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NON-LINEAR PARAMETER ESTIMATION OF EMC/ERH CORRELATIONS FOR GRAIN-TYPE PRODUCTS

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ABSTRACT

A mathematical prediction of corn sorption isotherm was developed for three-parameter EMC correlation such as Modified-Henderson, Modified-Chung-Pfost, Modified-Oswin, and Modified-Halsey. Moisture sorption experimental data were determined using a dynamic method at temperature 30 ^oC, 40 ^oC and water activity range from 0.07 to 0.75. The vapor pressure regulation of air surrounding the grains was adjusted by varying sulfuric acid solution. Non-linear regression algorithms such as Simplex and/or Rosenbrock algorithm were used to fit the measured data to the EMC relations. The generalized correlation coefficient (R^2) and the mean relative deviation were in the range of 0.90-0.99 and 2 % - 8 % respectively, in which comparison between predicted and experimental sorption isotherms. From the parameters of correlation, it is possible to get the best equations among them to represent equilibrium moisture content of corn grains. The Modified-Henderson and Modified-Oswin equations give the best model for predicting the adsorption and desorption EMC of corn grain for given range of temperature and water activity.

NOTATION

A,B,C	parameters used in EMC relations	
A_w	water activity or relative humidity	decimal
R^2	correlation coefficient	
T	absolute temperature	K
X^*	equilibrium moisture content	%
$\hat{X}_i$	calculated data	
$\overline{X}_i$	mean value of experimental data	
X_i	experimental data	
n	number of experimental data	

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1. INTRODUCTION

Grain products, such as corn, paddy rice, coffee beans, etc., are widely cultivated grains in the world. The most of grain products are harvested at high moisture content. Hence, it requires immediate treatment to prevent quality along decreasing during storage. Drying is the most widely practiced preservation method for grains in the post-harvesting technology. With drying processing, the moisture content of grains is lowered to a level at which there is no danger of the growth of undesirable microorganisms. The minimum moisture content to which corn can be dried under certain conditions is given by the equilibrium moisture content (EMC) [Istadi *et al.* (1999)]. The concept of equilibrium relative humidity (ERH) is often used as it measures the availability of water to microorganisms and hence gives an indication of the biological activity within corn grain. The relationship between EMC and ERH are described by the EMC/ERH sorption isotherm equations [Sitompul *et al.* (2000)].

In an extensive study conducted by Sun and Woods (1998) on comparing a number of commonly used EMC/ERH equations for the corn grains. It is found that the Modified-Oswin and Modified-Chung-Pfost equations are identified as the most appropriate equations for describing EMC/ERH sorption isotherms of shelled-corn based on the ability to describe the nineteen individual data sub-sets. The analysis of sorption isotherm of corn grain had been conducted by Sitompul *et al.* (2000) and Papadakis *et al.* (1993) for the two- and three-parameter of EMC correlation. However, the two-parameter EMC correlation (Papadakis and Henderson model) can not provide better fitting to experimental data of corn grain, comparing with three-parameter EMC relations (Halsey and Iglesias-Chirife equations).

The aims of this study is to analyze four sorption isotherm equations (Modified-Henderson, Modified-Chung-Pfost, Modified-Oswin, and Modified-Halsey), through non-linear regression of experimental data, and to find the best model representing the equilibrium moisture content of corn grains. The sorption isotherm data of corn grain were determined experimentally by the dynamic method at temperature of 30^{o}C and 40^{o}C [Sitompul *et al.* (2000), Makower *et al.* (1943), Molnar (1995)].

2. EQUILIBRIUM MOISTURE CONTENT CORRELATIONS

In air-drying system, when air is brought in contact with a wet-food material, equilibrium between the air and food material is eventually reached. The moisture content of grains at this stage is called the equilibrium moisture content (EMC) and the corresponding vapor pressure of surrounding air at the same temperature is called the equilibrium vapor pressure. The ratio of the equilibrium vapor pressure to the saturation vapor pressure is so called as the equilibrium relative humidity (ERH) or water activity [Sokhansanj *et al.* (1995), Marinos-Kouris *et al.* (1995)]. The equilibrium moisture content-equilibrium relative humidity (EMC/ERH) relationships are necessary to optimize drying and storing of food products, especially for grain products. The sorption data may be used for the proper choice of the end-point of drying process. Sorption isotherm vary drastically from one food product to another, depending on whether the product is being wetted - adsorption - or dried - desorption [Mujumdar *et al.* (1995)]. No single equation has been found to predict accurately the sorption isotherm of all types of foods in the entire range of water activity; consequently, many correlation have been reported to represent sorption isotherms [Parry (1985)].

A large number of theoretical, empirical or semi-empirical correlations have been proposed in the literature to estimate the equilibrium moisture of biological materials. The theoretical correlation are developed based on sorption kinetics theories such as that of Langmuir and BET. In many cases, the theoretical models can not predict the equilibrium moisture for grains in a wide range of temperature and water activity. Further, the empirical or semi-empirical models were used to increase the accuracy of the predicted values of interest. The most important correlation proposed available in the literature are given in Table 1. In these correlation, X^* is the equilibrium moisture content for grains, while A_w and T is the water activity of air and the solid temperature respectively. Note that A, B, and C are the involved parameters of the correlation.

Table 1. Equilibrium moisture content models [Barrozo *et al.* (1996), Stencl *et al.* (1998)]

No.	Name	Equation	Reference
1	Modified Henderson	$X^*=\left(\frac{\ln(1-A_w)}{-A(T+C)}\right)^{1/B}$	[Thompson *et al.* (1968)]
2	Modified Chung-Pfost	$X^*=\frac{-1}{B}\ln\left(\frac{(C+T)\ln A_w}{-A}\right)$	[Chung and Pfost (1967)]
3	Modified Oswin	$X^*=(A+B\,T)\left(\frac{A_w}{1-A_w}\right)^C$	[Stencl *et al.* (1998)]
4	Modified Halsey	$X^*=\left(\frac{\exp\,(A+B\,T)}{-\ln A_w}\right)^C$	[Stencl *et al.* (1998)]

Basically, the correlation (1) is the modification of Henderson equation (1952) based on sorption model of Gibbs in order to appropriate for grains [Thompson *et al.* (1968)]. The correlation (2) was introduced by Chung and Pfost (1967) based on potential theory and in a simplified equation of state. The correlation (3) is based on mathematical series expansion for sigmoidaly curve. The correlation (4) is the empirical modifications of the Halsey equation (1948), that are based on the theoretical model of BET.

3. MATERIAL AND METHODS

The materials used in this experimental study were shelled-corn grain and sulfuric acid solution. The technique used to obtain the equilibrium moisture content data was based on the dynamic method with the use of sulfuric acid solutions to provide a constant relative humidity. A series of different sulfuric acid solution was used, such that the relative humidity was between 7 % and 75 % [Wilson (1921)]. The EMC experiments were conducted in a temperature controlled at 30 ^oC and 40 ^oC [Sitompul *et al.* (2000)]. The dry matter content was then determined by drying the sample in an oven until constant weight. The moisture content at any time was calculated from the sample weight obtained [Molnar (1995)]. The equilibrium conditions were considered to be reached, when three-subsequent measurements of the sample weight give identical results. The moisture content of the material was determined by the time the equilibrium condition was reached.

4. RESULTS AND DISCUSSION

The experimental values of the equilibrium moisture contents corresponding to shelled-corn at 30 °C and 40 °C are presented in Fig.1 and Fig.2 for the range of water activity of 0.07-0.75, and they are best-fitted with the respective correlation. Generally, the curves have a sigmoid shape form. Equilibrium moisture content was found to increase with decrease in temperature at constant water activity. The increase in temperature causes an increase for desorped water and a decrease for adsorbed water, if A_w is kept constant. Similar trends for many food materials have been reported in the literature [McMinn *et al.* (1997), Sun (1998)]. The estimated constants of the Modified-Henderson, Modified-Chung-Pfost, Modified-Oswin, and Modified-Halsey and the corresponding correlation coefficient (R^2) together with percentage mean relative deviation are given in Table 2 and Table 3.

The non-linear regression method was used in order to estimate the best model parameters, i.e. Simplex method in the form of the algorithm of SIMPLEX subroutine [Sitompul *et al.* (2000)]. The objective function to be minimized is given by Eq.(1) below, which is an important error parameter during the non-linear curve fitting process. The correlation coefficient (R^2) measures the fitting ability of a model to a data set. The higher of R^2 value represents the better of fitting ability of an equation. However, the correlation coefficient only gives the fitting ability of a correlation, but it can not provide a correct visualization of the goodness-of-fit of the equation to the experimental data. For this reason, percentage of mean relative deviation given by Eq.(3) is used to measure the goodness-of-fit of the correlation. It represents the mean departure of the measured data from the predicted data. Further, the consistency of parameters is also important when the correlation applied to different temperatures.

Table 2. Regression results of parameters of Desorption isotherm correlation

Name	Temp. (°C)	Estimated parameter value			(R^2)	Mean Rel. Deviation (%)
		A	B	C		
Modified Henderson	30	2.4259×10^{-5}	1.8247	24.468	0.9952	3.18
	40	2.6075×10^{-5}	1.8497	23.299	0.9984	1.78
Modified Chung-Pfost	30	15008	0.19493	2300.4	0.9605	8.54
	40	15005	0.2108	2300.2	0.9681	7.34
Modified Oswin	30	-2.195×10^{-2}	3.6319×10^{-2}	0.43591	0.9797	5.68
	40	-4.8942×10^{-2}	3.2404×10^{-2}	0.43021	0.9866	4.79
Modified Halsey	30	-1.5147	1.2671×10^{-2}	0.77337	0.9755	7.99
	40	1.6999	3.7274×10^{-3}	0.68901	0.9433	10.41

Table 3. Regression results of parameters of Adsorption isotherm correlation

Name	Temp. (°C)	Estimated parameter value			(R^2)	Mean Rel. Deviation (%)
		A	B	C		
Modified Henderson	30	5.2293×10^{-5}	1.6675	23.665	0.9912	2.84
	40	6.2134×10^{-5}	1.6361	26.238	0.9869	4.81
Modified Chung-Pfost	30	10003	0.18563	2500.6	0.9906	4.31
	40	10004	0.20626	2500.7	0.98	7.08
Modified Oswin	30	1.7559	2.31×10^{-2}	0.47982	0.9975	2.94
	40	1.6233	2.0565×10^{-2}	0.48798	0.9986	1.87
Modified Halsey	30	-1.5147	1.2671×10^{-2}	0.77337	0.9755	7.99
	40	-2.7899	1.6416×10^{-2}	0.73534	0.9887	5.49

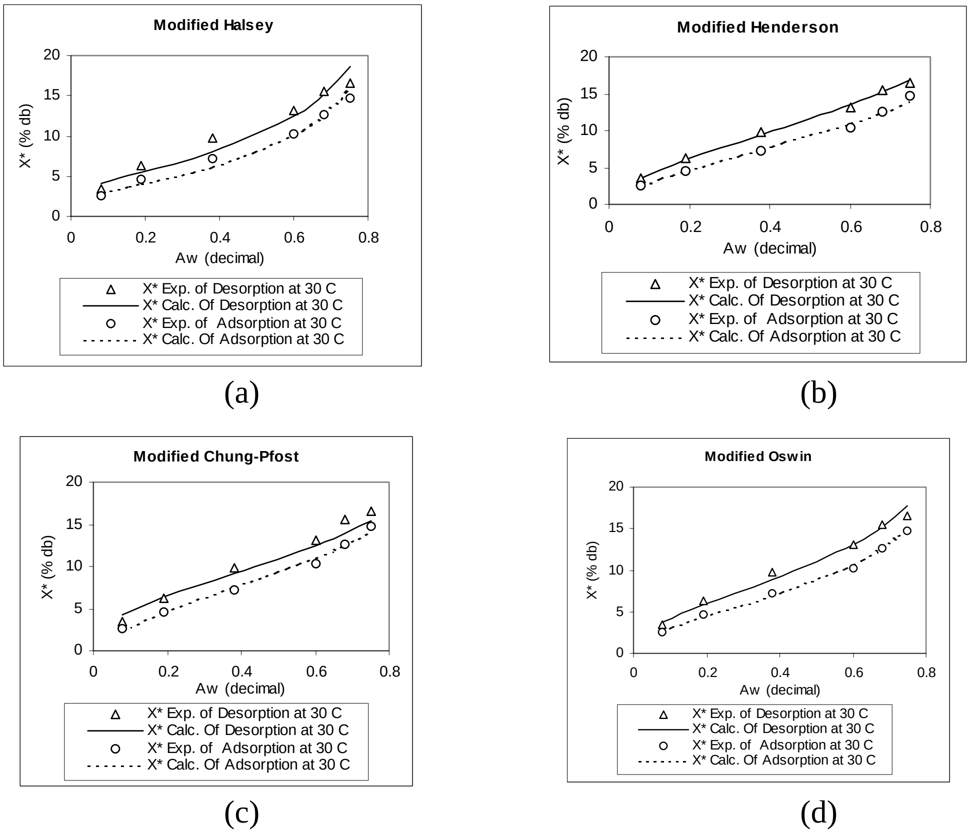

Fig.1. The comparison between the predicted isotherm and the experimental data at 30 ^{o}C

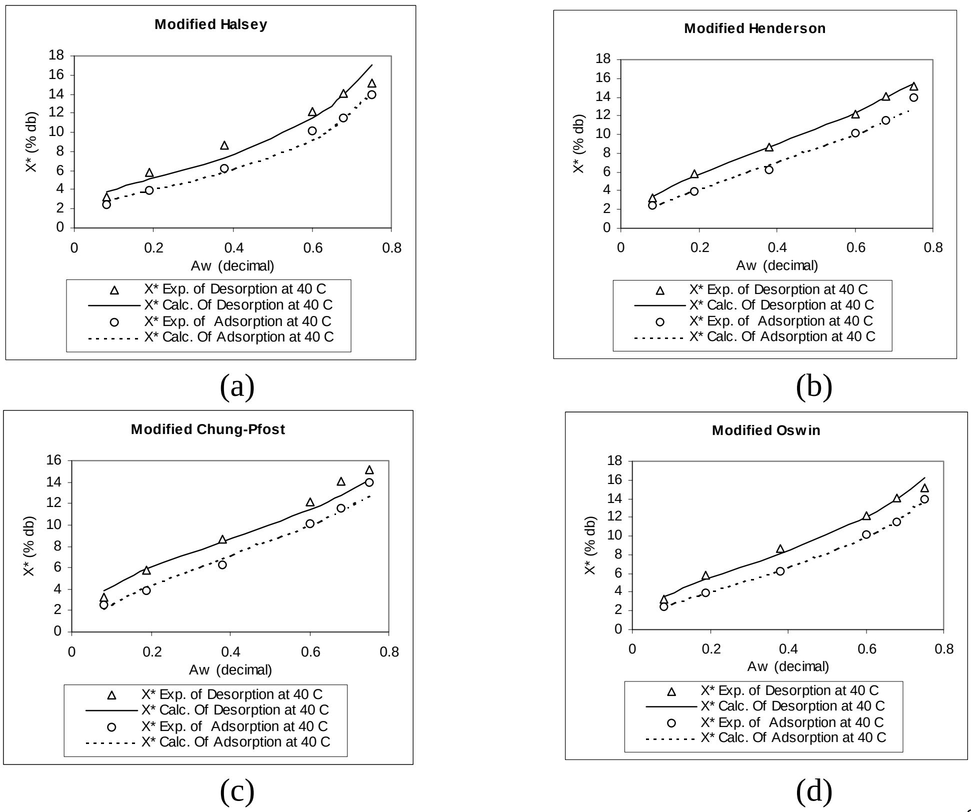

Fig.2. The comparison between the predicted isotherm and the experimental data at 40 ^{o}C

Objective function : $$OF = \frac{1}{n}\sqrt{\sum_{i=1}^{n}\left(\frac{\left|\hat{X}_i - X_i\right|}{X_i}\right)^2} \tag{1}$$

Correlation coefficient : $$R^2 = 1 - \frac{\sum_{i=1}^{n}\left(X_i - \hat{X}_i\right)^2}{\sum_{i=1}^{n}\left(X_i - \overline{X}_i\right)^2} \tag{2}$$

Mean relative deviation (%): $$\%\ Dev. = \frac{100}{n}\sum_{i=1}^{n}\left(\frac{\left|\hat{X}_i - X_i\right|}{X_i}\right) \tag{3}$$

The correlation coefficient was found very high in most cases (R^2>0.9) that calculated by Eq.(2). The Modified-Henderson model presents the highest R^2 and the minimum of mean relative deviation for this data. Therefore, the Modified-Henderson equation gives the best fit to the experimental data at the temperature range of 30 ^oC - 40 ^oC. The Modified-Oswin equation gives also better fitting than the Modified-Chung-Pfost and Modified-Halsey equations, but gives less fitting than the Modified-Henderson equation. In the case of comparison of temperature 30 ^oC and 40 ^oC, it is found that parameters correlation of the Modified-Henderson and Modified-Oswin relatively having constant value compared with others. It is noted that these models can be used to predict sorption equilibrium moisture content at different temperature.

5. CONCLUSIONS

An EMC experiment has been performed for shelled-corn by using dynamic method. The data obtained were used to determine the best model for predicting the adsorption and desorption EMC of corn grain for given levels of temperature and water activity. The equilibrium moisture content of corn grain decreases with an increase in temperature at constant relative humidity. The Modified-Henderson and Modified-Oswin equations are identified as the most appropriate equations for describing EMC/ERH sorption isotherms of shelled-corn based on the best ability to fit the equation on the set of experimental data. The Modified-Chung-Pfost and Modified Halsey equations have slightly better fitting ability than the Modified-Henderson and Modified-Oswin correlation. The non-linear regression based on Simplex and/or Rosenbrock algorithm is a good technique to fit non-linear correlation on the experimental data set. Therefore, the two correlations as describe above can be used to predict sorption isotherm of the shelled-corn grain and the other grain-type products.

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