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Modification of Oswin EMC/ERH equation[1]

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Abstract : An empirically modified Oswin equation is proposed to consider the effect of temperature on the sorption isotherms of several biolgical materials. Parameters of the sorption equations are presented. This three-parameter non-linear equation can fit the observed data adequately. It provides a simple form to describe the relation between EMC, ERH, and temperature.

Key Words : Temperature, Oswin equation.

INTRODUCTION

A number of theoretical, semi-theoretical, and empirical isotherm equations have been developed to model the relationship between EMC, or ERH, and temperature.

Empirical equations have found to be more accurate and convenient than theoretical and semi-theoretical relationships. Isotherm equations used most frequently are presented and discussed in the following section. In these equations, RH denotes relative humidity, M moisture content on dry basis, and T temperature.

1. The Henderson equation

The most widely used and best known model for the sorption isotherm of biological materials is this semi-empirical equation derived from Gibbs adsorption theory.

Henderson (1952) presented this equation:

$$1-RH=Exp(-K*T*M^N) \quad (1)$$

K and N are constants, thus the equation cannot predict the correct shift of the isotherm as the temperature changes.

2. The Modified-Henderson equation

To study the simulation of corn drying, Thompson et al. (1968) modified the Henderson equation by adding another constant into the temperature term. The practical effect of the modification is to move the temperature of absolute zero to a higher temperature.

The modified equation becomes:

$$1-RH=Exp(-A*\ (T+C)*M^B) \quad (2)$$

Where A, B, and C are constants.

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A different modification of the Henderson equation was presented by Zuritz et al. (1979) to describe the desorption isotherms of rough rice from 10 to 40 °C.

3. The Chung-Pfost equation

Based directly upon an assumption that the way the free energy changes for sorption is related to moisture content, Chung and Pfost (1967, Part II) presented a model of the form :

$$RH=Exp(-\frac{A}{RT}Exp(-B*M)) \quad (3)$$

Where R is the universal gas constant, and A and B are constants.

As with the Henderson equation, this equation cannot be used to predict the effect of temperature since the use of the T term does not eliminate the temperature dependence of parameters A and B.

In order to obtain a better fit, Pfost et al. (1976) added a new parameter to the temperature term and combined the R value in the constant term.

The new equation is:

$$RH=Exp(-\frac{A}{T+C}Exp(-B*M)) \quad (4)$$

Where A, B, and C are constants.

4. The Halsey equation

Halsey (1948) developed an equation to describe the condensation of multilayers at a large distance from the surface.

The equation is:

$$RH=Exp(-\frac{A}{RT}*M^{-c}) \quad (5)$$

Because the use of the RT term does not eliminate the temperature dependence of constants A and C, Iglesias and Chirife (1976d) simplified it to the form:

$$RH=Exp(-A*M^{-c}) \quad (6)$$

They found this equation could be used to describe the sorption behavior of 69 food materials reasonably well.

5. The Modified-Halsey equation

In studying the effect of temperature on water sorption isotherms, Iglesias and Chirife (1976a) analyzed the parameter A of the Halsey equation (Eq. 6) and found that it could be related to temperature by an empirical expopential function. A new Modified-Halsey equation was proposed:

$$RH=Exp(-Exp(A+B*T)*M^{-c}) \quad (7)$$

Where A, B, and C are constants.

6. The Day-Nelson equation

Because the T term in the Henderson equation does not eliminate the temperature dependence of constants K and N, Day and Nelson (1965) omitted the T term and replaced the constants with an empirical power function of temperature.

The new four-parameter equation is:

$$1-RH=Exp(-a*T^{b}*M^{cT^{d}}) \quad (8)$$

Where a, b, c, and d are constants.

7. The Chen-Clayton equation.

In order to predict the temperature dependence of the isotherm, Chen and Clayton (1971) propsed a four-parameter equation to describe the relation of moisture, temperature, and relative humidity. The model is:

$$RH=Exp(-a*T^{b}*Exp(-c*T^{d}*M) \quad (9)$$

Where a, b, c, and d are constants.

The equation is a modification of the Chung−Pfost equation (Eq. 3) with the constants A and B represented as empirical power functions of temperature.

Development of the Modified-Oswin equation

The objective of this study was to develop a simple equation for relating EMC, ERH, and temperature. A fully empirical isotherm equation with two parameters proposed by Oswin (1946) was further modified to consider the temperature effect.

Compared to the two-parameter sorption equation presented by Boquet et al. (1978), the Oswin equation was able to fit the sorption data better for protein and starchy foods. This equation is a mathematical series expansion of sigmoid shaped curves. It can be written as.

$$M=K*\left(\frac{RH}{1-RH}\right)^{N} \quad (4.43)$$

K and N are constant.

Presented by Oswin (1946), this equation primarily was adopted to solve a packaging problem. Since it is purely empirical, it received relatively little attention in the literature. Labuza et al. (1972) applied the equation to correlate EMC data in non-fat dry milk and freeze dried soluble tea. Andrieu et al. (1985) found that sorption data of Durum wheat pasta could be fitted by the Oswin equation with good precision.

Transformming into the linearized form, yields,

$$\ln M=\ln K+N*\ln(RH/1-RH) \quad (11)$$

The parameters K and N do not account for the temperature dependence.

A plot of ln M and ln (RH/(1−RH)) should be a straight line if this equation fits isotherm data well. If the parameters can be expressed as a function of temperature, then the equation can be modified to consider the temperature effect, in the same way as the Henderson equation was modified by Day and Nelson (1965), or the Chung equation by Chen and Clayton (1971).

Several original sets of isotherm data for biological materials were collected to find the parameters for the Oswin equation. The result are listed in Table 1. High R-square values strongly indicated that lnM and ln (RH/(1−RH)) had a linear relation.

Table 1. Parameters K and N for the Oswin equation

Products	Temp. (°C)	Range of RH	K	N	R-Square
Red beans (Guevara) 1963	21.1	0.12—0.80	13.4852	0.3287	0.969
	26.6	0.12—0.69	12.4578	0.3563	0.978
	32.2	0.12—0.69	12.4215	0.3761	0.976
	37.8	0.13—0.70	12.0973	0.4364	0.981
Winged beans (Ajibola) 1986a	40.0	0.12—0.82	8.9694	0.4348	0.993
	50.0	0.11—0.81	7.3550	0.4637	0.956
	60.0	0.11—0.80	6.6917	0.5373	0.967
	70.0	0.11—0.80	5.8700	0.5399	0.984
Corn (Rodriguze.) 1956	4.4	0.13—0.76	14.4950	0.3196	0.999
	15.6	0.32—0.95	12.8550	0.2817	0.997
	30.0	0.11—0.86	11.2967	0.3400	0.972
	37.8	0.11—0.97	10.6566	0.3039	0.955
	50.0	0.11—0.85	9.7263	0.3851	0.972
	60.0	0.12—0.81	8.3220	0.3921	0.985
Corn (Gustafson) 1973	10.0	0.13—0.96	13.6530	0.3054	0.998
	32.2	0.12—0.90	11.5178	0.3500	0.999
	48.9	0.12—0.85	10.3547	0.3851	0.993
	68.3	0.11—0.79	9.1879	0.3990	0.994
Popcorn (Flood) 1984	10.1	0.36—0.91	13.1895	0.3631	0.999
	20.1	0.19—0.91	12.2794	0.3695	0.996
	30.1	0.24—0.92	11.2185	0.3903	0.996
	39.8	0.29—0.93	10.3723	0.4111	0.996
	50.0	0.33—0.93	9.6044	0.4231	0.990
Peanut (Kososki) 1973	10.0	0.30—0.90	7.4851	0.3345	0.949
	15.0	0.30—0.90	6.7700	0.3643	0.965
	20.0	0.30—0.90	6.4268	0.3542	0.975
	25.0	0.30—0.90	6.1371	0.3500	0.990
	30.0	0.30—0.90	5.8249	0.3424	0.994
	38.0	0.30—0.90	5.4803	0.3605	0.991
Rapeseed Candle (Pixton) 1981	5.0	0.42—0.92	7.0346	0.4549	0.991
	15.0	0.22—0.92	7.0277	0.4418	0.993
	25.0	0.24—0.92	6.7326	0.4530	0.993
	35.0	0.27—0.92	6.3473	0.4742	0.994
Rice (Putranon) 1979	10.0	0.15—0.95	13.6300	0.2703	0.966
	20.0	0.23—0.93	12.9937	0.2791	0.979
	25.0	0.27—0.93	12.8192	0.2761	0.993
	30.0	0.22—0.77	12.5653	0.3565	0.991
	38.0	0.25—0.78	11.7872	0.3596	0.991
Rice (Zuritz) 1979	10.0	0.11—0.82	14.3754	0.2783	0.997
	20.0	0.11—0.87	13.2929	0.2973	0.992
	25.0	0.11—0.87	12.6575	0.3186	0.993
	30.0	0.11—0.86	12.0276	0.3189	0.982
	38.0	0.11—0.86	10.6320	0.3389	0.992
Sorghum (Dunstan) 1972	15.6	0.02—0.90	15.5266	0.2320	0.986
	23.9	10.02—0.89	14.5651	0.2637	0.997
	26.7	0.05—0.89	14.4220	0.2643	0.997
	40.6	0.05—0.89	13.4394	0.2818	0.997
	48.9	0.05—0.67	13.5288	0.3113	0.996
Soybean (Alam) 1972	5.0	0.14—0.89	10.8123	0.3942	0.967
	15.0	0.13—0.88	10.2087	0.4177	0.978
	25.0	0.12—0.87	9.9002	0.4361	0.976
	35.0	0.12—0.84	9.1659	0.4396	0.976
	45.0	0.12—0.85	8.3700	0.4859	0.988
	55.0	0.11—0.77	7.6494	0.5230	0.983
Wheat (Pixton) 1981	5.0	0.25—0.95	12.8138	0.3175	0.998
	15.0	0.27—0.95	12.3041	0.3290	0.999
	25.0	0.30—0.95	11.7014	0.4003	0.999
Gari (Ajibola) 1986b	40.0	0.12—0.82	10.1815	0.3500	0.979
	50.0	0.11—0.80	9.0613	0.3994	0.959
	60.0	0.11—0.80	8.3101	0.4003	0.973
	70.0	0.11—0.80	7.5892	0.3848	0.973

In this study, the main interest was to find the relation between parameters and temperature. Two type of function were selected:

a. Linear function:

$$K=a1+b1*T \quad (12)$$

$$N=d1+e1*T \quad (13)$$

b. Exponential function:

$$K=Exp(a2+b2*T) \quad (14)$$

$$N=Exp(d2+e2*T) \quad (15)$$

From a statistical analysis that compared the residual sum of the squares, the exponential function was not better than the linear function for describing K and N. The linear regression equation for the two parameters as a function of temperature are shown in Table 2. The result of an F−test indicated that the K parameters had a linear relation with temperature. While N did not exhibit a linear relation except for a few grains.

Table 2. The regression equation of K and N

Probuct	Regression Equation	R-square
Red beans	K=17.4705−0.182143*T	0.850
	N=0.1932+6.1557E−3*T	0.940
Winged beans	K=12.7003−9.9615E−3*T	0.958
	N=0.2801+3.8884E−3*T	0.900
Corn (Rodriguez−)	K=14.6985−0.10537*T	0.989
	N=0.2824+0.0165*T	0.609
Corn (Gustafson)	K=14.2209−7.6350E−2*T	0.986
	N=0.29397+1.6537E−3*T	0.961
Popcorn	K=14.0721−9.12375E−2*T	0.997
	N=0.34260+1.62528E−2*T	0.976
Peanut	K=7.92399−6.82593E−2*T	0.951
	N=0.34305+3.444E−4*T	0.100
Rapeseed	K=7.25690−0.02357*T	0.881
	N=0.4447+6.010E−4*T	0.333
Rice (Putranon)	K=14.3043−6.28147E−2*T	0.972
	N=0.21816+3.6614E−3*T	0.717
Rice (Zuritz)	K=15.7210−0.12495*T	0.996
	N=0.25956+2.03469E−3*T	0.961
Soyghum	K=15.1756−6.03475E−2*T	0.890
	N=0.20539+2.09464E−3*T	0.940
Soybean	K=11.24233−6.3043E−2*T	0.985
	N=0.3780+2.49234E−3*T	0.986
Wheat (Pixton)	K=13.1074−5.56187E−2*T	0.998
	N=0.31043+1.30992E−3*T	0.995
Gari	K=13.4760−8.5281E−2*T	0.988
	N=0.32174+1.05284E−3*T	0.335

With the above discussion a new Modified-Oswin equation was proposed that included the temperature term in the original Oswin equation, that is, K had a linear relation with temperature and N remained a constant.

The new modified nonlinear equation with three parameteres can be expressed as:

$$M=(A+B*T)*(\frac{RH}{1-RH})^N \quad (16)$$

The ERH value can be written as a function of M and T,

$$RH=\frac{1}{(\frac{A+B*T}{M})^c+1} \quad (17)$$

$$C=1/N \quad (18)$$

Mathematically, N reflects the sigmoid shape of the isotherm. A influences the magnitude of the ordinate at the temperature 0°C. B induces the temperature shift of the isotherm curve at a particular temperature, T.

A Fortran M77 program "NONLIN" which used the least squares method was written to estimate the parameters of the Modified-Oswin equation. The estimated parameters and the standard error of estimate of ERH (%) for several grains are shown in Table 3.

Table 3. Estimated parameters and S. E. of the Modified-Oswin equation for cereal grains

Product	Paramerers			S.E. of ERH
	A	B*(−100)	C	
Red beans	14.9607	8.2605	2.5183	3.2814
Winged beans	12.6259	9.9932	1.9106	4.7381
Corn (Rodriguez−)	14.6457	9.8022	2.9795	2.5332
Corn (Gustafson)	14.4014	8.4519	2.7545	2.7521
Popcorn	13.8135	8.2312	2.6189	1.0722
Peanut	7.7101	6.2351	2.9978	3.7386
Rapeseed	6.6909	1.8020	2.0773	0.8318
Rice (Putranon)	14.6362	7.2849	3.0930	2.7477
Rice (Zuritz)	15.6744	11.3673	3.3249	2.0342
Sorgrum	16.5271	6.7562	3.7721	1.9014
Soybean	10.9124	6.1544	2.1537	3.5133
Wheat	13.1009	5.2626	2.9987	0.8144
Gari	13.5656	8.6183	2.7891	3.6303

Calculated and experimented isotherm data for corn, popcorn, and soybeans at various temperatures are plotted in Fig. 1, 2, and 3. Values of S.E. (standard error for estimated value) and P (mean relative percentage deviation, different from the p value commonly used in statistical analysis) were calculated for purposes of comparing, the Modified-Henderson, the Chung-Pfost, and the Modified-Oswin equations (Table 4). Among these equations, the Modified-Oswin equation provided the best model for four grains.

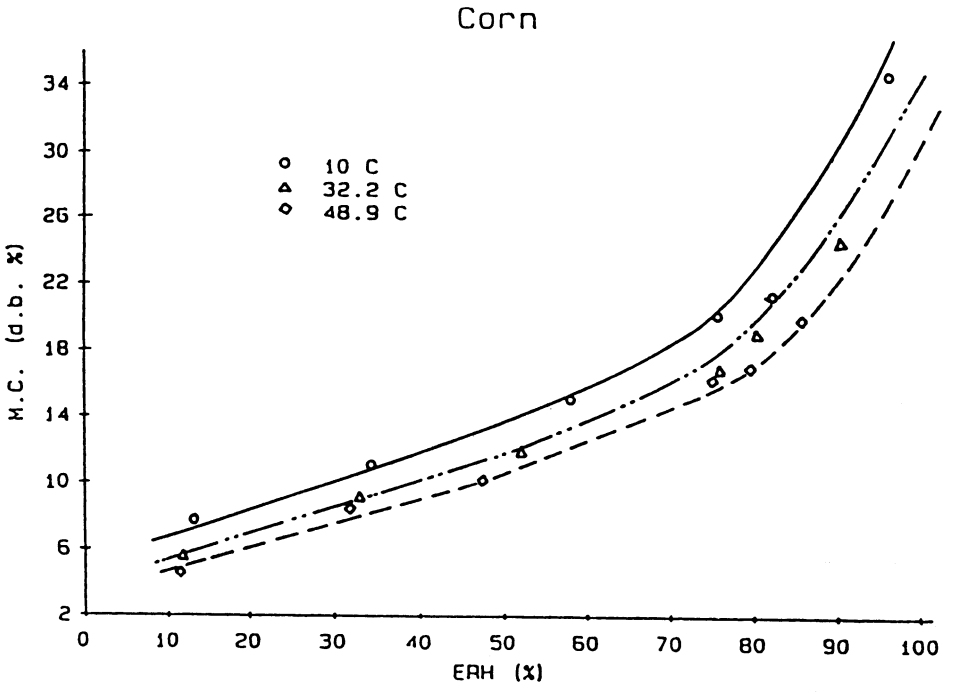


Fig. 1. Modified-Oswin equation and experimental data of Corn

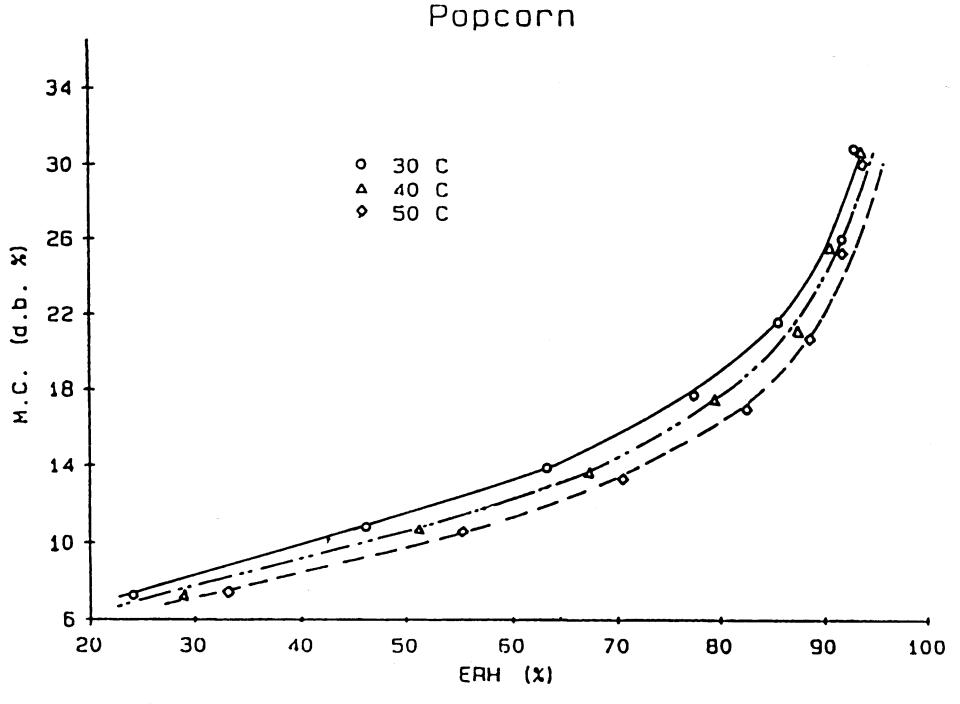


Fig. 2. Modified-Oswin equation and experimental data of Popcorn

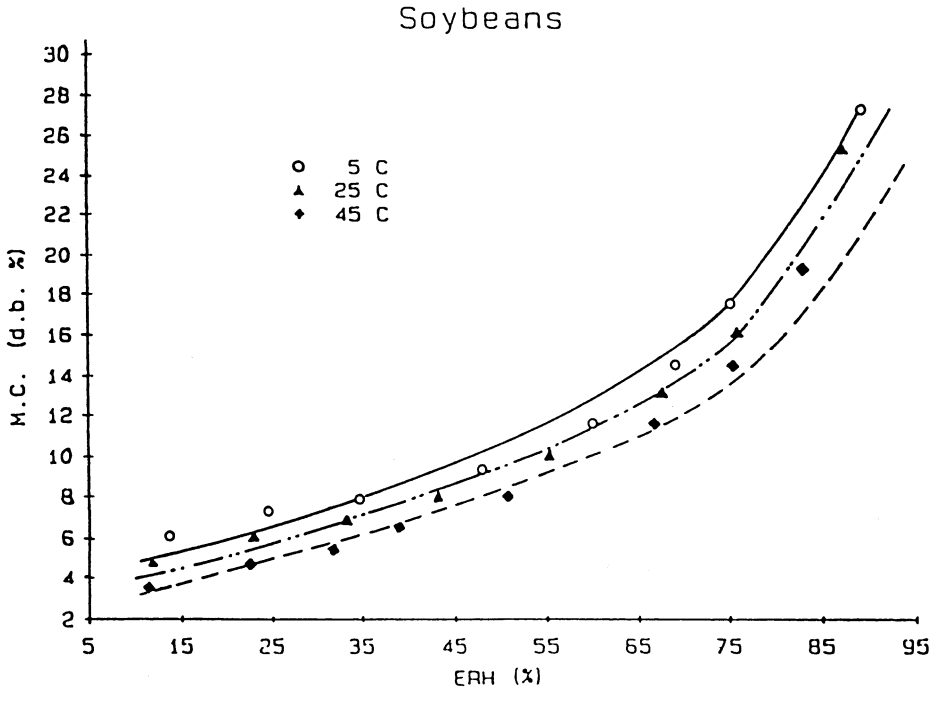


Fig. 3. Modified-Oswin equation and experimental data of soybeans

Table 4. Comparison of ERH equations for agricultural products

Product		Modified-Henderson	Chung-Pfost	Modified-Oswin
Red beans	S.E.	4.1231	3.7464	3.2814
	P	12.987	11.519	10.025
Corn (Gustafson)	S.E.	3.7230	2.8585	2.7521
	P	9.0137	6.3065	6.5762
Popcorn	S.E.	2.9810	2.5180	1.0720
	P	4.6250	3.5820	1.4870
Soybeans	S.E.	5.0188	4.9923	3.5133
	P	14.614	14.335	9.9601

1. S.E. : Standard error for relative humidity (%)
2. P : Mean relative percentage deviation

CONCLUSION

The Modified-Oswin equation,

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

could be used to predicted well for the effect of temperature on sorption isotherms for some biological materials. Apparaently, the proposed equation is not accurate for all ranges of ERH(0.01—0.99) and cannot be claimed as the best "fitting-agreement" equation for all biologicial materials. However, it is a simpler form than the three-parameter equations that are often used. It describes the isotherm curve adequately for some cereal grains. Its parameters are determined by temperature and characterstics of the products.

Since the equation was derived empirically, no conclusion can be drawn from it to explain the mechanism of water sorption phenomena. Its simplicity, however, should be valuable for those who are more concerned with engineering applications of ERH models.

REFERENCE

Alam, Anwar., 1972, Simulated drying of soybeans. Ph.D. Thesis, University of Illinois.

Andrieu, J., A. Stamatopoulos, and M. Zafiropoulos. 1985. Equation for fitting desorption isotherms of durum wheat pasta. J. Food Tech. 20 : 651-657.

ASAE. 1983. Moisture relationships of grains. ASAE Standards D. 245.4. Agricultural Engineering Yearbook. 30th edition. St.Joseph, MI. PP. 297-301.

Ajibola, O. O. 1986 a. Equilibrium moisture properties of Winged bean seed. Trans. of ASAE 29(5) : 1485 -1487.

Ajibola, O. O. 1986 b. Desorption isotherms of gari from 40 to 70 °C J.A.E.R. 35 : 207-210.

Becker, H. A. and H. R. Sallans 1956. A study of desorption isotherms of wheat at 25 and 50°C. Cereal Chem. 33 : 79-91.

Boquet, R., J. Chirife, and H. A. Iglesias. 1978. Equations for fitting water sorption isotherms of foods: Part II :
Evaluation of various two-parameter models. J. Food Tech.13 : 319-327.

Boquet, R., J. Chirife, and H. A. Iglesias. 1979. Equations for fitting water sorption isotherms of food : Part III :
Evaluation of various three-parameter models. J. Food Tech.14 : 527-534.

Chen, C. S. and J. T. Clayton. 1971. The effect of temperature on sorption isotherms of biological materials. Trans. of ASAE 14(5) : 927-929.

Chirife, J. and H. A. Iglesias. 1978. Equations for fitting water sorption isotherms of foods : Part I : a review. J. Food. Tech. 13 : 159-174.

Chung, D. S. and H. B. Pfost. 1967. Adsorption and desorption of water vapor by cereal grains and their products :
Part I : Heat and free energy changes of adsorption and desorption. Trans. of ASAE 10(4) : 549-551, 555.
Part II : Development of the general isotherm equation. Trans of ASAE 10(4) : 552-555.

Day, D. L. and G. L. Nelson. 1969. Desorption isotherms for wheat. Trans of ASAE 8 : 293

Dunstan, E. R., D. S. Chung, and T. D. Hodges. 1973. Adsorption and desorption characteristics of grain sorghum ASAE Paper No. 72-327 ASAE, St, Joseph, MI.

Flood, C. A. and Jr. G. M. White. 1984. Desorption equilibrium moisture relationships for popcorn. Trans. of ASAE 23(2) : 561-571.

Guevara-Guio, M. 1973. Equilibrium moisture content of beans. M.S. Thesis. Kansas State University.

Gustafson, R. J. 1973. Equilibrium moisture content of shelled corn from 50 to 155°F. M.S. Thesis. University of Illinois.

Henderson, S. M. 1952. A basic concept of equilibrium moisture. Agriculture Engineering 2 : 29-32.

Iglesias, H. A. and J. Chirief. 1976. Predication of effect of temperature on water sorption isotherms of food materials. J. Food Tech. 11 : 109-116.

Kumar, Ajit, F. L. Herum, and J. L. Blaisdell. 1978. Equilibrium moisture contents of intact corn ears and component parts. ASAE Paper No. 78-3054, ASAE. ST. Joseph, MI.

Kososki, A. R. 1977. Two methods of comparing equilibrium moisture of grains. M.S. Thesis, Kansas State University.

Labuza, T. P., S. Mizrahi, and M. Karel. 1972. Mathematical models for optimization of flexible film packaging of foods for storage. Trans of 15 : 150-155.

Oswin, C. R. 1946. The kinetics of package life. III. Isotherm. J. Chem. Ind., London. 65:419

Pfost, H. B., S. G. Mourer, D. S. Chung, and George A. Milliken. 1976. Sumarizing and reporting equilibrium moisture data for grains. ASAE paper 76-3520 ASAE, ST. Joseph, MI.

Pixton, S. W. and S. Henerson. 1981. The moisture content-equilibrium relative humidity relationships of five varieties of Candian wheat and Candle Rapeseed at different temperatures. J. Stored Prod. Res. 17 : 187-190

Putranon, R., R. G. Bowrey, and J. Eccleston. 1979. Sorption isotherms for two cultivars of paddy rice grown in Australia. Food Technology in Australia, 1979, Dec : 510-515.

Rodriguez-Arias, J. 1956. Desorption isotherms and drying rates of shelled corn in the temperature range of 40 to 140 °F. Ph. D. Dissertation, Michigan State University.

Thompson, T. L., R. M. Peart, and G. H. Forst. 1968. Mathematics simulation of corn drying-a new model. Trans. of ASAE 24(3) : 582-586.

Van den Berg, C. and S. Bruin. 1981. Water activity and its estimation in food systems : theoretical aspects. PP : 1-43. In : L. B. Rockland and G. F. Stewart (ed.). Water Activity : Influences on Food Quality. Academic Press. N. Y.

Zuritz, C., R. P. Singh, S. M. Meini, and S. M. Henderson. 1979. Desorption isotherms of rough rice from 10 to 40 °C. Trans. of ASAE 22(2) : 433-440.

歐思文平衡含水率模式之修正[1]

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摘 要

在此研究中提出一修正的歐思文模式以表示溫度對於數種農產品平衡含水率曲線的影響。各去濕方程式之參數列舉於此文中。此種含三參數的非線性模式能良好地適用於各實驗數據。即代表此模式能以簡單的形式描述農產品平衡含水率，平衡相對濕度和溫度三者之關係。

關鍵詞：修正歐思文模式，等溫曲線。

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