Sorption Isotherm Modelling Of Fermented Cassava Flour by Red Yeast Rice

M N Cahyanti¹, M N Alfiah², S Hartini³
¹,²,³Satya Wacana Christian University, Salatiga, Indonesia

Email: margareta.cahyanti@staff.uksw.edu

Abstract. The objective of the study is to determine the characteristic of moisture sorption isotherm from fermented cassava flour by red yeast rice using various modeling. This research used seven salt solutions and storage temperature of 298K, 303K, and 308K. The models used were Brunauer-Emmet-Teller (BET), Guggenheim-Anderson-de Boer (GAB) and Caurie model. The monolayer moisture content was around 4.51 – 5.99% db. Constant related to absorption heat in the multilayer area of GAB model was around 0.86-0.91. Constant related to absorption heat in the monolayer area of GAB model was around 4.67-5.97. Constant related to absorption heat in the monolayer area of BET model was around 4.83-7.04. Caurie constant was around 1.25-1.59. The equilibrium and monolayer moisture content on fermented cassava flour by red yeast rice was decreasing as increasing temperature. GAB constant value indicated that the process of moisture absorption on the fermented cassava flour by red yeast rice categorized in type II.

1 Introduction
The fermented cassava flour by red yeast rice is flour made from cassava made by the fermentation process by red yeast rice. In the process of making fermented cassava flour, cassava undergoes the drying process. Dehydrated food products are susceptible to damage due to rising moisture content. The moisture content in the food product will form the equilibrium with relative humidity. The relationship between equilibrium moisture content and relative humidity is illustrated in a moisture sorption isotherm curve. This curve is then modeled for further study. Earlier research suggests that GAB modeling is the most suitable model to illustrate the relationship between equilibrium moisture content and the relative humidity of cassava flour fermented by red yeast rice [1]. The purpose of this research is to determine the characteristics of cassava flour fermented by red yeast rice using GAB, BET, and Caurie models in depth.

2 Material and method
2.1 Material
The materials used were cassava and red yeast rice originally from Salatiga, aqua dest, NaOH, MgCl₂, K₂CO₃, Mg(NO₃)₂, KI, NaCl, and KCl. The tools used were drying cabinet, grinder, 61 mesh strainer, incubator, sorption container, and moisture analyzer Ohaus BM 25.
2.2 Method

The flour was made based on the previous research conducted by earlier study [2]. The cassava was peeled and then washed. Cassava is steamed for approximately 60 minutes, then drained and cooled until cassava reaches room temperature. Cassava is cut and weighed as much as 1 kg then inoculated with red rice yeast with a concentration of 12%, then fermented for three days at room temperature. The fermentation product was dried at 55 °C until dry and then mashed and sieved with mesh sieve 61.

The measurement of equilibrium moisture content was done based on the method by Budijanto et al. [3] which had been modifying the type of salt and the storage temperature. This research used seven kinds of saturated salt such as NaOH, MgCl₂, K₂CO₃, Mg(NO₃)₂, KI, NaCl, and KCl. It was done to form certain RH and storage temperature of 303K, 308K, and 313K.

The models used in this research were Brunauer-Emmet-Teller (BET), Guggenheim-Anderson-de Boer (GAB) and Caurie. The equation for each model can be seen in Table 1.

| Model | Equation | Description |
|-------|----------|-------------|
| GAB   | \[ m = \frac{m_0 k_b c a_w}{(1 - k_b a_w)(1 - k_b a_w + c k_b a_w)} \] | a_w : water activity m : equilibrium moisture content (% db) m_0 : monolayer moisture content((% db) c and k_b : constant (a) |
| BET   | \[ \frac{a_w}{(1 - a_w)m} = \frac{1}{m_0 c} + \frac{(c - 1)}{m_0 c a_w} \] | a_w : water activity m : equilibrium moisture content (% db) m_0 : monolayer moisture content (% db) c : constant (b) |
| Caurie| \[ \ln \frac{1}{m} = -\ln (Cm_0) + \frac{2C}{M_0} \ln \left( \frac{1 - a_w}{a_w} \right) \] | m : equilibrium moisture content (% db) C :Caurie Constant m_0 : monolayer moisture content (% db) a_w : water activity |

Monolayer moisture content can be determined from the equilibrium sorption isotherm data by fitting BET, GAB, and Caurie model. Monolayer moisture content is one of the important parameters. Estimates of monolayer moisture content are related to the stability of food products physically and chemically. In the range below the monolayer moisture content, various food damage reactions are infrequent. This is due to a very strong bound water with food products, and water does not participate in the reaction. Determination of monolayer moisture content can be used to calculate the surface area of solid from food product using BET and GAB model based on Equation 1.

Surface area of solid = \( m_0 \times 35.53 \) (1)

Monolayer moisture content in Caurie model and Caurie constant can be used to determine the properties of sorbed water. Number of the adsorbed monolayer can be calculated by Equation 2 and bound water content can be calculated by Equation 3. The density of adsorbed water in the monolayer calculation is done by Equation 4 and surface area by Equation 5.

Number of adsorbed monolayer = \( \frac{m_0}{c} \) (2)

Bound water content = \( m_0 \times \) Number of adsorbed monolayer (3)

Density of adsorbed water in the monolayer = Caurie Constant (4)
Surface area of adsorption \(= \frac{m_0}{C \times \text{diameter of a water molecule } \times 10^8} \) \( (5) \)

### 3 Result and Discussion

The equilibrium moisture content of fermented cassava flour by red yeast rice has been published earlier [1]. It is known that the equilibrium moisture content shows a decrease as the storage temperature increases. At high temperatures, the molecules are in a state of excitation, thereby increasing the distance between the water and the surface of the product that causes a decrease in attractiveness between them [4]. Another reason is that higher temperatures give higher energy to water molecules that cause water molecules tend to move and not bind to food products [5]. It was precisely correlated with the previous research about the equilibrium moisture content of dry merunggai leaves in several temperatures [6] and the research about moisture sorption isotherm on dry mung beans [5].

The data of equilibrium moisture content and water activity was then applied in the GAB, BET, and Caurie equations to get description about absorption process on the sample. The valuable constants from GAB, BET, and Caurie equations were shown in Table 2.

| Model                  | GAB   | BET   | Caurie |
|------------------------|-------|-------|--------|
| Constant               | \(m_0\) | \(C\) | \(k_0\) | \(m_0\) | \(c\) | \(m_0\) | \(C\) |
| Temperature            | Article | Article II | Article I | Article | Article V | Article | Article |
| 303K                   | 5.56   | 5.2641 | 0.8835 | 4.53   | 6.4751 | 5.98   | 1.2905 |
| 308K                   | 5.54   | 5.9704 | 0.8593 | 4.51   | 7.0381 | 5.99   | 1.2494 |
| 313K                   | 5.53   | 4.6685 | 0.9117 | 4.99   | 4.8345 | 5.06   | 1.5859 |
| Dried Cassava (303K)   | 6.16   | 12.9004 | 0.8939 | 5.55   | 15.1463 | -      | -      |
| Cassava Flour (303K)   | 7.28   | 15.550 | 0.8329 | -      | -      | -      | -      |
| Cassava Flour (308K)   | 6.32   | 30.390 | 0.8677 | -      | -      | -      | -      |
| Gari (303K)            | 5.9    | 38.64  | 0.811  | -      | -      | -      | -      |
| Enriched Gari (303K)   | 3.2    | 5.76   | 0.900  | -      | -      | -      | -      |

Monolayer moisture content for GAB model was around 4.51-5.99% db and for BET model was around 4.51-4.99% db. Monolayer moisture content of fermented cassava flour by red yeast rice lower than another cassava product except enriched gari using soy melon. The monolayer moisture content changed as the composition changed as well. Commonly, monolayer moisture content of starchy food supply in GAB model was around 3.2-16.3% [10]. In areas of low water activity, proteins and carbohydrates are preferred sites of absorption at lower temperatures than higher temperatures. Proteins and carbohydrates are preferred sites of absorption at lower temperatures is because proteins and carbohydrates have a polar hydrophilic part with a high water binding capacity in it. Water also forms hydrogen bonds with certain groups causing hydrophobic hydration [11]. But with rising temperatures, there is a decrease in the number of hydrophilic groups, and hydrophobic hydrogen biopolymers also begin to break at higher temperatures. It may cause a decrease in monolayer moisture content.

Constant (c) on GAB and BET models were connected to absorption heat in monolayer area. BET constants were related to absorption heat in accordance with an algorithm in a monolayer area. Whereas in accordance to algorithm BET constants were related to chemical potential differences of the water molecule in the form of pure liquid in a monolayer area. GAB constants were related to variation in the energy value in the monolayer area and the layers above [12]. BET constants score tended to be higher than the score of GAB constants. It was the same with the research of Koua et al. [7] which used samples from dry cassava. The decrease of c was an indication of more enthalpy and a gain in kinetic energy resulting in the loss of more moisture at higher temperature [13].
The $k_b$ constant was a constant related to absorption heat in the multilayer area [14]. The $k_b$ score was around 0.8593-0.9117. Increase in $k_b$ was an indication that at higher temperature, the multilayer molecules became more entropic [13].

The $k_b$ score was around 0.8593-0.9117, while the $c$ score was around 4.6685-5.9704. Those two constants indicated that sorption isotherm on "gaplek" flour fortified by protein from red bead tree flour was following isotherm type II. Blahovec[15] said that if $0<k<1$ and $c>2$, the sorption isotherm followed type II. Type II had a graphic about the relation of $aw$ and $m$ which is similar to letter S.

Once the monolayer moisture content was known, the solid surface area of the samples could be determined. The solid surface based on GAB and BET model for each temperature shown in Table 3.

| Temperature | GAB | BET | Cassava |
|-------------|-----|-----|---------|
| 303K        | 196.27 | 159.91 | 217.55 |
| 308K        | 195.56 | 159.20 | - |
| 313K        | 195.21 | 176.15 | - |

Monolayer moisture content in Caurie model and Caurie constant can be used to determine the properties of sorbed water. The properties of sorbed water based on Caurie model shown in Table 4.

| Constant | $m_0$ | $C$ | $N$ | Density | Surface area of Adsorption | Bound water |
|----------|-------|-----|-----|---------|-----------------------------|-------------|
| 303K     | 5.98  | 1.2905 | 4.6339 | 1.2905 | 126.1602 | 27.7107 |
| 308K     | 5.99  | 1.2494 | 4.7943 | 1.2494 | 130.5282 | 28.7179 |
| 313K     | 5.06  | 1.5859 | 3.1906 | 1.5859 | 86.8668 | 16.1444 |

A larger surface area means a large number of exposed polar groups, resulting in increased water absorption. Table 3 and Table 4 show the higher the temperature, the lower absorption surface area. This is in line with previous research conducted by Koua et al. [7] using cassava as a sample.

The highest density is achieved at the highest temperature. Possibly at higher temperatures, the rate of chemical reactions at the multimolar phase and capillary water condensation in region III also increased which may have led to the increased solubilization of sugars present in considerable amounts in food. This intermingling of the sugars with the water molecules may have caused an increase in the density of the sorbed water as adding sugar or salt to water increases its density [7].

4 Conclusions
The equilibrium and monolayer moisture content on fermented cassava flour by red yeast rice was decreasing as increasing temperature. GAB constant value indicated that the process of moisture absorption on the fermented cassava flour by red yeast rice categorized in type II.

References
[1] Alfiah, M. N., Hartini, S., and Cahyanti, M. N.. Mathematical Models and Thermodynamic Properties of Moisture Sorption Isotherms of Fermented Cassava Flour by Red Yeast Rice. Alchemy. 2017. 13(1), 29-40.
[2] Lakahina, O., Saputri, Y. L. I. D., and Hartanto, B. D., Mocaf Merah – Pangan Kaya Antioksidan Berbasis Kearifan Lokal. [Research report]. Salatiga : Universitas Kristen Satya Wacana. 2015.
[3] Budijanto, S., Sitanggang, A.B.and Kartika, Y.D. Shelf Life Study of Tortilla Using Accelerated Shelf Life Testing (ASLT) Method and its Mathematical Modeling of Moisture. Jurnal Teknologi dan Industri Pangan. 2010. 21(2), 165-170.
[4] Kaya A, Aydin O. An experimental study on drying kinetics of some herbal leaves. *Energy Convers Manag.* 2009. 50,118–124

[5] Chowdhury, M.M.I, Huda, M.D, Hosain, M.A., and Hassan, M.S.. Moisture Sorption Isotherms for Mungbean (Vigna radiata L). *Journal of Food Engineering*, 2006. 74 (4), 462-467.

[6] Sobolawe, S.S., Oke, M.O., Odunmbaku, L.A., and Adebio, O.A.. Equilibrium Sorption Isotherms of Moringa Oleifera Leaves at different temperatures. *African Journal of Science, Technology, Innovation and Development*, 2017. 9(1), 61-68.

[7] Koua, B.K, Koffi, P.M, Gbaha, P, and Toure, S. Thermodynamic analysis of sorption isotherms of cassava (Manihot esculenta). *Journal of Food Science and Technology*, 2014. 51(9), 1711–1723.

[8] Ayala-Aponte, A. A., Thermodynamic Properties of Moisture Sorption in Cassava Flour. *Dyna* 2015. 83 (197), 138-144.

[9] Oluwamukomi, M O. Adsorption isotherm modeling of soy-melon-enriched and un-enriched ‘gari’ using GAB equation. *African Journal of Food Science* 2009. 3(5), 117-124

[10] Lomauro, C. J., Bakshi, A. S., and Labuza, T. P. Evaluation of food moisture sorption isotherm equations. Part I: Fruit, vegetable and meat products. *Lebensmittel-Wissenschaft und Technologie*, 1985. 18(2), 111–117.

[11] Kinsella JF, Fox PF. Water sorption by milk proteins. *Bull Int Dairy Fed*. 1987. 209,12–40.

[12] Erbaş, M., Aykın, E., Arslan, S., and Durak, A. N. Adsorption behaviour of bulgur. *Food Chemistry*, 2016. 195, 87-90.

[13] Diosady LL, Risvi SSH, Cai W, Jagdeo DJ Moisture sorption Isotherms of Canola meals, and application to packaging. *J. Food Sci.* 1996. 61(1), 204-208.

[14] Basu, S., Shivhare, U.S., & Mujumdar, A.S.. Model for Sorption Isotherm for Food: A Review. *Drying Technology* 2006. 24(8), 917-930

[15] Blahovec, J. Sorption isotherms in materials of biological origin mathematical and physical approach. *Journal of Food Engineering* 2004. 65(4), 489-495.