</table>

Table 4. Parameters of enthalpy Equation (4) for the products

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rice</th>
<th>Potato starch</th>
<th>Oat flakes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>-7.78551</td>
<td>-15.271</td>
<td>-6.72043</td>
</tr>
<tr>
<td>( b )</td>
<td>1.082992</td>
<td>1.180543</td>
<td>1.226331</td>
</tr>
<tr>
<td>( c )</td>
<td>0.002803</td>
<td>0.001989</td>
<td>0.001326</td>
</tr>
<tr>
<td>( d )</td>
<td>0.212203</td>
<td>2.458917</td>
<td>0</td>
</tr>
<tr>
<td>( e )</td>
<td>-0.04208</td>
<td>-0.17139</td>
<td>0</td>
</tr>
<tr>
<td>( f )</td>
<td>0.022833</td>
<td>0.037968</td>
<td>0</td>
</tr>
<tr>
<td>Validity ( x_w ) (%)</td>
<td>1.02–8.01</td>
<td>0.72–15.86</td>
<td>0.63–7.2</td>
</tr>
<tr>
<td>Validity ( T ) (°C)</td>
<td>5–130</td>
<td>5–130</td>
<td>5–130</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.999</td>
<td>0.993</td>
<td>0.971</td>
</tr>
</tbody>
</table>

Figure 3. The enthalpy of rice as a function of temperature and moisture content.
the temperature and moisture content with rice, potato starch, and oat flakes. The water activity was used for predicting the ratio of the heat of evaporation as a function of the moisture contents of these products. The lower is the moisture content of the powder, the higher is the amount of the heat necessary for water evaporation from the product. Based on the water activity, we derived an equation for the heat of evaporation (Equations in Table 3).

The enthalpy necessary for the temperature increase of the product in a closed system (negligible evaporation) was measured. Optimum regression equations were found for these data expressing the enthalpy as a function of the temperature and water content (Equation 4).

By combining both equations is it possible to calculate the total energy necessary for the simultaneous heating and drying of these products.

**List of symbols**

- $a, b, c, d, e, f$ – regression coefficients
- $a_w$ – water activity
- $C$ – integration constant
- $E_c$ – total energy
- $ERH$ – equilibrium relative humidity (decimal, number between 0 and 1)
- $H$ – enthalpy
- $L$ – evaporation heat of water
- $L_w$ – heat of water evaporation from the product
- $L_w(x_{w1} \rightarrow x_{w2})$ – energy necessary for moisture content change from $x_{w1}$ to $x_{w2}$
- $m_w$ – mass of the product
- $p_v$ – partial water vapour pressure over the product
- $p_{vs}$ – partial saturated water vapour pressure
- $R$ – correlation coefficient
- $T$ – temperature
- $v_l$ – specific volume of liquid
- $v_v$ – specific volume of vapour
- $x_w$ – moisture (water) content of solids (wt basis)

**References**


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