Study of sorption isotherm and isosteric heat of Kepok Banana 
(*Musa paradisiaca F.*) slice

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Abstract. Kepok banana (*Musa paradisiaca F.*) is an abundant commodity in Indonesia. This 
commodity is a kind of horticulture that has high risk to be defect and damage, moreover if it is 
handled with poor of post-harvest technology, it makes the economic value of this commodity 
comes low. The processing is needed in order to preserve quality and to improve economic value. 
Kepok banana contains high amylose and starch around 29.50% so it is suitable to be processed as 
flour. The critical step of flour processing occurs in the drying process of banana slices so this 
research focused on slices form. Two important factors of drying process are the equilibrium water 
content and water activity (a<sub>w</sub>). The relationship between moisture content and a<sub>w</sub> at constant 
temperature is known as Moisture Sorption Isotherm (MSI). The MSI of Kepok banana slice was 
experimented by static gravimetric method with 5 types of saturated salt in a<sub>w</sub> range of 0.05-0.90 at 
30°C, 40°C, and 50°C. It was tested by BET (*Braunauer, Emmet and Teller*), Smith, Oswin, Caurie, 
and GAB (*Guggenheim-Anderson-de Boer*) model. Then the isosteric heat was calculated using the 
*Clausius-Clapeyron* equation. The results showed that the equilibrium moisture content at constant 
temperature increases with increasing of a<sub>w</sub> value, while at constant a<sub>w</sub> equilibrium moisture content 
decreases with increasing temperature. The most appropriate model in describing the characteristics 
of MSI Kepok banana slices is GAB model and is classified in type II. In addition, the isostreric heat 
for desorption is higher than adsorption.

1. Introduction

Kepok banana (*Musa paradisiaca F.*) belongs to the plantain banana group. This banana is more 
convenient to be consumed after processing [1]. Kepok bananas have a high starch content around 
29.50%, so it can be used for substituting flour production [2]. The process of making Kepok banana flour 
is closely related to the drying process, especially in the slices form. This is reinforced by research 
conducted by Hawa et al. [3] which states that the critical process in flour processing is in the chips drying 
process. The equilibrium moisture content and water activity are required regarding to the drying process 
information. A curve that describes the relationship between water activity and the equilibrium moisture
content of a product at constant temperature and constant pressure is known as the curve of moisture sorption isotherm. The determination of moisture sorption isotherm based on experimental data is always associated with the use of mathematical models to correlate the data obtained. In this study BET (Braunauer, Emmet and Teller), Smith, Oswin, Caurie, and GAB (Guggenheim-Anderson-de Boer) models were used to determine the characteristics of moisture isotherm for Kepok banana slice. Determination of moisture sorption isotherm for Kepok banana used static gravimetric method in the range of aw (0.05-0.90) at 30°C, 40°C, and 50°C for desorption and adsorption. From the data obtained, moisture sorption isotherm curve created by the most suitable model. The object of this study was to select the best model and analyze the characteristic behavior of moisture sorption isotherm for Kepok banana slice and to calculate and to construct the isosteric heat of sorption curve of Kepok banana slice.

2. Materials and Methods

2.1. Material

The materials that used in this research are Kepok banana purchased at nearby market in Malang area. Saturated salt such as KOH, MgCl₂, NaNO₂, NaCl, and KCl are used to maintain relative humidity, and aquabidest is used to dissolve saturated salt. The instruments that used in this research are incubator, oven, tray type of dryer, analytical scales. Air tight container clip to keep type from Lion Star with dimension 13.7 cm x 10.6 cm x 6.4 cm, vacuum desiccator, and slicer.

2.2. Experimental methods

This study used static gravimetric method to determine equilibrium moisture content. This method involved the use of saturated salt solutions to maintain relative humidity in the airtight container at constant temperature. Five saturated salt solutions (KOH, MgCl₂, NaNO₂, NaCl, and KCl) were used to keep a wide range of aw between 0.05 and 0.90. This study used 2 types of treatment including the adsorption process and desorption process at 30°C, 40°C, and 50°C in triplicate.

2.2.1. Preparation of saturated salt solution

Saturated Salt solutions with certain water activity (aw) values are used to control RH in airtight containers. The water activity (aw) value of the five types of saturated salts at 30°C, 40°C, and 50°C is shown in Table 1.

| Salt   | aw (30°C) | aw (40°C) | aw (50°C) |
|--------|-----------|-----------|-----------|
| KOH    | 0.074     | 0.063     | 0.057     |
| MgCl₂  | 0.324     | 0.316     | 0.305     |
| NaNO₂  | 0.633     | 0.620     | 0.588     |
| NaCl   | 0.751     | 0.747     | 0.744     |
| KCl    | 0.836     | 0.823     | 0.812     |

Source: Bell and Labuza [4]

The preparation of saturated salt solution was carried out by dissolving the salt solids and aquabidest with the number as shown in Table 2. After dissolution, the solution was allowed to stand for 24 hours in an incubator at 30°C [18].
Table 2. Number of salt solids and aquabidest.

| Solution | $a_w$ | Salt (g) | Aquabidest (ml) |
|----------|-------|----------|-----------------|
| KOH      | 0.07  | 15       | 3               |
| MgCl$_2$ | 0.32  | 15       | 2               |
| NaNO$_2$ | 0.63  | 15       | 4.5             |
| NaCl     | 0.75  | 15       | 4.5             |
| KCl      | 0.84  | 15       | 6               |

Source: Spiess and Wolf [5]

2.2.2. Sample preparation

Kepok banana ($Musa paradisiaca formatypica$) were purchased from a nearby market. Kepok banana was selected based on color level, uniform hardness and not defect then peeled and cleaned from dirt during the stripping process. Kepok banana slice lengthwise with a thickness of approximately 1 mm. Slice of Kepok banana then weighed 1 g and placed on aluminum foil dish that has been sterilized and stored in airtight container next to the saturated salt solution. Fresh banana slices were used as desorption samples, while the adsorption treatment used dried banana slices, which has been dried using a tray dryer at 50°C for 300 minutes and then stored in a vacuum desiccator containing silica gel 27°C for 48 hours.

2.2.3. Determination of equilibrium moisture content

The mass changes of the adsorption and desorption sample that placed in the incubator were observed by weighing the samples every 24 hours, until its mass is constant or changes in sample mass <0.005 g in 3 consecutive times of weighing. After the equilibrium moisture content of material is reached, the water content of the sample tested using an oven at 105°C for 24 hours and expressed on a dry basis using the following equation.

$$MC (bk) = \frac{\text{initial mass} - \text{final mass}}{\text{initial mass}} \times 100\%$$ (1)

2.3. Data analysis

The equilibrium moisture content and $a_w$ data was fitted using gnuplot software to obtain the constant values ($X_m$, $C$, $K$, $a$ and $b$) in each equation used. The fitting process is done based on the BET, Smith, Oswin, Caurie and GAB equations that can be seen on Table 3.

Table 3. Moisture sorption isotherm model.

| Model | Equation |
|-------|----------|
| BET   | $X_e = \frac{X_m C a_w}{(1 - C a_w)(1 + (C - 1)a_w)}$ |
| Smith | $X_e = a + b \ln(1 - aw)$ |
| Oswin | $X_e = a\left(\frac{a_w}{1 - a_w}\right)^b$ |
| Caurie| $X_e = \exp(a + b a_w)$ |
| GAB   | $X_e = \frac{X_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$ |
The plotting process is done using Ms. Excel 2013, aims to obtain the curve of moisture sorption isotherm which represented the relationship between $a_w$ and equilibrium moisture content. The test of model accuracy is conducted to determine the accuracy of a model in describing the moisture sorption isotherm curve for Kepok banana slice. The best fit model is obtained through three parameters, including $R^2$ (coefficient of determination), RMSE (Root Mean Square Error) and $P$ (mean relative modulus). The RMSE value of each model can be known using the following equation.

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (X_i - \bar{X})^2}$$

Seid and Hensel [21] stated that the best fit of the model is obtained if the RMSE value is close to zero. The coefficient of determination ($R^2$) is used to evaluate the accuracy of data on the five mathematical equation models [6]. $R^2$ value close to 1 indicates that predictive data and research data have good correlation. Mean relative modulus ($P$). $P$ value below 10% indicates that the curve formed has been in accordance with predictive data or model estimates [7]. The value of $P$ can be known through the following equation.

$$P(\%) = \frac{100}{N} \sum_{j=1}^{N} \left( \frac{X_j - X_P}{X_P} \right)$$

The isosteric heat ($q_{st}$) is obtained by a graphic relationship of $1/T$ (°K) and ln ($a_w$). The $a_w$ (equilibrium relative humidity) value is calculated based on the GAB equation by assuming the value of equilibrium moisture content is constant. The isosteric heat ($q_{st}$) is obtained from the slope formed from the graphic equation based on Clausius-Clapeyron Law [8].

$$\ln a_w = \frac{q_{st}}{R} \cdot \frac{1}{T} + k$$

Then the fitting process is done to get the $q_o$ and $x_o$ value based on the following equation.

$$q_{st} = q_o \exp(-x/x_o)$$

3. Results and Discussion

3.1. Moisture sorption isotherm modeling for kepok banana slice

Moisture Sorption Isotherm modeling for Kepok banana slice is done using BET, Smith, Oswin, Caupit and GAB models, then the model accuracy test is determined using the same parameters. The constants value and statistical error of each model can be seen in Table 4 and Table 5. Based on the fittings data in Table 4 and Table 5. The best model in describing the moisture sorption isotherm of Kepok banana slice is GAB (Guggenheim-Anderson-de Boer) model, because the GAB model gives the highest $R^2$ value, $P$ value below 10% and the lowest RMSE value compared to other models. GAB model is a model that has many advantages such as having a good theoretical background because it comes from perfection Langmuir and BET models and easy to use because it can describe the behavior of sorption in the range of water activity 0 to 0.9.
Table 4. Constant value and statistical error of adsorption on Kepok banana slice.

| Model | T (°C) | A  | B  | C   | K    | X_m | R²   | P (%) | RMSE |
|-------|--------|----|----|-----|------|-----|------|-------|------|
|       | 30     | -  | -  | 125.976 | -  | 3.084 | 0.971 | 11.794 | 1.059 |
|       | 40     | -  | -  | 130.675 | -  | 3.209 | 0.964 | 14.271 | 1.170 |
|       | 50     | -  | -  | 30.009  | -  | 2.648 | 0.952 | 20.369 | 1.008 |
| Smith | 30     | -  | -  | 7.722  | -  | 0.493 | 0.996 | 4.358  | 0.332 |
|       | 40     | -  | -  | 8.249  | -  | 0.448 | 0.989 | 5.357  | 0.529 |
|       | 50     | -  | -  | 6.591  | -  | 0.486 | 0.992 | 9.992  | 0.379 |
| Oswin | 30     | -  | -  | 0.776  | -  | 2.453 | 0.988 | 4.817  | 0.576 |
|       | 40     | -  | -  | 0.963  | -  | 2.212 | 0.972 | 10.687 | 0.831 |
|       | 50     | -  | -  | 0.597  | -  | 2.409 | 0.983 | 18.721 | 0.554 |
| Caurie| 30     | -  | -  | 0.776  | -  | 2.453 | 0.988 | 4.817  | 0.576 |
|       | 40     | -  | -  | 0.963  | -  | 2.212 | 0.972 | 10.687 | 0.831 |
|       | 50     | -  | -  | 0.597  | -  | 2.409 | 0.983 | 18.721 | 0.554 |

Table 5. Constant value and statistical error of adsorption on Kepok banana slice.

| Model | T (°C) | A  | B  | C   | K    | X_m | R²   | P (%) | RMSE |
|-------|--------|----|----|-----|------|-----|------|-------|------|
| BET   | 30     | -  | -  | 3.161 | 1194.64 | -  | 4.375 | 0.962 | 12.879 | 1.723 |
|       | 40     | -  | -  | 3.161 | 1194.64 | -  | 4.375 | 0.962 | 12.879 | 1.723 |
|       | 50     | -  | -  | 3.161 | 1194.64 | -  | 4.375 | 0.962 | 12.879 | 1.723 |
| Smith | 30     | -  | -  | 1.910 | 9.327  | -  | 6.591 | 0.978 | 16.355 | 0.861 |
|       | 40     | -  | -  | 1.910 | 9.327  | -  | 6.591 | 0.978 | 16.355 | 0.861 |
|       | 50     | -  | -  | 1.910 | 9.327  | -  | 6.591 | 0.978 | 16.355 | 0.861 |
| Oswin | 30     | -  | -  | 8.622 | 0.484  | -  | 0.465 | 0.998 | 4.181  | 0.349 |
|       | 40     | -  | -  | 8.622 | 0.484  | -  | 0.465 | 0.998 | 4.181  | 0.349 |
|       | 50     | -  | -  | 8.622 | 0.484  | -  | 0.465 | 0.998 | 4.181  | 0.349 |
| Caurie| 30     | -  | -  | 1.230 | 2.321  | -  | 0.424 | 0.993 | 3.983  | 0.612 |
|       | 40     | -  | -  | 1.230 | 2.321  | -  | 0.424 | 0.993 | 3.983  | 0.612 |
|       | 50     | -  | -  | 1.230 | 2.321  | -  | 0.424 | 0.993 | 3.983  | 0.612 |
| GAB   | 30     | -  | -  | 20.150 | 5.855  | 6.486 | 0.999 | 1.338 | 0.173 |
|       | 40     | -  | -  | 9.944  | 0.594  | 7.617 | 0.996 | 4.731  | 0.271 |
|       | 50     | -  | -  | 9.944  | 0.594  | 7.617 | 0.996 | 4.731  | 0.271 |

3.2. Characteristics of moisture sorption isotherm for Kepok banana slice

Moisture sorption isotherm of Kepok banana slice at temperature 30°C, 40°C, and 50°C are shown by Figure 1a, 1b, and 1c. Based on the three graphs it is known that at constant temperature the equilibrium moisture content increases with the increase of the water activity value (a_w). The results are consistent with the research conducted by Dalgiç et al. [9] with mint leaf material and Alfiah et al. [10] with cassava fermented starch powder.
Moisture sorption isotherm curve of Kepok banana slice have a shape like the letter S or sigmoid-shaped, so included in type II. Type II moisture sorption isotherm curves are also found in the characteristics of banana Matooke [11]. The sigmoid-shaped curve is caused by a combination of colligative effects, capillaries and inter-surface interactions [12].

Hysteresis phenomenon existed over the entire range of research temperatures. The hysteresis phenomenon represents the difference equilibrium moisture content value between adsorption and desorption. Based on these three graphs, equilibrium moisture content of desorption is higher than the adsorption in the entire \(a_w\) range. Similar results were obtained by Yogendarajah et al. [13] on black pepper. It shows that the adsorption and desorption process is irreversible because the fresh foods hold more moisture than dried foods over the entire range of \(a_w\), probably due to cell damage occurring in food that has been dehydrated [14].
3.3. Effect of temperature on moisture sorption isotherm for Kepok banana slice
Characteristics of moisture sorption isotherm of Kepok banana slice were observed at three different temperatures, at 30°C, 40°C, and 50°C which can be seen in Figures 2 and 3. The figures show that at a constant a_w value most of the equilibrium moisture content of the material decreases with increasing temperature. This result is consistent with Saad et al. [15] on the *Ziziphus* leaves and by Filho et al. [7] with fresh and blanched pumpkin, because the material adsorbs more water at low temperatures than at high temperatures because at low temperatures the equilibrium relative humidity values are higher than at high temperatures, so the equilibrium moisture content level will be higher.

![Figure 2. Effect of temperature on adsorption.](image)

![Figure 3. Effect of temperature on desorption.](image)

3.4. Isothermic heat
Isothermic heat adsorption is the amount of energy released during adsorption. While desorption isothermic heat is the energy required to break the inter-molecular forces between water vapor molecules and the surface of the adsorbent [16]. The GAB model is used to predict water activity values (a_w) at different moisture content values in isothermic heat analysis. In this analysis a graph is drawn that illustrates the relationship between water activity (a_w) and temperature, where the value of natural logarithmic as an ordinate and inverse temperature (1 / T) as abscissa that can be seen in Figure 4 and Figure 5.

![Figure 4. In (a_w) vs 1/T for adsorption](image)

![Figure 5. In (a_w) vs 1/T for desorption](image)
The isosteric heat is calculated from the slope formed from the graph following the equation (4). Isosteric heat of banana Kepok slice can be seen in Figure 6. From the figure, it is known that the isosteric heat of desorption is higher than the isotheric heat of adsorption at the same equilibrium moisture content. The results are consistent with Mariem and Mabrouk [8] for Tomato slices which suggest that can be associated with energy requirements in the desorption process is higher than desosrption process. In addition, it is known that the isosteric heat decreases with increasing the equilibrium moisture content. The results are consistent with Taitano et al. [17] on raw almonds and blanched ones and by Togrul and Arslan [19] on Walnut seeds, indicating that it takes the maximum energy to remove water present in the product at low moisture content. This phenomenon can be caused by the existence of a highly active polar site on the surface of a product covered by a water molecule forming a monomolecular layer [20].

The relationship between the equilibrium moisture content and isosteric heat is then fitted to obtain the $q_o$ and $x_o$ based on equation (5). The isosteric heat of adsorption and desorption of water on Kepok banana slicesd can be expressed mathematically by the exponential function of the water with the following equation.

For adsorption: $R^2=0.968$

$$q_{st} = 44.7457 \exp\left(\frac{-X_e}{4.03878}\right)$$

For desorption: $R^2=0.929$

$$q_{st} = 44.1316 \exp\left(\frac{-X_e}{8.67811}\right)$$

The equation can be used to calculate the isosteric heat of sorption on Kepok banana slice in the range 1% -15% for water content.

4. Conclusion
The GAB (Guggenheim-Anderson-de Boer) model is the most appropriate model in describing the moisture sorption isotherm for Kepok banana slice, because it gives the highest $R^2$ value, $P$ value below 10% and the lowest RMSE value compared to other models. Moisture sorption isotherm curve for Kepok banana slice is classified in type II, because it has shape like the letter S or sigmoid-shaped. From the
research it is known that the equilibrium moisture content increases with increasing water activity value (aw) at a constant temperature, and moisture sorption isotherm decreases with increasing temperature at a constant aw. The equation of isosteric heat of adsorption can be mathematically expressed as $q_{st} = 44.7457 \exp \left( \frac{-X_e}{4.03878} \right)$ while isosteric heat of desorption is expressed as $q_{st} = 44.1316 \exp \left( \frac{-X_e}{4.67812} \right)$.

References

[1] Astawan M 2005 Info of Food Technology. Bogor Agricultural University Bogor Indonesia. [In Indonesian]
[2] Rosida 2009 Effect of processing on banana starch (in-vitro) digestion Jurnal Rekapangan 3 1 1-11. [In Indonesian]
[3] Hawa L C, Dewi S R, Izza N, Wigati L P 2016 Analysis of physical characteristics of taro chips (Colocasia esculenta L.) Based on machine vision (study of drying with tray dryer) Jurnal Rekapangan 10 122-128. [In Indonesian]
[4] Bell L N, Labuza T P 2000 Moisture sorption: practical aspects of isotherm measurement and use American association cereal chemist Minnesota USA.
[5] Spiess W E L, Wolf W 1987 Critical Evaluation of Methods to Determine Moisture Sorption Isotherm In Water Activity Theory and Application to Food Marcell Dekker Inc New York.
[6] Widowati S, Heti H, Rizal S, Nugraha E S, Hendra A P 2010 Effect of water sorption isotherms on ubi rice stability Jurnal Teknologi dan Industri Pangan 21 2 123-128. [In Indonesian]
[7] Filho L M, Gonçalves A K R, Mauro M A, Frascareli E C 2011 Moisture sorption isotherms of fresh and blanched pumpkin (Cucurbita moschata) Ciênc. Tecnol. Aliment Campinas 31 3 714-722.
[8] Mariem S A, Mabrouk S B 2015 Moisture sorption isotherms and isosteric heats of sorption of tomato slices Am. J. Renew. Sustain. Energy 1 3 140-155.
[9] Dalgıç A C, Pekmez H, Belibağ K B 2012 Effect of drying methods on the moisture sorption isotherms and thermodynamic properties of mint leaves J. Food Sci. Technol. 49 4 439-449.
[10] Alfiah M N, Hartini S, Cahyanti M N 2017 Mathematical modeling and thermodynamic properties of isotherms angkak fermented cassava flour sorption Jurnal Penelitian Kimia 13 1 29-40. [In Indonesian]
[11] Kawongolo J B 2013 optimization of processing technology for commercial drying of bananas (Matooke) Dissertation Universität Kassel Fachbereich Ökologische Uganda.
[12] Labuza T P 1984 Moisture Sorption: Practical Aspects of Isotherm Measurement and Use American Association of Cereal Chemists Minnesota USA.
[13] Yogendrarajah P, Samapundo S, Devlieghere F, De Saeger S, De Meulenaer B 2015 Moisture sorption isotherms and thermodynamic properties of whole black peppercorns (Piper nigrum L.) Food Sci. Technol. 64 177-188.
[14] Gálvez A V, Palacios M, Lemus-Mondaca R 2008 Moisture sorption isotherms and isosteric heat determination in Chilean papaya (Vasconcellea pubescens) Quim. Nova 31 6 1417-1421.
[15] Saad A, Boumediene T, Belkacem D, Boufeldja B, Asma A, Said B 2014 Mathematical modeling of moisture sorption isotherms and determination of isosteric heats of sorption of Ziziphus leaves Model. Sim. Eng. 2014 1-8.
[16] Ciro H, Osorio J A, Cortes E A 2008 Determination of the isosteric heat of plantain pulp (Musa paradisiaca L.) by sorption isotherms DYNA 156 127-134.
[17] Taitano L A, Singh R P, Lee J H, Kong F 2012 Thermodynamic analysis of moisture adsorption isotherm of raw and blanched almonds J. Food Process Eng. 35 6 840-850.
[18] Herlina S W, Prima E S 2017 Modified save age analysis of cassava fermented results using Wikau Maombo lactic acid bacteria *J. Appl. Chem.* **2** 3 1-10. In Indonesian

[19] Togrul H, Arslan N 2007 Moisture sorption isotherms and thermodynamic properties of walnut kernels *J. Stored Prod. Res.* **43** 3 252-264.

[20] Tsami E 1991 Net isosteric heat of sorption in dried fruits *J. Food Eng.* **14** 327-335.

[21] Seid RM, Hensel O 2012 Experimental evaluation of sorption isotherms of chili pepper: an Ethiopian variety, Mareko Fana (*Capsicum annum* L.) *Agric Eng Int: CIGR J.* **14** 4 163-172.