PHYSICO-CHEMICAL EVALUATION AND MODELING OF CHIMARRITA AND Eragil PEACHES DEHYDRATED BY DIFFERENT DRYING PROCESSES

AVALIAÇÃO FÍSICO-QUÍMICA E MODELAGEM DE PÊSSEGOS DE CHIMARRITA E ERAGIL DESIDRATADOS POR DIFERENTES PROCESSOS DE SECAGEM

Abstract: The cultivars Chimarrita and Eragil stand out in fruitful productivity, with high quality of flavor, size and nutritional value. However, due to perishability and seasonality, there is a need for the development of conservation methods, among which dehydration can be used to increase the shelf life of the fruit, as well as add value to the peaches. In this sense, the objective of this work was to dehydrate Chimarrita and Eragil peach cultivars by oven, osmotic dehydration followed by oven and lyophilization methods, and to verify pH, soluble solids, water and moisture activity, and to adjust mathematical models to drying kinetics of the peaches in these different drying processes. The models used to adjust the drying kinetic curves were Lewis, Page and Silva. The drying kinetics of the peaches was followed by weighing the samples until constant weight. Significant differences (p <0.05) were found between the drying processes and between the evaluated parameters. Among the studied models, the Silva model obtained the best fit for all the kinetic curves of the different drying processes, corroborated by its statistical indicators. It was possible to conclude that both the Page and Silva models describe the drying curves satisfactorily, with results that can be considered equivalent.

Key-words: mathematical modeling. peaches cultivars. drying.

Resumo: As cultivares Chimarrita e Eragil destacam-se em produtividade frutífera, com alta qualidade de sabor, tamanho e valor nutricional. No entanto, devido à perecibilidade e sazonalidade, é necessário o desenvolvimento de métodos de conservação, entre os quais a desidratação pode ser usada para aumentar o prazo de validade da fruta, além de agregar valor aos pêssegos. Nesse sentido, o objetivo deste trabalho foi desidratar as cultivares de pêssego Chimarrita e Eragil por forno convencional, desidratação osmótica seguida de de forno e liofilização, verificar pH, sólidos solúveis, atividade de água e umidade e ajustar modelos matemáticos à cinética de secagem dos pêssegos nesses diferentes processos de secagem. Os modelos utilizados para ajustar as curvas cinéticas de secagem foram Lewis, Page e Silva. A cinética de secagem dos pêssegos foi seguida de pesagem das amostras até peso constante. Diferenças significativas (p <0,05) foram encontradas entre os processos de secagem e entre os parâmetros avaliados. Entre os modelos estudados, o modelo Silva obteve o melhor ajuste para todas as curvas cinéticas dos diferentes processos de secagem, corroboradas por seus indicadores estatísticos. Foi possível concluir que os modelos de Page e Silva descrevem satisfatoriamente as curvas de secagem, com resultados que podem ser considerados equivalentes.

Palavras-chave: modelagem matemática. cultivares de pêssegos. secagem.
1 Introduction

The peach (Prunuspérsica) is a climacteric and seasonal fruit, highly perishable. Worldwide are produced approximately 17.5 million of tons annually (ZHU & SHEN, 2014). Due to its accelerated metabolism, there are losses on postharvest, reaching values of 30 to 50%, so it is important to evaluate conservation methods, such as dehydration, that aim to reduce the water activity of food, reducing microbial growth and increasing shelf life (ORIKASA et al., 2013, KARAM et al, 2016).

The main dehydration processes are dehydration in an oven, osmotic dehydration, followed by oven drying, and lyophilization (freeze drying). Drying with heated air in oven is one of the oldest methods used to preserve food, consisting of exposing the food in hot air stream, removing the moisture (SOUZA NETO et al., 2005).

The osmotic dehydration process involves the partial removal of water from a given food, by dipping the product in solution with high osmotic pressure and low water activity (RAOULT-WACK, 1994) being used as a pre-treatment for the oven drying.

In the freeze drying process water is removed by sublimation of ice from previously frozen product at low temperatures and with vacuum. In this process the product practically preserves it’s biologically-physiologically and sensory characteristics, structure and shape. This technology has been developed to overcome the losses of compounds responsible for the aromas in foods, which become too susceptible when high temperatures are used, such as conventional drying (oven). Lyophilized foods, are products with high added value by retaining much of their original nutrients, since they employ low temperatures in their processing (VIEIRA et al., 2012).

Studies and analyzes of drying curves as well as determination of the water content, provide a better understanding and visualization of the drying process, besides choosing the process, the treatment, the equipment and the temperature, which are suitable elements for fruit dehydration (OLIVEIRA et al., 2002). According to Fang et al. (2009), the knowledge of the initial and final contents of water of the food, the relation of water to the solid structure, and the transport of water from the interior of the material to its surface, make it possible to understand the drying process, besides studies of heat and mass transfer.

Studies have been development to analyzing the different aspects of the drying process in fruits, where the modeling brings mathematical as well as physical insight into the process (CEYLAN et al., 2007; SIQUEIRA et al., 2013; ROSA et al., 2015). The modeling is based on having a set of mathematical equations that can characterize the system (BARATI & ESFAHANI, 2011).

Mathematical modeling of the drying process of fruits allows predicting their behavior during the removal of water. Among the models of drying that can be used are: Silva, Lewis and Page (MOHAPATRA & RAO, 2005; BEYE et al., 2019). The knowledge of the moisture distribution inside the drying fruits is very important for the control of quality of the product and process, and then, mathematical models to predict moisture distribution during drying could be contribute to this. The aim of this work was the dehydration of peaches Chimarrita and Eragil by oven, osmotic dehydration followed by drying in oven and lyophilization, characterization of the peaches and application of the mathematical modeling, looking for the most appropriate model to predict the dehydration.

2 Materialand Methods

The peach samples of the cultivars Chimarrita and Eragil were purchased in the local market of Erechim-RS, from the 2014 harvest.
Five kg of each peach cultivar were used, where they were washed in running water, dried on absorbent paper and stored at 10ºC in refrigerator (Consul). Subsequently the peaches were peeled manually, submerged in water with 1% citric acid for 4 min at 80 ºC and immediately immersed in ice water (0 ºC) for 2 min. After the peaches were manually destempered and sliced with average of 2 cm thickness and 4.6 cm length. Subsequently, 1kg of each cultivar was submitted to different dehydration processes: in oven, osmotic dehydration followed by drying in oven and freeze drying.

For the dehydration in oven (OD) the samples were separately placed on perforated trays and taken to the oven with air circulation (Marconi brand, model MA 037, Brazil) at 60 ºC (Boeira et al., 2007).

For osmotic dehydration, followed by dehydration in oven (ODOD) the osmotic agent was sucrose (Union). The osmotic solution was prepared with sucrose syrup at 65 ºBrix and fruit ratio: syrup 1:2. The peaches were immersed in the solution (syrup) at 30°C in a water bath for 2 h with manual shaking according to Souza Neto et al. (2003) methodology. The peach were removed from the osmotic solution and immersed in distilled water at 10ºC for 5s, and then dried on absorbent paper to remove excess water. After that, the peach where were arranged in trays for dehydration in oven with air circulation (Marconi brand, model MA 037, Brazil) at 60 ºC.

For freeze drying (FD) process, the samples were placed in aluminum paper, freezing in a freezer (Consul), with a temperature of -18ºC for 24 h. Afterwards they were placed in petri dishes, wrapped in plastic film, and placed in ultra-freezer (CL 600-80) at -80 ± 2ºC for 12 h. Then the frozen samples were placed into lyophilizer (LIOTOP L101AISI304) at -40 ºC under low pressure.

The drying kinetics of the peaches in the dehydration processes was followed by the loss of mass in relation to time, weighing the samples until obtaining constant mass. The dehydrated samples were packed in low density polyethylene film, vacuum sealed and stored at room temperature 25°C.

Samples were characterized in relation to pH, total soluble solids (ºBrix), water activity, ash and humidity. All analyzes were performed in triplicate. The methodologies for analysis were performed according to AOAC (2005).

The pH was determined with a digital potentiometer, the total soluble solids (ºBrix) was determined by therefractometric method using a refractometer (BEL Equipamentos Ltda, Brazil), moisture by the gravimetric method in a recirculation oven (Fanem - model 320 - SE) at 105ºC until constant weight and ash by incineration in an oven at 550ºC. Water activity was determined at 25ºC using the Aqualab series 3 (model TE, Decagon Device, Pullman, WA, USA).

Empirical equations are seen as a resource that only serves to describe the thin layer drying kinetics of a food product. However, several methods describe drying dividing the domain into many thin layers. Thus, an empirical equation, together with several others, could be used to describe the process in each layer. In this case, expressions involving the drying as a function of time, and the drying time as a function of moisture content are required, and are possible to use an empirical equation with this finality (DANTAS et al., 2011). Then, an expression involving the drying rate is required, in order to describe the heat penetration in a body during the water removal using hot air (MARIANI et al., 2008), and an empirical model is used to determine this rate.

The dimensionless moisture content $M^*$ at a time $t$ is given by Equation (1).

$$M^* = \frac{(M - M_{eq}) - (M_t - M_{eq})}{(M - M_{eq})}$$  \hspace{1cm} (1)
where $M$ is the moisture content (w/w) on dry basis, $M_{eq}$ is the equilibrium moisture (w/w) and $M_i$ is the initial moisture (w/w).

Several studies in the literature report the use of empirical models (AKPINAR & BICER, 2005, GHAZANFARI et al., 2006, GANESAPILLAI et al., 2008, DIAMANTE et al., 2010, KALET & GORNICKI, 2010 , KUMAR et al., 2010; SILVA et al., 2012) that best fit the drying kinetics.

Experimental drying curves of the peaches were modeled using the models of Lewis (Equation 2), Page (Equation 3), and Silva (Equation 4).

\[
M^* = \exp(-(a \cdot t)) 
\]  

(2)

\[
M^* = \exp(-a \cdot t^b) 
\]  

(3)

\[
M^* = \exp(-a \cdot t - b\sqrt{t}) 
\]  

(4)

Where $a$ and $b$ are the parameters of the empirical models to be estimated and $t$ is the drying time (min).

The empirical models were fitted to the experimental data using nonlinear regression using the software Scilab 6.0 and the results were evaluated through statistical indicators such as the coefficient of determination ($R^2$) and the mean error, root mean square error (RMSE). The results obtained from the physicochemical characteristics where used to evaluated the differences between means variance analysis (ANOVA) follow by t student using Statistic software, version 5.0, at a significance level of 95% of confidence.

3 Results and discussion

Table 1 shows the results of physical-chemical analyses for Chimarrita and Eragil cultivars dehydrated of: oven (OD), osmotic dehydration followed by oven drying (ODOD) and freeze drying (FD).

For the (OD), (ODOD) and (FD) process for both Chimarrita and Eragil cultivars, it is found that there are significant differences ($p<0.05$) between the processes and cultivars. In relation of pH and ash of Chimarrita are higher than Eragil in both dehydration process, this is because of the characteristic of each peach. Water activity for Chimarrita and Eragil cultivars showed statistical difference ($p<0.05$) for both dehydration processes. This is also related with the final moisture of the peach subject at the dehydration.

Water activity is a factor that directly influences food stability, because it represents water values, which are available in solid food matrix, and indicates the relationship of this content with chemical and microbiological reactions that determine the material deterioration. According to the Brazilian legislation (BRASIL, 1978), the maximum moisture content of dehydrated fruits is 25% and for the freeze-drying process is 5%. Therefore, with processes used for dehydration of the peaches it was possible to obtain moisture values within the required by the legislation, for both cultivars.

The FD process presented the less pH, wa, and moisture, and the highest Brix was obtained by ODOD process, for both peaches. According to Liu et al. (2017) the freeze drying process produce high levels of nutrient retention, with good sensory quality, in addition the low humidity and wa of the peaches with the DF process increases the shelf life of the product. The higher brix is expected in the ODOD process, because the osmotic dehydration with sugar provides brix increase (Germeret al., 2010).
Table 1-Results of physicochemical analysis of peaches chimarrita and eragil dehydrated in oven (od), osmotically dehydrated followed by oven drying (odod) and freeze drying (FD).

| Parameters                  | OD Chimarrita | ODOD Chimarrita | FD Chimarrita | OD Eragil | ODOD Eragil | FD Eragil |
|-----------------------------|---------------|-----------------|--------------|-----------|-------------|-----------|
| pH                          | 4.71±0.02     | 4.13±0.01       | 4.00±0.02    | 4.09±0.05 | 3.98±0.02   | 3.25±0.017 |
| soluble solids (Brix)       | 17.01±0.05    | 19.60±0.02      | 18.00±0.03   | 18.01±0.14 | 21.00±1.04  | 18.30±0.14 |
| wa                          | 0.658±0.001   | 0.676±0.002     | 0.487±0.002  | 0.617±0.002 | 0.652±0.001 | 0.448±0.002 |
| ash (g/100g)                | 3.78±0.01     | 1.80±0.01       | 3.52±0.01    | 2.25±0.11  | 0.79±0.12   | 1.89±0.13  |
| moisture(g/100g)            | 12.88±0.20    | 24.24±0.20      | 5.03±0.10    | 12.00±0.01 | 23.38±0.40  | 4.57±0.30  |

* Means followed by the same letter on the same line/column do not differ by Tukey’s test at 95% significance level.

Germeret al. (2010) performed osmotic dehydration (Aurora cultivar) in slices with 45°Brix sucrose and 30°C, which was followed by oven drying at 65°C/5h, and obtained 22% of moisture and 19.6% of soluble solids. This difference in osmotic dehydration in the study is due to the type of fruit and/or growth, fruit size: syrup in osmotic dehydration, drying time, among others.

Figures 1-6 shows the experimental data of the four drying processes and the respective kinetic curves adjustment and 95% confidence regions bounds obtained by the empirical models of Silva, Lewis and Page, for the two peach cultivars (Chimarrita and Eragil).

As can be seen in Figure 1-6, the Silva and Page models were the best to describe the kinetics curves for both dehydration process and for both peach cultivars. It is possible to observe compatibility between the two models, regardless of the drying time, different for each cultivar. A similar result was observed by Silva et al., (2014) on banana drying. In addition, the mathematical structure of the Lewis model entails in every error of the estimation algorithm on a single parameter, which corroborates the behavior of the profile adjusted by it.
Figure. Kinetic curves of osmotic dehydration drying of the *Chimarrita* cultivar adjusted using the empirical models of (a) Silva, (b) Lewis and (c) Page.
Figure 2. Kinetic curves of osmotic dehydration drying of the Eragil cultivar adjusted using the empirical models of (a) Silva, (b) Lewis and (c) Page.
Figure 3. Kinetic curves of freeze drying of the *Chimarrita* cultivar adjusted using the empirical models of (a) Silva, (b) Lewis and (c) Page.
Figure 4. Kinetic curves of freeze drying of the *Eragil* cultivar adjusted using the empirical models of (a) Silva, (b) Lewis and (c) Page.
Figure 5. Kinetic curves of oven drying of the *Chimarrita* cultivar adjusted using the empirical models of (a) Silva, (b) Lewis and (c) Page.
Figure 6. Kinetic curves of oven drying of the *Eragil* cultivar adjusted using the empirical models of (a) Silva, (b) Lewis and (c) Page.

Through non-linear regressions, the results obtained are presented in Table 2. An inspection of the statistical indicators provided by Table 2 provides a conclusion that the worst adjusted model was the Lewis model obtaining the highest root of the mean square error (RMSE) and the lowest coefficient of determination ($R^2$) among the three models studied for both drying and peach cultivars.
Table 2- Results for drying kinetics described by the empirical models studied.

| Process   | Model   | Model | a            | b            | R²     | RMSE |
|-----------|---------|-------|--------------|--------------|--------|------|
| ODOD      | Silva   | 6.292x10^3 | 9.993x10^-2 | 0.997        | 0.0173 |
|           | Page    | 6.296x10^-2 | 0.708        | 0.998        | 0.0163 |
|           | Lewis   | 0.017 | -            | 0.992        | 0.0279 |
| Eragil    | Silva   | 7.000x10^-3 | 9.390x10^-2 | 0.996        | 0.0233 |
|           | Page    | 6.597x10^-2 | 0.701        | 0.997        | 0.0213 |
|           | Lewis   | 0.019 | -            | 0.981        | 0.0481 |
| FD        | Chimarrita | Silva | 0.112       | -0.171       | 0.993  | 0.0376 |
|           | Page    | 3.160x10^-2 | 1.274       | 0.991        | 0.0427 |
|           | Lewis   | 0.067 | -            | 0.985        | 0.0482 |
|           | Eragil  | 5.751x10^-2 | -0.131       | 0.984        | 0.0522 |
|           | Page    | 8.701x10^-3 | 1.386       | 0.982        | 0.0556 |
|           | Lewis   | 0.034 | -            | 0.957        | 0.0722 |
| OD        | Chimarrita | Silva | 1.060x10^-2 | 6.100x10^-2 | 0.998  | 0.0139 |
|           | Page    | 4.300x10^-2 | 0.797        | 0.999        | 0.0124 |
|           | Lewis   | 0.019 | -            | 0.994        | 0.0269 |
| Eragil    | Silva   | 1.170x10^-2 | 3.550x10^-2 | 0.997        | 0.0188 |
|           | Page    | 2.970x10^-2 | 0.856        | 0.998        | 0.0164 |
|           | Lewis   | 0.016 | -            | 0.995        | 0.0234 |

Among the other empirical models, the Page model for osmotic dehydration presented the highest R² and lowest mean error, and the Silva model for lyophilization showed the highest R² and the lowest mean error, independent of the cultivar studied.

4 Conclusions

It is possible to conclude that the processes of dehydration by oven, osmotic dehydration followed by oven and lyophilization (freeze-drying) presented significant difference (p <0.05) between the processes of and among the evaluated parameters for the cultivars Chimarrita and Eragil.

Among the three empirical models investigated in this study, the worst results were obtained with Lewis model. According to the statistical indicators, Page and Silva models well describe the thin layer drying kinetics of whole peaches cultivars at all investigated drying process. A little disagreement between the two models occurs only in the final instants of the drying process. However, these two models enable to write mathematical expressions for the drying rate and the process time, and these expressions produce results that can be considered equivalent.

Dehydration is a method that can be used to conserve fruits, especially peaches, which are seasonal products with high perishability. Both processes of dehydration (lyophilization, dehydration by oven and osmotic dehydration followed by oven) presented moisture contents within the allowed by the legislation, being the freeze-drying presented the lowest value.

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