

# GRAVIMETRIC MEASUREMENT OF MOISTURE SORPTION ISOTHERM AND ISOSTERIC HEAT OF BLACK PEPPER

Yutthana Tirawanichakul<sup>1</sup>, Sae-Khow Atchara<sup>2</sup>, and Supawan Tirawanichakul<sup>2,\*</sup>

*Received: May 23, 2019; Revised: October 01, 2019; Accepted: October 02, 2019*

## Abstract

There are 4 objectives of Thailand 4.0 economic model, and 1 of the objectives is economic prosperity for creating a value-based economy, especially on agricultural sector. Thus, the principal physical, biological, chemical and physico-chemical properties data for each agriculture products and food should be studied and reported on for overall collection of agricultural product data. So, the main objectives of this work are to evaluate some thermo-physical properties of black pepper and to develop mathematical model of sorption isotherm for black pepper. Therefore, the thermo-physical properties in terms of equilibrium moisture content (EMC), apparent density ( $\rho$ ), void fraction ( $\epsilon$ ) and specific heat capacity ( $cp$ ) were determined in this research. In addition, the drying kinetics of black pepper was also studied and predicted by mathematical modeling. The EMC simulation results showed that the predicted data using the modified Halsey model gave the best fit to the exact desorption isotherms data of black pepper, providing the highest coefficient of determination ( $R^2 = 0.98$ ) and the lowest root mean square error value ( $RMSE = 0.68$ ). To determine 3 thermo-physical properties, the results stated that the apparent density, the percentage of the void fraction, and the specific heat capacity value of black pepper were linearly dependent upon moisture content.

**Keywords:** Equilibrium moisture content, isosteric heat of sorption, sorption isotherm, thermo-physical properties

---

<sup>1</sup> Plasma and Energy Technology Research Laboratory, Department of Physics, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, 90110, Thailand.

<sup>2</sup> Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla, 90110, Thailand. E-mail: supawan.t@psu.ac.th

\* Corresponding author

## Introduction

The post-harvesting process, such as drying and dehydration, is very important to maintain the quality of agricultural products before marketing. The conventional drying or dehydration methods of products are solar drying and hot-air drying. To optimize the stability and quality of a dry product during storage, the characteristics of the product's sorption behavior must be known (Soponronnarit, 1997; Tirawanichakul *et al.*, 2008; Tirawanichakul *et al.*, 2013). The moisture content of a moist material in equilibrium with the surrounding air of a given relative humidity and temperature is well-known and termed as the equilibrium moisture content (EMC); it is an important parameter which determines shelf life, drying, mixing, and packaging. Fresh agricultural products have different EMCs under similar surrounding conditions because of their different physical, chemical, biological, and physicochemical structures. The sorption isotherms are of interest because they provide information on the water activity of a product depending on the surrounding air temperature and relative humidity. There has been much previous research focusing on the sorption isotherms corresponding to agricultural products and their by-products (Timmermann, 1989; Soponronnarit, 1997; Timmermann *et al.*, 2001) which has mainly covered the effect of temperature on moisture sorption, heat sorption, and sorption modelling. Additionally, some research works have evaluated the isosteric heat of sorption and the properties of bound water from the moisture sorption properties (Timmermann, 1989; Wang and Brennan, 1991; Soponronnarit, 1997; Timmermann *et al.*, 2001; Chen, 2006; Tirawanichakul *et al.*, 2008). Pepper has remained 1 of the most precious and valuable forms of spice in the world, especially acting as the most added ingredient to food among the wide range of spices. Due to its bio-functional and health properties, dried black pepper has played a pivotal role in international trade. There have been a few research works that have reported on its thermo-physical properties, such as specific heat capacity, heat sorption, apparent density, void fraction, and

equilibrium moisture content correlation with temperature and humidity.

Thus, the main objectives of this research are to investigate various thermo-physical properties of black pepper in terms of its EMC value, apparent density, percentage of void fraction, and specific heat capacity and to evaluate the isosteric heat of sorption.

## Materials and Methods

### Materials

Black pepper (*Piper nigrum* L.) was purchased from a local market in Songkhla province, Thailand. To remove any impurity and seed immaturity, the pepper samples with an average dimension of  $0.6 \pm 0.1$  cm diameter were washed and halved. To provide a uniform moisture content of the samples, the pepper samples were stored in a refrigerator at a temperature of 4°C. Before the experiments, the pepper samples were taken out of the refrigerator and placed in a net basket until the samples' temperature was close to the ambient temperature. The moisture content of the pepper samples was determined by the standard AOAC method (AOAC International, 1995).

### Methods

#### Determination of Equilibrium Moisture Content

Five saturated salt solutions were used to achieve an equilibrium moisture content consisting of LiCl,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , NaCl, and  $\text{KNO}_3$ . These solutions provided relative humidity values of 10-90% correlated to the surrounding temperatures of 40-65°C (Oswin, 1942; Halsey, 1948; Henderson, 1952; Chung and Pfost, 1967; Timmermann, 1989; Soponronnarit, 1997; Tirawanichakul *et al.*, 2008). To avoid disruption of the results from direct contact with the salt solutions, the fresh pepper samples were placed in stainless steel baskets each hanging over a saturated salt solution in airtight vials. The 2 sample vials in each saturated salt solution were placed in an

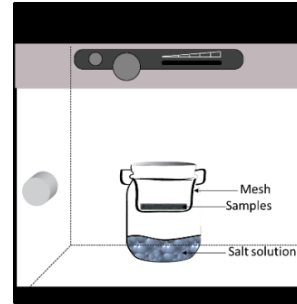
incubator at temperatures of 40, 45, 50, 55, 60, and 65°C to obtain final consistent matter weight. The time to achieve the equilibrium state between the sample and saturated salt solution was between 10 and 20 days (Pfoest *et al.*, 1976; Soponronnarit, 1997; Timmermann *et al.*, 2001; Cortés and Chejne, 2010). The experimental set-up for evaluation of the equilibrium moisture content was shown in the Figure 1. The moisture content was determined when the sample weight remained unchanged after 2 consecutive weighing ( $\pm 0.01$  g), implying that the sample was in an equilibrium state with the saturated salt solution and surrounding air condition. The samples were then weighed to determine the final moisture content (the EMC value) following the standard AOAC method (AOAC, 1995). The weight of a pepper sample was measured in triplicate and the isotherm models for predicting the EMC values was chosen to fit the experimental data as listed in Table 1.

The coefficient values in the 6 EMC models were determined by non-linear regression analysis. The coefficient of determination ( $R^2$ ) and root mean square error (RMSE) values were used as the primary criteria to select the best equation to describe the experimental data. The parameters were defined as follows:

$$R^2 = 1 - \frac{\sum_{i=1}^N (Data_{exp,i} - Data_{pre,i})^2}{\sum_{i=1}^N (Data_{exp,i} - Data)^2} \quad (1)$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (Data_{exp,i} - Data_{pre,i})^2} \quad (2)$$

where the subscripts exp,i and pre,i stand for the experimental and predicted values, respectively.



**Figure 1. Preparation of equilibrium moisture content experimental set-up**

### Thermodynamic Properties of Sorption

Differential enthalpy or isosteric heat of sorption and differential entropy were selected to calculate the thermodynamic properties of the black pepper. The isosteric heat of sorption was determined using the Clausius-Clapeyron equation relating the surrounding relative humidity and temperatures at a fixed moisture content (Cortés and Chejne, 2010; Tirawanichakul *et al.*, 2013). The following equation can be written as Equation (11):

**Table 1. The mathematical equilibrium moisture content models for pepper**

| Model name                | Model equation                                                |      |
|---------------------------|---------------------------------------------------------------|------|
| Oswin (1942)              | $M_{eq} = A \left[ \frac{RH}{(1 - RH)} \right]^B$             | (3)  |
| Modified Oswin (1942)     | $M_{eq} = (A + BT) \left[ \frac{RH}{(1 - RH)} \right]^C$      | (4)  |
| Halsey (1948)             | $M_{eq} = \left[ \frac{-A}{T \ln(RH)} \right]^{1/B}$          | (5)  |
| Modified Halsey (1948)    | $M_{eq} = \left[ \frac{-A}{(BT + CT^2) \ln RH} \right]^{1/D}$ | (6)  |
| Henderson (1952)          | $M_{eq} = \left[ \frac{-\ln(1 - RH)}{AT} \right]^{1/B}$       | (7)  |
| Modified Henderson (1952) | $M_{eq} = \left[ \frac{-\ln(1 - RH)}{A(T + B)} \right]^{1/B}$ | (8)  |
| Smith [3]                 | $M_{eq} = A + B/\ln(1 - RH)$                                  | (9)  |
| Modified Smith [3]        | $M_{eq} = -A + (BT + CT^2 \ln(1 - RH))$                       | (10) |

Note:  $M_{eq}$  is the equilibrium moisture content, (decimal);  $T$  is the absolute temperature, (K);  $RH$  is the surrounding relative humidity, (decimal);  $A$ ,  $B$ , and  $C$  are the arbitrary constants determined by non-linear analysis

$$\frac{\partial[\ln RH]}{\partial T} = \frac{\Delta H}{RT^2} \quad (11)$$

where  $RH$  is the relative humidity (decimal),  $T$  is the absolute temperature (K),  $\Delta H$  is the isosteric heat of sorption (kJ/mol), and  $R$  is the universal gas constant (8.314 kJ/kmol°C).

Integrating Equation (11) and assuming that the isosteric heat of sorption ( $\Delta H$ ) is temperature independent gives the following equation:

$$\ln(RH) = -\left(\frac{\Delta H}{R}\right)\frac{1}{T} + C. \quad (12)$$

where  $C$  is the intercept on the graph of Equation (12).

The slope of the plot of  $\ln(RH)$  versus  $1/T$  at a constant moisture content gave the isosteric heat of sorption, following the thermodynamic relationship:

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

where  $\Delta G$  is the Gibbs free energy (kJ/kmol) and  $\Delta S$  is the entropy (kJ/kmol K). For moisture sorption:

$$\Delta G = -RT \ln(RH). \quad (14)$$

By substituting  $\Delta G$  from Equation (13) into Equation (14), the following equation is obtained:

$$\ln(RH) = -\left(\frac{\Delta H}{R}\right)\frac{1}{T} + \frac{\Delta S}{TR}. \quad (15)$$

If  $\ln(RH)$  is plotted against  $1/T$ , a straight line graph is obtained with the y-intercept of  $\Delta S/R$ . From the values of this y-intercept and  $R$ ,  $\Delta H$  and  $\Delta S$  can be determined.

### Apparent Density ( $\rho$ )

To determine the apparent density of black pepper, the samples with different moisture content values of 10 to 200% dry-basis were put into a 250 ml volumetric flask until full volume and were weighed with an electronic balance with an accuracy of  $\pm 0.01$ g. The inspections were repeated 5 times for each

moisture content value. Then the apparent density was calculated by dividing the weight with the bulk volume as shown in Equation (16):

$$\rho = \frac{m}{V} \quad (16)$$

where  $\rho$  is the apparent density (kg/m<sup>3</sup>),  $m$  is the mass of the black pepper sample in each moisture content (kg), and  $V$  is the volume of the volumetric flask (m<sup>3</sup>)

### Void Fraction ( $\epsilon$ )

The percentage of the void fraction of a sample is normally defined as the fraction of the space in its bulk volume. So, in this research, the percentage of the void fraction of black pepper in different moisture content values of 10-200% dry-basis was determined. The black pepper samples were put into a 250 ml volumetric flask until full volume and then an exact volume of vegetable oil was put into the flask until there was no air bubble inside the flask. The volume of vegetable oil was then recorded and the inspections were measured with 4 replications for all the experiments. The void fraction was calculated as in the following Equation (17):

$$\% \epsilon = \frac{V_{oil}}{V_b} \times 100 \quad (17)$$

where  $\% \epsilon$  is the percentage of the void fraction,  $V_{oil}$  is the volume of the vegetable oil (m<sup>3</sup>), and  $V_b$  is the volume of the volumetric flask (m<sup>3</sup>).

### Specific Heat Capacity ( $c_p$ )

The specific heat capacity of the black pepper was measured at different moisture content values of 10-200% dry-basis. Seventy g of black pepper samples were placed into a bomb calorimeter and sealed with an insulated sheet. Then 40 g of hot distilled water (65°C) was added into the bomb calorimeter and mixed thoroughly. The experiment was carried out with a duration time of 10-20 min. Then the black pepper grains and surroundings (calorimeter, water, air) reached the equilibrium state at which all the temperatures including

the bomb calorimeter temperature, water, black pepper seed, and surroundings were recorded. Inspections were determined in triplicate for each experiment. Then the specific heat capacity was calculated by the energy balance equation as shown in Equation (18):

$$C_p = \frac{[m_c c_c (T_{eq} - T_{ci}) + m_w c_w (T_{eq} - T_{wi})]}{m_p (T_{eq} - T_{pi})} \quad (18)$$

where  $c_p$  is the specific heat capacity of the sample (kJ/kg °C),  $c_c$  is the specific heat capacity of the calorimeter (kJ/kg °C),  $c_w$  is the specific heat capacity of the water (kJ/kg °C),  $m_p$  is the mass of the sample (kg),  $m_c$  is the mass of the calorimeter (kg),  $m_w$  is the mass of the water (kg),  $T_{pi}$  is the temperature of the black pepper seed (°C),  $T_{ci}$  is the temperature of the calorimeter (°C),  $T_{wi}$  is the temperature of the water (°C), and  $T_{eq}$  is the equilibrium temperature (°C).

## Results and Discussion

### Equilibrium Moisture Content (EMC)

The raw EMC data from the experiment were statistically analyzed by following the mathematical EMC modelling (Table 1), and the statistical analysis results from the EMC model which had a high  $R^2$  (>0.8) are presented in Table 2. The results showed that the EMC value was relatively dependent on the surrounding relative humidity and temperature. These results corresponded to previous studies of other biomaterials [2-5, 8-15]. From Table 2, the non-linear regression analysis stated that the predicted data using the modified Halsey model gave the best fit to the experimental data ( $R^2 = 0.979$ , RMSE = 0.68). These EMC results are very useful in forecasting the effect of the surrounding air (relative humidity and temperature) on the evolution of the moisture transfer phenomena of the black pepper samples. So, entrepreneurs can use the results to maintain the quality of their black pepper for long periods of storage and drying with the temperature between 40 and 65°C.

### Thermodynamic Properties of Sorption

Determination of the isosteric heat of sorption mentioned previously in presented in this sub-section. The physical meaning is the amount of heat sorption for the evaporation of the water content for moist material. The net isosteric heat of sorption of black pepper decreased with increasing the moisture content. The relationship between the isosteric heat of sorption and the moisture content was non-linearly analyzed. The following Equation (19) was developed for the black pepper:

$$\Delta H = 43071e^{-13.5M} \quad (19)$$

### Apparent Density ( $\rho$ )

The apparent density of the black pepper was determined by Equation (16). It showed that an apparent density linearly related to the moisture content increased from 464.90 to 664.36 kg/m<sup>3</sup> for black pepper. The relationships of the apparent density with the moisture content of the pepper are expressed in Equation (20):

$$\rho = 1.071M + 452.2 \quad (20)$$

### Void Fraction ( $\epsilon$ )

The void fraction of black pepper was determined by Equation (17) showing that the percentage of the void fraction for pepper decreased with the increase of the moisture content. When the black pepper seed absorbs the water content, the structure will swell relating to the reduction of its void fraction. The percentage of the void fraction was linearly dependent on the moisture content and was expressed by the following Equation (21):

**Table 2. Statistical analysis results of the equilibrium moisture content (EMC) of black pepper in range relative humidity ranges of 10-90%**

| EMC Model              | $R^2$        | RSME        |
|------------------------|--------------|-------------|
| Oswin                  | 0.941        | 1.06        |
| Modified Oswin         | 0.835        | 1.78        |
| Henderson              | 0.908        | 1.32        |
| Modified Henderson     | 0.913        | 1.29        |
| Smith                  | 0.957        | 0.91        |
| Modified Smith         | 0.960        | 0.88        |
| <b>Modified Halsey</b> | <b>0.979</b> | <b>0.68</b> |

$$\varepsilon = 51.97 - 0.0194M. \quad (21)$$

### Specific Heat Capacity ( $c_p$ )

The experimental results were mathematically analyzed using the linear and non-linear regression methods. The results showed that the specific heat capacity of black pepper was directly proportional to the moisture content. The specific heat capacity increased from 6.95 to 9.92 kJ/kg °C with increasing the moisture content. Relationships between the specific heat capacity and the moisture content of 10-200% dry-basis was expressed as follows in Equation (22):

$$c_p = 0.015M + 6.771. \quad (22)$$

### Conclusions

Simulation modeling of water sorption isotherms was carried out in a relative humidity of 10-90% and a temperature of 40-65°C using traditional non-linear regression equations. Both the analytical and physical results showed good agreement in predicting the equilibrium moisture content of black pepper. The net isosteric heat of sorption of the pepper calculated using the Clausius-Clapeyron equation showed a power law relation with the moisture content ranging from 10-200% dry-basis. This net isosteric heat equation can be used to determine the heat of sorption of black pepper during the drying process and the moisture content during the period of storage of dried black pepper. For the rest of the physical analysis, the conclusion is that an apparent density, percentage of void fraction, and specific heat capacity of black pepper were relatively dependent on the moisture content.

### Acknowledgements

The authors would like to express their sincere thanks to the Department of Physics, Faculty of Science and the Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University for their experimental area support. The authors also appreciate and extend

special thanks to the Graduate School of Prince of Songkla University for student financial support.

### References

- AOAC International. (1995). Official Methods of Analysis. 16<sup>th</sup> ed. The Association of Official Analytical Chemists, Inc., Arlington, VA, USA.
- Chen, C. (2006). Obtaining the isosteric sorption heat directly by sorption isotherm equations. *J. Food Eng.*, 74:178-185.
- Chung, D. S. and Pfost, H. B. (1967). Adsorption and desorption of water vapor by cereal grain and their products. *T. ASABE*, 10:549-557.
- Cortés, F.B. and Chejne, F. (2010). A rapid and novel approach for predicting water sorption isotherms and isosteric heats of different meat types. *Meat Sci.*, 86:921-925.
- Halsey, G. (1948). Physical adsorption on non-uniform surface. *J. Chem. Phys.*, 16:83-92.
- Henderson, S.M. (1952). A basic concept of equilibrium moisture. *Agr. Eng.*, 3:29-32.
- Oswin, C.R. (1942). The kinetics of package life. III. The isotherm. *J. Soc. Chem. Ind.*, 65:419-421.
- Pfost, H.B., Mourer, S.G., Chung, D.S., and Milliken, G.A. (1976). Summarizing and reporting equilibrium moisture data for grains. *ASAE Paper No.76-3520*. American Society of Agricultural and Biological Engineers, St. Joseph, MI, USA.
- Soponronnarit, S. (1997). Drying Grains and Some Types of Foods. King Mongkut's University of Technology, Thonburi, Thailand, 338p.
- Timmermann, E.O. (1989). A BET-like three sorption stage isotherms. *J. Chem. Soc. Faraday T.I*, 85:1,631-1,645.
- Timmermann, E.O., Chirife, J., and Iglesias, H.A. (2001). Water sorption isotherms of foods and foodstuffs: BET or GAB parameters. *J. Food Eng.*, 48:19-31.
- Tirawanichakul, S., Tirawanichakul, Y., and Sniso, E. (2008). Paddy dehydration by adsorption: Thermo-physical properties and diffusion model of agriculture residues. *Biosyst. Eng.*, 99(2):249-255.
- Tirawanichakul, Y., Tasara, J., and Tirawanichakul, S. (2013). Artificial neural network approaches for the sorption isotherms, enthalpy and entropy of heat sorption of two types block rubber products. *Songklanakarin J. Sci. Technol.*, 35(1):69-80.
- Wang, N. and Brennan, J.G. (1991). Moisture sorption isotherm characteristics of potatoes at four temperatures. *J. Food Eng.*, 14:269-287.