

Desorption Isotherm Model for a Malaysian Rough Rice Variety (MR219)

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ABSTRACT

Moisture desorption model of long grain Malaysian rough rice variety (MR219) was experimentally obtained using the static gravimetric method for different combinations of temperature (40, 45, 50, 55°C) and water activities (0.0507 to 0.9331). Five most commonly used models with three parameters namely modified Chung–Pfoest, modified GAB, modified Halsey, modified Henderson and modified Oswin and a four parameters model (Zuritz *et al.*, 1978) were determined for their ability to fit the experimental data using non linear regression techniques. Comparisons between all models were made on the basis of standard error of estimate (SEE), residual sum squares (RSS) and residual plots. Based on the results of this study, the Zuritz *et al.*, modified Chung–Pfoest and modified GAB models could be useful to predict the desorption EMC of MR219. The modified Halsey, modified Henderson and modified Oswin presented a poor fitting to the experimental data. In addition, the model by Zuritz *et al.* was found to be the most appropriate equation for representing the desorption isotherm model for MR219 at the range of temperatures from 40°C to 60°C.

Keywords: Equilibrium moisture content, desorption, static gravimetric, fit ability, rough rice

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INTRODUCTION

Rough rice is known as a hygroscopic material that can gain or lose moisture even though its surrounding air conditions

undergo changes. A product can gain or lose its moisture when it is subjected to a continual supply of air at constant temperature, humidity and vapour pressure (p), until the vapour pressure of moisture in the product becomes equal to p. In this state, moisture content (MC) of a product is known as equilibrium moisture content (EMC) (Champagne, 2004). There is a relationship between the MC of a product and its equilibrium relative humidity (ERH) at a constant temperature which can be shown by an isotherm curve. It is necessary to have information on the adsorption or desorption isotherms of a particular food. These isotherms can be applied in food processing and engineering to improve product quality (Delgado & Sun, 2002b). The EMC affects the rate of moisture transfer from kernels to the surrounding air which can affect rice milling quality (Fan *et al.*, 2000., Kunze, 1979). Chen (1997) and Bonazzi, *et al.* (1997) claimed that variety, temperature and relative humidity were the main factors that lead head rice yield (HRY) to decrease. Adsorption and desorption are important factors that can affect fissure formation in the rice kernel, and the subsequent HRY during drying and storage. The EMC is developed as a result of an interaction between the material and the environmental condition (Molna' r, 2007):

$$\bar{X}^* = \bar{X}^*(p_v, T) \quad [1]$$

MC of products can be changed because of the condition (p_v, T) dominating on the surface of the products. After an adequately long time with stable limit conditions

an internal moisture diffusion balance occurred until the EMC is reached. The sorption equilibrium is a condition where the moisture adsorption and desorption does not occur in a product. The equilibrium vapour pressure (EVP) is the vapour pressure at which the sorption equilibrium takes place at a certain level of product MC (\bar{X}) at a certain temperature (T). EVP can be expressed as follows:

$$p_v^* = p_v^*(T) \bar{X} \quad [2]$$

In drying research, it is necessary to have enough information on EVP at a constant temperature. Therefore, when T is constant p_v^{*} is constant, the equilibrium relative vapour content is applied in drying process as a characteristic of the vapour pressure (Molna' r, 2007):

$$\psi = \frac{p_v}{p_{ov}^*} \quad [3]$$

Generally, the sorption isotherm ($\bar{X}^* = \bar{X}^*(p_v)_T$), sorption isobars ($\bar{X}^* = \bar{X}^*(T)_{p_v}$), and sorption isosteres ($p_v = p_v(T)_{x^*}$) are applied in drying process. They are derived from the sorption equilibrium function ($\bar{X}^* = \bar{X}^*(p_v, T)$). The sorption isotherms are most frequently applied to describe the sorption behaviour of a material. Sorption isotherms are determined from point to point (Molna' r, 2007):

$$\bar{X}_1^*(\psi_1)_T, \bar{X}_2^*(\psi_2)_T \dots \bar{X}_n^*(\psi_n)_T, \quad [4]$$

Each pair of values for determining a point is in general the result of a measurement. The elements of this measurement are as follows:

1. Presentation of the pair of values to be measured on the condition that T is constant.
2. Measurement of the value of p_v , and ψ should be done during or at the end of the sorption measurement.
3. The EMC (\bar{X}^*) of sample should be determined at the end of the sorption measurement.

Gal (1981) reviewed different methods and finally classified them into three basic techniques, namely, manometric, gravimetric and other special methods. Meanwhile, Molnár (2007) stated that the gravimetric technique is the common method used for EMC determination. In this technique, saturated salt solutions or sulfuric acid dilutions at different concentrations are used to maintain constant relative humidity in closed still moist air at certain temperature (Gal, 1981) and a thermostat is used to control the air temperature (Molnár, 2007). Champagne (2004) stated that different rice varieties equilibrate to slightly different moisture contents in a given environment. The same rice variety also equilibrates to slightly different MC depending on whether the grain is adsorbing or desorbing moisture while approaching the equilibrium state. Chio *et al.* (2010) reviewed different rice hygroscopic equilibrium studies and finally concluded that rice type and variety affect EMC/ERH relationship significantly. The

researchers added that since new varieties are introduced by rice industry, it is necessary to obtain suitable EMC/ERH equation for each to improve rice processing and storage. Since the EMC model is an important parameter in computer drying simulation, selecting a proper model can help to achieve good results. It must be noted that all EMC/ERH models applied in this study have been recommended by previous researchers for a limited range of temperature (10°C - 40°C). In addition, Zuritz *et al.* (1978) conducted an equilibrium isotherm for a medium grain. Therefore, the main goal of this study was to obtain a desorption equilibrium isotherm in the higher range of temperature (40°C - 60°C) for a selected Malaysian long rice variety (MR 219) using the existing models.

MATERIALS AND METHOD

Long grain rough rice, MR219 with approximately 18% moisture content (d.b.) was used in this experimental study. The gravimetric method was chosen to find suitable EMC equation. Sulphuric acid solutions were used to provide constant relative humidity. The following equation was applied to estimate ERH or water activity (Molnár, 2007):

$$\log a_w = \left(a_1 - \frac{a_2}{T}\right) + \log\left(\frac{133.3224}{P_0}\right) \quad [5]$$

Where:

T= absolute temperature (K)

P_0 = vapor pressure of water (Pa)

The empirical constant values (a_1 and a_2) which depend on the sulfuric acid weight percentage are presented by Molnár (2007). Water activity ranges from 0.9331 to 0.0507 was achieved by different concentrations of sulphuric acid from 10% to 70% (w/w). About 20 g of rough rice samples were put inside a cloth net and suspended from jars covers above 125 ml sulfuric acid solution. The jars with rough rice samples were put in temperature controlled incubator set at 40, 45, 50, 55, 60 °C. The measurement of samples masses commenced after 2 weeks. Sample masses were checked again every 72 h. Depending on the relative humidity and temperature, different times were required for samples to reach an equilibrium condition. The maximum time for the samples to reach equilibrium was 28 days. Moisture content of each sample was measured in duplicates by drying 13-15 g samples for 24 h in an oven set at 130°C (Jindal & Siebenmorgen, 1987). The following equation was used to calculate the EMC of the samples (ASAE, 2007):

$$MC(d.b.) = \frac{W_e - W_d}{W_d} \quad [6]$$

Where:

W_e = Sample weight at equilibrium before oven drying

W_d = Sample weight at equilibrium after oven drying

The experiments for each temperature and water activity were carried out in triplicate. Five three-parameter equations that had been recommended by the ASAE

standard D245.5 (ASAE, 2007) were used to determine their fit ability in this study. They can be expressed as follows:

Modified Chung–Pfof equation (Pfof *et al.*, 1976; ASAE, 2007; Basunia & Abe, 2001; Choi *et al.*, 2010):

$$M_e = \frac{\ln A}{B} - \frac{1}{B} \cdot \ln[-(T + C) \cdot \ln RH] \quad [7]$$

Modified Halsey equation (Iglesias & Chirife, 1976; ASAE, 2007; Basunia & Abe, 2001; Choi *et al.*, 2010):

$$M_e = \left[-\frac{\exp(A + B.T)}{\ln RH} \right]^{1/C} \quad [8]$$

Modified Henderson equation (Thompson *et al.*, 1968, ASAE, 2007; Basunia & Abe, 2001; Choi *et al.*, 2010):

$$M_e = \left[-\frac{\ln(1 - RH)}{A.(T + C)} \right]^{1/B} \quad [9]$$

and the modified Oswin's equation (Oswin, 1946; ASAE, 2007; Basunia & Abe, 2001; Choi *et al.*, 2010):

$$M_e = (A + B.T) \cdot \left[\frac{1 - RH}{RH} \right]^{-1/C} \quad [10]$$

The developed and modified GAB equation is as follows (Jayas & Mazza, 1993):

$$M_e = \frac{A.B.\left(\frac{C}{T}\right).RH}{(1 - B.RH)\left[1 - B.RH + \left(\frac{C}{T}\right).B.RH\right]} \quad [11]$$

Where,

M_e = Equilibrium moisture content (EMC, d.b., %)

RH = Equilibrium relative humidity (ERH, decimal)

T = temperature (°C)

A, B & C = parameters

A four-parameter equation by Zuritz *et al.* (1978) was also used for fitting the data. This particular equation was developed by Zuritz *et al.* (1978) for medium grain variety (CSM 5) at drying air temperature range of 10°C - 40°C and Rh of 11.2% - 87.9%. It can be expressed as follows:

$$M_e = \exp \left[\frac{\log \left[\frac{(\log(1 - RH) \cdot T)}{\left(1 - \frac{T}{T_c}\right)^A \cdot B} \right]}{C \cdot T^D} \right] \quad [12]$$

Where,

M_e = EMC (% d.b.)

RH = ERH (decimal)

T = Temperature (°K)

T_c = Critical temperature of water=647.1 (°K)

A, B, C & D = Equation parameters

The parameters in the sorption equations were estimated using non-linear regression analysis by applying the Lab Fit V7.2.44 software. Meanwhile, the sum of square

error (SEE) was used to measure the accuracy of the model and the coefficient of determination (R^2) to show the variability between the predicted and measured data. In a good mathematical model, the coefficient of determination should be close to 1 (one) and sum of square errors should be close to 0 (zero). The suitability of the equations was evaluated and compared using residual sum of square (RSS), standard error of estimate (SEE) and coefficient of determination (R^2):

$$R^2 = \frac{S_t - SEE}{S_t} \quad [13]$$

Where,

$$S_t = \sqrt{\frac{\sum_{j=1}^N (\bar{y} - y_i)^2}{N - 1}} \quad \bar{y} = \frac{\sum_{j=1}^N y_i}{N}$$

$$SEE = \sqrt{\frac{\sum_{j=1}^N (y_{jcal} - y_{jexp})^2}{df}}$$

The residual sum square (RSS) is defined as:

$$RSS = \sum_{j=1}^N (y_{jcal} - y_{jexp})^2 \quad [14]$$

df and N are the degree of freedom and the number of data points, respectively, and y_{jexp} and y_{jcal} are experimental and calculated values of y, respectively. The equation giving the smallest RSS and SEE and the highest R^2 value are considered to be the best fitted equation.

RESULTS AND DISCUSSION

Table 1 shows the desorption isotherm values for MR 219 at ERH of 93.31% to 5.07% and temperature of 40°C – 60°C with equilibrium moisture content (M_e) in decimal and dry basis.

The experimental data were used to estimate parameters of isotherms equations of Zuritz, modified Chung-Pfost, modified GAB, modified Oswin, modified Halsey and modified Henderson. Table 2 shows the estimated parameters of these models in which the EMC was taken as the dependent variable. Meanwhile, the corresponding correlation coefficient

between the experimental and predicted data (R^2), the standard error of estimate (SEE) and residual sum of square (RSS) which indicate the fitting ability of each equation are shown in Table 2. As illustrated, the correlation coefficients are very high in most cases ($R^2 > 0.97$).

The Zuritz model obtained the highest R^2 , the least SEE and the least RSS followed by modified Chung- Pfost, modified Gab and modified Oswin at selected temperature range (40°C – 60°C) and ERH (93.31% to 5.07%). According to Chen and Morey (1989) and Aviara *et al.* (2004), statistical parameters like R^2 or SEE may not be

TABLE 1
Desorption isotherm values for MR219 at different ERH (%) and temperatures.

T= 40 ° C		T= 45 ° C		T= 50 ° C		T= 55 ° C		T= 60 ° C	
ERH	M_e	ERH	M_e	ERH	M_e	ERH	M_e	ERH	M_e
92.97	0.2094	92.90	0.176	92.94	0.168	93.08	0.1587	93.31	0.1436
86.42	0.1755	86.44	0.1631	86.56	0.1483	86.78	0.1375	87.08	0.1193
73.96	0.1441	74.01	0.1413	74.14	0.1234	74.35	0.1089	74.63	0.0954
56.96	0.1167	57.18	0.108	57.46	0.1027	57.80	0.0862	58.19	0.0754
36.51	0.0852	36.89	0.0767	37.32	0.0688	37.77	0.0595	38.26	0.0520
17.86	0.0600	18.26	0.055	18.68	0.0414	19.11	0.0382	19.57	0.0321
5.07	0.0284	5.32	0.0235	5.59	0.0209	5.86	0.0191	6.15	0.0165

TABLE 2
The estimated coefficients and the statistical parameters for selected mathematical sorption equations

Equations	parameters				R^2	SEE	RSS
	A	B	C	D			
Zuritz	-2.5239×10^2	9.480×10^{-8}	1.1801×10^6	-2.307	0.9956	0.0037	0.1875
Modified Chung-Pfost	107.048	24.277	-28.320	-	0.9899	0.0078	0.2013
Modified GAB	463.148	1.068	1.701×10^{-2}	-	0.9871	0.0091	0.2392
Modified Oswin	0.1654	-1.673×10^{-3}	3.282	-	0.9726	0.0094	0.2650
Modified Halsey	-4.417	-5.396×10^{-2}	2.630	-	0.9321	0.0147	0.4229
Modified Henderson	1.797×10^{12}	1.932	2.247×10^{10}	-	0.9063	0.0169	0.9519

sufficient evidence for the goodness of fit of a moisture sorption isotherm model based on experimental data. Therefore, the nature of the residual plots should be considered. The residual plots of the Zuritz *et al.* modified Chung-Pfost and modified Gab models were random distributions over the range of temperature and EMC tested in this study. As shown in Fig.1 to Fig.3, the modified Oswin, modified Halsey and modified Henderson models presented a patterned distribution for MR219 under the tested conditions in this study.

Based on the results shown in Table 2 and the residual plots, the Zuritz *et al.*

modified Chung- Pfost, and the modified Gab models could be useful for predicting the EMC and its temperature dependence. From the three models, the Zuritz *et al.*'s model was the most appropriate model to predict moisture desorption isotherms of MR219 at the temperature ranges from 40°C to 60°C. The desorption isotherms obtained in this study have a sigmoid shape (Fig.4). Under fixed relative humidity condition with increasing air temperature, the EMC decreases. In addition, at fixed air temperature, EMC decreases with decreasing relative humidity.

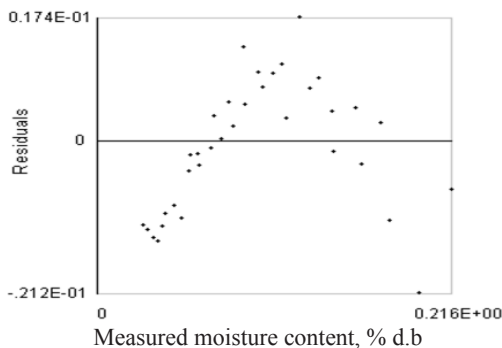


Fig.1: Residuals versus predicted EMC for the modified Oswin's equation

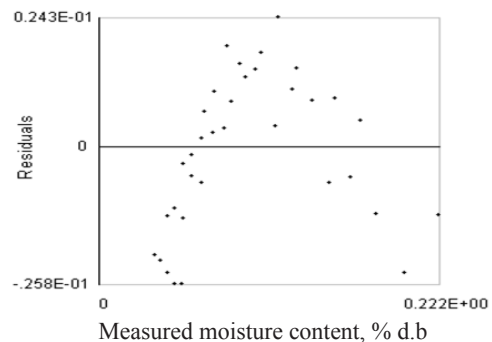


Fig.2: Residuals versus predicted EMC for modified Halsey equation

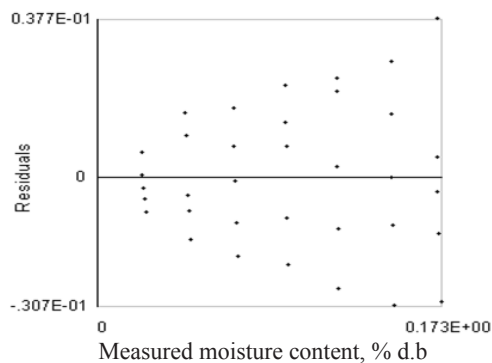


Fig.3: Residuals versus predicted EMC for modified Henderson equation

CONCLUSION

The desorption isotherm obtained in this study presented a sigmoid shape. The results illustrate that the EMC of rough rice decreases with an increase in temperature at constant ERH. The correlation coefficient (R^2) obtained for all the models was in the range of 0.9956 – 0.903. Among the moisture isotherm equations tested in this study, the four-parameter moisture isotherm equation of Zuritz *et al.* was identified as the most appropriate equation to represent EMC of the Malaysian rice variety (MR219) at the temperature ranges from 40°C to 60°C. Three parameter equations of the modified Chung-Pfost and the modified Gab were also found acceptable. However, the modified Oswin, modified Halsey and modified Henderson presented a poor fitting ability to the experimental data.

NOTATIONS

- A, B, C, D = Coefficients
- EMC = Equilibrium moisture content
- ERH = Equilibrium relative humidity
- EVP = Equilibrium vapor pressure
- M_e = Equilibrium moisture content
- P = Partial pressure
- R^2 = Correlation coefficient
- RSS = Residual sum square
- SEE = Standard error of estimate
- T = Temperature
- X = Moisture content of material
- ψ = Relative equilibrium vapor pressure

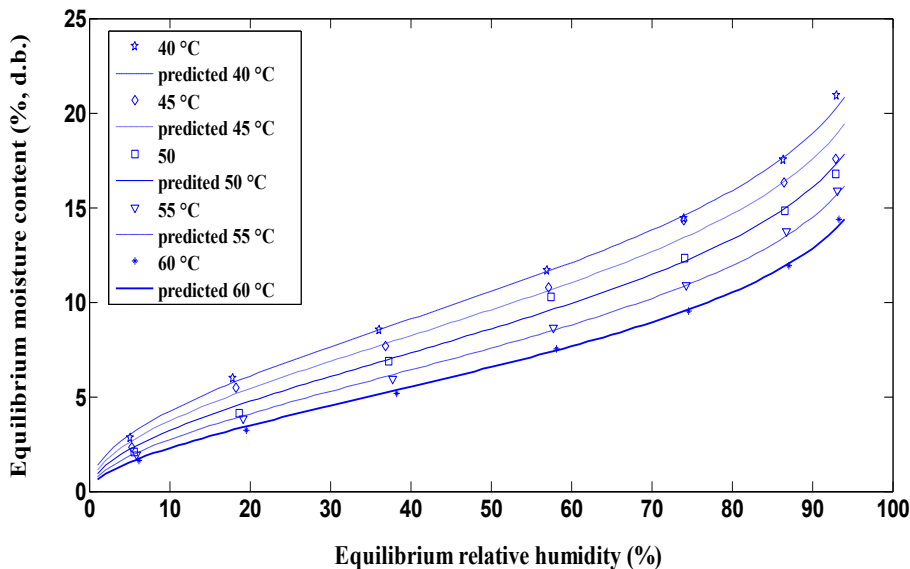


Fig.4: The experimental and Zuritz model predicted the desorption isotherms for MR219 at 40, 45, 50, 55, and 60°C

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