Moisture Sorption Isotherm and Isosteric Heat of Butterfly-pea Flowers (Clitoria ternatea)

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Abstract. Butterfly-pea (Clitoria ternatea) flowers are containing various active compounds such as flavonoids, myricetin, quercetin, flavonols, and anthocyanins which have potential as antioxidants. Dried butterfly-pea flower is often used as an ingredient of herbal tea drinks. The drying procedure for the butterfly-pea flower is important to maintain the shelf-life. However, during the drying process, anthocyanins are easily be degraded before reaching the balance of water content. Therefore, a study focus on moisture sorption isotherm of fresh butterfly-pea flowers is needed. This present study aims to determine the balance of water content and isosteric heat of butterfly-pea flowers using a static gravimetric method. Water activities were conditioned using chemical solutions of KOH, MgCl₂, K₂CO₃, NaCl, KCl, and BaCl₂ with a water activity range of 0.06-0.90. The hysteresis curve was determined using desorption and adsorption samples with various temperature variations of 30, 40, and 50°C. The isothermal behavior of butterfly-pea flowers was determined based on GAB, BET, Halsey, Oswin, and Peleg models. As a result, the Peleg model was found to be the most suitable model to represent the moisture sorption isotherm of butterfly-pea flowers and based on Brunauer classification including the Type II-sigmoid curve in which has been statistically analyzed using determination coefficient \( R^2 \), mean relative modulus \( P \), and root mean square error \( RMSE \). The hysteresis curve indicated that the balance of water content of the desorption sample is higher than the adsorption sample on the same water activity level. The net isosteric heat in the desorption and adsorption samples were 48.529 exp \( (-X_e/0.0734) \) and 53.591 exp \( (-X_e/-0.0797) \), respectively.

Keywords: GAB; BET; Static Gravimetric; Hysteresis Curve; Net Isosteric Heat

1. Introduction

In agriculture, drying is a method that is often used by most people in Indonesia. Various agricultural products often need this method before entering further processing steps. One of the crops that use this method is the butterfly-pea flower. The nature of butterfly-pea flowers that easily withers and senescence after harvesting make this plant cannot be used for a long time without special treatment. Thus, the drying method is needed to minimize mechanical damage and to extend its shelf-life. However, the drying process of butterfly-pea flowers by farmers today does not consider the length of time and the suitable moisture content during the storage period. These could develop a source of biological damage such as mold, which harms the farmers considering the dried butterfly-pea flower’s high price. Meanwhile, the quality of the dried product depends on the stability of the content in the product [1]. Based on that, it is necessary to observe the moisture sorption isotherm and isosteric heat which could
be used for designing, optimizing, and predicting changes in water content during the drying process, which finalized as determining requirements for butterfly-pea flowers packaging [2].

There is a relationship between water activity (aw) and equilibrium moisture content (EMC) in butterfly-pea flowers. According to Ayala-Aponte [3], the drying process will result in changes in biological, physical, and chemical properties and the cause stability of these changes must be determined. Moisture sorption isotherm shows the relationship between EMC and aw at constant temperature [2]. According to the report [4], generally, agricultural products have curves of type II and III. Net isosteric heat is used to determine energy requirements to remove the amount of water contained in foodstuffs.

This study aims to determine moisture sorption isotherm and net isosteric heat in butterfly-pea flowers using mathematical models of Guggenheim-Anderson-de Boer (GAB), Braunauer-Emmet-Teller (BET), Halsey, Oswin, and Peleg, with the static gravimetric method at a temperature of 30 ± 2°C, 40 ± 2°C, 50 ± 2°C. Furthermore, net isosteric heat was determined using the Clausius-Clapeyron equation.

2. Materials and Methods

2.1 Raw Materials

The raw materials used in this study were butterfly-pea flowers with an average moisture content of 8.394 (db) obtained from farmers in Banggle Village, Kediri Regency, East Java Province, Indonesia.

2.2 Sample and aw Preparations

This study used two samples (desorption and adsorption) to determine the hysteresis curve and net isosteric heat. At first, the fresh butterfly-pea flowers were dried at 50°C for 12 h until the average moisture content was 0.182 (db). Each sample was dried twice. The desorption sample was dried at 40°C for 4 hours until the average moisture content was 1.224 (db). The adsorption sample was dried at 40°C for 48 hours then put in a desiccator for 48 hours until the moisture content was 0.049 (db).

The aw preparations used a petri dish containing a chemical solution (5 ml) within an airtight container for 24 hours at each treatment temperature. At aw > 0.7, the airtight container was added with listerine (5 ml) in a petri dish and placed side by side with the chemical solution, then removed during the Moisture sorption isotherms measurement.

2.3 Moisture sorption Isotherms Measurements

Determination of moisture sorption isotherm in butterfly-pea flowers used a static gravimetric method with a strong alkaline solution and saturated salt to obtain aw conditions of 0.057 – 0.898. The chemicals used contain strong bases (KOH) and salts (MgCl2, K2CO3, NaCl, KCl, and BaCl2). Moisture sorption isotherms measurement used two types of samples, namely desorption (1 ± 0.001 g) and adsorption (1 ± 0.001 g) with fixed temperatures (30 ± 2°C, 40 ± 2°C, 50 ± 2°C), with triple repetition for each sample. Data were collected every 1 hour for the first 4 hours and every 24 hours for 10 days. Data collection was stopped when the sample mass measured constant for 3 time periods, thus considered as equilibrium has occurred. The sample was put in the airtight container line up with a dish containing a chemical solution. During the measurement, the temperature of the working room was 26 – 30°C and RH of 65 – 85%.

2.4 Mathematical Models

Mathematical models that are often used in several papers [5]–[8] to describe the isothermal activity of Moisture sorption can be seen in Table 1, where C, K, a, b, and n are mathematical model constants, aw is water activity, EMC is the balance water content (db), and M0 is the monolayer water content (db). Each model constant was determined using Microsoft Excel 2016 software. Mathematical models can describe the different Moisture sorption isotherms depending on the foodstuffs used in the study [9] and each model was determined with the smallest error value between the experimental results and the predicted results [10].
Table 1. Mathematical models of Moisture sorption isotherms in butterfly-pea flowers

| No | Model Name | Model |
|----|------------|-------|
| 1  | GAB        | \[EMC = \frac{M_o C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}\] |
| 2  | BET        | \[EMC = \frac{M_o C a_w}{(1 - a_w)(1 + (C - 1)a_w)}\] |
| 3  | Halsey     | \[EMC = \left(\frac{C}{\ln a_w}\right)^n\] |
| 4  | Oswin      | \[EMC = C \left(\frac{a_w}{1 - a_w}\right)^n\] |
| 5  | Peleg      | \[X_e = a a_w^b + C a_w^n\] |

2.5 Statistical Analysis

The data obtained from the mathematical modeling were evaluated using statistics, including the coefficient of determination (R²), Mean relative modulus (P), and Root-Mean-Square Error (RMSE). The statistical analysis was used to determine the best model which has a small deviation and was able to draw a good moisture sorption isotherms. The best model has a coefficient of determination close to 1 [6], a P-value of less than 10% [11], and has the smallest RMSE value [7].

2.6 Net Isosteric Heat Determination

Net isosteric heat (q_{st}) is the amount of heat needed to transfer the mass of water to change its form [12]. However, it was clarified by Jidher and Bagane [13] that net isosteric is the heat required by the material when transferring water (desorption) and adding water (adsorption). Based on the report [14] q_{st} can be determined using linear regression of –ln a_w vs 1/T (K⁻¹) curve. The determination was done by determining the equilibrium moisture content in sequence from the smallest to the maximum water content that can be predicted in the best mathematical models [14].

The value of q_{st} was determined using the Clausius-clapeyron equation [9] assuming that q_{st} is independent of temperature, as follows [11], [13], [15]:

\[\ln a_w = -\frac{q_{st}}{RT} + C\]  \hspace{1cm} (1)

where \(\lambda\) is the latent steam heat of pure water, \(R\) is the gas constant (8.314 J/mol.K), \(T\) is the temperature (K), and C is the integration constant.

3. Results and Discussion

3.1 Moisture sorption isotherms

The depiction of moisture sorption behavior in butterfly-pea flowers can be seen on the hysteresis curve to determine the amount of equilibrium moisture content. This equilibrium value is then used to determine a good storage conditions for butterfly-pea flower products. The characteristic of the butterfly-pea flower products hysteresis curve forms a closed Type II-sigmoid curve due to the pressure of the desorption and adsorption curves [16]. Furthermore, a report by S. Bennaceur, et al [17] revealed that a temperature of 30 ± 2 °C, 40 ± 2 °C, 50 ± 2 °C has a hysteresis effect on desorption and adsorption samples throughout the range of water activity (a_w 0 - 1). Moreover, the equilibrium moisture content in the desorption sample was greater than the adsorption sample at the same water activity [18]. Regarding the hysteresis curve of the moisture sorption isotherms, a study conducted by Bonner and Kenney [19] revealed that the initial and final moisture content values will be the same and cover the hysteresis curve at a_w >0.9.
3.2 Mathematical Models

Table 2 shows the parameters of the mathematical model used in this study were evaluated by using statistical analysis $R^2$, $P$, and RMSE. The statistical analysis shows only the Peleg model that can describe the behavior of moisture sorption isotherm well, which has a mean relative modulus of <10%, the $R^2$ value close to 1, and the lowest RMSE value. However, using the GAB and BET models, the monolayer ($M_o$) of moisture content can be determined. Monolayer moisture content indicates the amount of water that is strongly bound to the active part of the food which has a stable moisture content during the drying process [3]. As reported by Thanuja and Ravindra [20], the monolayer moisture content had physical and chemical stability which was still related to browning and enzyme activity.

| Model  | T (°C) | Desorption | Adsorption |
|--------|--------|------------|------------|
|        | $R^2$  | $P$        | RMSE       | $R^2$  | $P$        | RMSE       |
| GAB    |        |            |            |        |            |            |
| 30     | 0.993  | 0.166      | 0.013      | 0.998  | 0.113      | 0.007      |
| 40     | 0.964  | 0.239      | 0.013      | 0.979  | 0.051      | 0.002      |
| 50     | 0.989  | 0.243      | 0.011      | 0.989  | 0.167      | 0.016      |
| BET    |        |            |            |        |            |            |
| 30     | 0.972  | 0.308      | 0.032      | 0.992  | 0.214      | 0.015      |
| 40     | 0.965  | 0.340      | 0.022      | 0.956  | 0.038      | 0.003      |
| 50     | 0.916  | 0.036      | 0.036      | 0.988  | 0.175      | 0.016      |
| Halsey |        |            |            |        |            |            |
| 30     | 0.971  | 0.234      | 0.045      | 0.996  | 0.192      | 0.011      |
| 40     | 0.961  | 0.247      | 0.033      | 0.965  | 0.137      | 0.006      |
| 50     | 0.912  | 0.046      | 0.045      | 0.977  | 1.343      | 0.058      |
| Oswin  |        |            |            |        |            |            |
| 30     | 0.991  | 0.128      | 0.014      | 0.996  | 0.069      | 0.010      |
| 40     | 0.948  | 0.169      | 0.016      | 0.957  | 0.142      | 0.009      |
| 50     | 0.986  | 0.013      | 0.013      | 0.995  | 0.130      | 0.014      |
| Peleg  |        |            |            |        |            |            |
| 30     | 0.997  | 0.096      | 0.008      | 0.999  | 0.053      | 0.003      |
| 40     | 0.998  | 0.148      | 0.008      | 0.999  | 0.053      | 0.002      |
| 50     | 0.992  | 0.009      | 0.009      | 0.998  | 0.053      | 0.004      |

3.3 Net Isosteric Heat

The net isosteric heat is determined by plotting $-\ln a_w$ vs $1/T$ (K$^{-1}$) which shows that the higher the temperature, the lower the EMC [17]. From the Peleg model, it was determined that the net isosteric heat in butterfly-pea flowers showed a decrease in the heat along with increasing EMC (Fig 2). Desorption samples have a lower qst value than adsorption samples, due to the large energy-consuming process of releasing water from the materials [21]. Net isosteric heat has EMC stability at a moisture content of >0.25 (db). Meanwhile, moisture content of <0.25 (db) indicates that moving water from low moisture content requires a large amount of heat energy due to the water that is tightly bound to the solids. This event has also been reported by Ayala-Aponte [3] and Velázquez-Gutiérrez, et al [22] which alludes to the relationship of EMC and net isosteric to water binding in carbohydrates and proteins.

![Figure 1. Hysteresis curve of butterfly-pea flower. Desorption prediction (black dot); adsorption prediction (red dot); desorption experiment (black); adsorption experiment (red)](image-url)
Besides, R. Bahar, et al. [14] also reported that the high net isosteric heat indicates the low moisture content, due to the presence of high polar bonds on the surface of the food. The same isosteric heat reduction behavior has also been reported in studies of cassava [23], maize [24], yellow dragon fruit [25], orange juice powder [26], and oak woods [14].

The exponential equations from \( q_{st} \) data of the Peleg model can be used [5], [14], [15], [21] to describe the closeness between exponential prediction results and experimental predictions on desorption (Eq. 2) and adsorption (Eq. 3) samples, with \( R^2 \) values of 0.9917 and 0.9952.

\[
q_{st} = 48.529 \exp \left( -\frac{X_e}{0.0734} \right) 
\]

\[
q_{st} = 53.591 \exp \left( -\frac{X_e}{-0.0797} \right) 
\]

Figure 2. Net Isosteric Heat. Desorption prediction (red dot); adsorption prediction (black dot); desorption experiment (red); adsorption experiment (black)

4. Conclusions
The best mathematical model in describing the behavior of moisture sorption isotherms in butterfly-pea flowers is the Peleg model, which was represented by the Type II-sigmoid curve. The hysteresis curve shows that there is a relationship between \( a_w \) and EMC, where the increasing water activity also increases the equilibrium moisture content in butterfly-pea flowers. Furthermore, the hysteresis curve shows that the equilibrium moisture content in the desorption sample was greater than the adsorption sample at the same water activity. Results also unveil that the decrease of net isosteric heat is in line with the increase of EMC.

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