

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

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Abstract

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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 micro-organism 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 function 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_1 to the final temperature T_2 and during the simultaneous 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 – originated 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 KALEEMULLAH and KAILAPPAN (2005). CHEN (2006) 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:

$$\frac{dp_{vs}}{dT} = \frac{L}{(V_v + v_l) \times T} \quad (1)$$

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:

$$\ln(p_v) = \frac{L_w}{L} \times \ln(p_{vs}) + C \quad (2)$$

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

$$p_v = \text{ERH} \times p_{vs} \quad (3)$$

ERH (equilibrium relative humidity expressed as a fraction between 0 and 1, under the equilibrium 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 products. 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 $\pm 0.2^\circ\text{C}$, the reproducibility 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 vapour 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_w/L was predicted 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 $L_w/L(x_w)$ 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

Powder moisture content (% wet basis)	Equilibrium relative humidity of water vapour above powder ERH (-)			Partial pressure of water vapour p_v (kPa)		
	20°C	30°C	40°C	20°C	30°C	40°C
Potato starch						
15.86	0.516	0.533	0.586	1.206	2.260	4.322
13.58	0.400	0.422	0.476	0.935	1.790	3.510
11.58	0.268	0.318	0.355	0.626	1.349	2.618
9.51	0.185	0.218	0.245	0.432	0.925	1.807
7.66	0.125	0.152	0.176	0.292	0.645	1.298
5.80	0.075	0.086	0.113	0.175	0.365	0.833
3.72	0.035	0.042	0.058	0.082	0.178	0.428
1.55	0.010	0.015	0.018	0.023	0.064	0.133
1.16	0.007	0.008	0.013	0.016	0.034	0.096
0.72	0.005	0.008	0.010	0.012	0.034	0.074
Rice						
8.01	0.238	0.259	0.295	0.556	1.098	2.176
6.72	0.137	0.165	0.201	0.320	0.700	1.482
5.92	0.096	0.118	0.160	0.224	0.500	1.180
5.09	0.065	0.089	0.114	0.152	0.377	0.841
3.79	0.047	0.047	0.084	0.110	0.199	0.619
2.62	0.025	0.031	0.051	0.058	0.131	0.376
1.50	0.012	0.017	0.025	0.028	0.072	0.184
1.37	0.009	0.015	0.020	0.021	0.064	0.147
1.02	0.006	0.011	0.015	0.014	0.047	0.111
Oat flakes						
7.20	0.282	0.318	0.344	0.659	1.349	2.537
5.82	0.240	0.29	0.298	0.561	1.230	2.198
4.77	0.170	0.212	0.225	0.397	0.899	1.659
3.46	0.107	0.153	0.167	0.250	0.649	1.232
2.47	0.066	0.100	0.128	0.154	0.424	0.944
1.17	0.040	0.048	0.079	0.093	0.204	0.583
0.63	0.025	0.034	0.057	0.058	0.144	0.420

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 KAILAPPAN (2005) and calculating the total evaporation

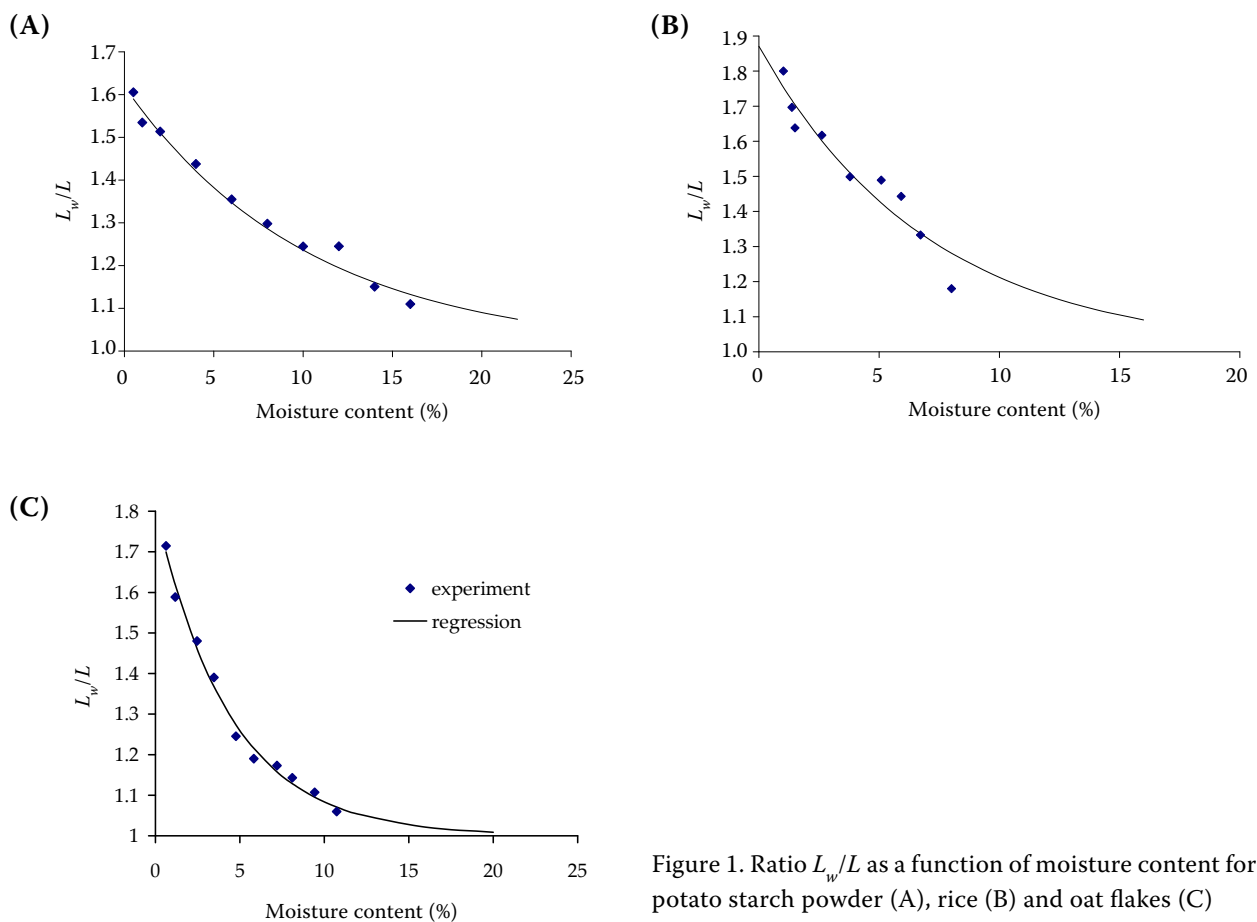


Figure 1. Ratio L_w/L as a function of moisture content for potato starch powder (A), rice (B) and oat flakes (C)

Table 2. Dependence of L_w/L ratio on the water content of the products

Product	$L_w/L = f(x_w)$	R^2
Rice	$L_w/L = 1 + 0.871 e^{(-0.141 \times x_w)}$	0.910
Potato starch	$L_w/L = 1 + 0.619 e^{(-0.096 \times x_w)}$	0.983
Oat flakes	$L_w/L = 1 + 0.807 e^{(-0.227 \times x_w)}$	0.996

heat necessary for the evaporation of water from the mass m_w of the product (changing the water content from x_{w1} to x_{w2}), 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 $H = f(T, x_w)$:

$$H = a + b \times T + c \times T^2 + d \times x_w + e \times x_w^2 + f \times T \times x_w \quad (4)$$

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)

$$E_c = m_w (H_2 - H_1) + L_{w(x_{w1} \text{ to } x_{w2})} \quad (5)$$

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

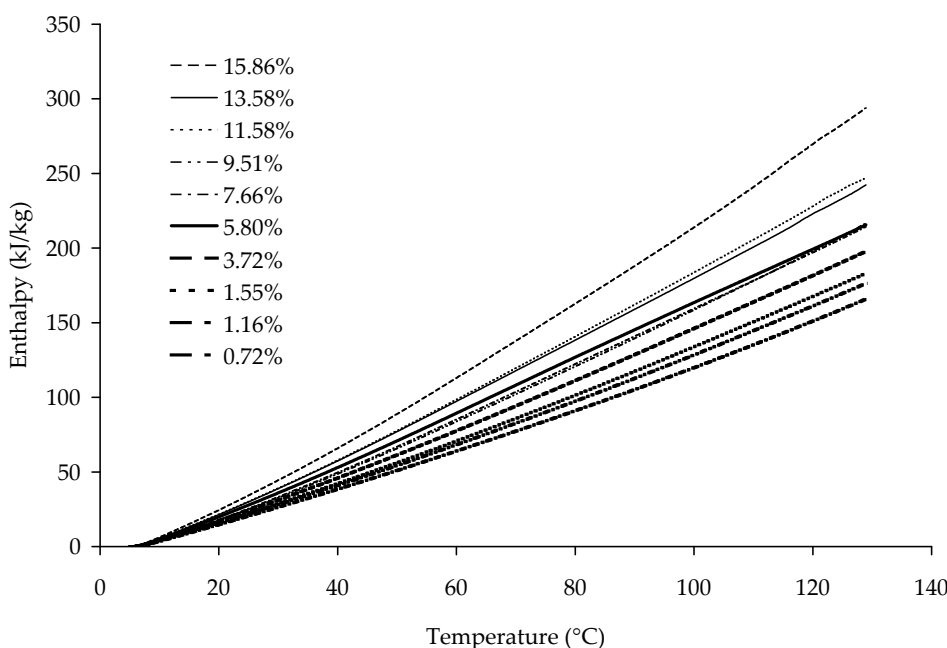


Figure 2. The enthalpy of potato starch as a function of temperature and moisture content

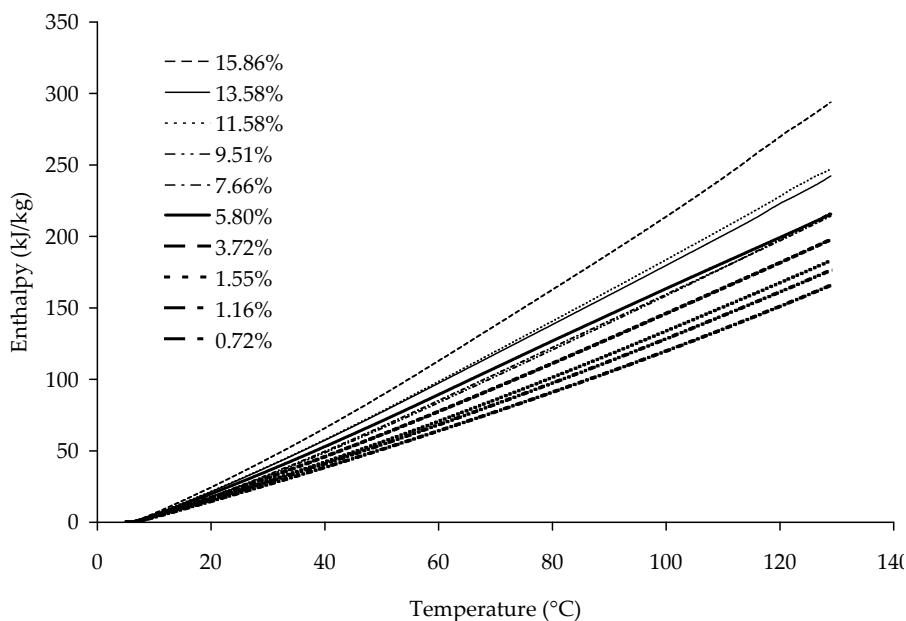


Figure 3. The enthalpy of rice as a function of temperature and moisture content

Table 3. Total evaporation heat necessary for the evaporation of water from the mass m_w of the product

Product	$L_{w(x_{w1} \text{ to } x_{w2})} = f(m_w, L, x_w)$	Validity x_w (%)
Rice	$L_{w(x_{w1} \text{ to } x_{w2})} = \frac{-m_w \cdot L}{100} [x_w - 6.1657 \cdot \exp(-0.141 \cdot x_w)]_{x_{w1}}^{x_{w2}}$	1.02–8.01
Potato starch	$L_{w(x_{w1} \text{ to } x_{w2})} = \frac{-m_w \cdot L}{100} [x_w - 6.4283 \cdot \exp(-0.096 \cdot x_w)]_{x_{w1}}^{x_{w2}}$	0.72–15.86
Oat flakes	$L_{w(x_{w1} \text{ to } x_{w2})} = \frac{-m_w \cdot L}{100} [x_w - 3.5594 \cdot \exp(-0.227 \cdot x_w)]_{x_{w1}}^{x_{w2}}$	0.63–7.2

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

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

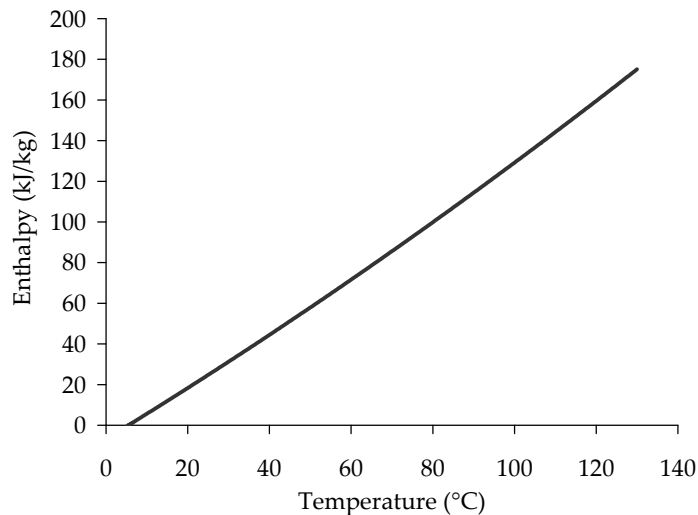


Figure 4. The average enthalpy of oat flakes as a function of temperature (range of moisture content 0.63–7.2 %)

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	kJ
ERH	equilibrium relative humidity (decimal, number between 0 and 1)	–
H	enthalpy	kJ/kg
L	evaporation heat of water	kJ/kg
L_w	heat of water evaporation from the product	kJ/kg

$L_w (x_{w1} \text{ to } x_{w2})$	energy necessary for moisture content change from x_{w1} to x_{w2}	kJ
m_w	mass of the product	kg
p_v	partial water vapour pressure over the product	kPa
p_{vs}	partial saturated water vapour pressure	kPa
R	correlation coefficient	(–)
T	temperature	°C
v_l	specific volume of liquid	m ³ /kg
v_v	specific volume of vapour	m ³ /kg
x_w	moisture (water) content of solids (wet basis)	%

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