Enhancement of the Halsey equation for canola isotherms

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Yang, W.H. and Cenkowski, S. 1995. **Enhancement of the Halsey equation for canola isotherms.** Can. Agric. Eng. 37:169-182. The goodness-of-fit of the Halsey, Modified-Henderson, and Chung isotherm equations, as they were applied to 56 canola isotherms, is discussed. The Halsey equation was modified to improve the goodness-of-fit of these isotherms. The modified model is valid for equilibration temperatures between 3.5 and 75°C, relative humidities from 15 to 92% and moisture contents in the range of 4 to 23 % db. The canola was exposed to five drying-rewetting cycles and to dehydration temperatures of 25 and 50°C. The modified Halsey equation was found to be capable of expressing canola isotherms exposed to multiple drying and rewetting cycles. The dependency of temperature and drying-rewetting cycles was also examined. A mathematical equation that related the equilibrium relative humidity (ERH) to equilibrium moisture content (EMC), equilibrium temperature, and drying-rewetting cycles is proposed.

Nous avons examiné la précision de l'ajustement des équations isotherms Halsey, Chung et Henderson-modifée, appliquées à cinquante-cinq isothermes de canola. Afin d'améliorer la précision de l'ajustement des isothermes, l'équation Halsey a été modifiée. Le modèle modifié est valable pour des températures d'équilibration entre 3.5°C et 75°C, pour des humiditiés relatives de 15% à 92% et pour des teneurs en eau allant de 4% à 23% sur sec. Nous avons soumis le canola à cinq cycles de séchage et de mouillage ainsi qu'à des températures de déshydratation de 25°C et de 50°C. Nous avons trouvé que l'équation modifiée Halsey peut exprimer les isothermes de canola soumis à de multiples cycles de séchage et de mouillage. Nous avons aussi examiné la dépendance entre la température et les cycles de séchage et de mouillage. Nous avons proposé une équation mathématique rattachant l'humidité relative à l'équilibre (equilibrium relative humidity, ERH) aux teneur en eau à l'équilibre (equilibrium moisture content, EMC), température à l'équilibre et cycles de séchage et de mouillage.

INTRODUCTION

More than 200 isotherm equations have been proposed to describe sorption data for biological materials alone (Van den Berg and Bruin 1981). No unique model, however, has been found to accurately describe the equilibrium moisture content versus equilibrium relative humidity (EMC-ERH) relationship of various types of materials in a broad range of relative humidities and temperatures. The absence of such an equation is due to differences between biological materials in terms of their composition, dimensions, physical, and/or chemical changes during maturation and stage of processing or storage (Chirife and Iglesias 1978).

The American Society of Agricultural Engineers has adopted two standard equations to describe EMC-ERH relationships for agricultural grains (ASAE 1994). The first one is the Modified-Henderson equation (Thompson et al. 1968):

$$RH = 1 - \exp\left[-K\,(T + C)\,M^{N}\right] \qquad (1)$$

and the second is the Chung equation (Pfost et al. 1976):

$$RH = \exp\left[-\frac{A}{T+C}\exp\left(-B\,\frac{M}{100}\right)\right] \qquad (2)$$

where:

RH = equilibrium relative humidity (fraction),
M = equilibrium moisture content (% db),
T = temperature (°C), and
A, B, C, K, N = constants.

Some researchers have reported rather poor fit of data when the recommended ASAE equations were used for canola (Sokhansanj et al. 1986), lentils (Cenkowski et al. 1989) and sunflower seeds (Mazza and Jayas 1990). The two recommended equations usually underestimate the experimental data at relative humidities above 80-85% (Sokhansanj et al. 1986). Also, Chen and Morey (1989) reported that Eqs. 1 and 2 give results which have a high standard error and clear patterns in residual plots when they are used to describe EMC-ERH relationship for high oil and protein content products.

Chen and Morey (1989) concluded that the two standardized equations were only satisfactory for starchy and fibrous materials. Protein rich or high oil content materials including canola were described better when the Modified Halsey equation was used.

Chen and Morey (1989) used sorption data of canola reported by Pixton and Warburton (1977), Pixton and Henderson (1981), and Sokhansanj et al. (1986) in their analysis. The data were reported for a temperature range of 5 to 35°C and equilibrium moisture obtained through one drying and rewetting cycle. In reality, a crop can be exposed to multiple drying and rewetting cycles during storage as a result of aeration with ambient air, temperature gradient build-up across a storage bin, or mixing grain of different initial moisture contents. Therefore, moisture sorption characteristics can be affected throughout the crop storage history (Rao 1941; Kapsalis 1987; Yang and Cenkowski 1993). Yang and Cenkowski (1993) used a simplified form of the Modified Halsey equation (Halsey 1948; Iglesias and Chirife 1976):

$$RH = \exp\left(-\frac{C}{M^{B}}\right) \qquad (3)$$

where B, C = constants. Unlike Eqs. 1 and 2, Eq. 3 does not take the temperature effect into account. It was statistically proven that Eq. 3 gave reasonably good fit to canola isotherms, when the canola seeds were exposed to multiple drying-rewetting cycles.

The objectives of this paper are: i) to enhance the performance of the Halsey equation for the determination of canola isotherms, where the canola has been exposed to sorption conditions of equilibrium temperatures between 3.5 and 75°C, ii) to compare the computation results of the two ASAE standardized equations against the original Halsey and enhanced Halsey equation proposed in this paper, and iii) to examine the effect of equilibration temperature and adsorption-desorption (A/D) cycles on the parameters of the enhanced Halsey equation.

MATERIALS AND METHODS

EMC-ERH data

The isotherms of canola *Brassica napus* L., cv. Westar were measured at temperatures of 6.0, 15.0, 35.0 and 45.0°C in this study. The same dynamic equilibration method and equipment described by Yang and Cenkowski (1993) were used. Briefly, the experimental set-up consisted of an equilibrium apparatus, heat exchanger, and aquarium air pump. These elements were connected with flexible plastic tubing forming an airtight loop. The major component of the system, the equilibrium apparatus, was comprised of six plastic rings stacked on top of one another with a wire mesh attached to the bottom of each ring for holding a thin layer of canola. A bulk polymer resistance humidity sensor (RH-2, General Eastern Instruments Inc., Watertown, MA) was used to measure the relative humidity in the headspace of the equilibrium apparatus. The sensors were calibrated against a Hygro-M1 dew point sensor (General Eastern Instruments Inc., Watertown, MA). Alternating wet and dry canola samples (approximately 15 g each) were placed on the wire meshes of the plastic rings and allowed to equilibrate by circulating air inside the apparatus for at least 24 hours (Bielewicz et al. 1993). This arrangement allowed us to simultaneously obtain both desorption and adsorption isotherms. The wet samples were prepared by adding a predetermined amount of distilled water to dry canola and then storing the canola overnight in a refrigerator maintained at 8°C to allow the water to distribute evenly across the kernels. The experimental set-up was placed in a temperature-controlled chamber.

The EMC-ERH data for Westar canola obtained in this study are presented in Table I. Also, canola isotherms from other sources were used for curve fitting purposes. A total of 56 canola isotherms from the following cultivars were analyzed: Candle (Pixton and Henderson 1981), Tobin (Sokhansanj et al. 1986), Global (Otten et al. 1990), and Westar (Bielewicz et al. 1993; Yang and Cenkowski 1993). These isotherms had relative humidities ranging from 15 to 94% and equilibrium moisture contents between 4 and 23% db. Equilibration temperatures were in the range of 3.5 to 75°C. The drying temperatures used in our experiments were 25 and 50°C and each sample was exposed to five drying-rewetting cycles.

Enhancement of the Halsey equation

The procedure for enhancing the Halsey equation was empirical with some component of analytical strategy. Enhancement of the Halsey equation was focused on the replacement of the numerator, *C*, of the vulgar fraction inside the exponential term of Eq. 3 with an algebraic expression being a function of the equilibrium moisture, *M*. The goal was to adjust the convexity of the isotherm curves, especially for relative humidities above 80%. A linear [$C=M$], parabolic [$C=M^2$], cubic [$C=M^3$], logarithmic [$C=\ln(M)$], and exponential [$C=\exp(M)$, $C=\exp(M^2)$, $C=A^M$, $C=A^{M\wedge 2}$ where *A* is a constant] algebraic expressions were tried. The above algebraic expressions were all confined to one parameter in order for the constants in the modified equation not to exceed three parameters. Non-linear regressions were then conducted, fitting each modified form to the 56 canola isotherms. Relevant statistical parameters of the modified equations were compared in order to select the best-fit model.

Statistical evaluation

Evaluation of selected modified versions of the Halsey equation was completed in two steps. First, the selected models were used to describe the EMC data of individual cultivars gathered at specific temperatures and drying-rewetting cycles, then their statistical performance was examined. The poorly performing selected formulae were rejected at this point. The formulae that passed the first step of the evaluation were then screened again. All the EMC data for one variety gathered at different temperatures were fitted to yield estimate parameters for the EMC-ERH relationship. In this case, moisture content, temperature, and drying-rewetting cycles were considered to be interacting independent variables.

The statistical criteria used to assess the goodness-of-fit were: i) the mean relative percentage deviation, *P*, ii) the standard error, *S.E.*, iii) the behaviour of the residual plot, i.e., randomly distributed, *R.D.*, or systematically patterned, *S.P.*, and iv) the sum of residuals, *Sum*. The mean relative percentage deviation, *P*, was defined as:

$$P=\frac{100}{N}\bullet\sum\frac{|Y-Y'|}{Y} \tag{4}$$

where:

Y = the measured value,
Y' = the estimated value,
N = the number of observations,

and the standard error, S.E., was determined as:

$$S.E.=\sqrt{\frac{\sum(Y-Y')^2}{df}} \tag{5}$$

where df = degrees of freedom of a regression model.

A non-linear regression program that uses a least squares procedure based on the Marquardt-Levenberg algorithm to minimize the sum of the squares of the differences between the estimated values and the measured values was used for curve fitting operations (SigmaPlot 5.0, Jandel Scientific 1992). The parameters and the sum of residuals for a tested equation were automatically recorded when a curve fitting was completed. The *P* values and *S.E.* values were calculated by pre-programming Eq. 4 and Eq. 5 into the TRANSFORM feature of the SigmaPlot 5.0 package mentioned above. Plots of residuals versus EMCs and estimated ERHs were con-

Table I: EMC-ERH data of canola cultivar Westar measured in this study

Equilibration temperature 6°C

RH (%)	92.0	76.6	53.6	30.8
Adsorption				
Mean	17.607	9.093	6.970	4.926
Std. Dev.*	0.037	0.038	0.036	0.007
95% Conf.*	0.093	0.094	0.089	0.017
Desorption				
Mean	17.927	9.987	7.386	6.094
Std. Dev.	0.038	0.066	0.011	0.065
95% Conf.	0.093	0.165	0.028	0.162

Equilibration temperature 15°C

RH (%)	72.6	46.9	41.1	39.8	39.4	34.9
Adsorption						
Mean	10.244	6.546	6.073	5.924	5.775	5.707
Std. Dev.	0.025	0.038	0.033	0.036	0.015	0.051
95% Conf.	0.062	0.095	0.083	0.088	0.036	0.128
Desorption						
Mean	10.474	7.118	6.342	6.104	5.962	5.901
Std. Dev.	0.036	0.050	0.008	0.013	0.072	0.016
95% Conf.	0.089	0.124	0.020	0.032	0.179	0.039

Equilibration temperature 35°C

RH (%)	76.2	65.4	55.3	51.8	48.9	20.9
Adsorption						
Mean	11.239	8.716	7.253	6.642	6.487	4.623
Std. Dev.	0.018	0.046	0.016	0.076	0.031	0.027
95% Conf.	0.044	0.115	0.040	0.189	0.077	0.067
Desorption						
Mean	11.212	9.047	7.495	6.887	6.717	4.897
Std. Dev.	0.012	0.079	0.040	0.121	0.016	0.070
95% Conf.	0.030	0.196	0.099	0.299	0.039	0.173

Equilibration temperature 45°C

RH (%)	69.9	66.7	58.5	46.3	44.8	44.2	35.4
Adsorption							
Mean	10.146	8.897	7.521	5.798	5.692	5.577	4.893
Std. Dev.	0.016	0.031	0.029	0.063	0.016	0.051	0.023
95% Conf.	0.040	0.077	0.072	0.155	0.039	0.127	0.056
Desorption							
Mean	10.302	9.197	7.770	5.810	5.736	5.618	4.902
Std. Dev.	0.046	0.050	0.013	0.037	0.025	0.016	0.014
95% Conf.	0.113	0.123	0.032	0.093	0.062	0.039	0.035

* Calculated from three observations

structed to aid the residual analysis.

The residuals were qualitatively identified as random or patterned based on their number of runs in contrast with the expected value of runs (Swed and Eisenhart 1943; Beck and Arnold 1977; Draper and Smith 1981). This was done by differentiating the plus and minus residuals and then analyzing the randomness of their grouping. The number of runs, R, equals the number of residual sign changes plus one. The expected value of runs, $E(R)$, equals the number of independent observations plus one divided by two (Beck and Arnold 1977). For large samples, the closer R is to $E(R)$, the more random the residuals, since the closeness indicates that there exists neither positive nor negative serial correlations. For small samples, like in the case of our experiments (six signs on the average), obtaining a high number of runs is not a concern. The reason for this is the most possible number of runs is six, which results from the combination of three plus signs and three minus signs occurring alternately, thus in this case, it is the desired residual distribution. On the contrary, a low R number is of concern, since it has every indication of a patterned distribution of residuals. For example, for the combination of three plus signs and three minus signs, the number of runs $R=2$ would very likely signal that the residuals were assigned on a straight line spanning across the plus and minus regions. Considering this, a guideline has been set up to enhance the analysis of the runs in this study. If the number of runs was greater or equal to the expected value of runs, $R \geq E(R)$, it was concluded that the residuals were randomly distributed. If the number of runs was less than the expected value of runs, $R < E(R)$, the residuals were discriminated as systematically patterned. The specific criteria associated with the grading of a tested mathematical model were the percentage of the mean relative deviation, P, the ratio of randomly distributed residual plots, *R.D.*, standard error, *S.E.*, and the sum of residuals, *Sum*. The P values were assigned into the four categories: i) $P<2$, ii) $2 \leq P<5$, iii) $5 \leq P<10$, iv) $P \geq 10$. The *R.D.* ratio is a ratio of the number of randomly distributed residual plots to the 56 tested isotherms (Table IV). A superior equation will have a high percentage of low *P*, *S.E.*, and *Sum* values and exhibit a great number of randomly distributed residual plots, for all the isotherms involved.

RESULTS AND DISCUSSION

The enhanced Halsey equation

As a result of the curve fitting operations and statistical criterion comparisons, Eq. 6 was found to give the best performance:

$$RH = \exp\left(-\frac{C\,A_1^M}{M^B}\right) \tag{6}$$

where A_1, B, C = constants. This equation resembles the combination of the Bradley equation (Bradley 1936) and Eq. 3.

Performance of Equation 6

The estimated parameters and goodness-of-fit criteria associated with Eq. 6 and Eq. 3 are listed in Table II and Table III, respectively. Equation 6 accurately expressed the majority of canola isotherms of Candle, Tobin, Global, and Westar cultivars. This is indicated by the statistical parameters listed in Table II. The only exception was for the Global canola isotherm at 75°C reported by Otten et al. (1990). In this case, when Eq. 6 was used, the P and *S.E.* values were abnormally high, 10.2 and 1.49, respectively. This might be related to the comment made by Otten et al. (1990) in their paper, that the EMC-ERH data at the relative humidity of 60 and 80% at 75°C were subject to verification. The best-fit model for this case was found to be the Guggenheim-Anderson-de Boer equation, GAB (Anderson 1946; de Boer 1953; Guggenheim 1966). This was concluded after a model search using equations reported by Bradley (1936), Brunauer et al. (1938), Harkins and Jura (1944), Anderson (1946), Hailwood and Horrobin (1946), Oswin (1946), Smith (1947), Halsey (1948), Henderson (1952), Chung and Pfost (1967), Kuhn (1964), Caurie (1970), Mizrahi et al. (1970), and Chen (1971).

As a summary of the performance of Eq. 6, Table IV lists the percentage of the P values which fell into each of the four categories: $P<2$, $2 \leq P<5$, $5 \leq P<10$, $P \geq 10$. The ratio of the number of randomly distributed residual plots over the total of the residual plots involved and the maximum *S.E.* for Eq. 6 are also given. For the purpose of comparison, the same statistical summary for Eq. 3 is also included in Table IV. When Eq. 6 was used, 95% of P values were below 5, and the R.D ratio was 41/56. The maximum standard error, *S.E.*, was below 1 percent.

The small values (usually less than 0.05) of the sum of residuals, *Sum*, shown in Table II indicated that the least square elimination has been done to a very low level. The statistical results in Table IV indicated Eq. 6 described precisely the isotherms of canola.

Comparison between Equation 3 and Equation 6

It is well known that a three-parameter mathematical model such as Eq. 6 can describe the isotherms more closely than a two-parameter model like Eq. 3. The estimated parameters of Eq. 3 and goodness-of-fit criteria for the isotherms of canola cultivar Westar were reported by Yang and Cenkowski (1993), therefore, they are not repeated here. Briefly, the investigation focused on the effect of various pretreatments like drying kinetics (25 vs 50°C drying temperature) and multiple adsorption and desorption cycles on sorption characteristics. After the pretreatments, canola samples were equilibrated at temperatures of 3.5, 25, and 40°C. Table III shows the additional results of the estimated parameters of Eq. 3 and the statistical information for canola cultivar Westar equilibrated at 6.0, 15.0, 35.0 and 45.0°C. Table III also contains the constants for Eq. 3 and the statistical parameters for isotherms of canola cultivars published by other researchers. Comparison of curve fitting results for Eq. 3 and Eq. 6 is summarized in Table IV. When Eq. 6 was used to represent the EMC-ERH data, the number of P values in the category of $P<2$ increased by 21% and simultaneously decreased by 20% in the category $5 \leq P<10$. The *R.D.* Ratio increased by 27% when Eq. 6 was applied. A slight increase of 1% for P values in the category of $P \geq 10$ was encountered with Eq. 6. This increase was caused by the 75°C isotherm data of canola cultivar Global reported by Otten et al. (1990). It seems that the greatest enhancement when applying Eq. 6 over Eq. 3 was placed in the categories of $P<2$ and $5 \leq P<10$.

Table II: Estimated parameters and goodness-of-fit criteria for Eq. 6 as fitted to the 56 isotherms from different

Investigator	A/D Cycle[1]	Fit constants			Statistical parameters			
		A_1	B	C	P^2	S.E.(%)[3]	Sum[4]	Residual[5]
		Treatment A[6] - Westar, Isotherm 3.5°C						
Yang and Cenkowski 1993	A1	1.0353	2.1900	45.763	3.49	0.82	0.033	R.D.
	D1	1.0089	2.0583	51.081	4.72	1.09	0.058	S.P.
	A3	1.0948	2.8104	75.897	3.07	0.66	0.038	R.D.
	D3	1.0556	2.4947	77.224	2.68	0.42	0.034	R.D.
	A5	1.0592	2.2648	38.872	0.69	0.43	0.007	R.D.
	D5	1.0358	2.1510	42.414	2.06	0.47	0.023	R.D.
		Treatment A[6] - Westar, Isotherm 25°C						
	A1	1.6237	5.4961	999.88	2.36	0.45	0.025	R.D.*
	D1	1.5684	5.3260	1023.80	5.43	0.82	0.045	R.D.
	A2	1.2621	3.4273	102.28	2.31	0.41	0.023	R.D.
	D2	1.2224	3.3560	123.12	2.13	0.37	0.020	R.D.
	A3	1.3877	4.2017	243.34	4.75	0.69	0.038	S.P.**
	D3	1.3337	4.0308	250.76	2.67	0.44	0.024	R.D.
	A4	1.2648	3.6176	150.82	3.20	0.42	0.023	R.D.
	D4	1.2346	3.4852	146.34	0.79	0.20	0.011	R.D.
	A5	1.3148	3.6996	126.81	5.28	0.79	0.043	S.P.
	D5	1.2938	3.6836	148.32	3.88	0.64	0.035	R.D.
		Treatment A[6] - Westar, Isotherm 40°C						
	A1	1.1642	2.7211	42.847	2.27	0.52	0.008	R.D.
	D1	1.1357	2.4905	33.461	1.34	0.36	0.012	R.D.
	A3	1.1146	2.2347	22.147	3.88	0.64	0.011	S.P.
	D3	1.1139	2.2367	23.205	0.85	0.26	0.018	R.D.
	A5	1.0570	1.9919	19.975	0.81	0.21	0.028	R.D.
	D5	1.0361	1.8312	17.121	1.12	0.32	0.020	R.D.
		Treatment B[6] - Westar, Isotherm 25°C						
	A1	1.2228	2.4253	31.716	2.72	0.73	0.047	S.P.
	D1	1.1554	2.9932	97.146	0.66	0.21	0.014	R.D.
	A2	1.2655	3.3846	90.628	0.98	0.29	0.016	R.D.
	D2	1.2734	3.8842	280.71	0.88	0.24	0.013	R.D.
	A3	1.1259	2.5754	45.683	1.08	0.29	0.022	R.D.
	D3	1.2205	3.5902	221.24	1.45	0.37	0.028	R.D.
	A5	1.1906	2.9957	68.675	0.86	0.23	0.013	R.D.
	D5	1.3304	4.2369	412.83	0.88	0.25	0.014	R.D.

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Table II: Continued

Investigator	A/D Cycle[1]	Fit constants			Statistical parameters			
		A_1	B	C	P[2]	S.E.(%)[3]	Sum[4]	Residual[5]
This study				Westar, Isotherm 6°C				
	A1	0.9908	2.1509	39.142	1.97	0.74	0.050	S.P.
	D1	1.1640	3.9531	533.45	2.59	0.92	0.032	S.P.
				Westar, Isotherm 15°C				
	A1	1.0633	2.4296	48.587	1.89	0.47	0.026	S.P.
	D1	0.7269	-0.5834	2.3017	2.47	0.56	1.162	S.P.
				Westar, Isotherm 35°C				
	A1	1.1838	3.1860	93.213	1.51	0.39	0.021	R.D.
	D1	1.1990	3.4266	146.64	1.99	0.50	0.027	R.D.
				Westar, Isotherm 45°C				
	A1	1.1175	2.2611	21.686	0.80	0.20	0.013	R.D.
	D1	1.0695	1.8984	15.022	1.22	0.26	0.017	R.D.
Pixton and Henderson 1981				Candle, Isotherm 5°C				
	A1	1.0224	2.0276	28.483	0.09	0.04	0.003	R.D.
	D1	1.0328	2.2693	47.488	0.20	0.07	0.004	R.D.
				Candle, Isotherm 15°C				
	A1	1.0114	1.8872	22.150	0.18	0.08	0.005	R.D.
	D1	0.9722	1.5403	16.028	1.62	0.36	0.027	S.P.
				Candle, Isotherm 25°C				
	A1	1.0107	1.8609	20.108	0.18	0.08	0.005	R.D.
	D1	0.9850	1.6323	16.152	1.14	0.26	0.020	S.P.
				Candle, Isotherm 35°C				
	A1	1.0173	1.9119	20.010	0.24	0.09	0.006	R.D.
	D1	0.9943	1.6685	14.852	0.55	0.14	0.010	S.P.
Sokhansanj et al. 1986	N/A			Tobin[7], Isotherm 5°C				
		0.9907	1.8311	33.257	2.30	0.51	0.028	S.P.
				Tobin[7], Isotherm 10°C				
		0.9364	1.1154	9.6936	2.17	0.74	0.041	R.D.
				Tobin[7], Isotherm 15°C				
		0.9735	1.4724	16.080	3.72	0.87	0.048	S.P.
				Tobin[7], Isotherm 20°C				
		0.9398	1.1219	9.5932	1.68	0.60	0.033	R.D.
				Tobin[7], Isotherm 25°C				
		1.0473	2.4758	61.797	0.23	0.12	0.005	R.D.

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Table II: Continued

Investigator	A/D Cycle[1]	Fit constants			Statistical parameters			
		A_1	B	C	P[2]	S.E.(%)[3]	Sum[4]	Residual[5]
				Global[7], Isotherm 25°C				
Otten et al. 1990	N/A	0.8792	0.9740	13.667	2.21	0.40	0.014	R.D.
				Global[7], Isotherm 50°C				
		0.9689	1.3525	10.342	3.32	0.52	0.018	R.D.
				Global[7], Isotherm 75°C				
		1.1119	1.8034	6.5356	10.2	1.49	0.052	R.D.
				Westar, Isotherm 25°C				
Bielewicz et al. 1993	A1	1.0900	1.9482	13.749	4.41	0.51	0.06	R.D.
	D1	1.1976	3.0042	65.902	4.27	0.60	0.07	S.P.

A/D cycles Adsorption - Desorption cycles
* Randomly distributed
** Systematically patterned
[1] Adsorption/Desorption cycle: A1 = first adsorption cycle, D3 = third desorption cycle, etc.
[2] Mean relative percentage deviation
[3] Standard error of the estimated value
[4] Root sum of residuals
[5] Behavior of residual plot
[6] Treatment A - kernels were successively rewetted and dried at 25°C prior to the EMC tests
Treatment B - kernels were successively rewetted and dried at 50°C prior to the EMC tests, Yang and Cenkowski (1993)
[7] Isotherms consisted of the mixture of adsorption and desorption EMC data

Equation 6 was especially advantageous over Eq. 3 in expressing canola isotherms of canola exposed to multiple drying and rewetting cycles. This was manifested by the P values for the first A-D cycle in comparison with the third or fifth A/D cycle (Table II). The percentage of *P* values for the category $5 \leq P < 10$ decreased to about 7% for the isotherm of the fifth A/D cycle. The percentage of *P* values in the category $P < 2$ increased from 30 to 43%, while in the category $2 \leq P < 5$ a small change from 43% to 46% occurred.

When Eq. 3 was used to describe isotherms of canola exposed to successive adsorption and desorption cycles, about 27% of $P < 2$ values (a total of 30 isotherms) fell into the category of $2 \leq P < 5$.

In many cases, constant A_1 in Eq. 6 was close to unity. This would make Eq. 6 similar in its form to Eq. 3. Deviation of constant A_1 from unity allowed the curve obtained by Eq. 6 to be more representative of the measured data. For example, constant A_1 was 1.6327 for the Westar canola cultivar isotherm at 25.0°C on the first drying-rewetting cycle (Table V), and the *P*, *S.E.* and *Sum* values for Eq. 6 were 2.36, 0.45% and 0.025, respectively. When Eq. 3 was used to describe the same set of data, the *P*, *S.E.*, and *Sum* values were 8.86, 1.34% and 0.066, respectively. The difference was further depicted in Fig. 1 where the regression curve for Eq. 6 is very close to the experimental data. Based on the "runs" guideline, systematically patterned residual plots existed for Eq. 3. The residuals for Eq. 6 were randomized. The residual magnitude at each point was much smaller for Eq. 6 than for Eq. 3 (Fig. 1).

The disadvantage of Eq. 6 is its form does not allow it to be transformed easily. This might be inconvenient in the case where an analytical solution necessitates the exact expression

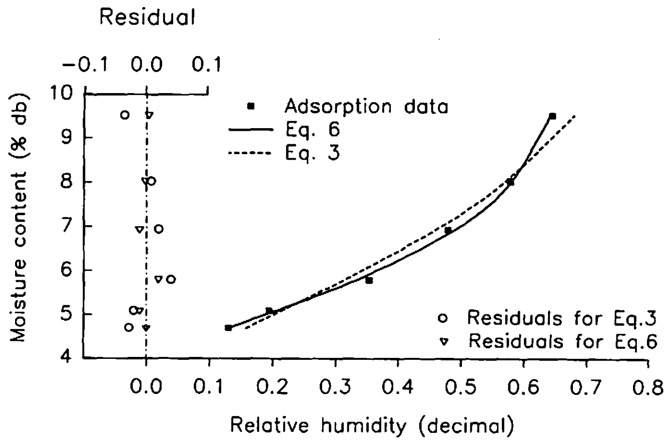

Fig. 1. Performance of Eq. 3 and Eq. 6 as applied to the adsorption isotherm of canola cultivar Westar at 25°C on the first drying-rewetting cycle based on data reported by Yang and Cenkowski (1993).

Table III: Estimated parameters and goodness-of-fit criteria for Eq. 3 as fitted to the isotherms measured in this study and from other sources

Investigator	A/D Cycle[1]	Fit Constants		Statistical parameters			
		B	C	P	S.E.(%)[3]	Sum	Residual
				Westar, Isotherm 6°C			
This study	A1[1]	2.2152	41.487	3.88	1.45	0.050	R.D.
	D1[2]	2.8702	202.94	2.80	1.10	0.037	S.P.
				Westar, Isotherm 15°C			
	A1	1.9551	30.072	1.99	0.48	0.026	R.D.
	D1	1.9264	30.938	3.39	0.73	0.040	R.D.
				Westar, Isotherm 35°C			
	A1	2.0046	31.516	3.72	0.76	0.042	S.P.
	D1	2.1127	41.867	4.02	0.81	0.044	R.D.
				Westar, Isotherm 45°C			
	A1	1.4759	10.492	1.30	0.30	0.019	R.D.
	D1	1.4168	9.5721	1.37	0.29	0.019	R.D.
				Candle, Isotherm 5°C			
Henderson and Pixton 1981	A1	1.7920	20.997	0.40	0.14	0.009	S.P.
	D1	1.9286	30.618	0.59	0.20	0.013	S.P.
				Candle, Isotherm 15°C			
	A1	1.7665	18.953	0.22	0.10	0.006	S.P.
	D1	1.7828	20.666	2.12	0.42	0.032	S.P.
				Candle, Isotherm 35°C			
	A1	1.7302	15.830	0.33	0.13	0.008	R.D.
	D1	1.7168	15.606	0.58	0.15	0.011	R.D.
				Tobin*, Isotherm 5°C			
Sokhansanj et al. 1986	N/A	1.1914	36.512	2.11	0.51	0.028	R.D.
				Tobin*, Isotherm 10°C			
		1.8010	23.440	2.79	0.83	0.046	R.D.
				Tobin*, Isotherm 15°C			
		1.7067	20.818	3.77	0.89	0.049	S.P.
				Tobin*, Isotherm 20°C			
		1.6744	17.572	2.45	0.76	0.042	R.D.
				Tobin*, Isotherm 25°C			
		2.0421	36.842	0.65	0.26	0.012	R.D.

CONTINUED

Table III: Continued

Investigator	A/D Cycle[1]	Fit Constants B	Fit Constants C	Statistical parameters P	S.E.(%)[3]	Sum	Residual
				Global*, Isotherm 25°C			
		1.9657	35.649	6.09	1.27	0.045	S.P.
				Global*, Isotherm 50°C			
Otten et al. 1990	N/A	1.5571	12.095	5.02	0.63	0.022	S.P.
				Global*, Isotherm 75°C			
		1.2227	4.7669	7.81	2.21	0.077	R.D.
				Westar, A-Sample, Isotherm 25°C			
Bielewicz et al. 1993	A1	1.4087	9.121	4.59	0.61	0.070	S.P.
	D1	1.6963	19.545	6.86	0.79	0.091	S.P.

* Isotherms consisted of the mixture of adsorption and desorption EMC data

[1] First adsorption cycle

[2] First desorption cycle

of EMC with respect to ERH. But if the relationship of ERH versus EMC or its numerical solution is satisfactory, Eq. 6 would be an accurate and comprehensive model for canola isotherms. In practice, it would be at the discretion of the user to decide whether Eq. 3 or Eq. 6 should be used. If a problem requires accuracy in prediction, the three-parameter Eq. 6 would be a better choice. If a problem requires simplicity and reasonable accuracy, Eq. 3 is an adequate option.

Comparison among the Modified-Henderson, Chung, Equation 3, and Equation 6

Performance of the Modified-Henderson equation, Chung equation, Eq. 3, and Eq. 6 was compared based on their statistical results from fitting the 56 isotherms. The temperature terms of the first two equations were simplified by replacing them with constants determined at specific temperatures. Thus, the Modified-Henderson equation (Eq. 1) was altered to:

$$RH = 1 - \exp(-A_1 M^B) \qquad (7)$$

and Chung equation (Eq. 2) was simplified to:

$$RH = \exp[-A_1 \exp(-B\,M)] \qquad (8)$$

where A_1 = constant that replaced the temperature term.

The performance of the Modified-Henderson equation, Chung equation, and Halsey equation, Eq. 3 for the 56 individual isotherms reflected the performance of the three-parameter Modified Henderson, Chung and Halsey equations being at the same temperatures. It was confirmed that the Modified-Henderson and Chung equations were not capable of expressing the majority of the 56 isotherms. To depict the differences among these four equations, the curve fitting results for the desorption isotherm at 15°C reported by Pixton and Henderson (1981), as listed in Table VI, are shown in Fig. 2 as an example. This isotherm was selected simply due to its broad range of relative humidities (21.5 to 91.7%). From both Table VI and Fig. 2, it is clear that the Modified-Henderson and Chung equations did not give a good fit to the isotherm data. They underestimated the isotherm at the relative humidities above 80% and below 40%, whereas, they all overestimated the isotherm between 40% and 80% relative humidities. This also confirmed the conclusion made by Chen and Morey (1989) regarding the poor suitability of the Modified-Henderson and Chung equations for the isotherms of canola.

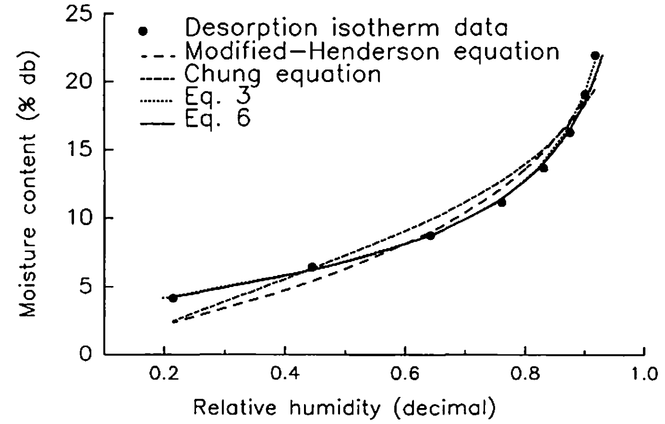

Fig. 2. Goodness-of-fit comparison among Modified-Henderson, Chung, Eq. 3 and Eq. 6 using the desorption isotherm data of canola cultivar Candle at 15°C as reported by Pixton and Henderson (1981).

Table IV: Summary of the performance of Eq. 3 and Eq. 6 as equally applied to the 56 isotherms from different sources

	$P<2$	$2\leq P<5$	$5\leq P<10$	$P\geq 10$	R.D. Ratio*	S.E.
Eq. 3	31%	44%	24%	0%	26/56	≤2.21%
Eq. 6	52%	43%	4%	1%	41/56	≤0.97%

* The number of the isotherms whose residual plots were randomly distributed over the 56 isotherms tested

Table V: Performance of Eq. 3 and Eq. 6 as applied to the adsorption isotherm of Westar canola at 25°C on the first drying-rewetting cycle obtained by Yang and Cenkowski (1993)

	A_1	B	C	P	S.E. (%)	Sum	Residual
Eq. 3		2.2097	51.213	8.86	1.34	0.066	S.P.
Eq. 6	1.6327	5.4961	999.88	2.36	0.45	0.025	R.D.

Both Eq. 3 and Eq. 6 were very representative of the experimental data throughout the whole relative humidity range involved in the above described case. The residual plots for the four models are shown in Fig. 3. The residual plots for the Modified-Henderson and Chung equations were alike and clearly patterned. The residual plots for Eq. 3 and Eq. 6 were also similar to each other and unfortunately patterned as well in this particular case. They had, however, a much smaller residual magnitude than the Modified-Henderson equation or Chung equations.

Equation 6 is the only equation among the others tested in this study that is capable of describing canola isotherms accurately, this is especially true for samples exposed to cyclic drying and rewetting treatment. In spite of the fact, that there were 15 out 56 isotherms that did not show R.D. pattern in their residual plots, Eq. 6 would still be considered the best performing model. Equation 6 gave very small *P* and *Sum* values (Table VI) which are far more important factors in assessing a model than residual behaviour. Supporting the above statement, Wallach and Goffinet (1989) recommended mean squared error as a single criterion for evaluating and comparing models.

Dependency on equilibrium temperature and drying-rewetting cycles

Constants A_1, B and C of Eq. 6; and B and C of the Halsey equation were found to be dependent on equilibrium temperature and the number of drying and rewetting cycles to which a sample was exposed. The dependency of constant C on these factors was much higher than the dependency of constants A_1 or B. To simplify the problem, only constant C was examined for its temperature dependence for canola samples exposed to the multiple drying and rewetting cycles. The analysis was conducted for both adsorption and desorption isotherms. The satisfactory relationship between constant C of Eq. 3 or Eq. 6 and equi-

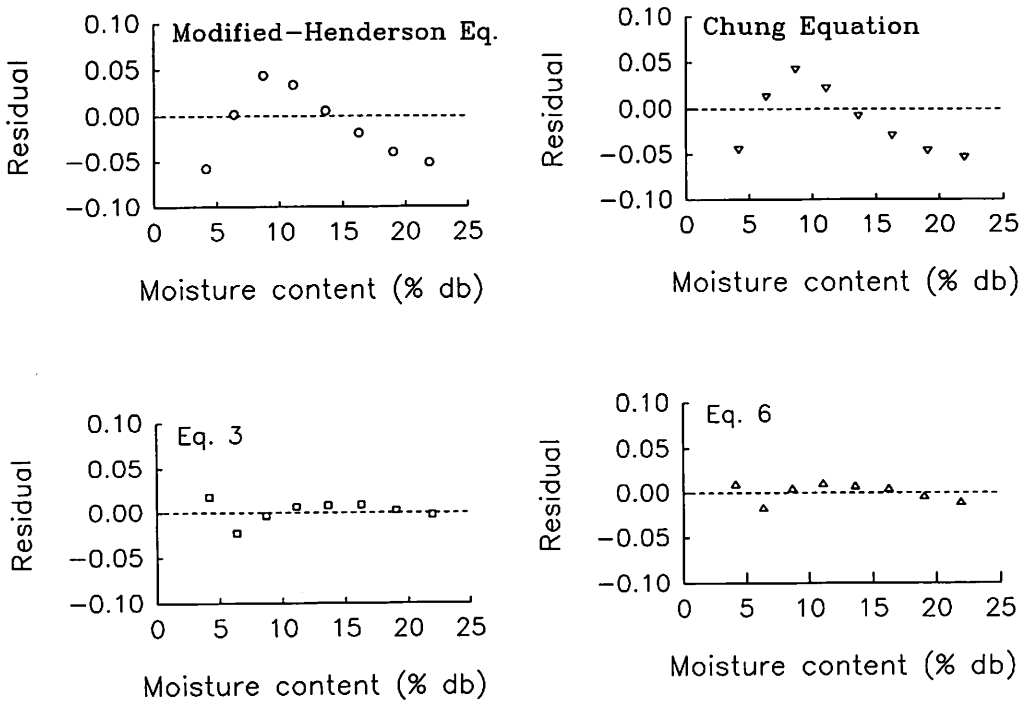

Fig. 3. Residual plots for the Modified-Henderson equation, Chung equation, Eq. 3 and Eq. 6 as applied to the desorption isotherm of Candle canola at 15°C based on data reported by Pixton and Henderson (1981).

Table VI: Curve fitting results for the Modified-Henderson equation (Eq. 7), Chung equation (Eq. 8), Eq. 3 and Eq. 6 with respect to the desorption isotherm of canola cultivar Candle at 15°C reported by Pixton and Henderson (1981)

	A_1	B	C	P	S.E (%)	Sum	Residual
Eq. 7	3.2990	0.2143		6.06	1.28	0.102	S.P.
Eq. 3		1.7828	20.666	2.12	0.42	0.032	S.P.
Eq. 8	0.0411	1.4330		6.40	1.34	0.104	S.P.
Eq. 6	1.5403	0.9722	16.028	1.62	0.36	0.027	S.P.

Table VII: Constants for Eq. 3 and Eq. 6 for the desorption and adsorption isotherms when their constant C is expressed by Eq. 10

	Adsorption		Desorption	
	Eq.6 + Eq.10	Eq.3 + Eq.10	Eq.6 + Eq.10	Eq.3 + Eq.10
A_1	1.0811	-	1.8220	-
B	2.4190	1.8220	2.1964	1.8391
c_1	-0.01173	-0.006614	-0.008036	-0.005623
c_2	0.2724	0.1417	-0.01128	-0.01268
F	49.6473	27.8327	48.6888	33.8938
G	-0.05790	-0.05571	-0.05105	-0.04999

librium temperature, T, was of the form of a quadratic polynomial:

$$C = c_1 \bullet T^2 + c_2 \bullet T + c_3 \qquad (9)$$

where:

T = temperature (°C), and

c_1, c_2, c_3 = constants.

Constants c_1, c_2, and c_3 were further related to the number of adsorption and desorption cycles. It was found that they were equally expressible by an exponential relation to the number of the cycles, but constant c_3 had a higher dependency than the others. Thus, the examination of the multiple drying and rewetting effect was done only for constant c_3 by replacing it with FN^G. Finally, constant C in Eq. 3 and Eq. 6 was expressed as:

$$C = c_1 \bullet T^2 + c_2 \bullet T + F \bullet N^G \qquad (10)$$

where:

N = number of drying and rewetting cycles (up to five), and

F, G = constants.

Table VII lists the constants A_1, B, c_1, c_2, F, and G of Eqs. 6 and 10 and Eqs. 3 and 10. As an example, Figs. 4, 5, and 6 show the goodness-of-fit of Eq. 3 and Eq. 6 when their constant C is replaced by the relationship given by Eq. 10. Some accuracy has been inevitably lost due to the decrease in degrees of freedom resulting from the introduction of more variables into one single model. In general, however, both models fit the experimental data fairly well. Figure 7 and Fig. 8 are the residual plots for Eqs. 3 and 6, respectively, when constant C was expressed by Eq. 10. The analysis was conducted on a model that was exposed to 1 to 5 drying-rewetting cycles and then equilibrated at temperatures between 3.5 and 40°C. It is noticeable that the residuals in Fig. 7 are patterned (R=17, $E(R)$=24.5), while those in Fig. 8 show considerable improvement towards randomized distribution (R=22, $E(R)$=24.5).

As the final stage, the verification of Eq. 6 with its constant C expressed by Eq. 10 against the measured data for the 2nd and 4th A/D cycle and for 25 and 40oC desorption isotherm was conducted. The data selected for verification were not used in the development of Eq. 6 and Eq. 10. As a result, P values ranged from 4 to 8 and S.E. values from 0.01 to 0.03. Figure 9 shows the verification results for the desorption

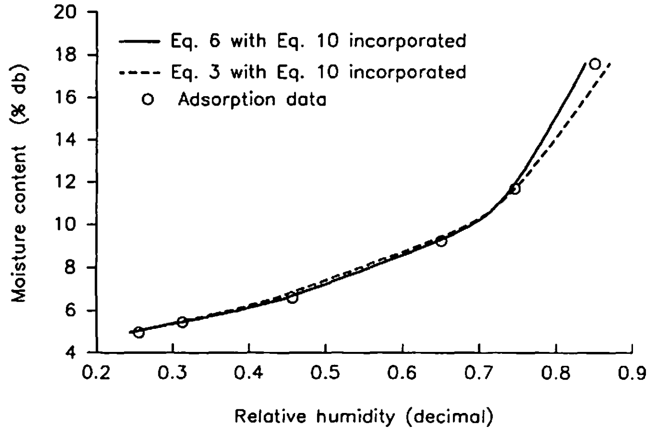

Fig. 4. Goodness-of-fit of Eq. 3 and Eq. 6 to the adsorption isotherm data of canola Westar at 3.5°C on the 5th drying-rewetting cycle when constant C was expressed by Eq. 10.

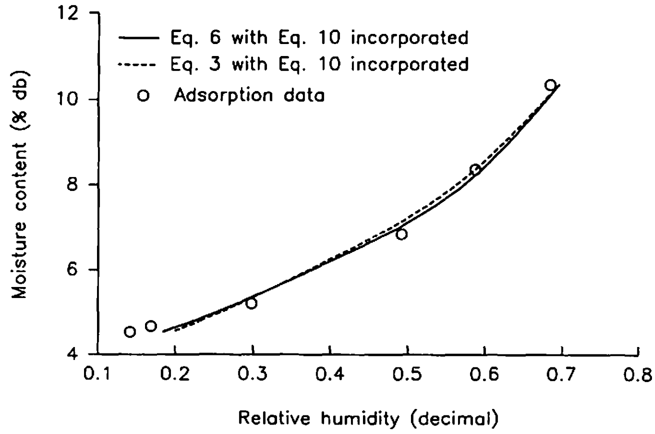

Fig. 5. Goodness-of-fit of Eq. 3 and Eq. 6 to the adsorption isotherm data of canola Westar at 25°C on the 3rd drying-rewetting cycle when constant C was expressed by Eq. 10.

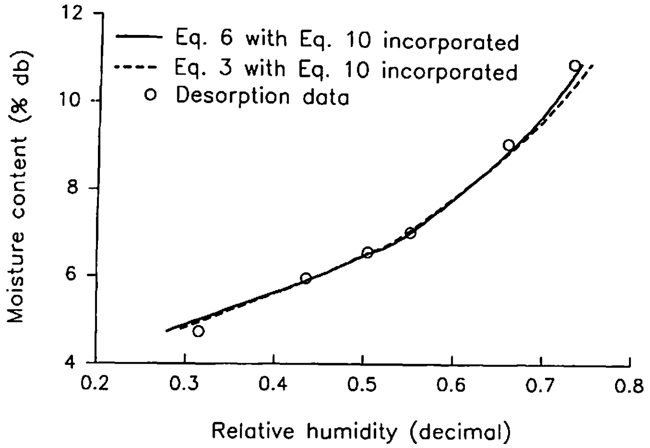

Fig. 6. **Goodness-of-fit of Eq. 3 and Eq. 6 to the desorption isotherm data of canola Westar at 40°C on the 3rd drying-rewetting cycle when constant C was expressed by Eq. 10.**

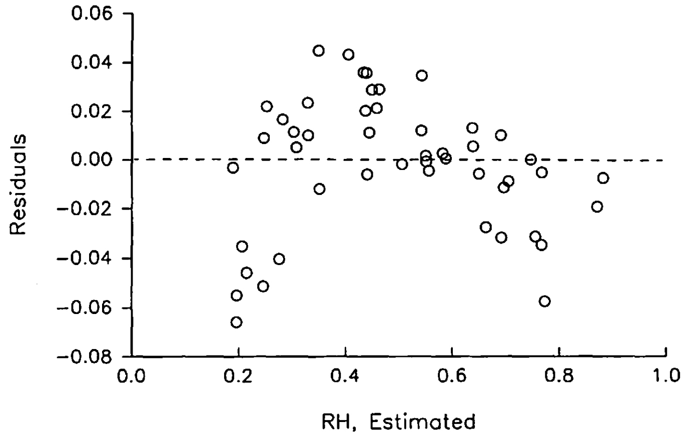

Fig. 7. **Residual plot for Eq. 3 when its constant C was expressed by Eq. 10 as applied to the adsorption isotherms (3.5 to 40°C) of Westar canola on multiple (1 to 5) drying-rewetting cycles.**

isotherm at 25°C after the 4th drying-rewetting cycle. The *P* value in this case is 5.07, and the S.E. value is 0.019. This indicates satisfactory prediction capability of Eq. 6 with Eq. 10 incorporated for the complex pretreatment case.

CONCLUSIONS

The Halsey equation was a marginally good model for describing canola isotherms exposed to drying and rewetting cyles. A new empirical equation proposed in this study showed statistically much better performance than the Halsey equation. The development of the empirical relationship was based on the statistical criteria including the mean relative percentage deviation, standard error, behaviour of residual plots, and the sum of residuals. A total of 56 adsorption and desorption isotherms were analyzed for this purpose. It was also statistically confirmed that the Modified-Henderson and Chung isotherm equations were not suitable for expressing the moisture sorption isotherms of canola. To correlate relative humidity with equilibrium moisture content, temperature, and the number of adsorption-desorption cycles, a six parameter model was proposed. Parameter estimates were given for the EMC-ERH relationship either for individual isotherms or for isotherms when the effects of equilibrium temperature and drying-rewetting cycles were simultaneously considered.

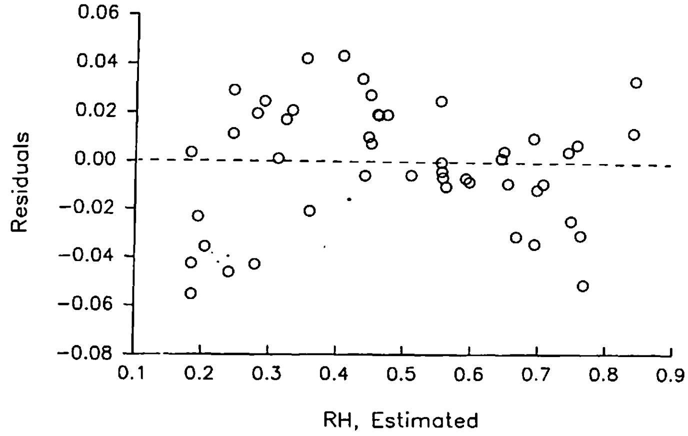

Fig. 8. **Residual plot for Eq. 6 when its constant C was expressed by Eq. 10 as applied to the adsorption isotherms (3.5 to 40°C) of Westar canola on multiple (1 to 5) drying-rewetting cycles.**

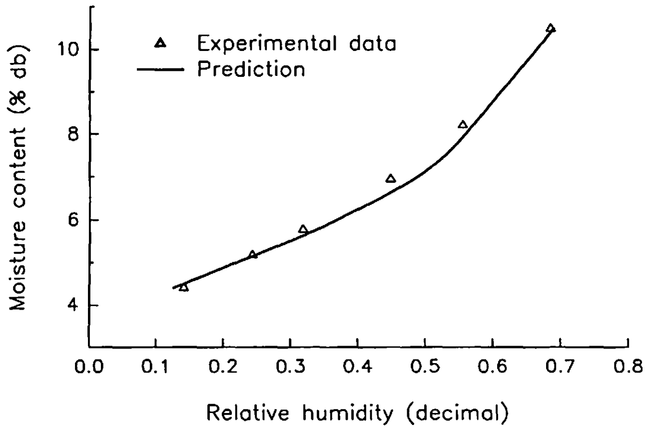

Fig. 9. **Verification of calculation results based on Eq. 6, when constant C was expressed by Eq. 10, against the experimental data. Canola cultivar Westar was exposed to four drying and rewetting cycles and then sorption characteristics were measured at 25°C.**

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