Abstract—The drying characteristics and moisture sorption isotherm (MSI) of batuan, an underutilized and commonly neglected fruit that is often found in tropical climate countries like the Philippines, were investigated. Whole and sliced fruits were dried using a convection dryer set at 50°C. The constant-rate period is absent from the drying curve, and the bulk of drying happened in the falling rate period. Drying data was fitted in four drying models, namely: Newton (Lewis), Henderson and Pabis, Page, and Logarithmic. The goodness of the fit of the model was evaluated by comparing the values of coefficient of determination \(R^2\) and Root Mean Square Error (RMSE) between the observed and predicted moisture ratios. Page model provided the best fit in describing the drying behavior of both whole and sliced fruits, with highest \(R^2\) of 0.9867 and 0.9994 and lowest RMSE of 0.0360 and 0.0078, respectively. MSI of the dried fruits was meanwhile determined at 25°C using the static gravimetric method, and was fitted in seven different isotherm models, namely: Brunauer-Emmet-Teller (BET), Guggenheim-Anderson-DeBoer (GAB), Adam and Shove, Halsey, Oswin, Henderson-Thompson, and Peleg. Fitness of models was evaluated using the values of \(R^2\) standard error (SE) and mean relative percentage deviation modulus (P). Among the models, Halsey showed the best fit for MSI with highest \(R^2\) of 0.9946, SE of 0.0185 and P of 7.0207%. Using the same model, the monolayer value of the dried batuan fruits was determined as 0.1542 g H2O/g solid, with corresponding water activity \(a_w\) of 0.3478.

Index Terms—Batuan, drying, moisture sorption isotherm, monolayer value

I. INTRODUCTION

Garcinia binucao (Blanco) Choisy, commonly known as “batuan”, is an evergreen tree that belongs to the family Guttiferae (alternatively Clusiaceae) and is a close relative of mangosteen (Garcinia mangostana). Most of the available references point out the use of batuan as a fruit tree and rootstock for a more popular member of Guttiferae – Mangosteen (Garcinia mangostana. L.) [1]. It can also be made into a good timber for its thick and wide trunk. The fruits are juicy and have a distinct acidity which makes it a good choice as a souring agent in some localities, particularly in the Philippines’ Visayas Region where it is used in a variety of dishes including kansi, sinigang, paksiw, and even chicken inasal. In Masbate, Philippines it is preferred over sampalok or tamarind as souring agent in their local dishes and is likewise the preferred souring agent for the Ilonggo dish Kadyos-Baboy-Langka (KBL) which literally translates to pigeon peas, pork, and jack fruit in English. It is also reported that batuan is the most abundant fruit tree found in Benguet province, Philippines but remains to be characterized as one of the underutilized and commonly neglected fruit trees in the area [2].

The underutilization of the fruit tree also relates to a lack of available thorough data about it. In fact, at present, there is a paucity of research studies made about batuan. Among those conducted is a comprehensive study on the use of the batuan fruit as food ingredient [3]. Findings showed that the fruit contains low amounts of total ash, crude protein, sugar, starch, total carbohydrates, total soluble solids, and sodium while having high amounts of vitamin C, potassium, phosphorus, calcium, magnesium, and iron, with trace levels of zinc, copper, and manganese. The same study consequently found that the seeds contain high amount of crude fat, crude protein, and tannin. With the expected increase in demand of the batuan fruit for food use, it is therefore necessary to establish its basic processing and preservation technologies. Dehydration or drying is one of the simplest methods of food preservation. Hot air drying is currently the most widely used method in post-harvest technology of agricultural products, providing a more hygienic and better appearance of the dried product [4]. It involves removal of moisture which in turn reduces the water activity \(a_w\) of the dried products. The low water activity levels extend the shelf-life by limiting the degradation reactions in food systems, as well as microbial growth. However, drying may also alter the quality of the food, including color deterioration (browning) and loss of volatiles and flavor. Moreover, dehydrated products may be susceptible to storage defects such as moisture sorption and other water activity-related reactions. A good understanding of the drying behaviors, as well as the storage stability of food commodities, is thus necessary to address these defects. Moisture Sorption
Isotherms (MSI) describe the relationship between moisture content and water activity in food. Knowledge of MSI data is important for the prediction of microbial, chemical, and enzymatic stability. It is also useful in designing drying processes, selecting the appropriate packaging materials, and choosing the right storage conditions for the food product [5]. Meanwhile, monolayer value is the moisture content (dry basis) which is regarded as the satisfactory specification of the lower limit of moisture in dehydrated food. Moisture content lower than the calculated monolayer value will render the product highly susceptible to oxidation and rancidification which is aggravated by drying to very low moisture level. On the other hand, moisture content higher than this value can contribute to increased rate of deteriorative reactions associated with increased water activity such as enzymatic and non-enzymatic reactions, oxidation, and microbial growth.

The main objective of the study is to evaluate the drying characteristics and MSI of the batuan fruits. Specifically, the study aims to (1) describe the drying behavior of whole and sliced batuan fruits by establishing the moisture content – drying time curve and subsequent model-fitting of related parameters to established dehydration models; (2) evaluate the MSI of dried batuan fruits as fitted to established MSI models; and (3) determine the monolayer value of the dried batuan fruits based on the fitted MSI model.

II. MATERIALS AND METHODS

A. Materials

Preparation of Fruits. Green-mature unripe batuan fruits with ≥ 3.0 cm in diameter were outsourced from La Granja Research and Training Station (LGRTS) in La Carlota City, Negros Occidental, Philippines. Selected fruits were washed and blot-dried. For the whole fruit treatment, blot-dried fruits were immediately placed on stainless drying trays, weighed, and dried accordingly. To prepare the sliced fruit treatments, representative fruits were cut lengthwise in quarters. Sliced fruits were then weighed and placed on stainless steel drying trays. The fruits were dried in a cabinet dryer set at 50°C until equilibration of weight was observed. The drying temperature was selected based on a preliminary study which optimized dried batuan powder in terms of physico-chemical, functional, and sensory properties.

Preparation of Relative Humidity (RH) bottles. RH bottles were prepared such that the samples can be equilibrated at different relative humidity, and therefore attaining equilibrium water activities. Environments of different relative humidity were generated using different concentrations of sulfuric acid. To attain RH (%) of 10, 20, 30, 45, 55, 65, 75, 85, and 95, sulfuric acid concentrations (% by weight) of 61.00, 57.76, 52.45, 45.51, 40.75, 35.80, 30.14, 22.88, and 11.02 were prepared, respectively.

B. Methods

Determination of Moisture Content of Fruits: Oven drying method [6] was used to determine the initial moisture content of the samples. One gram (1.0g) of homogenized sample was quantitatively weighed into tared crucibles. The crucibles were then placed inside an oven maintained at 100 ± 5°C for 6 hours. Thereafter, these were transferred into a desiccator to allow cooling before weighing. After the weight was recorded, the crucibles were placed back into the oven for 30 minutes, cooled afterwards in a desiccator, and reweighed. The procedure was repeated until a 0.001g change in weight was observed. Moisture content wet-basis (%MC_wb) was computed using (1).

\[
% \text{MC}_{wb} = \frac{\text{weight loss}}{\text{initial weight of sample}} \times 100 \quad (1)
\]

With initial moisture content determined, the initial mass of water and solids were then identified. Moisture content-dry basis (MC_db), expressed as grams water per gram of solids, was computed using (2).

\[
\text{MC}_{db} = \frac{\text{mass of water}}{\text{mass of solids}} \quad (2)
\]

MC_db of sample for each drying instance, t, of weighing (MC_dbw) was determined using the weight difference method and was computed using (3).

\[
\text{MC}_{dbw} = \frac{M_{w,t-1} + M_{s,t} - M_{s,t-1}}{\text{mass solids}} \quad (3)
\]

where: MC_dbw = MC_db at time t

M_{w,t-1} = mass of water at time t-1

M_{s,t} = mass of sample at time t

M_{s,t-1} = mass of sample at time t-1

Mathematical modelling of drying curve. The moisture ratio (MR) was fitted in different drying models [4] namely: Newton (Lewis), Handerson and Pabis, Page, and Logarithmic (Table I). Moisture ratio at any given time, t (MR_t) was determined using (4).

\[
\text{MR}_t = \frac{M_s - M_e}{M_i - M_e} \quad (4)
\]

where: MR_t = moisture ratio at time drying time t

M_i = MC_{db} at drying time t

M_s = equilibrium MC_{db}

M_e = initial MC_{db}

<table>
<thead>
<tr>
<th>Model name</th>
<th>Model*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newton (Lewis)</td>
<td>MR = \text{exp}(−k\ t)</td>
</tr>
<tr>
<td>Handerson and Pabis</td>
<td>MR = A\text{exp}(−k\ t)</td>
</tr>
<tr>
<td>Page</td>
<td>MR = \text{exp}(−k\ t^n)</td>
</tr>
<tr>
<td>Logarithmic</td>
<td>MR = A\text{exp}(−k\ t^n) + c</td>
</tr>
</tbody>
</table>

* A, n, k, and c are experimental constants

Dehydration models were assessed for goodness of fit based on the coefficient of determination (R²), as well as with root mean square error (RMSE) defined by (5), where N, MR, and MR_p represent number of observations, experimental moisture ratio, and predicted moisture ratio, respectively.
$$RMSE = \left[ \frac{1}{N} \sum_{i=1}^{N} (MR_i - MR_p)^2 \right]^{1/2}$$  \hspace{1cm} (5)

Drying rate (DR) was also computed to determine the changes in the rates of dehydration during the drying operation. DR was calculated using (6).

$$DR = \frac{M_{t+dt} - M_t}{dt}$$  \hspace{1cm} (6)

where: \(M_{t+dt}\) = MC at time \(t + dt\)
\(M_t\) = MC at time \(t\)
\(dt\) = time of differentiation

**Preparation of Moisture Sorption Isotherm (MSI) plot.**
Static gravimetric method was used in determining MSI. Pre-weighed portions of the dried homogenized samples were placed in tared and equilibrated crucibles and were placed in tightly sealed RH bottles. The samples were left for five days to equilibrate with the surrounding relative humidity and at average temperature of 25°C. Afterwards, successive weighing was done every other day. Samples were considered equilibrated when the weight difference in three successive instances did not differ by 0.001g. Experimental MSI was then developed as the plot of equilibrium moisture content (EMC) versus water activity.

**Mathematical modelling of MSI.** The EMC data were processed using Microsoft Excel 365 software (2018) and were plotted using seven different models namely: Brunauer, Emmett, and Teller (BET); Guggenheim-Anderson-DeBoer (GAB); Adam and Shove; Halsey, Henderson-Thompson, and Peleg [7], [8] (Table II).

Coefficient of determination (R²) and standard error were the primary indices for the selection of model. Fitness to the models was also evaluated using the mean relative percentage deviation modulus (P) as defined by (7), where \(n\), \(X_i\), and \(X_{ip}\) represent number of experimental data, experimental EMC, and predicted EMC, respectively.

$$P(\%) = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{X_i - X_{ip}}{X_i} \right|$$  \hspace{1cm} (7)

The model that showed the greatest fit was used to determine the monolayer value (MV) of the samples, which is considered as the good estimate of target moisture content during dehydration. Moreover, an estimate of the good storage condition in terms of relative humidity was also proposed based on the MV.

**TABLE II. LIST OF MODELS USED TO DESCRIBE THE MSI OF DRIED BATUAN FRUITS.**

<table>
<thead>
<tr>
<th>Model name</th>
<th>Model of EMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brunauer-Emmett-Teller (BET)</td>
<td>EMC = ( \frac{AB(a_w)}{(1 - a_w)(1 + (A - 1)a_w)} )</td>
</tr>
<tr>
<td>Guggenheim-Anderson-DeBoer (GAB)</td>
<td>EMC = ( \frac{CAB(a_w)}{(1 - Ba_w)(1 - Ba_w + ABa_w)} )</td>
</tr>
<tr>
<td>Adam and Shove</td>
<td>EMC = ( A + Ba_w + Ca_w^2 + Da_w^2 )</td>
</tr>
</tbody>
</table>

Halsey

$$EMC = A - \frac{B}{\ln(a_w)}$$

Henderson-Thompson

$$EMC = \left[ \frac{\ln(1 - a_w) - C}{A (1 + B)} \right]^2$$

Peleg

$$EMC = A + B a_w + C a_w^2 + D a_w^3$$

*\(A, B, C, \) and \(D\) are experimental constants while \(T\) is Temperature (°C).*

### III. RESULTS AND DISCUSSION

#### A. Drying Characteristics of Batuan Fruits

Fresh whole and sliced batuan fruits with both initial moisture content of 5.55 gH₂O/g solid were dried at 50°C to equilibration moisture content of 1.94 ± 0.28 gH₂O/g solid and 0.4859 ± 0.12 gH₂O/g solid, respectively. Images of fresh and dehydrated batuan fruit products are presented in Fig. 1. Noticeable browning of the products, as well as shrinking of the outer portion of the fruits were observed after the drying process.

![Fig. 1. Images of batuan fruit products: (a) whole fresh fruits; (b) sliced fresh fruits; (c) dried whole fruits; and (d) dried sliced fruits.](image)

Fig. 2 shows the drying curves of the fruit samples, illustrating the great variability in the rates and extent of dehydration between the whole and sliced fruits. Greater extent of dehydration of sliced fruits can be attributed to the increased surface area exposed to drying medium, permitting more surface moisture to diffuse into the dry air surrounding the samples.

![Figure 2. Drying curve of the whole and sliced batuan fruits at 50°C.](image)
Plot of the computed drying rates is presented in Fig. 3 where it can be observed that the constant rate period is absent for both samples. Moreover, this figure shows that the drying process of both samples occurred during the falling rate period. Same drying behavior is identified in the dehydration of other low sugar commodities such as okra slices [4] and saffron stigma [9]. Sliced batuan fruits exhibited higher drying rate at the beginning of the drying process as compared to whole fruits. The destruction of the tissue barriers, as well as the exposure of the interior part of the fruit during slicing and increased surface area exposed to drying air, contributed much to the ease in the moisture loss. Furthermore, it is observed that the drying rate falls rapidly where the rate of dehydration of sliced fruit is lower than that of whole fruits at around 25 hours of drying.

The dependency of the drying rate to the moisture ratio of the samples is shown in Fig. 4. As observed, the higher the amount of remaining water in the samples, the greater is the drying rate. This is due to the reduced concentration gradient between the surface moisture and the internal moisture of the samples, which is one of the driving forces in dehydration. The results support the idea that the exponential decrease in the moisture ratio as drying progresses is an indication that the internal mass transfer is governed by moisture diffusion [10].

B. Mathematical Modelling of Drying Curve

Moisture ratio of both whole and sliced batuan fruits were computed and fitted in different drying models as shown in Fig. 5 and Fig. 6, respectively. The best models describing the dehydration characteristics of the batuan fruits were chosen based on the highest $R^2$ and the lowest RMSE value. Result of the non-linear regression for the dehydration models is presented in Table III.
Based on the values for $R^2$ and RMSE, it was determined that the Page model had the greatest fit for the drying ratio of both whole and sliced batuan fruits, with highest $R^2$ value of 0.9867 and 0.9994, and lowest RMSE value of 0.360 and 0.0078, respectively. Page model is widely used in describing the behaviors of intermittent drying. However, it can also be used to evaluate continuous drying conditions such as continuous drying of bananas and other related commodities [11].

C. Moisture Sorption Isotherm and Monolayer Value of Dried Batuan Fruits

Fig. 7 shows the sigmoidal-shaped MSI of dried batuan fruit samples, as plotted against water activity using different models. The general shape of the sorption resembles Type II and Type IV isotherm. Type II isotherm is commonly exhibited by general foods, along with Type IV, while Type IV isotherm is typical for a swellable solids [12].

The MSI data were fitted to seven models that are commonly used to describe the isotherms in food systems. Estimated experimental constants, $R^2$ value, Standard Error (SE) and values for $P$ were summarized in Table 4. Results show that Halsey model is the most fitted to describe the MSI of dried batuan fruits, showing the highest $R^2$ value of 0.9946, and lowest SE of 0.0185. Its $P$ (%) with value of 7.0207 is also considered satisfactory since it is lower than 10%. Halsey model provides good representation of adsorption data regarding Type I, II, or III isotherms, and for isotherms of products containing starch. It has also been a good model to represent dehydration of pear, blueberry, and banana pulp [13]. Fitness to Halsey model suggests that dried batuan fruits exhibits a Type II isotherm.

The value of constant $A$ in Halsey equation is also considered as the MV [13], which in the case of the batuan samples, has a value of 0.1542 gH$_2$O / g solids. Using the selected model for MSI, MV can give a good estimate of proper storage relative humidity which is a useful parameter for packaging design. Using the Halsey equation, the $a_w$ corresponding to MV is 0.3478. This means that to keep the dried batuan fruits in good quality, it must be kept in area or packaging with relative humidity (RH) not exceeding 34.78% at 25°C.

IV. CONCLUSION

Drying characteristics of whole and sliced batuan fruits were investigated at 50°C. It was observed that bulk of the drying process occurred at a falling rate period with equilibrium moisture content determined as 1.94 ± 0.28 gH$_2$O/g solids and 0.4859 ± 0.12 gH$_2$O/g solids, respectively. Greater extent of dehydration of sliced fruits is attributed to the increased surface area exposed to drying medium. Browning and shrinking of the fruits were observed in both dehydrated products. An exponential decrease in the moisture ratio as drying progresses was also noted. Page model provided the best fit in describing the drying behavior of both whole and sliced fruits, with highest coefficient of determination ($R^2$) of 0.9867 and 0.9994 and lowest root mean square error (RMSE) of 0.0360 and 0.0078, respectively. Moisture Sorption Isotherm (MSI) of the dried batuan fruits at 25°C was also established where it was determined to be a sigmoidal-shaped Type II isotherm and likewise best fitted to Halsey model, with highest $R^2$ of 0.9946 and lowest mean relative percentage deviation modulus (P) of 7.0207%. The determined monolayer value was 0.1542 gH$_2$O/g solids with corresponding $a_w$ = 0.3478.

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