Accepted Manuscript

Convective drying of yellow discarded onion (Angaco INTA): Modelling of moisture loss kinetics and effect on phenolic compounds

María Celia Roman, Maria Paula Fabani, Lorena Celina Luna, Gabriela Egly Feresin, German Mazza, Rosa Rodriguez

PII:	\$2214-3173(19)30025-3
DOI:	https://doi.org/10.1016/j.inpa.2019.07.002
Reference:	INPA 209
To appear in:	Information Processing in Agriculture
Received Date:	6 February 2019
Revised Date:	28 June 2019
Accepted Date:	11 July 2019



Please cite this article as: M. Celia Roman, M. Paula Fabani, L. Celina Luna, G. Egly Feresin, G. Mazza, R. Rodriguez, Convective drying of yellow discarded onion (Angaco INTA): Modelling of moisture loss kinetics and effect on phenolic compounds, *Information Processing in Agriculture* (2019), doi: https://doi.org/10.1016/j.inpa. 2019.07.002

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Convective drying of yellow discarded onion (Angaco INTA): modeling

of moisture loss kinetics and effect on phenolic compounds

María Celia Roman^{a,#}, Maria Paula Fabani^{b,#}, Lorena Celina Luna^a, Gabriela Egly Feresin^b,

German Mazza^c, Rosa Rodriguez^{a, \Box}

^a Instituto de Ingeniería Química- Grupo Vinculado al PROBIEN (CONICET-UNCo)

Facultad de Ingeniería, Universidad Nacional de San Juan.

^b Instituto de Biotecnología, Facultad de Ingeniería, Universidad Nacional de San Juan.

^c Instituto de Investigación y Desarrollo en Ingeniería de Procesos, Biotecnología y

Energías Alternativas, CONICET-Universidad Nacional del Comahue, Neuquén,

Argentina

[#]Maria Celia Roman and María Paula Fabani have equal contribution.

^C Corresponding author. E-mail address: rrodri@unsj.edu.ar (R. Rodriguez).

Convective drying of yellow discarded onion (Angaco INTA): modelling of moisture loss kinetics and effect on phenolic compounds

Abstract

The Angaco INTA onion variety is the most cultivated and its production, mostly is destined for export. Due to their high-quality standards of these markets, many onions are discarded. The drying process seems to be a promising solution that not only give added value to this product, but also extend shelf life. In this work, the influence of convective drying process, at 60 and 70 °C, on the kinetic behavior, antioxidant activity, phenolic and flavonoid contents of discarded onion slices were investigated. Considering that, the Angaco INTA onion is a variety genetically developed to have shorter cultivation times in this region; the phenolic compounds content in this onion variety, the drying kinetics and its influence on this content have never been studied. In this study, the phenolic compounds contributions to dehydrated product quality was evaluated, observing that the convective drying increased the total soluble phenolic and flavonoid contents and antioxidant properties for both temperatures, being highest at 70 °C. The rehydration ratios were similar to the slices dried at 60 and 70°C. Several models were used for describing the obtained drying curve equation of onion slices, being the Midilli's model the one that presented the best fit. Ficks's model of water diffusion fitted all experimental data with acceptable correlation coefficients. Considering the achieved findings, 70°C is the optimum temperature to produce the dehydrated Angaco INTA onion.

Keywords: drying; antioxidant activity; phenolic content; kinetic model

1. Introduction

Onion (*Allium cepa L.*) is one of the most cultivated vegetables throughout the world, with around 86 million tons (t) of outfits [1]. China is the largest manufacture (22% of the total global onion production), followed by India and EEUU. Argentine generate between 600000 y 750000 t of onion, being San Juan one of the main producing provinces. The main onion varieties are Valenciana, Valencianita, Torrentina, Lona Inta, Valcatorce and Angaco INTA. The last variety was developed in order to have shorter cultivation times. It has light green leaves, medium bulbs, sub-conical shape, fine copper-yellow thin outer coat (golden yellow) and brief conservation time.

Onion is a versatile vegetable, being the bulb, the plant portion commonly used as a food ingredient, adds taste and flavor to the food [2]. Besides, onion contains several antioxidant compounds, mainly polyphenols such as flavonoids, fructo-oligosaccharides (FOS) and sulfur-containing compounds, so it's ingesting has been linked with health promotion, due to their beneficial effects against different pathologies [3], [4].

Considering the regional situation, it is important to remark that the most of Angaco INTA onion production is destined for export, however, due to the high-quality standards of these markets, many onions are discarded, principally by irregular shape and non-commercial sizes. Therefore, the use of these onions becomes an interesting topic. One of the utilization and revalorization alternatives, as well as preservation, is the drying. These aspects are gaining importance in the worldwide markets, considering that the dried onions could be used in the formulation of soups, sauces, comminuted meats, snacks, frozen foods, salad seasoning and condiment [5], [6]. In addition, the dehydrated onion may be marketed in different forms: flaked, minced and powdered, depending on its culinary uses.

In the actuality, the most used drying methods for onions are hot-air and freeze drying [7]. The dehydrated products have a better shelf life, up to one year, but generally their nutritional properties are affected and are closely connected to the processing operations and conditions [8]. This is the reason that the principal objectives during drying onions is to diminish the moisture content, maintaining the properties of their nutrients [9]. The processing effects on the overall quality of onions are lost/improvement of own components. It is known that the drying process has no influence in the ash, fat, protein and fiber contents. However, sugars, acidity and vitamin C contents are very affected by the drying, diminishing when the drying temperature increases [10].

Onions contain several phytochemicals, as the phenolic compounds, which are linked with health promotion and disease risk decrease; falling the cancers occurrence and preventing vascular and heart diseases, neurodegenerative disorders and cataract formation [11]. Considering the importance that onions have created in the antioxidant's topic, different studies have addressed the need to evaluate the antioxidant capacity of different onion varieties. On the other hand, considering the wide large variation of the phenolic compounds content among different varieties, it is important its determination. So, Perez-Gregorio et al. [12] reported the flavonol content in cultivars of white and red onions. Rodrigues et al. [13] studied the effect of meteorological conditions on this compound content in Portuguese onions in the same cultivars. Moreover, Perez-Gregorio et al. [14] studied changes during freeze-drying of the red onion in the flavonols and anthocyanins, observing that flavonols increased with the freeze-drying process. Otherwise, Rodrigues et al. [15] reported the postharvest storage systems affect the phytochemical content and quality of traditional Portuguese white and red onion cultivars concluding that flavonols content augmented up to 64% after six or 7seven months of storage. On the other hand, after 7seven months total anthocyanin content was diminished between 40 and 60%. Perez- Gregorio et al. [16]

reviewed the main factors that influence ion the flavonoid content of onions. These authors observed that red and resistant cultivars have higher flavonoid quantities and the nitrogen content of soil does not affect the flavonol content in onions. Considering the antioxidant compounds, during the drying process, novel formed constituents or the interaction between existing phenolic compounds can increase or diminish the antioxidative potential [17], Additionally, the kinetic analysis is indispensable for equipment design of drying process and choose the appropriate operating conditions [18]. Numerous mathematical models, theoretical, semi-empirical and empirical models, can fit the experimental kinetic data drying [19] and were studied in different varieties of onion by several researchers [20], [21]. Nevertheless, up to now there are no published works on chemical composition and drying kinetics of the Angaco INTA onion variety.

Thus, the main goal of this work was to evaluate the discarded onion drying at two different temperatures 60 and 70 °C analyzing the kinetic behavior during the process and its effect on total soluble phenolic, flavonoids and antioxidant activity. The obtained results will allow to advance in knowledge about the revalorization of a regional variety of onion, diminishing economic losses of producers.

2. Materials and methods

2.1. Reagents

Ultra-pure water (0.056 mS/cm, containing 5 mg/L TOC) was obtained from a water purification system Arium 126 61316-RO, plus an Arium 611 UV unit (Sartorius AG, Goettingen, Germany). Methanol (HPLC grade) was obtained from Fluka (Steinheim, Germany). Commercial Folin–Ciocalteu (FC) reagent and HCl (37%) were acquired in Merck Química Argentina (Buenos Aires, Argentina). 2,2-Diphenyl-1-picrylhydrazyl

(DPPH), gallic acid (GA) and quercetin were purchased from Sigma Aldrich (Buenos Aires, Argentina). All other chemicals were of analytical grade.

2.2. Samples

Fresh discarded (second quality) Angaco INTA variety onions were provided by local farmers from Pocito Department, Province of San Juan, Argentina. This place is located: latitude 31° 39'32" south, longitude 68° 34 '45" west and altitude 650–750 m.a.s.l. The climate is continental with hot summers (temperatures up to 40 °C) and cold winters.

Onions were harvested when 95 % or more of the stems have been folded (fallen) and packed in mesh bags in the dark at 20 °C until analysis within 30 days. To carry out the analyses, three independent samples (5 Kg/sample) were used. Onions (10, randomly taken from each sample) were hand-peeling, weighed, cut manually in the direction parallel to the vertical axis and diameters (D1 and D2), height, and cataphylls number were measured (Table 1).

Variety / Denomination	Angaco INTA			
Origin	Pocito INTA, San Juan - Argentina			
Shape	Sub-spinning or spinning Copper yellow			
Color				
Average weight (g)	137±22 D1: 6.9±0.8 / D2: 7.1±0.3			
Average diameter (D1 y D2) (cm)				
Average height (cm)	5.2±0.5 between 6 and 7 88.7±0.9			
Cataphylls number				
Moisture (%)				
Ash (%)	0.56±0.01			
Acidity (g citric acid /L)	$0.17{\pm}0.04$			
Soluble solids (°Brix)	9.5±0.3			
рН	5.09±0.08			

Table 1. Physical and chemical characterization of fresh onion Angaco INTA.

2.3. Chemical characteristics

The soluble solid content (%), pH, titratable acidity (g citric acid /L) were determinate in fresh onions (Table 1).

Ash and moisture contents were analyzed in both, fresh and dried onions [22].

2.4. Bioactive compounds: total soluble phenolic content (TSP), flavonoids (F) and antioxidant activity (AA)

Onion extract. Methanol extracts from fresh and dried onion samples were prepared according to the methodology described by Siddiq et al. [23]. The onions were ground in a coffee grinder and blended to obtain a homogeneous product. Samples were weighed (ca. 5.0 g of fresh or dried material), and extracted by sonication (40 kHz, 45 min, 25 °C, ultrasound bath model TB02TACA, TESTLAB S.R.L, Buenos Aires, Argentina) using 20 ml methanol: water (80:20, MeOH: H₂O). The homogenate was then centrifuged at 10000 g during 10 min using a Biofuge 28RS Heraeus Sepatech Centrifuge (Heraeus Instruments, Hanau, Germany) and filtered. Each homogenate was extracted two times and the combined fractions diluted to a final volume of 40 ml and used for further analyses.

The total soluble phenolic content (TSP) was determined by the Folin-Ciocalteu method, using linear regression from a calibration plot constructed using gallic acid [24]. The results were expressed as mg of gallic acid equivalents (GAE) per 100 g of onion on a fresh weight (fw) (mg GAE/100 g fw) and on dry weight (dw) expressed (mg GAE/100 g dw).

Flavonoid content (F) was determined using the AlCl₃ method according to the modified methodology proposed by Ismail et al. [25]. F content was calculated by linear regression from the construction of a calibration curve using quercetine. The results were expressed as mg of quercetine equivalents (QE) per 100 g of onion on a fresh weight (fw) (mg QE/100 g fw) and on a dry weight (dw) (mg QE/100 g dw).

Antioxidant activity (AA) was determined using the FRAP assay as described by Oyaizu [26]. Trolox (0-50 μ M) was used as a standard antioxidant and the AA of the extracts were expressed as microMolar Trolox equivalent (μ Mol TE) per g of onion on a dried weight (dw) basis (μ Mol TE /g dw). Free radical scavenging effects were assessed according to the procedure described by Brand-Williams et al. [27] with slight modifications to reduce the test time [28]. Quercetin was used as the reference compound. The extract concentration providing 50% of radicals scavenging activity (EC₅₀) was calculated. Absorbance measurements were carried out at 25 °C, using a Multiskan FC spectrometer (Thermo Fisher Scientific Corporation). All measurements were carried out in triplicate.

2.5. Drying equipment and experimental procedure

To carry out the drying experiences, a convective oven was used (Fischer Turbo 2.4). The onions were cut into circular shape, the diameter was approximately 6-7 cm and the thickness varied between 2 and 4 mm. The isothermal drying temperatures were 60 and 70 °C for each experiment and air velocity was equal to 1 m/s. This oven was equipped with the control system to fix these operating parameters. A sample was placed in the dryer and their weight was measured with a precision balance coupled to a data acquisition system via the communication port interface. The data were registered at two-minute intervals for each drying temperature. Drying tests were replicated three times and average weight loss were reported.



Figure 1. Onion slices dried at (a) 50 °C, (b) 60 °C, (c) 70 °C and (d) 80 °C.

To work at 60 and 70 °C, previous experiences were carried out at 50, 60, 70 and 80 °C. The drying time, when the work temperature was lower than 60 °C, was very long (between 300 and 330 min). On the other hand, when considering temperatures higher than 70 °C, the visual aspects of the onion was deteriorated, presenting important texture and colour changes. Figure 1 shows the final product after drying at temperatures previously cited.

2.6. Rehydration ratio

After the drying process, the rehydration was evaluated in order to observe the possible structural alterations produced by the drying process. Rehydration was carried out at 25±1 °C. The dried samples (3 slices dried at each temperature) were put into 50 ml of distilled water in Petri dishes for 3 hours (to constant weight). Samples were removed from the water and then, their surfaces were covered with a piece of filter paper to soak the water excess. Three replicates were performed and the rehydration ratio was calculated as the relation between the initial and final weight weights of the sample [29].

2.7. Modelling of drying curves

From the obtained experimental data of moisture at each time interval, the *MR* was calculated utilizing the following equation:

$$MR = \frac{(M_t - Me)}{(M_0 - Me)} \tag{1}$$

Me was determined from a plot of *MR* vs t, when the mass loss was equal to zero, assuming that no more moisture can be exchanged from the samples into the surrounding atmosphere of the chamber [9]. The plot of *MR* vs t was denominated drying curves of onions. These curves can be represented using different semi-theoretical and empirical models, from which, twelve of them were used in this work (Table 2).

Nº.	Model name	Model equation		
1	Newton	$MR = \exp(-kt)$		
2	Page	$MR = \exp(-kt^n)$		
3	Modified Page	$MR = \exp((-kt)^n)$		
4	Henderson and Pabis	$MR = a \exp(-kt)$		
5	Modified Henderson and Pabis	$MR = a \exp(-kt) + b \exp(-gt) + c \exp(-ht)$		
6	Wang and Singh	$MR = 1 + at + (bt^2)$		
7	Logarithmic	$MR = a \exp(-kt) + c$		
8	Midilli	$MR = a \exp(-kt^n) + bt$		
9	Two term	$MR = a \exp(-kt) + b \exp(-nt)$		
10	Two term exponential	$MR = a \exp(-kt) + (1-a) \exp(-kat)$		
11	Noomhorm and Verma	$MR = a \exp(-kt) + b \exp(-nt) + c$		
12	Approximation of diffusion	$MR = a \exp(-kt) + (1-a) \exp(-bkt)$		

Table 2. Semi-theoretical and empirical models applied to drying curves [30].

The fitting quality of each tested model to the experimental data was evaluated with the sum of squared errors (*SSE*), the root means square error (*RMSE*), and chi-square (χ^2):

$$SSE = \frac{1}{N} * \sum_{i=1}^{N} (MR_{pre,i} - MR_{exp,i})^{2}$$

$$RMSE = \sqrt{\frac{1}{N} * \sum_{i=1}^{N} (MR_{pre,i} - MR_{exp,i})^{2}}$$

$$X^{2} = \frac{\sum_{i=1}^{N} (MR_{exp,i} - MR_{pre,i})^{2}}{N-z}$$
(2)
(3)
(4)

The lowest of these statistical variables corresponds to the better fit to the experimental data [31]. These calculations were carried out using the statistical analysis software Origin.

2.7.1. Effective diffusivity

To model and calculate various onion processing operations, the moisture diffusivity is a significant mass transport property of any food product [32] and it varies with the temperature and moisture content variation [33]. To obtain it, a simple diffusion model based on Fick's second law, in the falling rate drying period, was used. An analytical solution of this law is:

$$MR = \frac{8}{\pi^2} \exp\left(-\pi^2 \frac{Deff.\ t}{L^2}\right)$$
(5)

This expression is applicable when the initial moisture is distributed uniformly and it is used by various regular shaped and for a long drying period [34]. The effective moisture diffusivity can be calculated by using the slope method. So, the equation (5) is converted into:

$$\ln (MR) = \ln \left(\frac{8}{\pi^2}\right) - \frac{\pi^2 . Deff.}{4L^2}$$

$$Slope = -\frac{\pi^2 D_{eff}}{4 L^2}$$

2.8. Statistical analysis

All analysis was carried out in triplicates and the data were reported as mean \pm standard deviation (SD). The results were analysed by one-way ANOVA and significant differences between mean values were determined by Tuckey's test (p < 0.05) using the software InfoStat [35]. Pearson's correlation analysis was used to determine statistically significance.

3. Results and discussion

3.1. Physical and Chemical characteristics of fresh onion

The physical and chemical characteristics of the Angaco INTA onion are shown in Table 1. Its appearance was copper yellow at maturity, with 6 to 7 cataphylls. The weight per unit was 137 ± 22 g, being 6.9 ± 0.8 cm the major diameter (D1) and 7.1 ± 0.3 cm the minor diameter (D2), while the height was 5.2 ± 0.5 cm. The content of dry matter (DM) was $11.2\pm0.9\%$ and the values of soluble solids (SS) was 9.5 ± 0.3 °Brix. SS value was similar to those reported by National Horticultural Production Research Program (2010), for short cycle onions (5.8 -10.2 ° Brix). The onion has a pH value of 5.13 ± 0.08 , and a level acidity of 0.17 ± 0.04 g citric acid/L, while ash content was 0.56 ± 0.01 %. These parameters have not been reported previously for this variety.

3.2. Bioactive compounds: total soluble phenolic content (TSP), flavonoids (F) and antioxidant activity (AA) of fresh and dried onions. Drying temperature effect.

(6)

Figure 2 shows the average total soluble phenolic (TSP) and flavonoid (F) content of fresh and dried onion slices expressed as fresh weight (fw) and dry weight (dw). The results were transformed from a fresh weight basis to a dry weight basis to avoid differences arising from the moisture content between fresh and dried onions.

Concerning the TSP content reported for fresh yellow onions from other locations, the found current values (40±6 mg GAE/100 g fw) are comparable to those cited by Siddiq et al. [16]. These authors reported a TSP content equal to 44.92 mg GAE/100 g fw from USA, considering the local market onion. Furthermore, Kaur et al. [11] reported TSP concentrations from 41.74 to 146.90 mg GAE/100 g for a great variety of fresh onion cultivars from India. On the other hand, several researchers informed major TSP for the yellow variety Marusino 330 and Sinsunhwang, from Muan, Republic of Korea [36], and for the variety Dorata di Parma from Cannara, Italy [37].





Related to the TSP content in the fresh onion slices (356±49 mg GAE/ 100g dw), this was significant smaller than quantified on the dry onion. Values ranged from 681 to 763 mg GAE/ 100g dw (Figure 2), being the relation TSP dried/TSP fresh onions equal to 1.8. Figure 2 shows that TSP values were significant increased from fresh onion to dried onions, for the two analyzed drying temperatures, not finding significant differences between both. The phenolic content of onions, dried at 70°C (722±41 mg GAE/100 g fw) was closer to the values reported by Arslan and Özcan [5]. These authors informed a value equal to 780 mg/100 g fw. The major quantity of found phenolic compounds in samples dried at 70°C, is possibly due to the liberation of these substances from the matrix during the drying process. According to Chang et al. [38], drying accelerates the release of bound phenolic compounds during the breakdown of cellular constituents.

Seeing the obtained results concerning to flavonoid content (F), the values for fresh Angaco INTA onion, 23 ± 4 mg QE/100 g fw, were lower than reported by Sharma et al. [36] for yellow skinned onions from Muan, Republic of Korea. Similar to the TSP content, flavonoid concentrations were lower in fresh (202±31 mg QE/100 g dw) than in dried onions (from 348 to 379 mg QE/100 g dw) (Figure 2), not showing significant differences between both evaluated drying temperatures. Then, the F dried/F fresh onions rate was calculated and it was equal to 1.6. Considering the obtained results, the convective drying of fresh onions at 60 and 70 °C not affect significantly their levels of TSP and F (Tuckey, p < 0.05).

In relation to the antioxidant activity (DPPH and FRAP assays), the results were shown in Figure 3. According to the revised literature, the high temperature usually degrades native bioactive compounds, oxidising the polyphenols, however these still exhibited higher antioxidant activity, more than of non-oxidized phenols. Moreover, the Maillard reaction/caramelization contributes to the formation of new compounds with proven strong

antioxidant capacity [39]. The two different performed assays, FRAP and DPPH, shown similar tendency, presenting significant differences between analyzed samples of fresh and dried onions. The obtained results revealed that the antioxidant activity of dried onions at 60 and 70 °C were significantly higher (p < 0.01) than fresh onions (Figure 3).

Regarding FRAP assay, Figure 3 shows that the reducing antioxidant power was the highest in onions, dried at 70 °C (15.5±0.4 μ mol TE/g dw). Moreover, the highest DPPH radical scavenging capacities of MeOH-E extracts were detected for onions, dried at 70 °C (EC₅₀ = 23±1 mg/mL dw), in agreement with the highest content of TSP and F observed for these dried onions. FRAP values for the Angaco INTA fresh onions were smaller than finding by Sharma et al. [36], but greater than informed by Lisanti et al. [37].



Figure 3. Effect of heating on antioxidant activity of onion, as assessed by Frap and DPPH. Data are presented as the mean \pm standard deviation. Values with same superscripts within the same treatment indicate no significant difference (Tuckey p < 0.05).

3.3. Drying characteristics

The time taken to reach the equilibrium moisture content for the drying at 60 and 70°C were 180 min and 176 min, respectively. As predictable, with the temperature increase, the drying time of samples diminished due to the growth of the drying rate. This phenomenon is produced by an augmentation of a surface temperature and the subsequent growth of water vapor pressure in the slice and consequently, higher evaporation rate [40].

After the drying process, the final moisture contents were 2.68 and 1.71 % for 60 and 70°C, correspondingly. These values allow an efficient storage and processing. Figure 4 shows the drying curves of onion slices at both studied temperatures. These curves follow an exponential moisture reduction, showing two stages: the first, the MR falls linearly with time at a higher rate, and the second phase, this weight loss is produced at a lower rate. This phenomenon is produced due to accessibility of surface water and its subsequent diffusion to maintain the constant drying rate at the beginning, resulting in higher moisture diffusion and consequently, in high drying rates [41].



Figure 4. Evolution of the moisture ratio with time, at 60 and 70°C.

This phenomenon was observed by other researchers, and it indicates that the falling rate is a main drying mechanism in controlling the water evaporation rate [42]. When moisture diffusion from the internal core to the surface decelerated down, the drying rate of subsequent stage also decreases. Instead, the obtained drying curves of onion correspond to material porous or cellular structures [43]. Additionally, and considering that the water is present in a solid as free and bound water, at a moderately low drying temperature, the removed moisture is habitually considered to be the free moisture that is feebly bound to the solid [44].

3.4. Rehydration ratio

The rehydration ratio is considered an important quality parameter of drying products [45]. It is influenced by preceding pre-treatments, vegetables properties (injury caused by drying), drying and rehydration conditions [46]. The rehydration ratio values varied between 7.38 - 7.41 and 7.48-7.52 at 25 ± 1 °C, for the onion dried at 60 and 70 °C, respectively. It is not observed drying temperature influence on this parameter. Figure 5 shows the rehydration slices. Sharma et al. [45] reported values of this parameter between 4.5 and 5.3 for dried onion slices. The found rehydration values were greater compared with the values reported by these authors.



Figure 5. Rehydrated onion slices previously dried at (a) 60 °C, y (b) 70 °C.

3.5. Application of different empirical models of thin layer drying process

Twelve models listed in Table 2 were used for predicting the changes in the onion particle moisture content with the drying time at different temperatures. The used criterion for model selection was the magnitude of the average value of *SSE*, *RMSE* and χ^2 . Model 8 (Midilli model) has minimum average values of the statistical variables between these models. Therefore, this model can be proposed to evaluate the moisture ratio of onion particles for drying temperature (60–70 °C). This model also, describes the drying behavior of carrot [47] and mushroom slices [48] and poplar sawdust [49]. Table 3 shows the parameter values of Midilli model for each temperature and the average values of *SSE*, *RMSE* and χ^2 . The dried onion parameters at 70 °C present the lowest values of the statistical variables. Similar results were obtained by Gazor and Mohsenimanesh [50]. Mota el al. [10] used three models to predict the empirical results of onion drying: Newton, Logaritmic and Modified Page, being the last one which presented the best fit. However, these authors do not use the other models as the Midilli expression.

Table 3. Coefficients of Midilli model to predict the onion particles drying at different temperatures. Values of statistical variables.

	Onion shape	Temperature (°C)	Model constants	R ²	X ²	SSE	RMSE
-		60	<i>k</i> =0.0029, <i>n</i> =1.406, <i>a</i> =0.969, <i>b</i> =0.0006	0.9995	0.00008	0.00007	0.0086
	Slices	70	<i>k</i> =0.0038, <i>n</i> =1,374, <i>a</i> =0.981, <i>b</i> =0.0006	0.9995	0.00004	0.00004	0.0062

Figure 6 shows the comparison between the experimental and predicted moisture ratio (*MR*) for the two studied temperatures. It is important to note that the suitability of these models was analyzed by Praveen Kumar et al. [9].

3.6. Effective moisture diffusivity

The Fick diffusion model was used to determine the D_{eff} from the experimental drying data. It is important to note that this parameter represents the onion intrinsic moisture mass transfer characteristics involving liquid and molecular diffusion, hydrodynamic flow, vapor diffusion and other mass transport mechanisms [51]. So, the obtained D_{eff} values for the slice onion are 8.11×10^{-11} and 1.22×10^{-10} m²/s at 60 and 70 °C, respectively. The fitting was satisfactory because the obtained regression coefficients were lower than 0.97.



Figure 6. Comparison between the experimental and predicted MR values for 60 and 70 °C

On the other hand, it is obvious that D_{eff} increases gradually with the temperature growths, reducing the drying time significantly. This behavior can be explained considering that the temperature increase produces fast heating of the onion particles, growing the activity among water molecules and the vapor pressure in these particles, augmenting the moisture diffusion rate to the sample surface. The obtained values are within the suitable range of various food products, 10^{-11} to 10^{-9} m²/s, reported in the literature [52], [53], [54]. Mota et al. [10] determined that D_{eff} values are equal to 9.5324×10^{-09} m²/s when the onion is dried at 60°C. This value is lower than the one determined in this work due to the different onion variety and the slice diameter (equal to 3 cm).

Conclusions

This is the first study reporting the characterization of yellow discarded onion (Angaco INTA variety) and the influence of the drying process on its phenolic compound contents. The results showed that the convective drying increased the total soluble phenolic and flavonoid contents for both temperatures, being highest at 70 °C. In relation to the antioxidant properties, the onions, dried at 70 °C, showed also the major values. The founding rehydration ratios are not influenced by the drying temperature. Additionally, the effect of drying process on kinetic behavior and moisture diffusivity was evaluated. Twelve mathematical models were tested, presenting the Midilli model the better fit of the experimental dehydration data. The obtained effective moisture diffusivity exhibited that onion drying process varied with the drying temperature. Comparing the achieved findings at 60 and 70 °C, the last temperature is better to produce the dehydrated Angaco INTA onion. It is considered that this study is the first step to obtain the optimum temperature with the objective of the onion drying keeping the nutritional characteristics and to design a dryer to industrial scale.

Acknowledgements

The authors wish to thank the support of the following Argentine institutions: ANPCvT -MINCyT (PICT No. 2014-2078), CONICET and SECITI - San Juan (PIO - CONICET -SECITI No. 15020150100042CO). Maria Paula Fabani, Gabriela Egly Feresin and Germán Mazza are researchers from CONICET, Argentina. Celia Román has a Doctoral Fellowship 3908 of CONICET.

Nomenclature

MR: moisture ratio, dimensionless.

- *Mt*: moisture content at time equal t, kg water/kg dry matter.
- M_0 : initial moisture content, kg water/kg dry matter.
- Me: equilibrium moisture content, kg water/kg dry matter.
- t: time, min.
- $MR_{exp,i}$: ith experimentally observed moisture ratio, dimensionless.
- $MR_{pre,i}$ is the ith predicted moisture ratio, dimensionless.
- *N*: Observations number.
- z: Constant number in the model.
- D_{eff} : Effective diffusivity, m²/s.
- L: Half thickness of the particle, m.

References

- FAO. United Nations Organization for Food and Agriculture. 2015. [1]
- [2] Choi S, Lee D, Kim J, Lim S. Volatile composition and sensory characteristics of onion powders prepared by convective drying. Food Chem 2017;231:386–92.
- Vidyavati H, Manjunatha H, Hemavathy J, Srinivasan K. Hypolipidemic and [3]

antioxidant effi cacy of dehydrated onion in experimental rats 2010;47:55-60.

- [4] Pérez-Gregorio M.R., García-Falcón M.S., Simal-Gándara J. Flavonoids changes in fresh-cut onions during storage in different packaging systems. Food Chem 2011;124:652–8.
- [5] Arslan D, Özcan MM. Study the effect of sun, oven and microwave drying on quality of onion slices. LWT - Food Sci Technol 2010;43:1121–7.
- [6] Lee B, Seo JD, Rhee J-K, Kim CY. Heated apple juice supplemented with onion has greatly improved nutritional quality and browning index. Food Chem 2016;201:315–9.
- [7] Ren F, Perussello CA, Zhang Z, Kerry JP, Tiwari BK. Impact of ultrasound and blanching on functional properties of hot-air dried and freeze dried onions. LWT -Food Sci Technol 2018;87:102–11.
- [8] Ratti C. Hot air and freeze-drying of high-value foods: a review. J Food Eng 2001;49:311–9.
- [9] Praveen Kumar DG, Hebbar HU, Ramesh MN. Suitability of thin layer models for infrared-hot air-drying of onion slices. LWT - Food Sci Technol 2006;39:700–5.
- [10] Mota CL, Luciano C, Dias A, Barroca MJ, Guiné RPF. Convective drying of onion: Kinetics and nutritional evaluation. Food Bioprod Process 2010;88:115–23.
- Kaur Charanjit, Joshi S, Kapoor H.C. Antioxidants in Onion (Allium cepa 1)
 Cultivars Grown in India. J Food Biochem 2009;33:184–200.
- [12] Pérez-Gregorio RM, García-Falcón MS, Simal-Gándara J, Rodrigues AS, Almeida DPF. Identification and quantification of flavonoids in traditional cultivars of red and white onions at harvest. J Food Compos Anal 2010;23:592–8.
- [13] Rodrigues AS, Pérez-Gregorio MR, García-Falcón MS, Simal-Gándara J, Almeida DPF. Effect of meteorological conditions on antioxidant flavonoids in Portuguese

cultivars of white and red onions. Food Chem 2011;124:303-8.

- [14] Pérez-Gregorio MR, Regueiro J, González-Barreiro C, Rial-Otero R, Simal-Gándara
 J. Changes in antioxidant flavonoids during freeze-drying of red onions and subsequent storage. Food Control 2011;22:1108–13.
- [15] Rodrigues AS, Almeida DPF, García-Falcón MS, Simal-Gándara J, Pérez-Gregorio MR. Postharvest storage systems affect phytochemical content and quality of traditional Portuguese onion cultivars. Acta Hortic 2012:1327–34.
- [16] Pérez-Gregorio MR, Regueiro J, Simal-Gándara J, Rodrigues AS, Almeida DPF. Increasing the Added-Value of Onions as a Source of Antioxidant Flavonoids: A Critical Review. Crit Rev Food Sci Nutr 2014;54:1050–62.
- [17] Figiel A, Michalska A. Overall Quality of Fruits and Vegetables Products Affected by the Drying Processes with the Assistance of Vacuum-Microwaves. Int J Mol Sci 2016;18:71.
- [18] Perea-Flores MJ, Garibay-Febles V, Chanona-Pérez JJ, Calderón-Domínguez G, Méndez-Méndez JV, Palacios-González E, et al. Mathematical modelling of castor oil seeds (Ricinus communis) drying kinetics in fluidized bed at high temperatures. Ind Crops Prod 2012;38:64–71.
- [19] Amiri Chayjan R, Kaveh M. Physical Parameters and Kinetic Modeling of Fix and Fluid Bed Drying of Terebinth Seeds. J Food Process Preserv 2014;38:1307–20.
- [20] Krokida MK, Karathanos VT, Maroulis ZB, Marinos-Kouris D. Drying kinetics of some vegetables. J Food Eng 2003;59:391–403.
- [21] Yaldýz O, Ertekýn C. Thin layer solar drying of some vegetables. Dry Technol 2001;19:583–97.
- [22] AOAC Association of Official Agricultural Chemistry, Washington D. Official Methods of Analysis, eighteenth ed. 2010.

- [23] Siddiq M, Roidoung S, Sogi DS, Dolan KD. Total phenolics, antioxidant properties and quality of fresh-cut onions (Allium cepa L.) treated with mild-heat. Food Chem 2013;136:803–6.
- [24] Blainski A, Lopes GC, De Mello JCP. Application and analysis of the folin ciocalteu method for the determination of the total phenolic content from limonium brasiliense
 L. Molecules 2013;18:6852–65.
- [25] Ismail HI, Chan KW, Mariod AA, Ismail M. Phenolic content and antioxidant activity of cantaloupe (cucumis melo) methanolic extracts. Food Chem 2010;119:643–7.
- [26] Oyaizu M. Studies on products of browning reaction. Antioxidative activities of products of browning reaction prepared from glucosamine. Japanese J Nutr Diet 1986;44:307–15.
- [27] Brand-Williams W, Cuvelier ME, Berset C. Use of a free radical method to evaluate antioxidant activity. LWT - Food Sci Technol 1995;28:25–30.
- [28] Tapia A, Rodriguez J, Theoduloz C, Lopez S, Feresin GE, Schmeda-Hirschmann G. Free radical scavengers and antioxidants from Baccharis grisebachii. J Ethnopharmacol 2004;95:155–61.
- [29] Seremet L, Botez E, Nistor OV, Andronoiu DG, Mocanu GD. Effect of different drying methods on moisture ratio and rehydration of pumpkin slices. Food Chem 2016;195:104–9.
- [30] Ayadi M, Mabrouk S Ben, Zouari I, Bellagi A. Kinetic study of the convective drying of spearmint. J Saudi Soc Agric Sci 2014;13:1–7.
- [31] Lee JH, Kim HJ. Vacuum drying kinetics of Asian white radish (Raphanus sativus L.) slices. LWT - Food Sci Technol 2009;42:180–6.
- [32] Joardder MUH, Karim A, Kumar C, Brown RJ. Determination of Effective MoistureDiffusivity of Banana Using Thermogravimetric Analysis. Procedia Eng

2014;90:538-43.

- [33] Feng H, Tang J, John Dixon-Warren S. Determination of moisture diffusivity of red delicious apple tissues by thermogravimetric analysis. Dry Technol 2007;18:1183–99.
- [34] Sun J, Hu X, Zhao G, Wu J, Wang Z, Chen F, et al. Characteristics of thin-layer infrared drying of apple pomace with and without hot air pre-drying. Food Sci Technol Int 2007;13:91–7.
- [35] Di Rienzo J., Casanoves F., Balzarini M., Gonzalez L., Tablada M., Robledo C. InfoStat versión 2014. Grup InfoStat 2014:FCA, Universidad Nacional de Córdoba, Argentina.
- [36] Sharma K, Mahato N, Lee YR. Systematic study on active compounds as antibacterial and antibiofilm agent in aging onions. J Food Drug Anal 2018;26:518–28.
- [37] Lisanti A, Formica V, Ianni F, Albertini B, Marinozzi M, Sardella R, et al. Antioxidant activity of phenolic extracts from different cultivars of Italian onion (Allium cepa) and relative human immune cell proliferative induction. Pharm Biol 2016;54:799–806.
- [38] Chang C-H, Lin H-Y, Chang C-Y, Liu Y-C. Comparisons on the antioxidant properties of fresh, freeze-dried and hot-air-dried tomatoes. J Food Eng 2006;77:478–85.
- [39] Manzocco L, Calligaris S, Mastrocola D, Nicoli MC, Lerici CR. Review of nonenzymatic browning and antioxidant capacity in processed foods. Trends Food Sci Technol 2000;11:340–6.
- [40] Datta AK, Ni H. Infrared and hot-air-assisted microwave heating of foods for control of surface moisture. J Food Eng 2002;51:355–64.
- [41] Sadin R, Chegini G-R, Sadin H. The effect of temperature and slice thickness on

drying kinetics tomato in the infrared dryer. Heat Mass Transf 2014;50:501-7.

- [42] Saavedra J, Córdova A, Navarro R, Díaz-Calderón P, Fuentealba C, Astudillo-Castro C, et al. Industrial avocado waste: Functional compounds preservation by convective drying process. J Food Eng 2017;198:81–90.
- [43] Pakowski Z, Adamski A. The Comparison of Two Models of Convective Drying of Shrinking Materials Using Apple Tissue as an Example. Dry Technol 2007;25:1139– 47.
- [44] Khan MIH, Wellard RM, Nagy SA, Joardder MUH, Karim MA. Experimental investigation of bound and free water transport process during drying of hygroscopic food material. Int J Therm Sci 2017.
- [45] Sharma GP, Verma RC, Pathare PB. Thin-layer infrared radiation drying of onion slices. J Food Eng 2005;67:361–6.
- [46] Noshad M, Mohebbi M, Shahidi F, Mortazavi SA. Kinetic modeling of rehydration in air-dried quinces pretreated with osmotic dehydration and ultrasonic. J Food Process Preserv 2012;36:383–92.
- [47] Toğrul H. Suitable drying model for infrared drying of carrot. J Food Eng 2006;77:610–9.
- [48] Taghian Dinani S, Hamdami N, Shahedi M, Havet M. Mathematical modeling of hot air/electrohydrodynamic (EHD) drying kinetics of mushroom slices. Energy Convers Manag 2014;86:70–80.
- [49] Chen D, Zheng Y, Zhu X. Determination of effective moisture diffusivity and drying kinetics for poplar sawdust by thermogravimetric analysis under isothermal condition. Bioresour Technol 2012;107:451–5.
- [50] Gazor HR, Mohsenimanesh A. Modelling the drying kinetics of canola in fluidised bed dryer. Czech J Food Sci 2010;28:531–7.

- [51] Nachaisin M, Jamradloedluk J, Niamnuy C. Application of Combined Far-Infrared Radiation and Air Convection for Drying of Instant Germinated Brown Rice. J Food Process Eng 2016;39:306–18.
- [52] Coskun S, Doymaz İ, Tunçkal C, Erdogan S. Investigation of drying kinetics of tomato slices dried by using a closed loop heat pump dryer. Heat Mass Transf 2017;53:1863–71.
- [53] Parveen S, Kailappan R, Dhananchezhiyan P. Studies on Shrinkage of Turmeric Rhizomes During Drying. Int J Food Nutr Sci 2013;2:30–4.
- [54] Thuwapanichayanan R, Prachayawarakorn S, Kunwisawa J, Soponronnarit S. Determination of effective moisture diffusivity and assessment of quality attributes of banana slices during drying. LWT - Food Sci Technol 2011;44:1502–10.

Conflicts de interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

We understand that the Corresponding Author is the sole contact for the Editorial process (including Editorial Manager and direct communications with the office). He/she is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs.

Celia Román, Paula Fabani, Lorena Luna, Gabriela Feresin, Germán Mazza, Rosa Rodriguez