四種農產品平衡相對濕度模式適用性之評估

Evaluation of the Fitting-Agreement Four ERH/EMC Equation on Agricultural Products

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要 要

四個包含溫度項目的平衡相對濕度模式已完成其適用性評估。兩種量化標準和殘差 圖被用以比較上弛模式的合適性。研究結果發現沒有一種模式可適合所有平衡相對濕度 數據。修正漢得生和鐘方程式適用含高澱粉和高纖維的農產品。修正荷西方程式是適用 含高油量和高蛋白質的農產品。修正歐思文方程式可適用於玉米花加工用玉米、玉米粳,帶殼花生與某些品種的玉米和麥類。

ABSTRACT

Four ERH models incorporating temperature terms are evaluated for sorption data of many agricultural products. Two quantitative standards and residual plots are used to compare the fit of these models. The research results indicate that no universal equation could be found to fit all isotherms. The Modified-Henderson and Chung-Pfost equations are good models for most starchy grains and fibrous materials. The Modified-Halsey equation is a good model for products of high oil and protein content. The Modified-Oswin equation could serve as a good model for popcorn, corn cobs, pods of peanut, and some varieties of corn and wheat.

INTRODUCTION

Data relating equilibrium moisture content (EMC) and equilibrium relative humidity (ERH) are necessary to design handling, storing and drying systems for agricultural products.

Many theoretical, semi-theoretical and empirical EMC/ERH models have been proposed for calculating EMC/ERH values of cereal grains and oilseeds. The accuracy of these equations is important for suc-

cessful modeling of processing work. The agreement of these equations for various grains needs to be compared and evaluated.

In this study, the fitting-agreement of four ERH models on sorption isotherm data of agricultural products are compared by two quantitative standards and the residual plots. The results are tabulated and recommended as the standards for modeling sorption isotherm of agricultural products.

LITERATURES REVIEW

Van den Berg (1985) stated the following ideal requirements for EMC equations: (1) the experimental curve should be described mathematically for practical applications such, as drying, packaging, and storing, (2) the equation should have a relatively simple form with a limited number of parameters, (3) the parameters should have a physical significance, (5) the equation should be able to correct for the influence of hysteresis. Based on these criteria, no perfect EMC model eixsts for sorption isotherms of biological materials.

From the review of 23 equations for EMC models, Chriife and Iglesias (1978) found that each model had some success and agreement in reporting the EMC data of a given food and in the given range of relative humidity and temperature. However, the correspondance of the experimental data with the EMC equation calculated for a particular model did not provide enough evidence to validate the theory from which the model was derived. A curve for a set of data may be described by many different equations.

Chirife and Iglesias (1978) summarized the difficulties in finding a unique mathematical model to describe sorption isotherms over the entire range of relative humidity and for different foods. They concluded: (1) the condition of moisture content and equilibrium relative humidity in foods was due to the combination of several factors, each factor dominating for a given range of Aw, (2) the EMC properties of biological materials are integrated from many constituents whose sorption properties may change as a consequence of physical or chemical interaction, and (3) the change of the moisture

content usually changes the constituents, dimensions, and other properties of the material.

Iglesias and Chrifie (1976b) compared the Halsey and the Henderson equations for 220 food isotherms. the average percentage of relative differences between the experimental and calculated values was adopted as the standard of comparison. They found that the Halsey equation had a better fit than the Henderson equation in most cases.

By studying the moisture sorption isotherms for bacon slices, Konstance et al. (1983) developed an empirical equation to fit the data. Coefficient of correlation, R-value, was used to validate the model. After measuring the EMC value of meat emulsion, Mittal and Usborne (1985) modified 11 models by considering the parameters of models as the functions of temperature and fat-protein ratio. The R-value and mean sum of square of residuals were applied to compare these modified models.

Boquet et al. (1978; 1979) used 39 experimental water isotherms to compare two and three parameters models. The value of P, mean relative percentage deviation, was adopted to compare the fitting ability of the different models applied to the same experimental data. From their study, no model was found to fit all the foods.

Adopting a value of P below 5% as the criterion, Iglesias et al. (1983) proposed an empirically developed equation for fitting some uncommon shapes of sorption isotherms for foods.

Lomauro et al. (1985) evaluated the goodness of fit of three two-parameter equations and the GAB equation. An equation having a value of P equal to or less than 5 was considered to represent a

good fit to the sorption data. After evaluating 163 sorption isotherms for 10 kinds of food products, the GAB equation was found to describe sorption isotherms much better than the two-parameter equations. With the same standard, Gencturk et al. (1986) compared the accuracy of the fit for four equations on wild rice isotherms. They found the GAB equation provided an extremely good fit to the experimental data.

Pixton and Howe (1983) used the linear transformation method to convert several sorption curves into straight lines. The deviations between the transformed data and the straight line were selected as the criterion for fitting agreement. The Chung-Pfost equation with two-parameters was found to give satisfactory results for cereal grains. However, this method cannot be applied to a nonlinear equation tht cannot be transformed into a linear type.

Pfost et al. (1976) used a nonlinear regression analysis method to analyze the EMC data. The standard error of estimate was adopted as the criterion to evaluate the fitting performance of the model. Five equations, the Modified-Henderson, Chung-Pfost, Day-Nelson, Chen-Clayton, and Strohman-Yoerger were tested. Comparing the sum of square residual of the EMC data for corn kernels, they found the residuals of four-parameter equations were not significantly lower than those of three-parameter equations and that three parameters were easier to use. The Modified-Henderson and Chung-Pfost equations were selected to find the parameters for other grains. These equations and parameters were adopted as the ASAE Standard (ASAE, ASAE Data D254.4 1983).

Kumar et al. (1978) modified the

Henderson equation by allowing parameters K and N to be linear functions of temperature, thus establishing a four-parameter EMC equation. They then claimed that the value of residual sum of squares (RSS) obtained with their model for the EMC data of intact corn ears and component parts was smaller than those of the Modified-Henderson equation. However, when the degrees of freedom on RSS were taken into account, their proposed model did not show any significant improvement.

Duggal et al. (1982) used EMC data for wheat kernels to study the fit of six isotherm equations. They adopted the standard error of estimate of EMC as the criterion to compare these equations and found the Chung-Pfost equation had the mininum value. The four-parameter equations did not improve the fit over the three-parameter models. In the study of EMC data for winged bean seed, Ajibola (1986) indicated that the Modified-Halsey model gave the best fit of the experimental data. The standard error of estimate of EMC for the model was lower than for four-parameter models.

Flood and White (1984) suggested that the stadard error as a percentage of the mean could be used to compare the relative "goodness-of-fit" for nonlinear regression analysis on popcorn sorption isotherms. They proposed that the Chung-Pfost equation had a lower standard error than the Modified-Henderson equation. In the study of rapeseed, Sokhansanj et al. (1986) suggested that the Modified-Henderson model had a slightly better regression statistic.

Selecting a sorption model for fitting EMC (ERH) data is a difficult problem. Labuza (1968) suggested that the usefulness of a sorption model would depend on

the desired objectives of the user. For example, to predict the drying time, the user is interested in an equation which fits as closely as possible the experimental data, rather than the correctness of the theory. Boquet et al. (1978) noted that another important factor in selecting a sorption model was simplicity which improved the usability in engineering applications.

Comparing the GAB equation and the Chung-Pfost equation, Bakker-Arkema (1986) suggested that a better equation for design purposes was the one that best represented the experimental data over the range of moisture contents and temperature for the situation of interest.

As far as application ERH models is concerned, empirical equations are more precise and convenient than theoretical and semitheoretical relationships, although they provide little insight into the interaction of water and food components. The accuracy of EMC equations is important for successful modeling and optimization of grain-dryer design (Brooker et al. 1974); therefore, criteria used to compare the fitting-agreement deserve more detailed study.

ERH/EMC EQUATIONS

Four empirical equations that incoparating temperature term were selected in the study to fit the ERH data of cereal grains. They are the Modified-Henderson, Chung-Pfost, Modified-Oswin, and Modified-Halsey equations.

Each of these four equations can be solved explicitly for relative humidity as a function of temperature and moisture content, or for mositure content as a function of temperature and RH. In following equations, RH denotes relative humidity, M moisture content on a dry

basis, and T temperature in C, A, B and C are constants.

As ERH data are expressed as a function of temperature and moisture content, these four equations are:

1a. Modified-Henderson equation (Thompson, et, 1968)

$$1-RH = Exp(-A*(T+C)+M^B)--(1)$$

2a. Chung-Pfost equation (Pfost, et, 1976)

3a. Modified-Halsey equation (Iglesias, et, 1976b)

RH = Exp
$$(-Exp(A+B*T)*M^{-C})$$

4a. Modified-Oswin equation (Chen, 1988)

RH =
$$\frac{1.0}{\left[\frac{A + B*T}{M}\right]^{c} + 1}$$
 -----(4)

As EMC data are calculated as the function of temperature and RH, these four equations are:

1b. The Modified-Henderson equation

$$M = \left[\frac{\ln(1-RH)}{-A*(T+c)} \right]^{1/B} ----(5)$$

2. The Chung-Pfost equation

$$M = \frac{\ln A}{B} - \frac{1}{B} * \ln (-(T+C)*_{\ln I})$$
RH) -----(6)

2c. The Modified-Halsey equation

$$M = \frac{(Exp(A+B*T))^{1/C}}{-\ln RH}$$
 ----(7)

2d. The Modified-Oswin Equation

$$M = (A+B*T)*(\frac{RH}{1-RH})^{1/C}$$

A program "NONLIN" based on the least squares method has been written in Fortran M77 language to estimate the parameters for nonlinear regression models with three parameters.

Two four-parameter models also be selected to compare the effect of the parameter number on the fitting-agreement of medium rice. They are:

5. The Day-Nelson equation (Day and Nelson, 1965)

$$1 - RH = Exp(-a*T^b*M^{C*T}^d)-(9)$$

Where a, b, c and d are constants.

6. The Chen-Clayton equation (Chen and Clayton, 1971)

RH = Exp
$$(-a*T^b*Exp$$

 $(-C*T^d*M)$) -----(10)
where a, b, c and d are constants.

DATA COLLECTION

A large number of sorption data of foods and food components was complied by Iglesias and Chirife (1982). The sorption data were collected from a diversity of available sources, most of them scientific and technical journals. Unfortunately, they presented sorption isotherms in plotted form and only at a fixed temperature.

Forty-two sets of sorption data for twnety-one agriculturl products over a wide range of RH value and at several temperatures were collected in the present study (Table 1). Most of the isotherms were constructed from original data. Some of the data were taken from scatterred points on figures.

CRITERIA OF COMPARSION

a. The quantitative standards for comparison

Many quantitative criteria have been proposed to compare the fit of the sorption isotherms to the EMC/ERH models. The definition of these criteria are discussed in this section. In the following equations, Y denotes the measured value, Y' denotes the value predicted by the model, and N denotes the number of data points.

1. R-square

The R-square value (coefficient of determination) is given by,

$$R^2 = 1 - \frac{SSR}{SST}$$
 ----(11)

Where SSR = Residual Sum of Squares. SST = Total Sum of Squares.

If all data fit the regression model, SSR will be zero and the R-square value will be equal to one. This measure is easy to calculate but is usually not a reliable criterion for a proposed model (Weisberg, 1980), since high R-square values can only express the quantitative relationship between the dependent variable and independent variables, but not the deviation of the regression model.

2. Mean relative percentage deviation (P)

$$P = {100 \over N} * \Sigma {|Y - Y'| \over Y}$$
 ----(12)

The value of P reveals the relative errors of the measured value. Larger errors for larger measured data have a smaller effect on the value of P than other

Table 1. Experimental moisture sorption data adopted for comparing the ERH models

	Prodcut	Relative Humidity (%)	Temp.	Spec	cification		Reference
Α.	Starchy grains						
	1. Barley	18-95	5-25	Des.	Hyg.	Ori.	Henderson (1987)
	2. Corn:						
	a.	11-86	4-60	Des.	Gra.	Ori.	Gustafson (1973)
	b.	11-96	10-68	Des.	Gra.	Ori.	Gustafson (1973)
	c.	11-86	20-80	Des.	Gra.	Ori.	Kumar et al. (1978)
	d.	11-98	5-45	Des.	Hyg.	Ori.	Chen (1988)
	3. Ear corn	11-87	20-80	Des.	Gra.	Fig.	Kumar et al. (1978)
	4. Popcorn	19-93	10-50	Des.	Hyg.	Ori.	Flood et al (1984)
	5. Oats	15-92	25-65	Ads.	Gra.	Fig.	Berry et al (1973)
	6. Rough rice:						
	a. Austra. (long)	19-97	10-38	Des.	Hyg.	Ori.	Putranon et al. (1979)
	b. Austra. (short)	15-95	10-38	Des.	Hyg.	Ori.	Putranon et al. (1979)
	c. Calif. (short)	11-88	10-40	Des.	Gra.	Ori.	Zuritz et al. (1979)
	d. Japan. (short)	11-85	20-40	Des.	Gra.	Ori.	Kameoka et al. (1979)
	7. Brown rice	11-85	20-40	Des.	Gra.	Ori.	Kameoka et al. (1986)
	8. Sorghum	2-90	16-49	Des.	Gra.	Ori.	Dunstan et al. (1972)
	9. Wheat:						
	a. Sinton (hard, red)	26-94	5-25	Des.	Hyg.	Ori.	Pixton et al. (1981)
	b. Napaya (Durum)	18-92	5-25	Des.	Hyg.	Ori.	Pixton et al. 91981)
	c. Wakooma	25-95	5-25	Des.	Hyg.	Ori.	Pixton et al. 91981)
	(hard, red)						·
	d. Waldron	11-93	5-45	Des.	Gra.	Fig.	Van den Berg. (1985)
	(hard, red)						
В.	Fibrous materials						
	10. Corn cobs						
	a.	11-87	20-80	Des.	Gra.	Fig.	Kumar et al. (1978)
	b.	29-95	10-50	Des.	Gra.	Ori.	White et al. (1985)
	11. Peanut hull	21-97	10-32	Des.	Gra.	Ori.	Beasley (1962)
	12. Rice bull	11-85	20-40	Des.	Gra.	Ori.	Kameoka et al. (1986)

Table 1. Experimental moisture sorption data adopted for comparing the ERH models (Con.)

Prodcut	Relative Humidity (%)	Temp.	Spec	cification	ı	Reference
C. High protein and	oil products					
13. Edible beans						
a. Red	11-90	21-38	Des.	Gra.	Ori.	Guevara-Guio (1973)
b. Baby Lima	11-90	21-38	Des.	Gra.	Ori.	Guevara-Guio (1973)
c. Pinto	11-90	21-38	Des.	Gra.	Ori.	Guevara-Guio (1973)
d. Black	30-90	10-38	Des.	Gra.	Ori.	Kososki (1977)
e. White	18-90	16-49	Des.	Gra.	Ori.	Otten (1987)
f. Winged	11-82	40-70	Des.	Gra.	Ori.	Ajibola (1986)
14. Peanut pods	21-97	10-32	Des.	Gra.	Ori.	Beasley (1962)
15. Peanut Kerne	ls 21-97	10-32	Des.	Gra.	Ori.	Beasley (1962)
Rapeseed						
a. Candle	21-93	5-35	Des.	Hyg.	Ori.	Pixton et al. (1981)
b. Tower	27-90	5-35	Des.	Hyg.	Ori.	Pixton et al. (1977)
c. Canola	18-90	5-25	Ads.	Hyg.	Ori.	Sokhansanj et al. (1985
17. Canola meal	5-84	10-50	Des.	Hyg.	Ori.	Jayas. (1988)
18. Soybeans						
a. U.S.A	11-90	5-55	Des.	Gra.	Ori.	Alam (1972)
b. England	18-96	15-35	Des.	Hyg.	Ori.	Pixton et al. (1975)
19. Sunflower see	ds 11-90	5-45	Des.	Hyg.	Ori.	Chen (1988)
O. Others						
20. Jew's Ear	11-87	10-36	Des.	Gra.	Ori.	Chang et al. (1983)
21. Jew's Ear	11-87	10-36	Ads.	Gra.	Ori.	Chang et al. (1983)
22. Tea Leaf	11-85	20-50	Des.	Gra.	Ori.	Yoshitomi (1985)
23. Tea Leaf	11-85	20-50	Ads.	Gra.	Ori.	Yoshitomi (1985)
24. Tea stem	11-85	20-50	Des.	Gra.	Ori.	Yoshitomi (1985)
25. Tea stem	11-85	20-50	Ads.	Gra.	Ori.	Yoshitomi (985)
/ Des: desorption	Ads: adso	orption				
Gra: gravimetric	Hyg: hyg	romettic				
Ori: original data	Fig. data	from figu	re			

standards. In contrast, larger errors occurring at lower measured values contribute to a greater increase in the value of P.

3. Other criteria

There are four other criteria, which are related to one another. There are:

(1) Residual sum of Square (RSS)

$$RSS = \Sigma (Y-Y')^2$$
 ----(13)

(2) Mean sum of square of residuals (MSE)

$$MSE = \frac{RSS}{df} \qquad ---- (14)$$

Where df = Degree freedom of RSS

(3) Standard error of estimated value (S.E.)

S.E. =
$$(MSE)^{0.5}$$
 ----(15)

(4) Standard error as a percentage of the mean (SEPM)

SEPM =
$$\frac{S.E.}{(Y)ave}$$
 ----(16)

Where (Y)ave = mean value of dependent variable

It is worth noting that only MSE, S.E., and SEPM values consider the effect of the number of parameters in the regression model. These standards provide a reasonable criteria to compare models with different numbers of parameters for the same sorption data.

For most regression analysis, high R-square values correspond to lower values of the other criteria. But this condition does not hold true for all model evaluation cases. In this study, P and S.E. are adopted

as the quantitative criteria to compare the "fitting-agreement" for four EMC/ERH models for the same sets of isotherm data.

b. The analysis of residual plots

Draper and Smith (1981) devoted a whole section of their text on regression to residual analysis. The analysis is appliable to nonlinear ss well as linear regression models.

The residuals are defined as the N differences, ei = Yi-Y'i, where Yi is an observated value and Y'i is the corresponding value obtained from the regression equation. If the model is correct, only the observed errors exist. These errors are assumed to be independent with a zero mean and constant variance, and to follow a normal distribution. This idea provides a very useful tool to validate a nonlinear regression model.

A model is selected because it can be exected to explain the observed values of the dependent variable in terms of the independent variables. If the model is correct then the residuals should be only due to random errors, for which data points in a plot of the residual values versus the predicted values should tend to fall in a horizontal band centered around zero, displaying no systematic tendencies toward a clear pattern. If the residual plots indicate the failure of the model in explaining the variation of the data, the model should not be accepted.

In this study, the method of examining the distribution of residuals is to plot them vs the predicted values or the independent variables. For four ERH models, RH is selected as the dependent variable with moisture content and temperature as independent variables. The residual verse predicted RH values are plotted to check the residual pattern.

RESULTS AND DISCUSSION

Because sorption isotherms for biological materials represent the integrated hygroscopic properties of their constituents. There were four groups in his study: starchy grains, fibrous materials, high protein and oil products, and others. Partial results are showed detailedly in following.

1. Barley

The parameters and comparison criteria are listed in Table 2. Residual plots for four models are shown in Fig. 1.

Based on the three criteria, the Chung-Pfost equation has the highest R-square value and smallest values of S.E. and P. The normal distribution of residual plot also indicated that the equation is a good choice for fitting sorption isotherm data for barley. The values of P and S.E. for the Modified-Henderson equation are not significantly larger than those for the Chung-Pfost equation. The R-square value for the Modified-Henderson and

Modified-Oswin equations are relative high (0.9971 and 0.9948). Even the Modified-Halsey equation has a relative high R-square value (0.9766). However, the clear patterns displayed in the residual plots for the latter equations indicate that these models do not adequately explain th relation between dependent and independent variables. These comparisons illustrate that quantitative measures alone are not reliable to establish the adequency of it of any models.

2. Corn kernel

Four sets of EMC data from different sources are compared, Table 3.

Comparing the results of three sets of data, the Modified-Halsey equation was found to be a poor model for the corn kernel. Definite patterns exist in the residual plots. The largest values for P and S.E. occur for this model.

The residual plots for both the Modified-Henderson and Chung-Pfost equa-

Table 2. Estimated parameters and criteria for ERH models of barley

	Modified- Henderson	Chung-Pfost	Modified-Oswin	Modified-Halsey
A	3.90687E-5	475.115	14,8317	5.2731
В	1.9793	0.14843	-7.6446E-2	-1.2249E-2
C	79.6867	71.9961	3.0283	2.1224
S.E.	1.629	0.910	2.173	4.610
P.	2.346	1.350	4.202	8.686
R-Squ.	0.9971	0.9991	0.9948	0.9766
Residual	Pattern	U.S.	Pattern	Pattern

Note: U.S.: Uniformly scattered points shown in the residual plot.

Pattern: A systematic pattern shown in the residual plot.

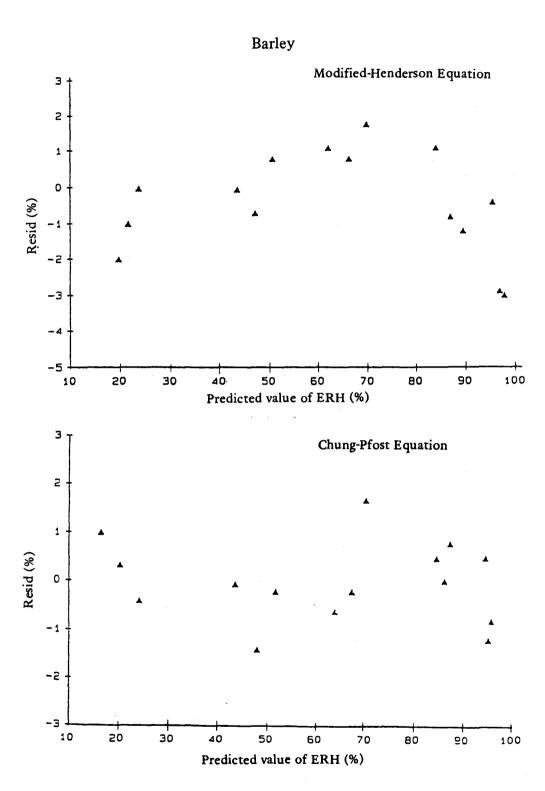


Figure 1a. Residuals vs predicted values of ERH models for barley

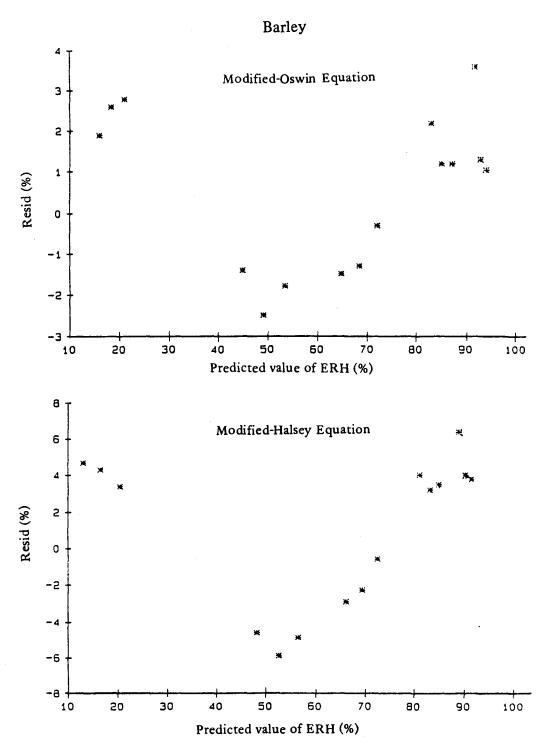


Figure 1b. Reiduals vs predicted values of ERH models for bareley

Table 3. Estimated parameters and criteria for ERH models for yellow dent corn.

	Modified- Henderson	Chung- Pfost	Modified- Oswin	Modified- Halsey
Rodriguez-Arias	s (1965)		· · · · · · · · · · · · · · · · · · ·	
Α	8.8181E-5	341.30	14.6457	5.3918
В	2.0210	0.28713	-9.8022E-2	-1.8902E-2
C	30.9095	27.4531	2.9794	2.1359
S.E.	3.101	3.1207	2.5579	4.2162
P	6.2118	5.6275	6.3638	11.8878
R ²	0.9827	0.9825	0.9883	0.9681
Residual	U.S.	U.S.	U.S.	Pattern
Gustafson (197:	3)			
Α	9.5569E-5	366.55	14.4014	4.8540
В	1.8543	0.1752	-9.4520E-2	-1.549E-2
C	44.2130	35.7580	2.7545	1.960
S.E.	3.8106	2.9263	2.9168	4.321
P	9.0137	6.307	6.576	4.321
R ²	9.0.9831	0.9901	0.9921	0.9784
Residual	U.S.	U.S.	U.S.	Pattern
Kumar et al. (19	978)	,		
Α	5.5831E-5	457.00	15.2843	4.7002
В	2.06651	0.1817	-7.923E-2	-1.3546E-2
C	33.7767	33.6804	2.9054	1.8482
S.E.	3.6950	3.9226	4.0893	6.1849
P	9.1890	9.8276	9.9164	17.253
R ²	0.9830	0.9808	0.9791	0.9522
Residual	U.S.	Pattern	Pattern	Pattern
Chen (1988) —	Variety R			
A	6.6612E-5	374.335	15.3034	5.5386
В	1.96767	0.18662	-0.101836	-1.6850E-2
C	42.1426	31.6956	3.0358	2.1937
S.E.	1.8771	4.9616	2.6924	4.5051
P	2.8690	4.2640	4.7770	9.0050
R ²	0.9953	0.9903	0.9928	0.9727
Residual	U.S.	Pattern	Pattern	Pattern

tions show uniformly scattered data points. For the Modified-Oswin equation, a very definite pattern shows up in the residual plot with data collected by kumar (1974).

For the Rodriguez-Arias and Gustafson data sets, the Modified-Oswin equation had the smallest value of S.E.. However, its value of P was larger than for the Chung-Pfost equation. Therefore, P and S.E. criteria do not always provide the same ranking for all ERH models. These results again point out the inadequancy of quantitative measures as the sole method for evaluting the fit of a model.

The results of the four equations fit to the variety R data of Chen (188) are compared to the experimental data at a 25°C isotherm termperature in Figure 2. The plots demonstrate the lack of fit for the Modified-Oswin and Modified-Halsey equations.

Based on the above comparisons, no ERH model can be recognized as the best ERH model for corn kernel sorption isotherms. Relatively high R-square values can be found for all models on the three sets of data. This fact suggests that R-square is an undependable criterion for evaluation of ERH models.

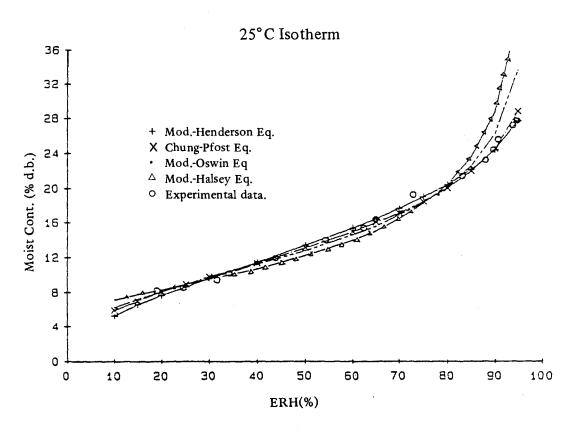


Figure 2. Comparison of the four ERH models at the 25°C isotherm temperature with the Variety R data of Chen (1988).

3. Popcorn

Compared to yellow dent corn, popcorn has higher protein and oil content. The comparisons for four models are shown in Table 4. Only the Modified-Oswin equation had a uniformly scattered residual plot. Other equations showed clear patterns in the residual plots although their values of P and S.E. were not particularly large.

Three ERH models are plotted with the experimental data in Fig. 3. They indicate that only the Modified-Oswin equation is good model.

4. Rough rice

Six ERH models were compared for the desorption data of rough rice (California, medium). The results are shown in Table 5. As a four-parameter model, the Day-Nelson equation has smaller values for S.E. and P than the Modified-Henderson equation. Compared to the Chung-Pfost equation, the Chen-Clayton equation does not have significant improvement, even though the value of P is larger than that of the Chung-Pfost equation. For the residual plots, similar residual patterns are found, respectively, for the Modified-Henderson and DayNelson equations, for the Chung-Pfost equation and Chen-Clayton equations. The reason is that each pair of equations are derived from the same original equations.

Although the Modified-Oswin equation does not have significantly larger values of P and S.E., its residual plot exhibits a clear pattern, therefore, it is not a good model for medium rice.

Table 6 shows the results of model evaluation of four ERH equations for three other varieties. The Modified-Henderson and Chung-Pfost equations can be recognized as good models for rough rice, but neither of them always has the smallest values for S.E. and P. The Modified-Oswin equation is not a good model for the short variety from Australia based on its clear residual pattern.

The Modified-Halsey equation was always found to be an inadequate model for all sorption isotherms of rough rice.

5. Rice hull

Table 7 shows the results of the comparison for four models. The Modified-Henderson equation is a good ERH model for rice hull. Although the residual plot of the Chung-Pfost equation does not have a clear pattern as those of

Table 4. Estimated	parameters and	criteria for	ERH mod	els of	popcorn

	Modified- Henderson	Chung- Pfost	Modified- Oswin	Modified- Halsey
A	1.54520E-4	283.93	13.8135	4.8296
B.	1.59933	0.14820	-8.23122E-2	-1.4897E-2
C	61.1665	44.4600	2.6189	1.9847
S.E.	3.029	2.558	1.0894	1.9607
P	4.625	3.5817	1.4870	3.3062
Resid.	Pattern	Pattern	U.S.	Pattern

Table 5. Estimated parameters and criteria for ERH models of rough rice (California, medium)

	Modified- Henderson	Day- Nelson	Chung- Pfost	Chen- Clayton	Modi Oswin	Modi Halsey
A(a)	3.5502E-5	-5.9672E-57	363.06	-3.8837E-9	15.6744	5.9061
B(b)	2.30997	21.597	0.1804	-3.5249	-0.1137	-1.962E-2
C(c)	27.3961	2.75096E-6	26.674	-1.1205E-4	3.3249	2.2888
D(d)		2.4535		1.3005		
S.E.	1.9623	1.4165	1.7827	1.6282	2.064	4.284
P	5.1875	2.9450	4.0390	4.22632	5.892	13.846
Resid.	U.S.	U.S.	U.S.	U.S.	Pattern	Pattern

Note: a, b, c, and d are constants of four-parameter models

the Chung-Pfost equation does not have a clear pattern as those of the Modified-Oswin and Modified-Halsey equation, the residuals do not have a constant variance, resulting in larger values of P and S.E..

6. Beans

Six different varieties of beans are compared. Representative residual plots of red beans are shown in Fig. 3. Only the Modified-Halsey equation exhibits uniformly scattered data points in the residual plot. All other equations have a clear pattern. For the black beans, the value S.E. for the Modified-Oswin equation is smaller than that of the Modified-Halsey equation, but a clear pattern in the residual plots indicated the inadequacy of this equation.

7. Soybeans

Two sorption isotherms of soybeans (U.S.A. and England) are compared in Table 8. Only the Modified-Halsey equa-

tion can be accepted as a good model for this product. A clear pattern in the residuals plot is found for other equations.

Three ERH models are plotted, along with the experimental data of U.S.A. tion can be accepted as a good model for this product. A clear pattern in the residuals plot is found for other equations.

Three ERH models are plotted, along with the experimental data of U.S.A. soyybeans, in Fig. 4. The Modified-Halsey equation is good, but the Chung-Pfost and Modified-Henderson equations have serious discrepancies at low and high RH values.

EVALUATION OF ERH/EMC MODELS

The RH models found suitable for various cereal grains and seeds are summaried in Table 9. The constants and

Table 6. Estimated parameters and criteria for ERH models of rough rice (long and short)

	Mofiied- Henderson	Chung- Pfost	Modified- Oswin	Modified- Halsey
1. Austr. sh	ort	·		
Α	3.43820E-5	494.091	14.6362	5.3873
В	2.1305	0.16652	-7.2849E-2	-1.2160E-2
C	59.5350	57.3831	3.09302	2.1592
S.E.	1.6334	1.7739	2.7867	4.3355
P	3.2448	3.3275	4.7952	8.0061
Resid.	U.S.	U.S.	Pattern	Pattern
2. Austr. lo	ng			
Α	4.12764E-5	412.015	14.4309	5.5991
В	2.1191	0.17528	-7.866E-2	-1.513E-2
C	49.8281	39.016	3.13695	2.2445
S.E.	2.3856	1.8986	2.9618	4.2235
P	4.9053	3.5752	5.7785	7.1894
Resid.	U.S.	U.S.	U.S.	Pattern
3. Japan, sh	ort			
A	4.8542E-5	433.876	14.8156	4.5865
В	2.0794	0.1686	-8.7027E-2	-1.3541E-2
C	45.6458	48.2820	2.8368	1.8361
S.E.	1.8470	1.9204	2.2815	4.1514
P	3.4238	3.7811	5.2987	11.868
Resid.	U.S.	U.S.	U.S.	Pattern

Table 7. Estimated parameters and criteria for ERH models of rice hull

	Modified- Henderson	Chung- Pfsot	Modified- Oswin	Modified- Halsey
A	1.44493E-5	285.443	12.6440	4.3658
В	1.94667	0.19738	-9.42097 - 2	-1.8064E-2
C	24.2644	27.7329	2.74652	1.86055
S.E.	0.8817	1.6936	2.1133	4.1985
P	1.753	4.195	5.1315	11.160
Resid.	U.S.	U.S.	Pattern	Pattern

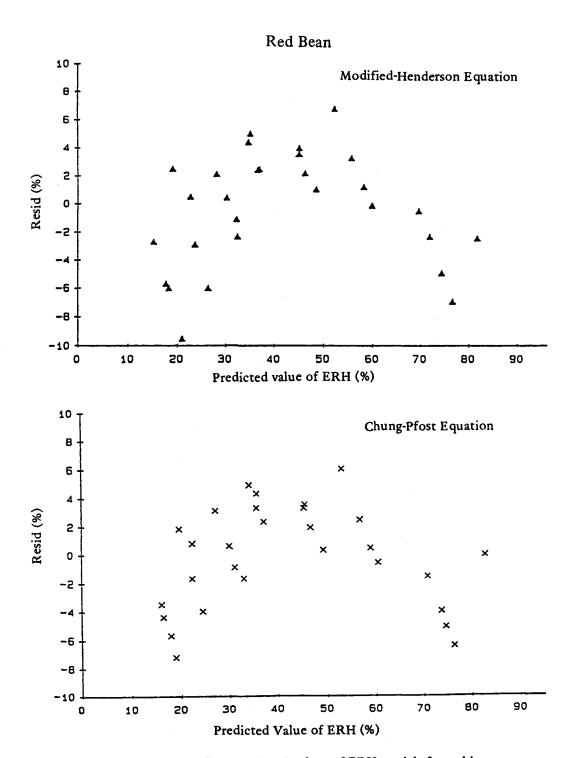


Figure 3a. Residuals vs predicted values of ERH models for red beans

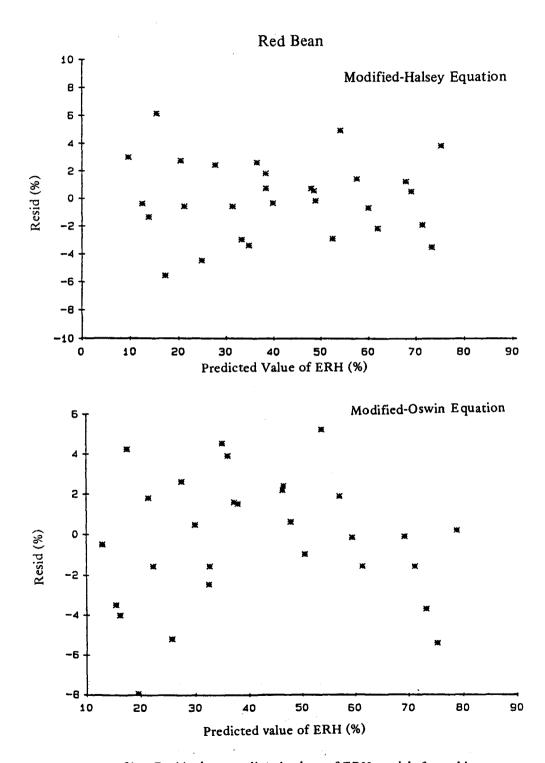


Figure 3b. Residuals vs predicted values of ERH models for red beans

Table 8. Estimated parameters and criteria for ERH models of soybeans

	Moified- Henderson	Chung- Pfost	Modified- Oswin	Modified- Halsey
1. Adam (U.	S.A)			
Α	2.31460E-4	394.920	10.91237	3.3109
В	1.4377	0.166236	-6.1544E-2	-1.16352E-2
C	89.7547	88.3295	2.15367	1.543065
S.E.	5.0731	5.0463	3.5513	2.9023
P	14.614	14.335	9.6895	8.2378
Resid.	Pattern	Pattern	Pattern	U.S.
2. Pixton et	al. (England)			
Α	1.95471E-4	453.326	9.4444	3.0446
В	1.2575	0.1425	-3.06379E-2	-5.4321E-3
C	207.374	161.207	1.97943	1.52446
S.E.	2.4359	2.7029	1.3243	0.5868
P	3.7325	4.084	2.0174	0.8690
Resid.	Pattern	Pattern	Pattern	U.S.

values of S.E. and P for acceptable models are summaried in Table 10.

The Modified-Henderson and Chung-Pfost equation are suitable for most starchy grains and high fiber materials. It may be the reason that both equations are adopted in the ASAE Standards. The Modified-Halsey equation is not a good model for these products except for one sorption isotherm of corn cobs. The newly developed Modified-Oswin equation can serve as an excellent model for popcorn, corn cobs, and some varieties of corn kernel and wheat.

For the high protein and oil products, the Modified-Halsey equation is a good model except for the sorption isotherms of whole pods of peanut. However, the Modified-Oswin equation can be applied to this product, and to peanut kernel and one variety of rapeseed. The popular Modified-Henderson and Chung-Pfost equation, were both found to have the clear patterns in the residual plots and relatively large values of P and S.E for all high oil and protein products. This result suggests that some parts of the ASAE Standard need to be revised.

For many products, the model that had the smallest value of P usually also had the smallest value of S.E. and a residual plot of uniformly scattered points. But this condition did not hold true for all products. Therefore, it was necessary to evaluate the fit of the ERH models by both quantitative measurement and observation of the residual plots.

In some cases the sorption isotherm data be fit by more than one ERH model. For starchy grains, no ERH model was sutiable for sorption isohterms for all grains and varieties. Therefore, no ERH

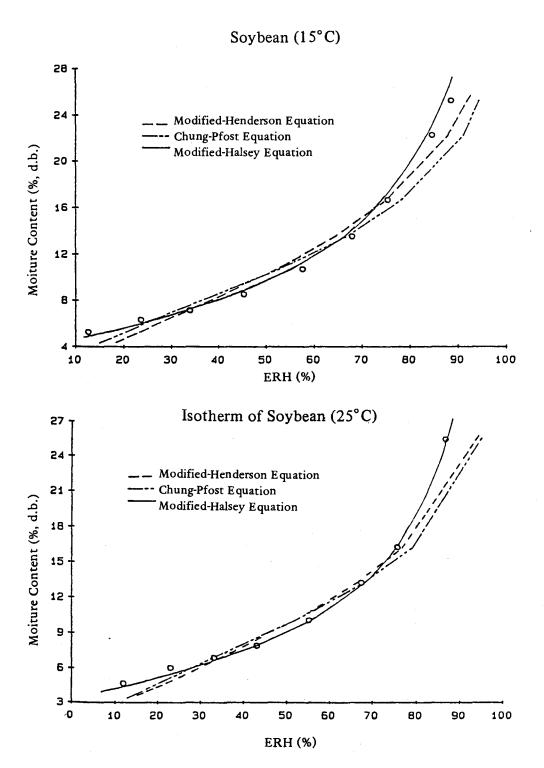


Figure 4. Comparing the experimental EMC data of Soybeans and three ERH models

Table 9. Summary of comparisons for the four models for data sets defined in Table 1.

Product/Variety		Modified- Henderson	Chung- Pfost	Modified- Oswin	Modified- Halsey
<u> —</u> А.	Starchy grains			<u></u>	
	1. Barley		*2/		
	2. Corn				
	a. (Rodriguez)1/	*	*	*	
	b. (Gustafson)	*	*	*	
	c. (Kumar et al.)	**3/	*		
	d. (Chen)	*			
	3. Ear corn	**	*		
	4. Popcorn			*	
	5. Oats	*	**	*	
	6. Rough rice:				
	a. Calif.	*	**		
	b. Austr. (short)	**	*		
	c. Austr. (long)	*	**	*	
	d. Japan	**	*	*	
	7. Brown rice	*			
	8. Sorghum		*		
	9. Wheat:				
	a. Napayo			*	
	b. Wakooma			*	
	c. Sinton		*		
	d. Waldron	*	*	**	
3.	Fibrous materials				
	10. Corn cobs				
	a. (White et al)			*	*
	b. (Kumar et al)			*	
	11. Peanut hull	**	*	•	
	12. Rice hull	**	*		
Ξ.	High protein and oil products				
	13. Edible beans				*
	a. Red				*
	b. Baby Lima				*
	c. Pinto				*
	d. Black				*
	e. White				*
	f. Winged				*

Table 9. Summary of comparisons for the four models for data sets defined in Table 1. (Cont.)

Product/Variety	Modified- Henderson	Chung- Pfost	Modified- Oswin	Modified- Halsey	
14. Whole pods of peanut			*		
15. Peanut kernel			*	*	
16. Rapeseed					
a. Candle				*	
b. Tower				*	
c. Canola			*	**	
17. Canola meal			*	**	
18. Soybeans					
a. U.S.A.				*	
b. England				*	
19. Sunflower seeds				*	
D. Others					
20. Jew's Ear (Des)	*	**	*		
21. Jew's Ear (Ads)	**	*	*		
22. Tea Leaf (Des)				*	
23. Tea leaf (Ads)				*	
24. Tea stem (Des)				*	
25. Tea stem (Ads)				*	

^{1/} If no variety was indicated, data set was defined by researcher's in parentheses.

^{2/} Asterisk (*) indicates that the model was acceptable based on a criterion of uniformly scattered residuals.

^{3/} Double asterisk (**) indicates that the model was acceptable and had the smallest values of S.E. and P compared to the other models.

Table 10. Parameters and values of S.E. and P for models defined as acceptable to fit the data sets defined in Table 1.

	TO = 1					
	Product/Variety	Α	В	C	S.E.	P
<u>-</u> А.	Starchy grains		· · · · · · · · · · · · · · · · · · ·			
	1. Barley					
	Chung-Pfost	475.155	0.14843	71.9961	0.910	1.350
	2. Corn (see Table 3)					
	3. Ear corn					
	Mod.—Henderson	6.4424E-5	2.0855	22.1501	4.158	9.753
	Chung-Pfost	447.051	0.1872	30.4450	4.717	11.99
	Mod.—Oswin	15.30624	-8.4674E-2	2.9764	4.564	11.63
	4. Popcorn					
	Mod.—Oswin	13.8135	-8.2312E-2	6.6189	1.089	1.487
	5. Oats					
	Mod.—Henderson	8.5511E-5	2.00873	37.8111	2.546	5.124
	Chung-Pfost	442.85	0.21228	35.8082	2.022	3.776
	Mod.—Oswin	12.41242	-6.0707E-2	2.9397	2.335	4.928
	6. Rough rice:					
	a. Calif.					
	Mod.—Henderson	3.5502E-5	2.30997	27.3961	1.962	5.188
	Chung-Pfost	363.06	0.1804	26.674	1.783	4.039
	b. Austr. (short)					
	Mod.—Henderson	3.4382E-5	2.1305	59.535	1.633	3.245
	Chung—Pfost	494.091	0.16665	57.3832	1.774	3.328
	c. Austr. (long)					
	Mod.—Henderson	4.1276E-5	2.1191	49.8281	2.386	4.905
	Chung-Pfost	412.015	0.17528	39.016	1.899	3.575
	Mod.—Oswin	14.4309	-7.866E-2	3.13695	2.962	5.779
	d. Japan					
	ModHenderson	4.8524E-5	2.0794	45.6458	1.847	3.424
	Chung-Pfost	433.876	0.1686	48.2820	1.920	3.781
	Mod.—Oswin	14.8156	-8.7027E-2	2.8368	2.828	5.299
	7. Brown rice					
	Mod.—Henderson	3.2301E-5	2.2482	34.2673	0.901	1.911
	8. Sorghum					
	Chung-pfost	797.333	0.18159	52.2375	1.373	2.485
	9. Wheat:	. ,	0.10107	52.25 15	1.575	2.403
	a. Napayo					
	Mod.—Oswin	14.7356	-5.4590E-2	3,33567	1.746	3.522
	b. Wakooma			32207	,,	
	Mod.—Oswin	13.1009	-5.26268E-2	2.9987	0.831	1.267
		13.1007	=3.20200E=2	2.7701	0.051	2.207

Table 10. Parameters and values of S.E. and P for models defined as acceptable to fit the data sets defined in Table 1. (Cont.)

	D - 14/371-4					
	Product/Variety	Α	В	С	S.E.	P
	c. Sinton					
	Chung-Pfost	610.337	0.15526	93.2125	0.932	0.991
	d. Waldron					
	Mod.—Henderson	4.3295E-5	2.1119	41.565	3.795	8.531
	Chung-Pfost	377.518	0.16456	35.5896	2.459	5.585
	Mod.—Oswin	15.8678	-0.10378	3.0842	2.149	4.307
В.	Fibrous materials					
	10. Corn cobs					
	a. (white et al).1/					
	Mod.—Oswin	12.6284	-8.8889E-2	2.13095	1.045	1.26
	Mod.—Halsey	3.88767	-1.4623E-2	1.68869	1.075	1.042
	b. (Kumar et al)					
	Mod.—Halsey	12.4168	-8.2680E-2	2.83895	3.458	9.816
	11. Peanut hull					
	Mod.—Henderson	1.1321E-4	1.8075	42.1544	2.785	4.044
	Chung-Pfost	254.721	0.14307	39.8359	2.789	4.076
	12. Rice hull					
	Mod.—Henderson	1. 444 9E-5	1.94667	24.2644	0.882	1.753
	Chung-Pfost	285.443	0.19738	27.7329	1.694	4.195
C.	High protein and oil produc	ets				
	13. Edible beans					
	a. Red					
	Mod.—Halsey	4.26685	-1.3382E-2	1.69325	2.895	8.125
	b. Baby Lima					
	Mod.—Halsey	4.3867	-1.2080E-2	1.72697	3.263	8.273
	c. Pinto					
	Mod.—Halsey	4.4181	-1.18745E-2	1.75708	1.779	4.881
	d. Black					
	Mod.—Halsey	5.20026	-2.26848E-2	1.98562	2.362	2.953
	e. White					
	Mod.—Halsey	4.2277	-1.47513E-2	1.72513	1.629	2.863
	f. Winged					
	ModHalsey	8.6440	-1.9600E-2	1.3600	4.4732	10.6
	14. Whole pods of peanut	0.6500	5 50000 P	2 (20:	1.040	1000
	Mod.—Oswin	8.6588	-5.79038E-2	2.6204	1.249	1.909
	15. Peanut Kernel	6.0012	4.0050= .0	0.5004	0.701	
	Mod.—Oswin	6.9812	-4.3870E-2	3.7021	2.786	4.001
	Mod.—Halsey	3.9916	-1.78556E-2	2.2375	2.547	4.282

Table 10. Parameters and values of S.E. and P for models defined as acceptable to fit the data sets defined in Table 1. (Cont.)

	D 1 //27 * .	Model Perameters				
	Product/Variety	Α	<u>B</u>	С	S.E.	P
	16. Rapeseed					
	a. Tower					
	Mod.—Halsey	2.8748	-7.4848E-3	1.7007	0.793	1.098
	b. Candle					
	Mod.—Halsey	3.00256	-4.8967E-3	1.76067	0.351	0.353
	c. Canola					
	Mod.—Oswin	8.12336	-4.5390E-2	2.3970	2.764	4.308
	Mod.—Halsey	3.4890	-1.0553E-2	1.8600	2.388	3.583
	17. Canola meal					
	Mod.—Oswin	13.0494	-4.47673E-2	2.2372	2.652	4.215
	Mod.—Halsey	3.5668	-5.54665E-3	1.5572	2.632	3.786
	18. Soybeans					
	a. U.S.A.	•				
	Mod.—Halsey	3.3109	-1.1635E-2	1.54307	2.902	8.238
	b. England					
	Mod.—Halsey	3.0446	-5.4321E-3	1.52446	0.587	0.869
	19. Sunflower seeds					
	Mod.—Halsey	4.43083	-1.55315E-2	2.12015	1.751	3.369
D.	Others					
	20. Jew's Ear (Des)					
	ModHenderson	5.38139E-5	1.94353	44.1251	3.781	9.582
	Chung-Pfost	343.4205	0.134810	43.9403	3.229	7.737
	Mod.—Oswin	17.8454	-0.14160	2,71787	3.723	8.249
	21. Jew's Ear (Ads)					
	ModHenderson	1.533032E-2	1.56748	53.6482	2.2012	4.868
	Chung-Pfost	339.3517	0.12217	72.0886	2.2932	5.7578
	Mod.—Oswin	15.11917	-0.0963	2.13576	2.1357	5.484
	22. Tea Leaf (Des					
	Mod.—Halsey	3.46287	-1.99285E-2	1.56708	2.370	7.953
	23. Tea Leaf (Ads)					
	Mod.—Halsey	2.22093	-5.91064E-3	1.32317	2.395	8.161
	24. Tea Stem (Des)					
	Mod.—Halsey	2.92353	-1.66123E-2	1.21566	3.197	8.251
	25. Tea Stem (Ads)					
	Mod.—Halsey	2.208571	-8.44205E-3	1.1466	2.145	6.542

^{1/} If no variety was indicated data set was defined by resercher's name in parentheses.

model can be claimed as the "universal ERH/EMC equation" for cereal grains and seeds.

REVISION OF ASAE STANDARDS

Based on the above discussion, it is recommended that the ASAE Standard (ASAE D254.4). Moisture Relationships of Grains, be partially revised.

Sereval limitations are found in the standard. For the corn kernel, the standards were developed by Pfost et al. (1976). They pooled four sets of desorp-Rodriguez-Arias tion data. (1956),Gustafson (1973), Chung et al. (1967), and Pixton et al. (1971). The estimated parameters for the Modified-Henderson and Chung-Pfost Equations were calcuated from these 143 data points. This method provided a simple technique to obtain the parameters of the ERH models from all available sorption data. However, the effect of the variety, determination methods, and other factors were not addressed.

In addition, the standard only includes nine cereal grains and seeds. The effect of variety was included only for wheat. Adsorption isotherms were not included.

Only two ERH/EMC equations were included in the Standard. These equations were found to be inadequate for some grains and seeds, especially for high protein and oil products. The Modified-Oswin and Modified-Halsey equations should be included for certain products. Also more agricultural products could be included in the standard.

Finally, detailed and accurate sorption data are required to estimate the parameters and compare the fit of the models.

CONCLUSION

The following conclusions can be drawn from this study.

- 1. The quantitative standards, values of S.E. and P. appear to be unreliable criteria for evaluating the fitting-agreement of nonnlinear ERH models for isotherms. Residual plots provide a more reliable evaluation criterion.
- 2. No ERH/EMC model can be claimed as the "universal" model for sorption data of agricultural products. The Modified-Henderson and Chung-Pfost equations can serve as good models for many starchy grains and fibrous materials. The Modified-Halsey equation is good for high oil and protein products. The newly develoed Modified-Oswin equation, is a good model for popcorn, corn cobs, whole pods of peanut, and some other varieties of corn and wheat.
- 3. The ASAE Standard D245.4, Moisture Relationships of Grains, needs to be partially revised. It should include more grains. The Modified-Halsey and Modified-Oswin equations should be considered for certain products.
- 4. Detail and Precision ERH/EMC data for the agricultural products of Taiwan should be deteriminated. The Standard of ERH/EMC models for indigenous grains need to be established.

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