Moisture Sorption Isotherms of Millet Seeds*

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Abstract

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The equilibrium moisture contents were determined for millet seeds of two cultivars using the gravimetric static method at 10, 25 and 40°C over a range of relative humidities from 0.112 to 0.868. The sorption capacity of the seeds decreased with an increase in temperature at constant relative humidity. The hysteresis effect is not distinctly expressed but statistically significant. The differences between equilibrium moisture contents of the cultivars are small. Four models were applied for analyzing the experimental data using the following equations: modified Chung-Pfost, modified Halsey, modified Oswin, and modified Henderson. The modified Chung-Pfost model was found to be the most suitable for describing the relationship between equilibrium moisture content, relative humidity and temperature.

Key words: millet; equilibrium; sorption; model

Millet (*Panicum miliaceum* L.) is a valuable foodstuff and forage plant due to its high content of vegetable protein and oil (CHOWDHURY, PUNIA 1997; JAIN, BAL 1997). The millet seeds meant for food or sowing are a product which is subjected to long-term storage. During that time, important physicochemical and biological changes take place with a strong impact on the nutritive properties. The equilibrium relationship binding the moisture content of a foodstuff with the temperature and humidity of the surrounding air is of primary interest for design, modelling and optimization of many food processes. A number of models have been previously suggested for the dependence between the equilibrium moisture content (EMC) and the relative humidity (RH) of the air (VAN DEN BERG, BRUIN 1981). Some of them take into account the effect of temperature. The modified Chung-Pfost, modified Henderson, modified Halsey, and modified Oswin equations have been adopted as standard equations by the American Society of Agricultural Engineers for describing sorption isotherms (ASAE 1995).

The object of this work was to obtain the equilibrium moisture isotherms for millet seeds at 10, 25 and 40°C and to develop a suitable model describing the isotherms.

MATERIAL AND METHOD

Material: Seeds of two millet cultivars grown in Bulgaria were investigated: Mironovskoe 85 and Kanelskoe skorospeloe. The weight of 1000 seeds of both cultivars was about 7 g, the oil content about 4% dry basis (d.b.).

Procedure: The EMC of the millet seeds was determined at 10, 25 and 40°C. The static gravimetric method was applied (WOLF *et al.* 1985). For the adsorption process, seeds were dehydrated in a desiccator with P_2O_5 at room temperature for 20 days prior to the beginning of the experiment (initial moisture content < 2% d.b.). The desorption isotherms were determined on samples hydrated in a glass jar over distilled water at 4°C to approximately 25% d. b. moisture content. Samples of 3 ± 0.2 g were weighed in weighing bottles. The weighing bottles were then placed in hygrostats with nine saturated salt solutions, used to obtain constant relative humidities environments (GREENSPAN 1977; WEISSER 1986). All used salts were of reagent grade. At high relative humidities (RH > 0.70), crystalline thymol was placed in the hygrostats to prevent microbial spoilage of the seeds (WOLF *et al.* 1985). The hygrostats were kept in thermostats at 10, 25 and 40 ± 0.2°C. Samples were weighed (balance with an accuracy of 0.0001 g) every three days. Equilibrium was acknowledged when three consecutive weight measurements showed a difference less than 0.001 g. The moisture content of each sample was determined by the air-oven method at 130°C (ROBERTS, ROBERTS 1972). The EMC was determined by calculating the means of triplicate measurements.

Analysis of data: The description of the EMC/RH relationship was verified according to the following models:

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Modified Chung-Pfost $$H_r = \exp\left[\frac{-A}{t+B}\exp(-CM)\right] \quad [1]$$

Modified Halsey $$H_r = \exp\left[\frac{-\exp(A+Bt)}{M^C}\right] \quad [2]$$

Modified Oswin $$M = (A+Bt)\left(\frac{H_r}{1-H_r}\right)^C \quad [3]$$

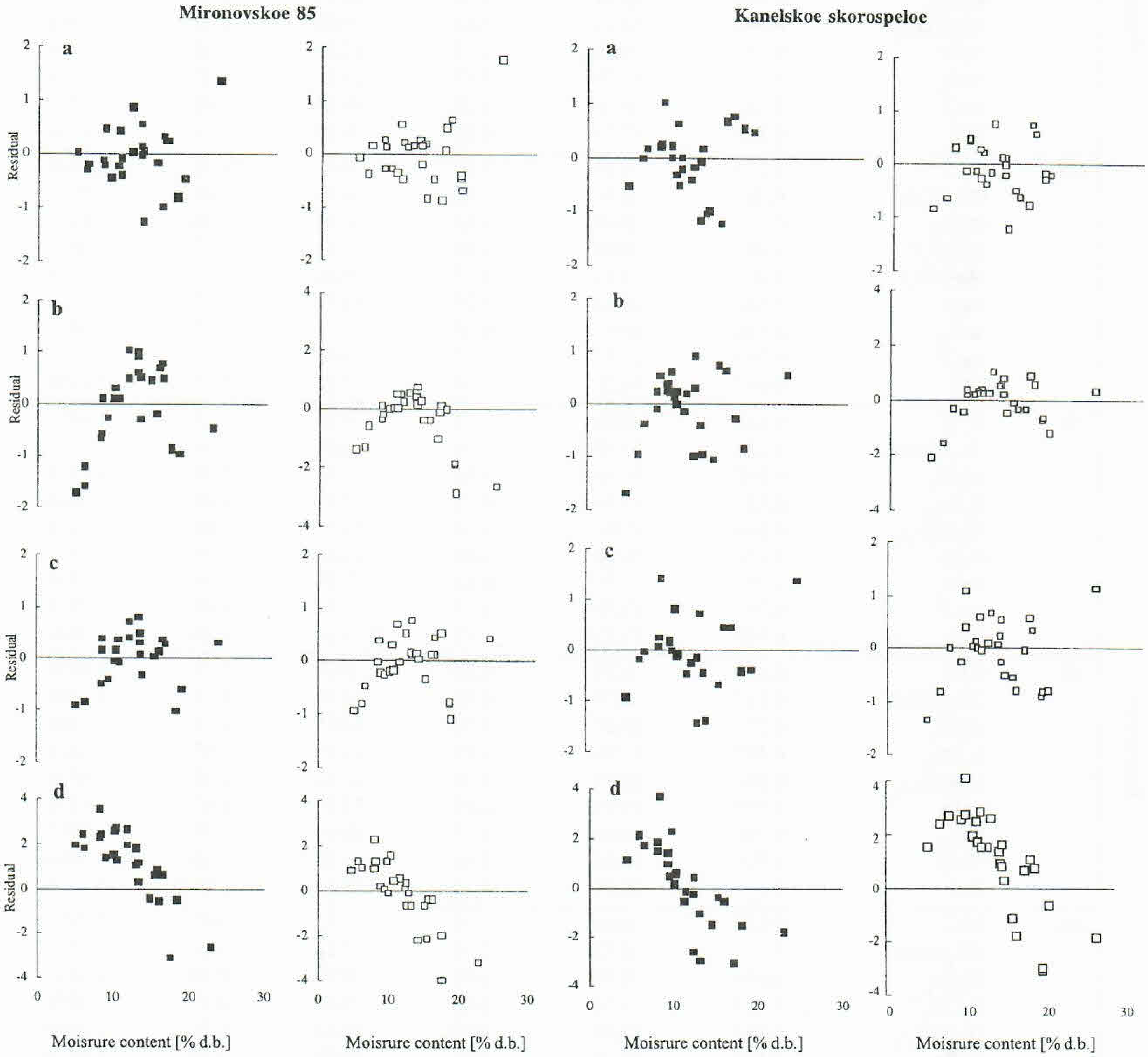
Modified Henderson $$1-H_r = \exp[(-A(t+B)M^C] \quad [4]$$

where: M – EMC [% d.b.]
H_r – relative humidity as a decimal
A, B, C – coefficients
t – temperature [°C]

A nonlinear, least squares regression program, was used to fit the four models to the experimental data (all replications). The suitability of the equations was evaluated and compared using the mean relative error (MRE in %), standard error of estimate (SEE) and randomness of residual (CHEN, MOREY 1989). The residuals obtained for each model were plotted against measured EMC and were assessed visually as random and patterned.

RESULTS AND DISCUSSION

The mean values M and the standard deviations, based on the triplicate measurements for the respective relative humidity and temperature, obtained after adsorption and after desorption are presented in Table 1. The values for



a – Modified Chung-Pfost; b – Modified Halsey, c – Modified Oswin, d – Modified Henderson; ■ adsorption; □ desorption

Fig. 1. Plot of residuals fit of four models to sorption data of millet seeds cultivar Mironovskoe 85 and Kanelskoe skorospeloe

Table 1. Equilibrium moisture content (EMC in % d.b.), standard deviation (SD) and *t*-statistic of the seeds of two millet cultivars obtained by adsorption and desorption at different relative humidities (RH as a decimal) and temperatures [°C]

	Temperature	Salt	RH	Mironovskoe 85		Kanelskoe skorospeloe		*t*-statistic
				EMC	SD	EMC	SD	
Adsorption	10	LiCl	0.113	8.09	0.07	8.42	0.07	5.7738
		CH_3COOK	0.234	10.48	0.10	9.83	0.18	5.4675
		$MgCl_2$	0.335	11.73	0.18	10.30	0.22	8.7135
		K_2CO_3	0.431	12.62	0.04	11.24	0.17	13.6864
		$Mg(NO_3)_2$	0.574	14.30	0.06	12.38	0.10	28.5163
		NaBr	0.622	15.56	0.15	13.26	0.13	20.0697
		$SrCl_2$	0.757	17.54	0.19	17.20	0.13	2.5580
		NaCl	0.757	17.59	0.12	17.18	0.06	5.2931
		KCl	0.868	22.93	0.26	23.21	0.25	1.3446
	25	LiCl	0.113	5.88	0.11	6.03	0.08	1.9101
		CH_3COOK	0.231	8.23	0.03	8.03	0.15	2.2646
		$MgCl_2$	0.331	9.97	0.20	9.33	0.13	4.6471
		K_2CO_3	0.432	10.84	0.12	10.34	0.24	3.2275
		$Mg(NO_3)_2$	0.544	12.46	0.15	11.60	0.07	8.9988
		NaBr	0.591	13.08	0.13	12.39	0.08	7.8295
		$SrCl_2$	0.725	15.70	0.13	15.35	0.23	2.2946
		NaCl	0.755	16.45	0.20	16.03	0.08	3.3772
		KCl	0.851	17.73	0.20	18.23	0.08	4.0204
	40	LiCl	0.112	4.72	0.08	4.48	0.02	5.0410
		CH_3COOK	0.201	6.36	0.10	6.56	0.08	2.7050
		$MgCl_2$	0.316	8.03	0.21	8.14	0.06	0.8726
		K_2CO_3[34]	0.432	8.98	0.08	9.31	0.12	3.9632
		$Mg(NO_3)_2$	0.484	9.58	0.17	9.64	0.14	0.4719
		NaBr	0.532	10.12	0.07	10.10	0.12	0.2494
		$SrCl_2$	0.658	12.65	0.14	12.61	0.22	0.2657
		NaCl	0.747	13.37	0.13	13.02	0.21	2.4545
		KCl	0.823	15.21	0.20	14.65	0.15	3.8798
Desorption	10	LiCl	0.113	8.42	0.12	8.89	0.14	4.4149
		CH_3COOK	0.234	10.49	0.10	10.48	0.10	0.1225
		$MgCl_2$	0.335	11.98	0.06	11.38	0.14	6.8229
		K_2CO_3	0.431	13.18	0.15	12.83	0.08	3.5660
		$Mg(NO_3)_2$	0.574	15.03	0.10	14.11	0.08	12.4430
		NaBr	0.622	16.18	0.05	14.68	0.09	25.2348
		$SrCl_2$	0.757	17.71	0.11	17.45	0.14	2.5293
		NaCl	0.757	17.70	0.11	17.54	0.05	2.2935
		KCl	0.868	23.12	0.17	23.56	0.16	3.2646
	25	LiCl	0.113	6.19	0.06	6.07	0.11	1.6588
		CH_3COOK	0.231	8.29	0.03	8.38	0.13	1.1684
		$MgCl_2$	0.331	10.20	0.06	10.05	0.16	1.5204
		K_2CO_3	0.432	11.96	0.11	11.79	0.07	2.2583
		$Mg(NO_3)_2$	0.544	13.17	0.24	12.59	0.16	3.4828
		NaBr	0.591	13.39	0.17	12.92	0.07	4.4279
		$SrCl_2$	0.725	16.00	0.11	16.08	0.11	0.8907
		NaCl	0.755	16.56	0.18	16.51	0.13	0.3900
		KCl	0.851	18.55	0.12	18.25	0.06	3.8730
	40	LiCl	0.112	5.04	0.10	4.60	0.03	7.2996
		CH_3COOK	0.201	6.32	0.12	7.16	0.11	8.9375
		$MgCl_2$	0.316	8.56	0.08	8.83	0.10	3.6518
		K_2CO_3[34]	0.432	9.18	0.08	9.66	0.17	4.4250
		$Mg(NO_3)_2$	0.484	10.07	0.09	10.18	0.11	1.3405
		NaBr	0.532	10.58	0.11	10.69	0.19	0.8678
		$SrCl_2$	0.658	13.07	0.15	12.90	0.08	1.7321
		NaCl	0.747	13.42	0.19	13.32	0.20	0.6279
		KCl	0.823	15.63	0.28	15.60	0.11	0.1727

Table 2. Coefficients (*A*, *B*, *C*); mean relative error (MRE in %) and standard error of estimate (SEE) of three-parameter models for cv. Mironovskoe 85 and Kanelskoe skorospeloe

	Process	Parameter	Modified Chung-Pfost	Modified Halsey	Modified Oswin	Modified Henderson
Mironovskoe 85	Adsorption	*A*	341.6704	7.027309	14.67732	0.000172
		B	16.04695	−0.027222	−0.118068	15.15052
		C	0.214066	2.767814	0.271347	1.884244
		MRE	3.12	5.95	3.97	10.34
		SEE	0.56	0.76	0.54	1.76
	Desorption	*A*	354.0791	7.283891	15.06517	0.000303
		B	16.86774	−0.027035	−0.118484	16.43500
		C	0.208293	2.837346	0.264521	1.703580
		MRE	3.21	6.54	4.30	16.62
		SEE	0.59	0.82	0.57	2.02
Kanelskoe skorospeloe	Adsorption	*A*	488.6612	6.344758	13.63704	0.000107
		B	33.23216	−0.021030	−0.094414	19.43358
		C	0.222382	2.591473	0.288515	0.482620
		MRE	4.64	5.39	4.58	8.51
		SEE	0.95	0.68	0.71	1.25
	Desorption	*A*	457.0354	7.066208	14.61170	0.000311
		B	22.34223	−0.024180	−0.106142	17.80618
		C	0.221535	2.791105	0.267670	1.610400
		MRE	4.25	6.00	4.64	17.65
		SEE	0.77	0.77	0.66	2.17

EMC, as expected, decreased with an increase in the temperature at constant RH. Similar trends for many seeds and foodstuff have been reported in the literature (ASAE 1995; MASKAN, KARATAS 1997; SUTHAR, DAS 1997; WALTERS, HILL 1998; MENKOV, DINKOV 1999). The differences between EMC of both cultivars are small but in some experimental points the statistic $t < t_{0.05,4} = 2.77$ (level of significance 0.05, degree of freedom 3 + 3–2). The sorptive capacity of the millet seeds grown in Bulgaria is lower than the Nigerian millet (AJISEGIRI, SOPADE 1990).

The sorption isotherms have a S-shape profile typical for the seeds (WALTERS, HILL 1998). The hysteresis effect was not distinctly expressed but statistically significant (level of significance 0.05).

The values of coefficients, MRE and SEE for the four three-parameter models are presented in Table 2 for adsorption and for desorption. Analysis of the residuals for the both cultivars are presented in Fig. 1. The values of MRE and SEE obtained by modified Chung-Pfost and modified Oswin models were lower than that obtained by the other models. For the modified Henderson (both cultivars), modified Halsey (both cultivars) and modified Oswin (Mironovskoe 85) equations, the residual plots were patterned, which makes them unsuitable. This gives some justification for recommending the modified Chung-Pfost model to describe the equilibrium isotherms of millet seeds.

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Souhrn

MENKOV N. D., GELYAZKOV D. I. (2000): **Sorpční izotermy vlhkosti semen prosa**. Czech J. Food Sci., **18**: 86–90.

Pomocí gravimetrické statické metody jsme při teplotě 10, 25 a 40 °C a relativní vlhkosti vzduchu v rozsahu 0,112–0,868 stanovili rovnovážnou vlhkost semen dvou odrůd prosa. Při konstantní relativní vlhkosti klesala sorpční kapacita semen se stoupající teplotou. Hysterezní efekt se výrazně neprojevil, ale byl statisticky významný. Rozdíly v rovnovážné vlhkosti mezi odrůdami jsou malé. K analýze pokusných dat jsme použili čtyři modely s modifikovanými rovnicemi Chunga-Pfosta, Halseyho, Oswina a Hendersona. Jako nejvhodnější se pro charakteristiku vztahu mezi rovnovážnou vlhkostí, relativní vlhkosti a teplotou ukázal modifikovaný model Chunga-Pfosta.

Klíčová slova: proso; rovnováha; sorpce; model

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