Influence of the temperature and granulometry on the hygroscopic behavior of tapioca flour

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Abstract

The morphological difference between two types of tapioca flour motivated this research, which aims to evaluate the hygroscopic behavior of these products via moisture sorption isotherms (MSI). The MSI of the products were obtained at 25°C, 35°C, 45°C, and 55°C and the experimental data were fitted at seven mathematical models that concern the effect of temperature. MSI had type-II behavior and hysteresis were observed between the moisture adsorption and desorption isotherms, whose magnitudes decreased with higher temperatures. According to adsorption, the two flour are microscopically stable if they have moisture below 11% and they are less susceptible to becoming moist if they are stored at relative humidity below 70%. The MSI indicated that the tapioca flour more expanded is more hygroscopic and with higher moisture decreases as temperature increases, suggesting distinct storage conditions for the two flour. The modified Oswin model had a good fit to the sorption data.

1. Introduction

Cassava (Manihot esculenta Crantz) is one of the most widely grown plants worldwide, particularly in the tropics, and stands out as one of the main crops in Brazil (Léotard et al., 2009), where it is broadly used as human and animal food (Franck et al., 2011; Nwokocha, Aviara, Senan, & Williams, 2009). It is a valuable crop, mainly for the economies of countries in development, due to the versatility of in natura and industrialized sub-products and by-products (Zanetti, Cardoso, Dourado, Reina, & Muraishi, 2014). Brazil is the fourth-largest producer of cassava in the world, after Nigeria, Thailand, and Indonesia. In the growing season of 2016, 23.71 million tons of cassava roots were harvested. Currently, the Pará state leads the cassava production in Brazil, followed by Paraná and Bahia (Conab, 2017).

In turn, cassava is more susceptible to spoilage than other tuberous roots such as potato, sweet potato, yam, and corn in regular environmental conditions (An, Yang, & Zhang, 2012). This has been attributed to the fact that in the root of cassava, the storage organ, has no dormancy, has no function in propagation and possesses no bud primordia from which regrowth can occur (Cooke, Rickard, & Thompson, 1988). Thus, cassava is best used with the aid of appropriate preservation technologies, especially those that reduce water activity (aw) and that limit microorganism action and product spoilage (Dias & Leonel, 2006; Falade & Akingbala, 2010). The main product obtained from cassava is flour, whose types include tapioca flour (Adebowale, Sanni, & Onitilo, 2008).

Tapioca flour is a granulated product obtained from the starch of cassava, which has uneven, polyhedral, or spherical granules (Chisté, Silva, Lopes, & Pena, 2012). To obtain the product, the starch with 40% moisture is manually rubbed over an extended cloth into a frame, for the formation of the granules, which are classified into a 3.35 mm mesh (Silva, Cunha, Lopes, & Pena, 2013b). According to Silva, Cunha, Lopes, and Pena (2013a), the product may have two forms: tapioca flour expanded type – ET and tapioca flour rounded shape – RS. To obtain tapioca flour ET, the starch granules are submitted to scolding in a metallic plate at ≈ 180°C for...
5 min followed by sitting at room temperature for 24 h. Scolding gellifies starch and forms an impermeable layer on the surface of the granules, which prevents water diffusion from within the granules during roasting (≈240°C) and causes their rupture and expansion. In tapioca flour RS, the starch granules are directly submitted to the roasting step (≈240°C), which reduces the possibility of the formation of the impermeable layer on the surface of the granules. Since that favors the diffusion and evaporation of the water contained in the granules, their rounded shape is maintained. Silva et al. (2013a) reported that the apparent densities of the products are 100 kg/m³ (tapioca flour ET) and 610 kg/m³ (tapioca flour RS).

The hygroscopicity study based on moisture adsorption and desorption isotherms of a product provides important information for process development and optimization; helps select packaging which maximize the retention of aroma, color, texture, nutrients, and biological stability; as well as allows estimating product stability over storage (Van Den Berg & Bruin, 1981). Additionally, knowing the effect of temperature on moisture sorption is very important as it may significantly affect equilibrium conditions and lead to changes in moisture and aw (Labuza, Tannenbaum, & Karel, 1970). Mathematical models that contemplate the effect of temperature on moisture sorption behavior, such as the modified equations of Chung-Pfost, Halsey, Henderson, GAB, and Oswin have been used to represent moisture sorption isotherms of different products (Argyropoulos, Alex, Kohler, & Müller, 2012; He et al., 2013; Jamali, Kouhila, Mohamed, Idlimam, & Lamharrar, 2006).

Chisté et al. (2012) investigated moisture sorption isotherms for tapioca flour; however, the study assessed the sorption behavior of only a single flour type (tapioca flour ET) and at a single temperature (25°C). As a more effective contribution for the study of the hygroscopicity of tapioca flour, the present research aimed to obtain the moisture sorption isotherms of both types of tapioca flour at different temperatures in order to indicate processing and storage conditions for the products.

2. Materials and methods

2.1. Raw material

Samples of both types of tapioca flour (1 kg each) were purchased in the municipalities of Santa Isabel (01°17’55” S and 48°09’38” W) (tapioca flour ET) and Santarém (02°26’35” S and 54°42’30” W) (tapioca flour RS), both in Pará, Brazil. Each flour type is largely produced and consumed in these localities. The samples were packaged with low-density polyethylene (LDPE) film under vacuum and room temperature (≈27°C) until the analyses. Granulometry analysis showed the flour had mean particle size of 4.46 mm (tapioca flour ET) and 2.41 mm (tapioca flour RS).

2.2. Physicochemical characterization of tapioca flour

The recommended methods of the Association of Official Analytical Chemists (AOAC) (2010) were adopted to determine the moisture, ashes, total lipids, total proteins (5.75 nitrogen-protein conversion factor), total sugars, and starch contents. The water activity (aw) was determined at 25°C with a digital thermohygrometer (AquaLab 4TE, Decagon, USA). All analyses were performed in triplicate and the results were presented as the replicates mean.

2.3. Obtaining the sorption isotherms

For the hygroscopicity study of the flour, moisture adsorption and desorption isotherms were built at 25°C, 35°C, 45°C, and 55°C in order to simulate bland and extreme conditions of storage for the product. The isotherms were obtained in a vapor sorption analyzer (Aqualab VSA, Decagon, Puma, WA, USA) using the DVS (dynamic vapor sorption) method, which consists of monitoring the moisture and aw values of a sample exposed to environments with different relative humidity (RH) levels. The different RH levels are generated by injection of dry and saturated vapor.

In order to obtain the sorption isotherms, the sample was initially submitted to complementary dehydration in a desiccator with silica gel under vacuum at working temperature for 24 h (Souza, Souza, & Pena, 2013). Next, an approximately 1 g sample was weighed in a stainless-steel capsule in the microanalytical balance of the VSA. To obtain equilibrium data, the sample was submitted to different levels of RH induced by changes in the injection of dry and saturated vapor. The data were obtained for an aw range between 0.1 and 0.9 used as convergence criterion for the equilibrium of two consecutive measurements with dm/dt ≥0.05, where dm/dt is the ratio between mass variation and time variation between consecutive measurements.

2.4. Monolayer and storage time of the flour determination

The moisture of the monolayer (Mmax) for the adsorption and desorption processes was determined from the linear and angular coefficients of the straight obtained through the linear regression of the aw/(1–aw)M versus aw correlation, using the linearized form of the BET equation (Equation (1)) (Brunauer, Emmet, & Teller, 1938).

$$M = \frac{M_0 C_{aw}}{(1 - a_w)/(1 - a_w + C_{aw})}$$

where M = equilibrium moisture (g H₂O/100 g dry basis – d.b.); aw = water activity (dimensionless); M₀ = monolayer moisture content (g H₂O/100 g d.b.;); and C = constant related to the heat of sorption of the first layer on primary sites.

Equation (2) proposed by Costa, Carmo, and Pena (2018) was used to estimate the storage time required for the tapioca flour to reach critical moisture. This equation involves both packaging and product properties, which are easily determined.

$$t = \frac{M}{1000A} \left[ m_{max} - \left( \frac{m_{max}}{100} + 1 \right) m_i \right]$$

where t = storage time of the product (days); M = product mass in packaging (g); mmax = maximum moisture to be reached by the product (g H₂O/100 g d.b.); m_i = initial moisture content of the product (g H₂O/100 g); Φ = water vapor permeability of the packaging material (g H₂O/m²·day); A = packaging contact area (m²).
2.5. Mathematical modeling of sorption isotherms

The mathematical models presented ahead (Equations (3)–(9)), which concern the effect of temperature, were adjusted to the experimental moisture sorption data of the flour. Goodness of fit was assessed using coefficient of determination ($R^2$), root mean square error (RMSE) (Equation (10)), and mean relative deviation (P) (Equation (11)). The trend of the distribution of residues regarding the fits was also assessed (Equation (12)).

Modified Chung-Pfost (Pfost, Mourer, Chung, & Milliken, 1976):

$$M = \frac{1}{c} \ln \left( \frac{T + b}{a \ln a_w} \right)$$  \hspace{1cm} (3)

Copace (Corrêa, Martins, & Melo, 1995):

$$M = \exp[a - (bT) + (ca_w)]$$  \hspace{1cm} (4)

Modified Halsey (Iglesias & Chirife, 1976b):

$$M = \left[ -\exp(a + bT) \right]^{1/c} / \ln a_w$$  \hspace{1cm} (5)

Modified Henderson (Thompson, Peer, & Foster, 1968):

$$M = \left[ \frac{1}{a(T + b)} \ln(1 - a_w) \right]^{1/c}$$  \hspace{1cm} (6)

Modified GAB (Jayas & Mazza, 1993):

$$M = \frac{M_0 \left( \frac{T}{1 + \frac{1}{T} - \frac{1}{a_w}} \right) k a_w}{(1 - a_w) \left( 1 - \frac{k a_w}{1 - \frac{1}{T} + \frac{1}{a_w}} \right) k a_w}$$  \hspace{1cm} (7)

Modified Oswin (Chen & Morey, 1989):

$$M = (a + bT) \left[ \frac{a_w}{1 - a_w} \right]^{1/c}$$  \hspace{1cm} (8)

Sigma Copace (Corrêa, Martins, Christ, & Mantovani, 1998):

$$M = \exp[a - bT + c \exp(a_w)]$$  \hspace{1cm} (9)

where $M =$ equilibrium moisture ($g$ H$_2$O/100 g d.b.); $a_w =$ water activity (dimensionless); $T =$ temperature ($K$); and $a$, $b$, $c$, $M_0$, $C$, and $k$ are the models’ parameters.

$$\text{RMSE} = \left( \frac{1}{N} \sum_{i=1}^{N} (M_{p,i} - M_{e,i})^2 \right)^{1/2}$$  \hspace{1cm} (10)

$$P = \frac{10^6}{100} \frac{\sum_{i=1}^{N} |M_{p,i} - M_{e,i}|}{M_{p,i}}$$  \hspace{1cm} (11)

$$e_{\text{ave}} = \frac{1}{N} \sum_{i=1}^{N} |M_{p,i} - M_{e,i}|$$  \hspace{1cm} (12)

where $M_{p,i} =$ predicted equilibrium moisture ($g$ H$_2$O/100 g d.b.); $M_{e,i} =$ experimental equilibrium moisture ($g$ H$_2$O/100 g d.b.); $N =$ number of experimental determinations; $e_{\text{ave}} =$ residue ($g$ H$_2$O/100 g d.b.).

2.6. Statistical analysis

The sorption models were fitted by non-linear regression using Statistica 7.0 software and the Levenberg-Marquardt algorithm with a convergence criterion of $10^{-6}$. The models whose fits had $R^2$ values close to 1, low RMSE and $P$ values, and random distribution of residues (Arslan & Togrol, 2005; Lomauro, Bakshi, & Labuzka, 1985) were considered effective. Trends in residue distribution indicate the model under- or overestimates the real condition in some regions, which makes it inappropriate to represent the phenomenon investigated (Draper & Smith, 1998). According to Peng, Chen, Wu, and Jiang (2007), $P$ values lower than 10% can be adopted as an indicative of a good fit for practical purposes.

3. Results and discussion

3.1. Moisture sorption of tapioca flour

Tapioca flour ET and tapioca flour RS studied had 11.30% and 9.0% moisture, 0.08% and 0.05% ashes, 0.33% and 0.14% lipids, 0.25% and 0.36% proteins, 0.94% and 0.98% total sugars, 82.77% and 80.82% starch and 0.62 and 0.46 $a_w$, respectively. Similar values of composition were observed by Chisté et al. (2012) and Silva et al. (2013a) for this product. The fiber crude content in this flour type varies between 0.20% and 0.22% (Ijoma, Ihediohanma, Okafor, Ofoedu, & Ojimba, 2016).

The moisture sorption data for tapioca flour at different temperatures are shown in Table 1. The moisture sorption isotherms obtained from these data are presented in Figure 1, showing the hysteresis phenomenon, and in Figure 2, highlighting the effect of temperature. The adsorption isotherms indicate ET and RS tapioca flour are microbiologically stable ($a_w < 0.6$) (Jay, 2005) when stored between 25°C and 55°C if their moisture levels are up to 14.7% d.b. (12.8% wet basis – w.b.) and 12.4% d.b. (11.0% w.b.), respectively. These results indicate tapioca flour ET required greater care during storage. A value in the same order of magnitude was observed for cassava flour of the dry and water groups (11.3% d.b.) (Chisté, Cardoso, Silva, & Pena, 2015).

According to the BET classification, the isotherms of the tapioca flour in the temperature range studied had type-II behavior (sigmoidal shape) (Figure 1) (Iglesias & Chirife, 1982). It is known that water molecules are strongly bound to hydrophilic biopolymers like proteins and polysaccharides, such as starch. Starchy foods show more Langmuir-like type-II isotherm Blahovec and Yanniotis (2009). Thus, although the product presents other biopolymers in the composition, like fibers and proteins, the sigmoid behavior is primarily attributed to the starch, being the major constituent. Type-II moisture sorption isotherms have been also observed for other cassava-derived products (Ayala-Aponte, 2016; Chisté et al., 2015, 2012; Mishra & Rai, 2006; Perdomo et al., 2009).

The hysteresis loop observed between the moisture adsorption and desorption isotherms of the flour comprehended the monolayer region until approximately 0.85 $a_w$, while its amplitude reduced as temperature increased (Figure 1). Studies involving starchy products such as rice (Arslan & Togrol, 2006; Bingol, Prakash, & Pan, 2012), corn flour (Oyelade, Tunde-Akintunde, Igbekac, Okeb, & Rajid, 2008), and millet (Raji & Ojediran, 2011) exhibited a hysteresis loop nearly throughout the entire $a_w$ range.

For constant $a_w$, the moisture of ET and RS flour decreased as temperature increased, an effect that was more representative of the former than the latter. The behavior observed is explained by the excitation state of water (McLaughlin & Magee, 1998). Studies on other starchy products such as cassava flour (Farias, Ferreira, Conceição, &
The tapioca flour ET had higher moisture content than the tapioca flour RS for a constant \( \alpha_w \) and temperature (Figure 2). The greater affinity for the water molecules of the first one is due to its mean particle size – 4.46 mm (more expanded), since it is submitted to scolding and has smaller density than tapioca flour RS (Silva et al., 2013a). Regarding the effect of temperature, the sorption isotherms of this latter were closest (Figure 2(b,d)), in other words, lower moisture decreases (0.7% b.s.) in relation to tapioca flour ET (9.0 g H\(_2\)O/100 g d.b.) at 25°C (Chisté et al., 2012) and cassava starch (Ayala-Aponte, 2016) for 80 µm thick LDPE film exposed to 38°C and 90% RH was used.

The storage time was estimated as 24 days for ET flour with 11.3% moisture and 31 days for RS flour with 9.0% moisture. These are the limit times for the flour to reach critical moisture. The water vapor permeability value of 4.94 g H\(_2\)O/m\(^2\)·day estimated by Alves, Ito, Carvalho, Melo, and Godoy (2012) for 80 µm thick LDPE film exposed to 38°C and 90% RH was used.

Means of the triplicate ± standard deviation; ET – expanded type; RS – rounded shape; \( \alpha_w \) – water activity; M – equilibrium moisture.

Medias de la prueba por triplicado ± desviación estándar; ET – tipo redondo; a – actividad del agua; M – humedad de equilibrio.
Figure 1. Moisture adsorption (○ tapioca flour ET; ● tapioca flour RS) and desorption (△ tapioca flour ET; ▲ tapioca flour RS) isotherms at (a) 25°C; (b) 35°C; (c) 45°C; (d) 55°C.

Figura 1. Adsorción de humedad (○ harina de tapioca ET; ● harina de tapioca RS) y desorción (△ harina de tapioca ET; ▲ isotermas de harina de tapioca RS) a (a) 25°C; (b) 35°C; (c) 45°C; (d) 55°C.

Figure 2. Influence of temperature on moisture adsorption ((a) tapioca flour ET; (b) tapioca flour RS) and desorption ((c) tapioca flour ET; (d) tapioca flour RS) isotherms. Experimental (○ 25°C; □ 35°C; ◊ 45°C; Δ 55°C) and predicted values using the modified Oswin model (line).

Figura 2. Influencia de la temperatura en la adsorción de humedad (a) harina de tapioca ET; (b) harina de tapioca RS) y desorción (c) harina de tapioca ET; (d) isotermas de harina de tapioca RS). Valores experimentales (○ 25°C; □ 35°C; ◊ 45°C; Δ 55°C) y pronosticados utilizando el modelo (línea) modificado de Oswin.
3.2. Mathematical modeling of sorption isotherms

According to the values of the statistics used to assess goodness of fit ($R^2$, $P$ and RMSE) and on the random distribution of the residues (Table 2), the modified Oswin model best described the moisture adsorption and desorption processes of the tapioca flour in the experimental domain. The isotherms generated by the modified Oswin model are presented in Figure 2. Overall, the literature indicates the GAB and Halsey models as having the best fits to the moisture sorption data of starch products such as potato starch (Al-muhtaseb, McMinn, & Magee, 2004), cassava flour (Chisté et al., 2015; Farias et al., 2010), rice (Bingol et al., 2012), tapioca flour (Chisté et al., 2012), and cassava (Koua, Koffi, Ghaba, & Toure, 2014).

4. Conclusion

The hygroscopic assessment of tapioca flour expanded type (ET) and tapioca flour rounded shape (RS) showed the moisture sorption isotherms of the products are type II (sigmoid) and that the microbiological stability between 25°C and 55°C is assured if the moisture of the products is below 12.8% for the former and 11.0% for the latter. In order to meet such conditions, the storage time of the products at 38°C and 90% RH packaged in low-density polyethylene film was estimated as 24 and 31 days, respectively. The tapioca flour ET has grater affinity with water molecules than tapioca flour RS, as function of the larger surface area of the former. Moreover, the tapioca flour ET presents higher moisture decreases as temperature increases, so this flour requires greater control during handling and storage. Finally, the modified Oswin model can be used with good precision to describe the sorption isotherms of both flour.

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References

Adebawale, A. A., Sanni, L. O., & Onitilo, M. O. (2008). Chemical composition and pasting properties of tapioca grits from different cassava varieties and roasting methods. African Journal of Food Science, 2, 77–82.

Al-muhtaseb, A. H., McMinn, W. A. M., & Magee, T. R. A. (2004). Water sorption isotherms of starch powders. Part II: Thermodynamic characteristics. Journal of Food Engineering, 62(2), 135–142. doi:10.1016/S0260-8774(03)00202-4

Alves, R. M. V., Ito, D., Carvalho, J. L. V., Melo, W. F., & Godoy, R. L. O. (2012). Stability of biofortified sweet potato flour. Brazilian Journal of Food Technology, 15(1), 59–71. doi:10.1590/S1981-67232012000100007

An, D., Yang, J., & Zhang, P. (2012). Transcriptome profiling of low temperature treated cassava apical shoots showed dynamic responses of tropical plant to cold stress. BMC Genomics, 13–64. doi:10.1186/1471-2164-13-64

Argyropoulos, D., Alex, R., Kohler, R., & Muller, J. (2012). Moisture sorption isotherms and isosteric heat of sorption of leaves and stems of lemon balm (Melissa officinalis L.) established by dynamic vapor sorption. LWT – Food Science and Technology, 47(2), 324–331. doi:10.1016/j.lwt.2012.01.026

Arslan, N., & Togrul, H. (2005). Modelling of water sorption isotherms of macaroni stored in a chamber under controlled humidity and thermodynamic approach. Journal of Food Engineering, 69(2), 133–145. doi:10.1016/j.jfoodeng.2004.08.004

Arslan, N., & Togrul, H. (2006). Moisture sorption behavior and thermodynamic characteristics of rice stored in a chamber under controlled humidity. Biosystems Engineering, 95(2), 181–195. doi:10.1016/j.biosystemseng.2006.06.011

Association of Official Analytical Chemists (AOAC). (2010). Official methods of analysis of Association of Official Analytical Chemists International (18th ed.), Arlington, VA: Author.

Ayala-Aponte, A. A. (2016). Thermodynamic properties of moisture sorption in cassava flour. DYN A, 83(197), 139–145. doi:10.15446/dyna.v83n197.5145

Bingol, G., Prakash, B., & Pan, Z. (2012). Dynamic vapor sorption isotherms of medium grain rice varieties. LWT – Food Science and Technology, 48(2), 156–163. doi:10.1016/j.lwt.2012.02.026

Blahovec, J., & Yanniotis, S. (2009). Modified classification of sorption isotherms. Journal of Food Engineering, 91(1), 72–77. doi:10.1016/j.jfoodeng.2008.08.007

Brunauer, S., Emmet, T. H., & Teller, F. (1938). Adsorption of gases in multimolecular layers. Journal of the American Chemical Society, 60(2), 390–399. doi:10.50190/j.physchem.60(2),390–399

Chen, C., & Morey, R. V. (1989). Comparison of four EMC/ERH equations. Transactions of the ASAE, 32(1), 983–990. doi:10.3221/030713.31103

Chisté, R. C., Cardoso, J. M., Silva, D. A., & Pena, R. S. (2015). Hygroscopic behaviour of cassava flour from dry and water groups. Ciência Rural, 45(8), 1515–1521. doi:10.1590/0103-8478cr20140338

Chisté, R. C., Silva, P. A., Lopes, A. S., & Pena, R. S. (2012). Sorption isotherms of tapioca flour. International Journal of Food Science and Technology, 47(4), 870–874. doi:10.1111/j.1365-2621.2011.02900.x
