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EFFECT OF TEMPERATURE ON MOISTURE SORPTION PHENOMENA IN AGRICULTURAL PRODUCTS

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Abstract

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The paper demonstrates importance of temperature influence on dehydration processes using drying model equations in introductory part and further presents results of water sorption tests of parsley leaves. Measurements were carried out under laboratory conditions in the temperature range of 10–40 °C and relative air humidity from 30 to 100%. Moisture sorption isotherms were tested using a gravimetric dynamic method with continuous recording of changes in sample weight. Five mathematical models available in the literature (Chung-Pfost, GAB, Halsey, Henderson, and Oswin) were statistical evaluated. The Henderson equation was found to be a good model both for moisture adsorption and desorption. Part of the sorption isotherms measured in parsley leaves show the type II BET classification shape. An increase in temperature causes an increase in water activity for the same moisture content and, if water activity is kept constant, an increase in temperature causes a decrease in the amount of absorbed water.

equilibrium moisture content, modeling, sorption isotherm, water activity

Reliable predictions of temperature effects on moisture sorption properties of agricultural products are needed when designing storage, packaging or drying systems, and particularly in the mathematical modelling of such systems. Water transport is a basic phenomenon occurring in foods during processing. The movement of water may be by diffusion within the material or by moisture exchange between the material and the environment. Several models are used to describe the drying characteristics of biological products (Ertekin and Yaldiz, 2004; Krokida et al., 2003). Among them are important for drying processes of agricultural products the one-term exponential model, the Page model, and the two-term exponential model.

As early as in 1921 Lewis (1921) suggested a one-term exponential model to describe the drying rate of a particle analogous to Newton´s law of cooling:

$$\frac{dM}{dt} = -k(M - M_e) \qquad (1).$$

The solution of equation (1) is obtained after variable separation:

$$\frac{dM(t)}{-k[M(t) - M_e]} = dt \qquad (2),$$

or

$$\frac{1}{-k} \int \frac{1}{M(t) - M_e} dM(t) = \int dt \qquad (3).$$

It is possible to receive after integration and after defining boundary condition, $M(t) = M_0$ at $t = 0$:

$$\ln\left[\frac{M(t) - M_e}{M_0 - M_e}\right] = -kt \qquad (4)$$

or

$$\frac{M(t) - M_e}{M_0 - M_e} = \exp(-kt) \qquad (5),$$

where $M(t)$ is the moisture content of the particle at the time t, Me is the equilibrium moisture content (EMC) of the particle, M_0 is initial moisture content and k is the drying constant. In equation (5), there are two parameters to be estimated, k and Me. Determination of the drying constant for wet materials was a subject of numerous studies (Krokida et al., 2004; Pancharyia et al., 2002; Rotz and Chen, 1985; Savoie, Brook and Rotz, 1982). For example Rotz and Sprott (1984) neglected equilibrium moisture content ($M_e = 0$) when they calculated the drying constant k. The error is minimal for moisture contents above 1g water/g d.b., but becomes significant when moisture content approaches the real equilibrium moisture content, as shown by Pitt (1993). In such cases, which are most important in practice, it is necessary to estimate equilibrium moisture content M_e. This value is limited for borderline conditions of drying processes, see equation (4) or (5). The fraction in equation (5) is called moisture ratio, M_r:

$$M_r = \frac{M(t) - M_e}{M_0 - M_e} \qquad (6).$$

Equation (1) is then commonly expressed as a function of M_r:

$$M_r = \exp(-kt) \qquad (7).$$

Page (1949) proposed a modification of the one-term exponential drying model in describing the drying of shelled corn. The model has the following form:

$$M_r = \exp(-k_0 t^n) \qquad (8),$$

where k_0 and n are drying constants. Equation (8) has been successfully used to describe the drying rate of corn products (Huizhen and Morey, 1984, Chhinnan, 1984).

Two-term exponential model

Henderson (1974) suggested that thin-layer drying of biological products can be represented by a two term exponential model of the form:

$$M_r = A_0 \exp(-k_1 t) + A_1 \exp(-k_2 t) \qquad (9),$$

where A_0 and A_1 are empirical constants, and k_1 and $k_2$2 are drying constants. Equation (9) is a simplified form of the solution to Fick´s law of diffusion (Mechlová and Košťál, 1999). This model predicts the drying process of solids during the falling rate period.

The process of dehydration, equations (7), (8), and (9), is described under constant temperature and relative air humidity of the environment in all cases. The limiting parameter is M_r, see equations (6), (7), (8), and (9), which primary depends on M_e.

The objective of this study is to show influence of the temperature on the drying process, M_e, and consequently on water sorption isotherms. Sorption tests of fibre material, parsley leaves, were chosen as an example. Water sorption tests with samples of dried parsley leaves at different temperatures (range of 10–40 °C) and relative air humidities (range of 30 to 99%) were carried out. The relationship among M_e, equilibrium relative air humidity (ERH), water activity (a_w), and temperature was analysed and described by existing isotherm equations available in the literature sources.

MATERIAL AND METHODS

There are numerous models for predicting the relationship of M_e, a_w, and temperature (Vitázek et al., 2003; Jouppila and Roos, 1994; Mazza and Jayas, 1991; Wolf et al., 1990; Chen and Morey, 1989). These water sorption isotherm models may be theoretical, semi-theoretical or empirical and the choice of the model is depend on many factors. Chen and Moray (1989) evaluated four EMC/ERH models (Halsey, Henderson, Chung-Pfost, and Oswin) for their ability to fit data from 18 grain, fibrous, and seed crops. The modified Henderson and Chung-Pfost equations were good for fibrous and starchy materials while the modified Halsey fitted well for oil and protein products. A European COST 90 project (Wolf et al., 1990) on physical properties of agricultural products revealed that the GAB (Guggenheim – Anderson – de Boer) equation was superior to four other models (Halsey, Henderson, Chung-Pfost, and Oswin) in characterising the sorption behaviour on the level of monolayer moisture content. Similar results have been confirmed by a study of Mazza and Jayas, (1991).

These five mentioned models are:

Chung-Pfost

$$w_e = \frac{1}{a} \ln\left(\ln a_w \frac{(b - t)}{c}\right) \qquad (10),$$

Halsey

$$w_e = \left(\frac{\exp(a + bt)}{-\ln a_w}\right)^c \qquad (11),$$

Henderson

$$w_e = \left(\frac{\ln(1 - a_w)}{a(t + b)}\right)^c \qquad (12),$$

Oswin

$$w_e = (a + bt)\left(\frac{a_w}{1 - a_w}\right)^c \qquad (13),$$

the GAB:

$$w_e = \frac{W_m \cdot C \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot (1 - K \cdot a_w + C \cdot K \cdot a_w)} \qquad (14),$$

$$W_m = W_{m0} \cdot \exp \cdot \frac{W_{m1}}{R \cdot T} \qquad (15),$$

$$C = C_0 \cdot \exp \frac{H_m - H_n}{R \cdot T} \qquad (16),$$

$$K = K_0 \cdot \exp \frac{H_e - H_n}{R \cdot T} \qquad (17),$$

where:
w_e = equilibrium moisture content (EMC), %w.b.,
a_w = water activity,
t = temperature, °C
a, b, c = constants for the particular equation,
W_m = mono-layer moisture content,
W_{m1} = temperature coefficient,
W_{m0}, C_0, K_0 = pre-exponential constants,
C, K = equilibrium constants,
H_m = heat of sorption of mono-layer,
H_n = heat of sorption of multi-layer,
H_c = heat of condensation of multi-layer,
R = universal gas constant,
T = temperature, K.

The gravimetric dynamic method with continuous registration of sample weight changes was used for determining the sorption characteristics of parsley leaves. Freshly harvested plants were stored at room temperature conditions for two weeks. The final moisture content of leaves was about 15% (w.b.). Moisture equilibrium data for adsorption and desorption of such prepared samples were investigated at a temperature range of 10–40 °C in 10 °C steps and relative humidities from 30 to 100% in 10% steps. The procedure of each test was as follows: after reaching the equilibrium moisture content of the sample at a certain relative air humidity (at a constant air temperature, velocity and pressure), the relative humidity was automatically increased (adsorption) or decreased (desorption) and the new equilibrium was obtained under these conditions. Each test was repeated three times. The experimental EMC data were processed using specially developed software and analysed using the non-linear regression procedure of UNISTAT (1995).

The precision of fit of a model (Halsey, Henderson, Chung-Pfost, Oswin, and GAB) was determined using several statistics: the standard error of the estimate for EMC (s.e. of estimate) (Chen and Morey, 1989; Mazza and Jayas, 1991), the mean relative percentage deviation (P) (Chen and Morey, 1989; Mazza and Jayas, 1991), the Durbin-Watson statistic (d) (Draper and Smith, 1981), the plot of residuals – probable Chi-squared value (Chen and Morey, 1989; Thakor et al., 1995; Suthar and Das, 1997) and also coefficient of determination (R2) (Lamond and Graham, 1993; Menkov et al., 1999).

RESULTS AND DISCUSSION

Equations (Halsey, Henderson, Chung-Pfost, Oswin, and GAB), which model the dependence of EMC of leaves of parsley on aw in the temperature range of 10–40 °C were investigated and reviewed. Convergence could not be achieved for GAB model in the tested range of EMC and temperature. Analysis of residuals and goodness-of-fit tests were carried out after determining parameters. The comparisons of accepted Chung-Pfost, Halsey, Henderson, and Oswin models are given in Tab. I.

I: *Comparison of Chung-Pfost, Halsey, Henderson and Oswin models for adsorption and desorption of parsley leaves*

Model	s.e. of estimate	P	d	Probable Chi-squared value	R^2
Chung-Pfost ads	0.8091	6.8643	1.3904	0.013	0.9442
Halsey ads	0.9757	12.8269	1.0814	0.097	0.9188
Henderson ads	0.3482	3.3633	1.8999	0.171	0.9897
Oswin ads	0.8643	10.7889	1.1167	0.001	0.9363
Chung-Pfost des	0.8045	6.9638	1.3608	0.002	0.9424
Halsey des	0.9551	12.1246	1.0814	0.085	0.9187
Henderson des	0.3540	3.3460	1.8810	0.176	0.9888
Oswin des	0.8479	10.2833	1.1178	0.194	0.9360

ads = adsorption
des = desorption

The statistical values in Tab. I show, that Henderson´s model for leaves of parsley, both for water adsorption and desorption, has the smallest standard error (s.e.) of estimate and the smallest mean relative percentage deviation. The standardized residuals of these models are normally distributed (Chi-square test) and uncorrelated (Durbin-Watson test).

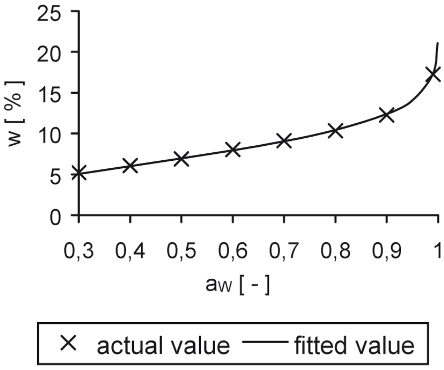
Adsorption and desorption parameters estimated for Henderson´s model of EMC for leaves of parsley are presented in Tab. II.

II: *Parameter values of constants in Henderson´s model of EMC for parsley*

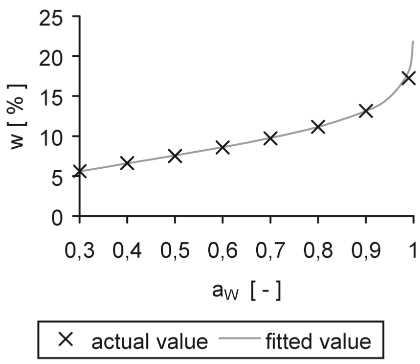
Constants for ads	Estimate	s.e.	Constants for des	Estimate	s.e.
a	–0.0007	0.00005	a	–0.0005	0.00004
b	–2.1493	1.07180	b	–2.9666	1.05750
c	0.4826	0.00790	c	0.4602	0.00790

ads = adsorption
des = desorption

As an example, the experimental adsorption and desorption isotherms of leaves of parsley at 20 °C and for aw ranging from 0.3 to 1.0 are shown in Fig. 1 and 2. Curves represent Henderson´s model.

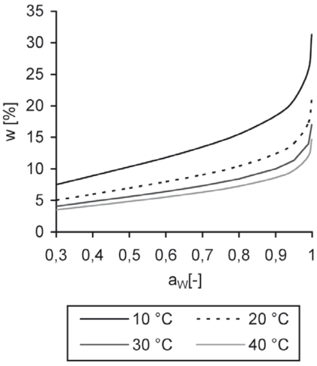


1: *Adsorption isotherm for leaves of parsley at 20 °C (Henderson´s model)*

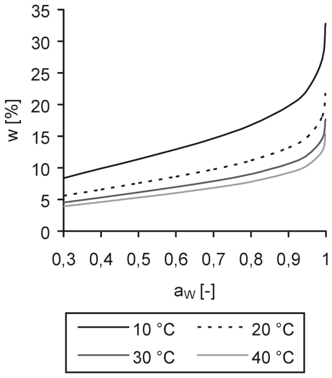


2: *Desorption isotherm for leaves of parsley at 20 °C (Henderson´s model)*

Fig. 3 and 4 was generated to illustrate predictions of the adsorption and desorption Henderson´s model given by equation (12) and using fitted parameters in Tab. II for near ambient air temperature in the range of 10–40 °C and aw ranging from 0.3 to 1.0.



3: *Adsorption isotherms for leaves of parsley (Henderson´s model)*



4: *Desorption isotherms for leaves of parsley (Henderson´s model)*

Temperature effects the mobility of water molecules and the dynamic equilibrium between the vapour and adsorbed phases. Fig. 3 and 4 show schematically the effect of temperature shifts on both the moisture content and a_w. If a_w is kept constant, an increase in temperature causes a decrease in the amount of absorbed water. This indicates that the material becomes less hygroscopic. As pointed out by Rao and Rizvi (1995), this is necessitated by the thermodynamic relationship. As a result, an increase in temperature represents a condition unfavourable to water sorption. An exception to this rule is shown by certain sugars and other low molecular weight constituents which become more hygroscopic at higher temperatures because they dissolve in water. This effect is explained by an increase of the solubility of these constituents in water. The shift of sorption isotherms with temperature has an important practical effect on microbiological and chemical reactivity related to the quality deterioration of agricultural products during storage. Part of the sorption isotherms measured show the type II BET classification shape. The critical EMC of parsley leaves was approximately 8% (w.b.) at 20 °C as it is in equilibrium with $a_w = 0.6$. Below this value the growth of micro-organisms, especially moulds, does not occur (Beuchat, 1981).

SOUHRN

Vliv teploty na sorpční chování vlhkých zemědělských produktů

Teplota vnějšího prostředí ovlivňuje nejen kinetiku sorpcí vlhkosti u zemědělských produktů, ale i jejich vodní aktivitu a v návaznosti mikrobiální stabilitu. Článek dokumentuje význam teploty pro rovnovážné vlhkosti a pro matematické modelování sušení. Prezentuje a analyzuje tři základní rovnice (jednoparametrickou exponenciální, Pageovu, dvouparametrickou exponenciální) a dále výsledky laboratorních sorpčních testů vlhkosti u vzorků lístků petrželové natě. Rozsah měření byl 10 až 40 °C při relativních vlhkostech okolního vzduchu 30 až 100 %. Pro stanovování sorpčních izoterem vlhkosti byla použita gravimetrická dynamická metoda s kontinuálním snímáním změn hmotnosti. Na základě literárních zdrojů bylo analyzováno pět modelů sorpčních izoterem: Chung-Pfost, GAB, Halsey, Henderson a Oswin. Přesnost přiřazených matematických rovnic byla hodnocena následujícími statistickými kritérii: standardní chybou odhadu, střední relativní odchylkou, Durbin-Watsonovou statistikou, Chi-kvadrátem a také koeficientem determinace. Na základě provedených statistik byla vyhodnocena Hendersenova rovnice jako odpovídající model pro adsorpci desorpci vlhkosti u testovaných vzorků. Tvar vytvořené sorpční izotermy odpovídal v rozsahu provedených měření typu II BET klasifikace. Pro konstantní obsah vlhkosti se s nárůstem teploty zvyšovala vodní aktivita a pro konstantní vodní aktivitu se s nárůstem teploty snižovalo množství absorbované vody. Kritická hodnota rovnovážné vlhkosti testovaných lístků petržele, odpovídající vodní aktivitě 0,6, činila 8 % při 20 °C.

rovnovážná vlhkost, modelování, sorpční izoterma, vodní aktivita

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REFERENCES

BEUCHAT, L.: Microbial stability as affected by water activity, Cereal Foods World, 1981, 26, 4: 345-351. ISSN 0146-6283.

BROOKER, D. B., BAKER-ARKEMA, F. W., HALL, C. W.: Drying cereal grains, The AVI Publishing Co. Westport, Connecticut, 1981.

CHHINNAN, M. S.: Evaluation of selected mathematical models describing thin-layer of in-shell pecans, Transactions of the ASAE, 1984, 27, 5: 610-615. ISSN 0001-2351.

CHEN, C. C., MOREY, R. V.: Comparison of four EMC/ERH equations, Transactions of the ASAE, 1989, 32, 7: 983-990. ISSN 0001-2351.

DRAPER, N. R., SMITH H.: Applied Regression Analysis. New York: J. Wiley & Sons Publishing, 1981, pp. 72-115.

ERTEKIN, C., YALDIZ, O.: Drying of eggplant and selection of suitable thin layer drying model, Journal of Food Engineering, 2004, 63, 3: 349-359. ISSN 0260-8774.

JOUPPILA, K., ROOS, Y. H.: Water sorption and time-dependent phenomena of milk powders, Journal of Diary Science, 2004, 77, 7: 1798-1808. ISSN 0022-0302.

HENDERSON, S. M.: Progress in developing the thin-layer drying equation, Transactions of the ASAE, 1974, 17, 6: 1167-1168. ISSN 0001-2351.

HUIZHEN, L. and MOREY, R. V.: Thin-layer drying of yellow dent corn, Transactions of the ASAE, 1984, 27, 1: 581-585. ISSN 0001-2351.

IGLESIAS, H. A., CHIRIFE, J.: Equilibrium moisture contents of air dried beef: dependence on drying temperature, Journal of Food Technology, 1976, 11, 7: 565-573. ISSN 0022-1155.

KAMINSKI, W., STRUMILLO, C.: The influence of temperature on sorption isotherms of protein-containing mixtures, Drying Technology, 1994, 12, 12: 1263-1276. ISSN 0737-3937.

KROKIDA, M. K., KARATHANOS, V. T., MAROULIS, Z. B., MARINOS-KOURIS, D.: Drying kinetics of some vegetables, Journal of Food Engineering, 2003, 60, 4: 391-403. ISSN 0260-8774.

KROKIDA, M. K., FOUNDOUKIDIS, E., MAROULIS, Z. B.: Drying constant: literature data compilation for foodstuffs, Journal of Food Engineering, 2004, 6+, 3: 321-330. ISSN 0260-8774.

LEWIS, W. K.: The rate of drying of solid materials, Journal of Industrial Engineering, 1921, 13,5: 427-432.

LABUZA, T. P.: Typical sorption isotherms. In: Moisture sorption, published by the American Association of Cereal Chemists, St. Paul, Minnesota, 1984, pp. 8-21. ISBN 0-913250-34-1.

LAMOND, W. J., GRAHAM, R.: The relationship between the equilibrium moisture content of grass mixtures and the temperature and humidity of the air, Journal of Agricultural Engineering Research, 1993, 56, 3: 327-335. ISSN 0021-8634.

MAZZA, G., JAYAS, D. S.: Equilibrium moisture characteristics of sunflower seeds, hulls and kernels, Transactions of the ASAE, 1991, 34, 4: 534-538. ISSN 0001-2351.

MECHLOVÁ, E., KOŠŤÁL, K.: Výkladový slovník fyziky, Fick´s laws. Prometheus Praha, 1999, p. 262. ISBN 80-7196-151-5

MENKOV, N. D., PASKALEV, H. M., GALYAZKOV, D. I., KEREZIEVA-RAKOVA, M.: Applying the linear equation of correlation of Brunauer-Emmett-Teller (BET) – monolayer moisture content with temperature, Nahrung, 1999, 43, 2: 118-121.

PAGE, G.: Factors influencing the maximum rates of air drying shelled corn in thin layers, M.S. Thesis, Purdue University, 1949.

PANCHARIYA, P. C., POPOVIC, D., SHARMA, A. L.: Thin-layer modelling of black tea drying process, Journal of Food Engineering, 2002, 59, 4: 349-357. ISSN 0260-8774.

PITT, R. E.: Forage drying in relation to pan evaporation, Transactions of the ASAE, 1993, 36, 6: 1933-1937. ISSN 0001-2351.

RAO, M. A., RIZVI, S. S. H.: Chemical potential and phase equilibria. In: Engineering properties of foods, Marcel Dekker, Inc., NY, 1995, 226-241. ISBN 0-8247-8843-1.

ROTZ, C. A., CHEN, Y.: Alfalfa drying model for the field environment, ASAE paper no. 85-1025, ASAE St. Joseph, Michigan, 1985.

ROTZ, C. A., SPROTT, D. J.: Drying rates, losses and fuel requirements for mowing and conditioning alfalfa, Transactions of the ASAE, 1984, 27, 3: 715-720. ISSN 0001-2351.

SAVOIE, P., BROOK, R. C., ROTZ, C. A.: Empirical model for field drying of alfalfa, ASAE paper no. 82-1528, ASAE St. Joseph, Michigan, 1982.

SUTHAR, S. H., DAS, S. K.: Moisture sorption isotherms for karingda seed, kernel and hull, Journal of Food Process Engineering, 1997, 20, 3: 349-366. ISSN 0145-8876.

THAKOR, N. J., SOKHANSANJ, S., PATIL, R. T., DESHPANDE, S. D.: Moisture sorption and volumetric changes of canola during hydrothermal processing, Journal of Food Process Engineering, 1995, 18, 2: 233-242. ISSN 0145-8876.

VITÁZEK, I., HAVELKA, J., PIRŠEL, M.: Sorption isotherms of maize grains, Agriculture, 2003, 49,3: 137-142. ISSN 0551-3677

WOLF, W., SPIESS, W. E. L., JUNG, G.: Standardization of isotherms measurements, COST - Project 90 and 90 bis, 1990. 97 p.

UNISTAT: Users Guide, Unistat Limited, London. 1995.

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