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Moisture Desorption Isotherms of Squids

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Abstract— Moisture desorption isotherms of squids were determined by the method of saturated salt, at temperatures of 30℃, 40℃ and 50℃ in the range of air relative humidity from 11.10% to 80.27%. The initial moisture contents were in the range of 83.5% - 84% wet basis. The final moisture content was considered as the equilibrium moisture content. Twelve different mathematical equations are brought into comparison to determine the effects of temperature and relative humidity on equilibrium moisture content of squids. The criteria, including correlation coefficient, root mean square error and chi-squared distribution, are examined in this study to select the appropriate equations. The analysis results show that modified Halsey is the most appropriate equation to predict the equilibrium moisture content of squids. Modified Oswin, modified Chung-Pfost and modified Henderson equations are also efficient, respectively, while Smith and Caurie equations are not consistent with the experimental results.

Keywords— **dried Squid, equilibrium moisture content, relative humidity, saturated salt.**

INTRODUCTION

Dried squid is a favorite seafood due to a delicious smell and high content of protein and nutrients (Wang et al., 2014). People in Asian region also prefer this food in a daily meal. Dried squid was prepared by dried fresh squid with reducing the moisture of about 84% (Kang et al., 2011) down to 25% (TCVN, 1992). In compared with fresh squid, dried squid is better to prevent microbial growth and prolong expiry date. Sun drying is the most traditional and economical one which does not involve the use of supported devices. However, Sun drying has some disadvantages such as time-consuming, weather dependent, nutrient loss, easy pollutants from environmental (Jain et al., 2007). Therefore, it is imperative to optimize processing conditions to produce high-quality dried products. Drying methods has the advantages of controlling the temperature parameters, the velocity of drying agents and other pollution sources. As the result, the dried squid has higher quality than sun drying method. To optimize the squid drying process, equilibrium moisture content (EMC) is considered as one of the most important factors.

Equilibrium moisture content is a major parameter to predict the changes of product moisture during drying and storage. The desorption isotherm determines the lowest attainable moisture content of squids at a particular drying temperature and relative humidity. The relationship between the equilibrium moisture content and equilibrium relative humidity (ERH) is essential to control the squid drying process.

There have been more than 200 equations which are developed theoretically, semi-theoretically or empirically to describe the relationships between EMC and ERH. Furthermore, the temperature of different biological materials is modelled by these equations. After studying 23 different EMC/ERH models, Chirife and Iglesias (Basunia et al., 2001) found that each model has achieved a certain success in predicting EMC for a specific type of food in a certain range of relative humidity and temperature. However, Chen and Morey (Chen et al., 1989) concluded that none of them has the true ability to describe the relationships between EMC and ERH for different type of materials in a wide range of relative humidity and temperature. Therefore, choosing and determining appropriate models to describe the relationship between EMC and ERH of squid are very essential.

Although many studies have discussed the equilibrium moisture content of different types of fresh food like fish, pork, beef, etc., very few of them has examined the equilibrium moisture content of squid. Hence, this study was performed to clarify the EMC of squid.

MATERIALS AND METHODS

A. Materials

The experiment was carried out with fresh squids. Each sample weighs from 250 to 300 gram and is free of defects. After cutting in a transverse direction, the middle part of each squid which weighs from 10 to 11 g was selected. The moisture content of the sample was determined by using drying oven at 105 ± 0.1℃ in 24 hours (AOAC, 1979).

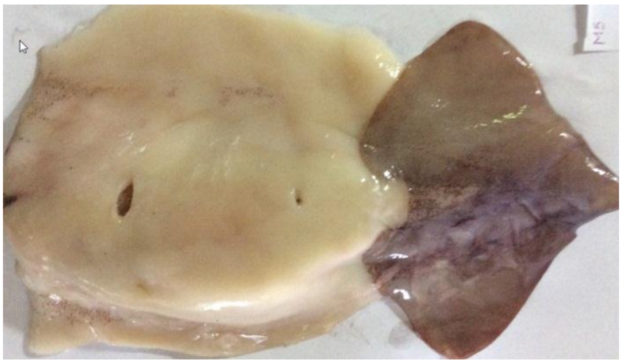

Fig. 1 Fresh squid use to experiment

B. Experiment equipment

The equipment used include a temperature control chamber with a capacity of 50 liters, adjusting the temperature is in the range of 30-55℃, with ±0.1℃ accuracy; Seven desiccators with a volume of 1 liter is used to contain the sample and saturated saline solution (Trujillo et al., 2003); HZX-310 electronic scales with ± 0,001 g precision.

C. Method for determining equilibrium moisture content of squid

Equilibrium moisture content is determined by saturated salt solution method; which salt is used to create an environment with stable relative humidity content at different temperatures. Seven different saturated salts were used to create the environment with humidity from 11.10% to 80.27% (Greenspan L., 1977) which is presented in Table 1. The experiment samples were placed on the mesh in each desiccator, with a saturated salt solution at the bottom (Fig. 2), then closed the cover tightly and placed the bottles in temperature control cabinet. The samples were numbered and experiments were conducted at three temperature levels of 30℃, 40℃ and 50℃. To avoid the samples being damaged, potassium sorbate preservative was used for samples with relative humidity of 50% or higher (Magnesium Nitrate, Potassium Iodide, Sodium Chloride, and Potassium Bromide). So, 25 mg Potassium sorbate was poured onto each sample (5 mg Potassium sorbate for each gram of sample). At this rate, the preservative did not affect equilibrium moisture content of the product as mentioned in study of Singh (Singh et al., 2006).

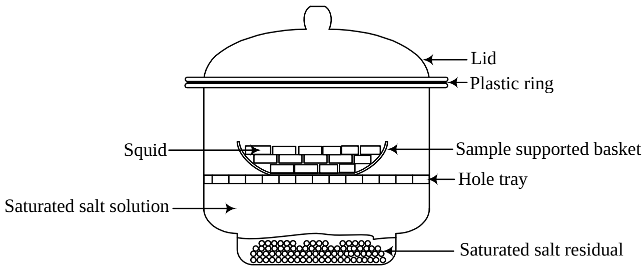

Fig. 2 Layout of equilibrium moisture experiment

In the course of the experiment, the sample was weighed after two days until the difference of two consecutive weighing times was less than 0.005 g. The moisture content of the samples was determined using drying oven at 105 ± 0.1℃ in 24 hours (Chen et al., 1989) to determine the equilibrium moisture content of squid, using equation (1). The average value of three experiments:

$$M = \left(\frac{m_{eq} - m_a}{m_a} \right) \times 100 \tag{1}$$

Where m_{eq} represents the mass of the sample in equilibrium and m_a is the anhydrous mass.

Table 1: relative humidity of saturated salt at different temperature levels

Salts	30℃	40℃	50℃
Lithium chloride	11.28 %	11.21 %	11.10 %
Potassium Fluoride	27.27 %	22.68 %	20.80 %
Magnesium Chloride	32.44 %	31.60 %	30.54 %
Magnesium Nitrate	51.40 %	48.42 %	45.44 %
Potassium Iodide	67.89 %	66.09 %	64.49 %
Sodium Chloride	75.09 %	74.68 %	74.43 %
Potassium Bromide	80.27 %	79.43 %	79.02 %

D. The mathematical equations used to determine the equilibrium moisture content

Many mathematical equations have been developed to describe the equilibrium moisture content for various types of foods. The studies on equilibrium moisture content of foods such as: barley (Basunia et al., 2005), bananas (Phoungchandang et al., 2000), fish (Basu et al., 2006) rice (Basunia et al., 2001) verifies the suitability of Smith and Caurie equations (Boquet et al., 1978), modified Chung–

Pfost equations (Pfost et al., 1976), modified Halsey equation (Iglesias et al., 1976), modified Henderson equation (Thomson et al., 1968) and modified Oswin equation (Oswin et al., 1946) to describe equilibrium moisture content of the product. While the studies on equilibrium moisture of pork (Clement et al., 2009) and beef (Ahmat et al., 2014) show that GAB equation is the most suitable one; however, GAB equation has a large number of parameters, so the authors recommend using the modified Halsey equation. Twelve mathematical equations presented below are used to describe the relationship between EMC of squid and ERH.

Smith (Smith 1947):

$$RH = 1 - \left(\frac{\exp(A)}{\exp(M)}\right)^{1/B} \quad (2)$$

$$M = A - B\ln(1 - RH) \quad (3)$$

Caurie (Caurie 1970):

$$RH = \frac{\ln(M) - A}{B} \quad (4)$$

$$M = \exp(A + B.RH) \quad (5)$$

Modified Halsey equation (Iglesias and Chirife 1976):

$$RH = \exp[-\exp(A + BT)M^{-C}] \quad (6)$$

$$M = [\exp(A + BT)]^{1/C}(-\ln RH)^{-1/C} \quad (7)$$

Modified Henderson equation (Thompson et al 1968):

$$RH = 1 - \exp[-A(T + B)(M)^{C}] \quad (8)$$

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

Chung-Pfost equation (Pfost et al 1976):

$$RH = \exp\left[-\frac{A}{T + B}\exp(-CM)\right] \quad (10)$$

$$M = A - C.\ln[-(T + B).\ln(RH)] \quad (11)$$

Modified Oswin equation (Oswin 1946):

$$RH = \frac{1}{(A + BT/M)^{1/C} + 1} \quad (12)$$

$$M = (A + BT)\left(\frac{RH}{1 - RH}\right)^{C} \quad (13)$$

E. Method for determining the parameters in the equation

The equation parameters are put under nonlinear regression statistical analysis by using SPSS 22.0 software. The experimental values and predicted values are compared. Then, the results were statistically analyzed to determine the most suitable equation; the equation is selected on the basis of analysis and evaluation of 3 criteria: correlation coefficient (R^2), root mean square error (RMSE) and Chi-squared distribution (χ^2). The highest R^2, the lowest RMSE and χ^2 are used as criteria for conformity.

$$\chi^2 = \sum_{i=1}^{N}\frac{(V_{exp} - V_{pre})^2}{V_{pre}} \quad (14)$$

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}\left(V_{exp} - V_{pre}\right)^2\right]^{0.5} \quad (15)$$

where V_{exp} and V_{pre} are the experimental and predicted values, respectively. N is the number of experimental data point

RESULTS AND DISCUSSIONS

After 16-18 days, the changes in the weight of all samples are less than 0.005g; the experiment was stopped. Experimental values of equilibrium moisture content of squid with a relative humidity level of the air in the range of 11.10% to 80.27%, at three levels of temperature 30℃, 40℃ and 50℃ are shown in Table 2 and are represented by the graph in Fig. 3.

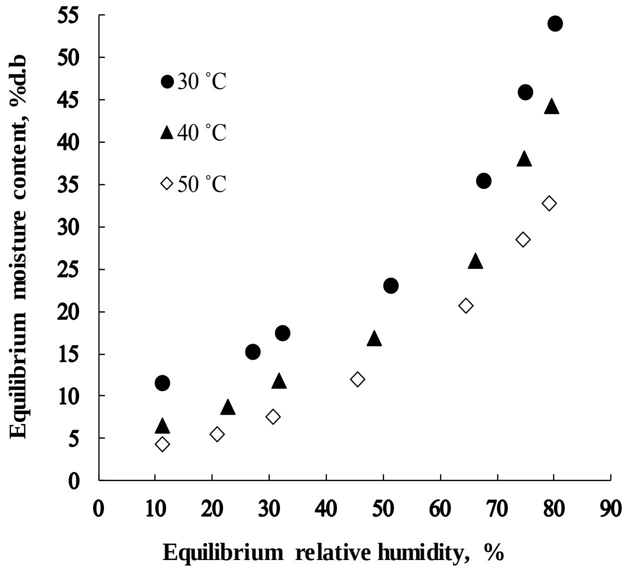

Fig. 3 Equilibrium moisture content of the squid at different temperatures

The EMC of squid decreased with a higher temperature at a given ERH and increased with increasing ERH at a given temperature. For example, EMC of squid at 30℃ with 32.44% ERH and 50℃ with 30.54% ERH were 17.35% and 7.58%, respectively. These results are similar with the findings of Ahmat (Ahmat et al., 2014) about equilibrium moisture content of pork.

The value of the parameters, including root mean square error RMSE, Chi-squared distribution χ^2 and correlation coefficient R^2 of twelve proposed equations are presented in Table 3. The results of nonlinear regression analysis show that evaluation criteria for the equilibrium moisture content and relative humidity obtained by modified Halsey, modified Henderson, modified Chung - Pfost and modified Oswin equations are quite similar. These equations have a high correlation coefficient R^2, root mean square error RMSE and low chi-squared distribution χ^2 compared with experimental data. In details R2 value is 0.950 to 0.991, RMSE is from 0.138 to 0.055 and χ^2 is from 0.025 to 0.128. Therefore, it can be used to predict the EMC of squid. While Smith and Caurie equation gives a low R^2 and high RMSE, so it is not suitable for predicting the EMC of squid.

Table 2: Equilibrium moisture content of squid at different temperatures

Temp. °C	ERH, %	EMC, % (w.b.)	EMC, % (d.b.)
30	11.28	10.23	11.39
	27.27	13.05	15.01
	32.44	14.78	17.35
	51.40	18.61	22.88
	67.89	26.03	35.20
	75.09	31.34	45.64
	80.27	34.98	53.81
40	11.21	6.12	6.52
	22.68	8.01	8.707
	31.60	10.59	11.86
	48.42	14.36	16.77
	66.09	20.64	26.02
	74.68	27.53	37.98
	79.13	30.65	44.19
50	11.10	4.18	4.37
	20.80	5.21	5.50
	30.54	7.05	7.58
	45.44	10.69	11.98
	64.49	17.16	20.71
	74.43	22.19	28.53
	79.02	24.65	32.72

Results of comparing predicted EMC values with experimental values at temperatures 30°C, 40°C and 50°C are represented on the graphs of Fig. 4, 5, and 6. The predicted curve uses four equations (7), (9), (11), and (13) with regression coefficients as defined in Table 3

For relative humidity from 45.44% to 80.27% at 30°C, 40°C and 50°C, modified Halsey equation has the smallest predicted error, followed by the equation of modified Oswin. Results described in Table 3 shows the errors obtained from the modified Halsey and modified Oswin equations are lower than those of modified Henderson and modified Chung – Pfost equations. The predicted curves show that modified Halsey equation closely describes the experimental data than modified Oswin equation

Table 3: Regression indicators and parameter values of the twelve proposed equation

Equation	Parameter A	Parameter B	Parameter C	R^2	χ^2	RMSE
Smith (Eq.(2))	0.015	0.265		0.876	0.443	0.087
Caurie (Eq.(4))	-3.256	3.156		0.856	0.507	0.094
Modified Halsey (Eq.(6))	-0.870	-0.040	1.192	0.985	0.063	0.030
Modified Henderson (Eq.(8))	0.1540	-7.628	1.195	0.968	0.128	0.044
Modified Chung - Pfost (Eq.(10))	89.756	-5.291	6.496	0.950	0.125	0.055
Modified Oswin (Eq.(12))	0.410	-0.005	0.583	0.981	0.184	0.050
Smith (Eq.(3))	0.026	0.250		0.866	0.263	0.052
Caurie (Eq.(5))	-3.085	2.814		0.870	0.248	0.052
Modified Halsey (Eq.(7))	-1.383	-0.029	1.267	0.991	0.025	0.014
Modified Henderson (Eq.(9))	0.110	0.528	1.133	0.972	0.115	0.025
Modified Chung -	0.705	-10.045	0.162	0.938	0.137	0.036

Pfost (Eq.(11))						
Modified Oswin (Eq.(13))	0.369	-0.004	0.592	0.988	0.062	0.023

The results presented in Table 3 show that modified Halsey equation has the lowest RMSE value, i.e. 0.014 for EMC and 0.030 for ERH. The R2 value is higher than that of other equations, 0.991 for EMC and 0.985 for ERH. This result proves that modified Halsey equation is the most suitable equation to predict the equilibrium moisture content of squid. The most appropriate factors for EMC/ERH of modified Halsey equation ((6), (7)) are rewritten as follows:

$$RH = \exp[-\exp(-0.870 - 0.040.T)M^{-1.920}]$$

$$M = [\exp(-1.383 - 0.029.T)]^{1/1.267}(-\ln RH)^{-1/1.267}$$

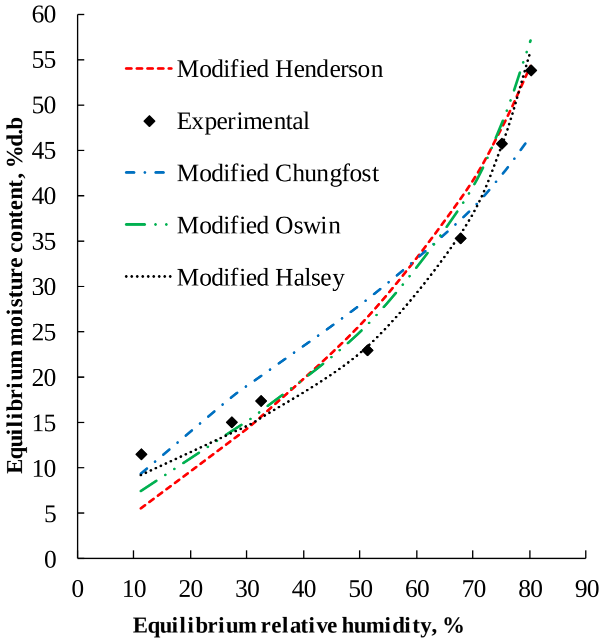

Fig. 4 Predicted and experimental equilibrium moisture content of the squid at 30℃

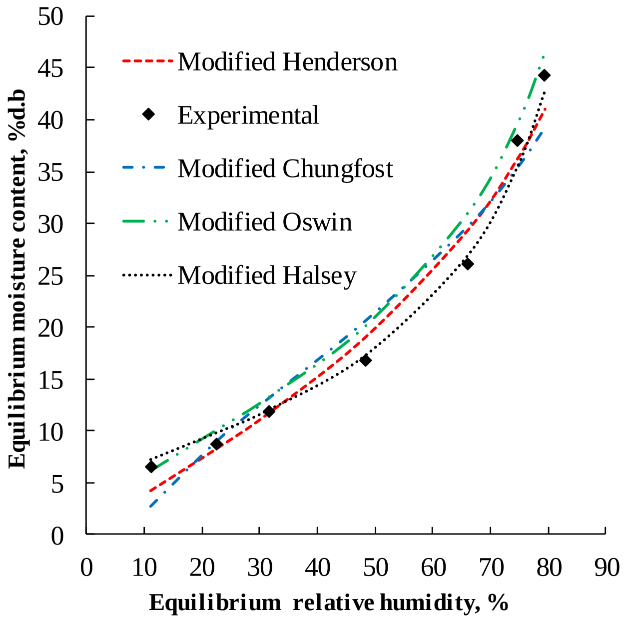

Fig. 5 Predicted and experimental equilibrium moisture content of the squid at 40℃

The graph for comparing the predicted value (modified Halsey equation) and experimental value of EMC is shown in Fig. 7 This result shows that experimental data is scattered around the predicted curve. Within the range of relative humidity from 35% to 80.27%, it gives predicted EMC results which are better than those in relative humidity range from 10% to 35%.

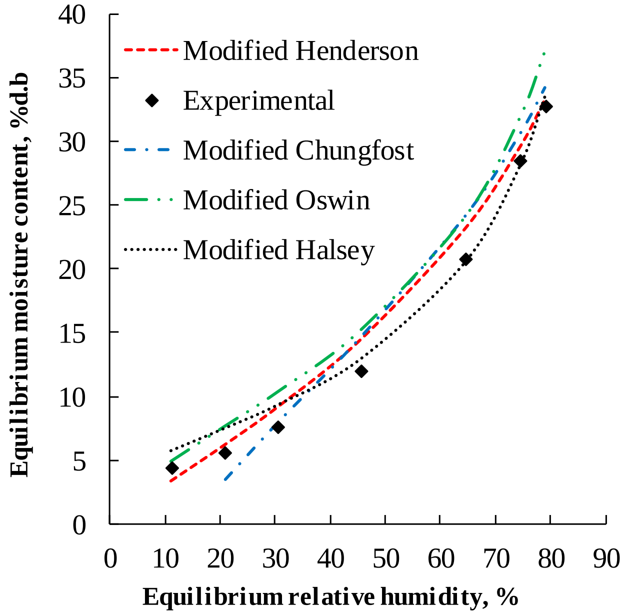

Fig. 6 Predicted and experimental equilibrium moisture content of the squid at 50℃

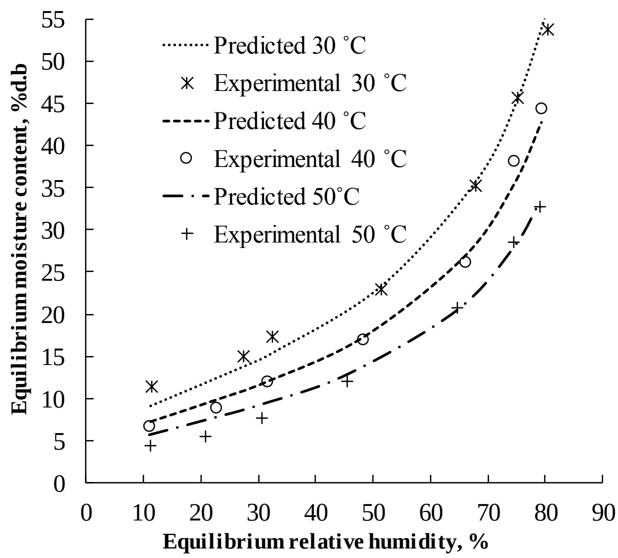

Fig. 7 Predicted and experimental equilibrium moisture content at 30℃, 40℃ and 50℃ (modified Halsey equation)

CONCLUSIONS

Twelve EMC/ERH equations are used to predict the equilibrium moisture content of squid which has relative humidity from 11.10% to 80.27%, at three temperatures of 30℃, 40℃, and 50℃, by saturated salt solution method. The results showed that modified Halsey, modified Oswin, modified Chung-Pfost, and modified Henderson equations are suitable to predict the equilibrium moisture content of squid.

Modified Halsey equation is the most appropriate equation to predict the equilibrium moisture of squid. RMSE value for EMC is 0.0134% and ERH is 0.030. R^2 value for EMC and ERH is 0.991 and 0.985, respectively, while Smith and Caurie equation gives inconsistent results to predict EMC of squid.

The result may provide a meaningful reference to help other researchers in finding a very useful resource for data for future work on drying and storage

Future researchers should also address to effects of different drying methods on equilibrium moisture content of squid and compare with other authors in the same field of study.

NOMENCLATURE

A, B, C	constant
RH	relative humidity
M	equilibrium moisture content
T	temperatures ℃
R^2	correlation coefficient
RMSE	mean square error
χ^2	chi-squared distribution
m_{eq}	equilibrium mass
m_a	anhydrous mass
V_{exp}	experimental
V_{pre}	predicted values
N	number of experimental data point.

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