COMMUNICATION

Effect of Air Temperature on Drying Kinetics, Vitamin C, Antioxidant Activity, Total Phenolic Content, Non-enzymatic Browning and Firmness of Blueberries Variety O´Neil

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Abstract Effect of air temperature on drying kinetics, vitamin C, antioxidant capacity, total phenolic content (TPC), colour due to non-enzymatic browning (NEB) and firmness during drying of blueberries was studied. Drying curves were satisfactorily simulated with the Weibull model at 50, 60, 70, 80 and 90°C. The scale parameter (β) decreased as air temperature increased and an activation energy value of 57.85 kJ mol^{-1} was found. Important losses of vitamin C were reported during drying for all the working temperatures ($p<0.05$). Although TPC decreased as air-drying temperature increased ($p<0.05$) in comparison to its initial value, the dehydration at high temperatures (e.g., 90°C) presented high values for these antioxidant components. Discoloration due to NEB reaction was observed at all the working temperatures showing a maximum value at 90°C ($p<0.05$). The radical scavenging activity showed higher antioxidant activity at high temperatures (80 and 90°C) than at low temperatures (50, 60 and 70°C) ($p<0.05$). A tissue firmness reduction was observed with increasing temperature ($p<0.05$).

Introduction

Fruit quality has become a significant issue for consumers who are concerned about the healthy aspect of food, defining a modern concept of food quality that combines ripening features and nutritional contents (Sinelli et al. 2008). In this respect, studies of the effects of processing on natural components of fruits have intensified because of increasing awareness of the possible health benefits of some of food micronutrients. In particular, blueberries contain many bioactive compounds which are associated with a strong antioxidant activity, namely phenolic compounds as well as vitamin C, which play important roles in human nutrition due to free radical scavenging activities (Skrede et al. 2000; Giovanelli and Buratti 2009). Moreover, texture is considered one of the decisive sensorial attributes in which the consumers base their subjective decision of buying some fruits and vegetables (Gutierrez et al. 2007). Because of the brief blueberries harvest season, processing after collection must be rapidly performed to extend shelf life of the fruits. Dehydration is a post-harvest operation being the main objective the removal of water to the level at which microbial spoilage and deterioration reactions are minimised. From an engineering point of view, the control of the air-drying temperature presents a challenging problem to be solved in a complex system with simultaneous heat and mass transfer phenomena (Di Scala and Crapiste 2008). Thus, by careful selection of this operative variable value, the product quality can be maximised leading to an increased and/or preservation of the activity and bioavailability of the fruit original components.

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Therefore, the aim of this work was to determine the effect of air-drying temperature on drying kinetics by modelling the drying curves with the Weibull distribution as well as to study the influence of temperature on antioxidant activity, total phenolic content, vitamin C, non-enzymatic browning, and firmness during the hot air drying of blueberries.

Materials and Methods

Sample Preparation and Modelling of Drying Kinetics

Blueberries variety O'Neil were cultivated and purchased in the province of Salamanca, Chile and stored at 5.0±0.2°C for a maximum time period of 5 days before processing. Samples were selected visually by colour, size and freshness, and with no sign of mechanical damage. Then, they were dried in a laboratory-scale convective dryer at 50, 60, 70, 80 and 90°C (Vega-Gálvez et al. 2008). The air flow rate, sample size, sample mass and load density were 2.0±0.1 ms^{-1}, 0.7–1.5 cm diameter, 14.67±1.81 g and 2.9±0.3 kg m^{-2}, respectively. Before drying, the samples were pretreated with a Pectinex® solution to speed up the vapour exchange process (Ochoa et al. 2002). Then, they were dried until they reached constant weight (equilibrium condition). The dehydrated samples were then packed and sealed in polyethylene bags. All the drying experiments were done in triplicate.

The Weibull model Eq. 1 was used to simulate the drying kinetics. This equation has been successfully applied to describe kinetics of chemical, enzymatic and microbiological degradation processes as well as in the drying process (Marabi et al. 2003; Uribe et al. 2009). In this equation, the dependent variable is the moisture ratio, Eq. 2.

$$MR = \exp\left[-\left(\frac{t}{\beta}\right)^{\alpha}\right] \tag{1}$$

$$MR = \frac{X_{wt} - X_{we}}{X_{wo} - X_{we}} \tag{2}$$

where X_{wo}, X_{wt} and X_{we} are the initial, at a real time, and at equilibrium moisture content, respectively (g water g^{-1} d.m.), α is the shape parameter (dimensionless), β is the scale parameter (min) of the Weibull model and t is the sampling time.

Quality Parameters

Physico-chemical Analysis of Raw Material

The crude protein content was determined using the Kjeldahl method with a conversion factor of 6.25 (AOAC

no. 960.52). The lipid content was analysed gravimetrically following Soxhlet extraction (AOAC no. 960.39). The crude fibre was estimated by acid/alkaline hydrolysis of insoluble residues (AOAC no. 962.09). The crude ash content was estimated by incineration in a muffle furnace at 550°C (AOAC no. 923.03). The available carbohydrate was estimated by difference. All methodologies followed the recommendations of the Association of Official Analytical Chemists (AOAC 1990). The pH was measured using an EXTECH Instruments microcomputer pH-vision 246072 (Waltham, Massachusetts, USA); the level of titrimetric acidity was expressed as malic acid. The water activity (a_w) was measured at 25°C by means of a water activity meter (Novasina, model TH-500, Pfäffikon, Lachen, Switzerland). Soluble solids were measured using a refractometer (ABBE, 1T, Tokio, Japan). All measurements were done in triplicate.

Determination of Vitamin C

Vitamin C, ascorbic acid (AA), was determined based upon the quantitative discolouration of 2,6-dichlorophenol indophenol (Merck KgaA, Darmstadt, Germany) titrimetric method as described in AOAC no. 967.21 (AOAC 2000). Comparative evaluations of vitamin C contents in fresh and dehydrated blueberries were carried out, where 5.0±0.1 g of each sample was weighed, crushed and diluted in 1 L distilled water. The vitamin C content was expressed as mg AA 100 g^{-1} dry matter. All measurements were done in triplicate.

Determination of Total Phenolic Content

Total phenolic content (TPC) was determined on the extract by Folin–Ciocalteau method with modifications (Chen et al. 2008). Two 0.5 mL aliquot of the blueberry extract solution, prepared using absolute ethanol, were added 0.5 mL of Folin–Ciocalteau reactive and 2 mL of 20% Na_2CO_3 solution and mixed well in a vortex. After 15 min of incubation at ambient temperature, 10 mL of ultra pure water was added and the formed precipitate was removed by centrifugation during 5 min at 4,000×g. Finally, the absorbance was measured in a spectrophotometer (Spectronic 20® Genesys™, Illinois, USA) at 725 nm and compared to a gallic acid equivalents (GAE) calibration curve. Results were expressed as mg GAE 100 g^{-1} dry matter. All measurements were done in triplicate.

Determination of Antioxidant Activity (DPPH Method)

Free radical scavenging activity of the samples was determined using the 2,2,-diphenyl-2-picryl-hydrazyl (DPPH) method of Turkmen et al. (2005) with some modifications. An aliquot of 2 mL of 0.15 mM DPPH radical in ethanol was added to a test tube with 1 mL of the
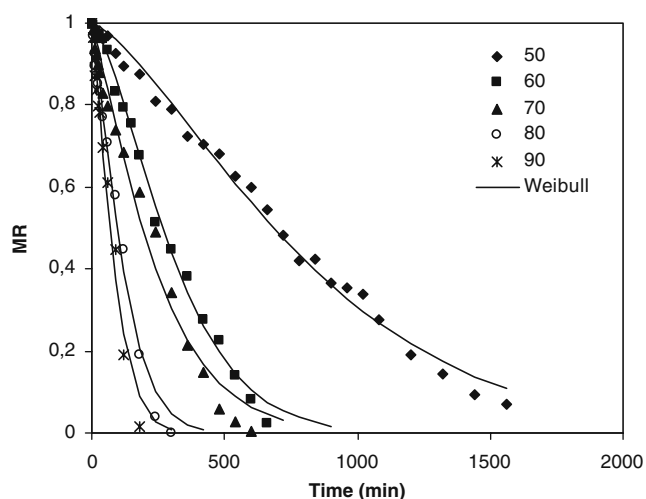
Fig. 1 Effect of air-drying temperature (°C) on experimental and Weibull-simulated drying curves of blueberries samples

sample extract. The reaction mixture was vortex-mixed for 30 s and left to stand at room temperature in the dark for 20 min. The absorbance was measured at 517 nm, using a spectrophotometer (Spectronic® 20 Genesys™, Illinois, USA). 80% (v v^{-1}) ethanol was used to calibrate the spectrophotometer. Total antioxidant activity (TAA) was expressed as the inhibition percentage of the DPPH radical and was determined by Eq. 3:

$$(\%)\ \mathrm{TAA} = \left(1 - \frac{\mathrm{Abs_{sample}}}{\mathrm{Abs_{control}}}\right) \times\ 100 \tag{3}$$

where TAA is the total antioxidant activity and Abs is the absorbance. IC$_{50}$, which is defined as the concentration of substrate, brings about 50% loss of the DPPH that was determined from a graph of antioxidant activity (%) against extract concentration (μg mL^{-1} sample), (Locatelli et al. 2009).

Determination of Non-enzymatic Browning

Non-enzymatic browning (NEB) was determined according to the work of Vega-Gálvez et al. (2008). The rehydration water, which is obtained when blueberries are rehydrated with a solid to water ratio of 1:25 during 24 h at ambient temperature, was clarified by centrifugation at 3,200×g for 10 min. Then, the supernatant was diluted with an equal volume of ethanol (Sigma Chemical CO., St. Louis, MO, USA) at 95% and centrifuged again at 3,200×g for 10 min. The browning index (absorbance at 420 nm) of the clear extracts was determined using a spectrophotometer (Spectronic® 20 Genesys™, Illinois, USA). NEB was expressed in terms of the absorbance Abs g^{-1} initial dry matter. All measurements were done in triplicate.

Determination of Firmness

Firmness of samples was measured using a Texture Analyzer (Texture Technologies Corp., TA, XT2, Scardale, NY, USA). The puncture diameter was 2 mm with a travel distance of 20 mm and 1.7 mm s^{-1} test speed. The maximum force was measured by making one puncture in each rehydrated blueberry sample. For each measurement, ten replications were collected to estimate the mean values. The mean value of maximum firmness for each treatment was then calculated and the results were expressed as N mm^{-1}.

Statistical Analysis: Experimental Drying Data and Quality Parameters

The parameters of Weibull model were obtained using the function *lsqcurvefit* of the optimization toolbox of MATLAB (v7.0 R14 Service Pack 2, The Mathworks Inc., MA, USA). For the modelling of drying kinetics, the goodness of fit between the predicted and experimental data was evaluated based on statistical analysis including coefficient of determination (R^2); chi-square (χ^2) and sum-squared errors (SSE).

The effect of air-drying temperature on each quality parameter was estimated using Statgraphics® Plus 5 (Statistical Graphics Corp., Herndon, VA, USA). The results were analysed by an analysis of variance with a significance level ($\alpha = 0.05$). In addition, the multiple range test was used to demonstrate the existence of homogeneous groups within each of the parameters.

Results and Discussion

Proximate analysis of blueberry (based on 100 g of fresh matter) presented an initial moisture content of 78.5±1.27 g, crude protein (nitrogen x 6.25) of 0.80±0.05 g, total lipids of 0.13±0.03 g, crude fibre of 1.91±0.23 g, crude ash of 0.34±0.02 g, available carbohydrates (by difference) of 16.2±0.54 g. The results were comparable to those reported by Skupien (2006) and Vega-Gálvez et al. (2009). Soluble solids, pH and tritimetric acidity for the fresh samples were 14.67±0.23

Table 1 Parameters and statistical tests of Weibull model for simulating blueberry drying curves at different temperatures

T (°C)	α	β (min)	R^2	χ^2	SSE
50	1.41	887.22	0.99	7.17×10^{-4}	6.61×10^{-4}
60	1.45	343.33	0.99	5.77×10^{-4}	5.22×10^{-4}
70	1.20	258.34	0.98	2.20×10^{-3}	1.97×10^{-3}
80	1.30	126.93	0.99	1.61×10^{-3}	1.38×10^{-3}
90	1.31	91.30	0.98	2.11×10^{-3}	1.76×10^{-3}

Fig. 2 Effect of air-drying temperature on vitamin C and total phenolic content of fresh and dehydrated blueberries samples. *Identical letters above the bars* indicate no significant difference
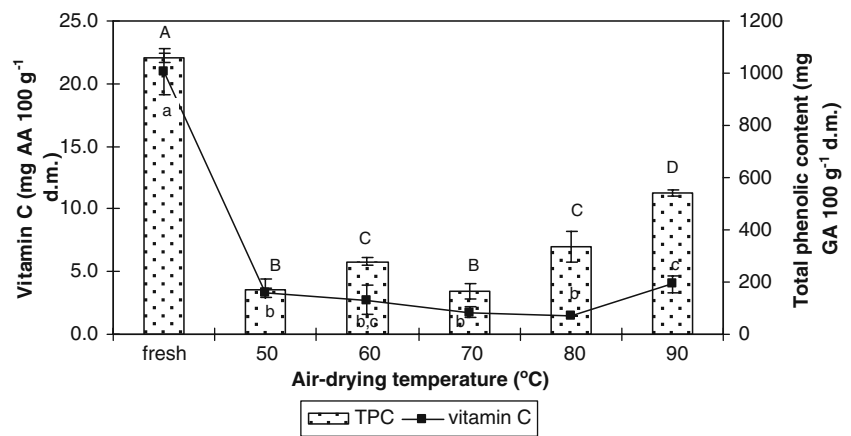

ºBrix, 4.22±0.04 and 0.157±0.007%, respectively. The equilibrium moisture contents were 0.0913, 0.0694, 0.0524, 0.0391, 0.0285 g water g^{-1} g d.m. for 50, 60, 70, 80 and 90°C, respectively (Vega-Gálvez et al. 2009).

Figure 1 shows both experimental and simulated drying curves of blueberries at 50, 60, 70, 80 and 90°C. In this figure, a clear influence of air-drying temperature on drying kinetics is observed. Thus, as the air-drying temperature increased the drying time decreased to reach similar final moisture content. Similar drying characteristics were also reported by other researchers (MacGregor 2005; Kavak Akpinar and Bicer 2006; Shi et al. 2008; Vega-Gálvez et al. 2009). The shape and scale parameters of Weibull distribution as well as the statistical tests applied are presented in Table 1 for the five temperatures under study. The shape parameter did not show a clear trend with temperature, its mean value (α=1.33±0.098) would indicate that the drying curve assumes a sigmoidal shape (Marabi et al. 2003). The scale parameter (β) decreased as air temperature increased and it was temperature dependent according to an Arrhenius type equation. An activation energy value of 57.85 kJ mol^{-1} was found when fitting ln (β) versus T^{-1}, which is within the range of activation energy reported by other authors working

with blueberries: 61.2 kJ mol^{-1} (Shi et al. 2008) and 54.45 kJ mol^{-1} (Vega-Gálvez et al. 2009).

The determination coefficients presented values higher than 0.98 for all drying temperatures with a mean value of 0.988, the chi-square (χ^2) values were low ($\chi^2 < 2.20 \times 10^{-3}$) as well as the SSE values (SSE$<1.97 \times 10^{-3}$). The results of R^2, χ^2 and SSE tests indicated a satisfactorily fitting to the experimental data suggesting that the Weibull distribution model is a suitable model for estimating loss of moisture of blueberries during drying for further optimization of process time.

Figure 2 shows the vitamin C as well as the fresh and dehydrated samples at the five drying experiments ($p<$ 0.05). The initial content of vitamin C in blueberries was 20.97±1.85 mg ascorbic acid 100 g^{-1} dry sample. Vitamin C is considered as a relevant nutritional quality index of food during processing due to its low stability during thermal treatments (Di Scala and Crapiste 2008). Thus, it can be seen that dehydration had an important effect on the blueberries vitamin C content. Indeed, drying from 50 to 90°C produced approximately the same nutritional degradation of the product from the ascorbic acid retention standpoint. A
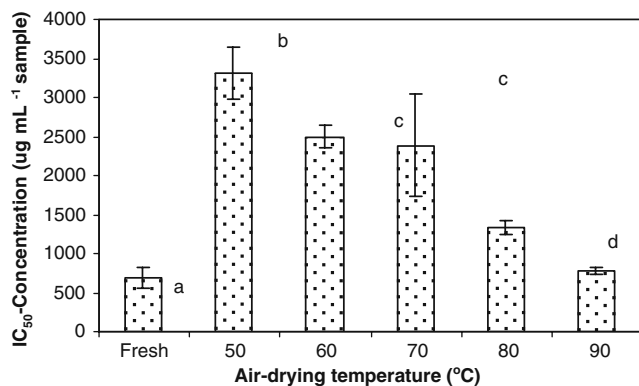
Fig. 3 Effect of air-drying temperature on DPPH free-radical scavenging activity of fresh dehydrated blueberries samples. *Identical letters above the bars* indicate no significant difference
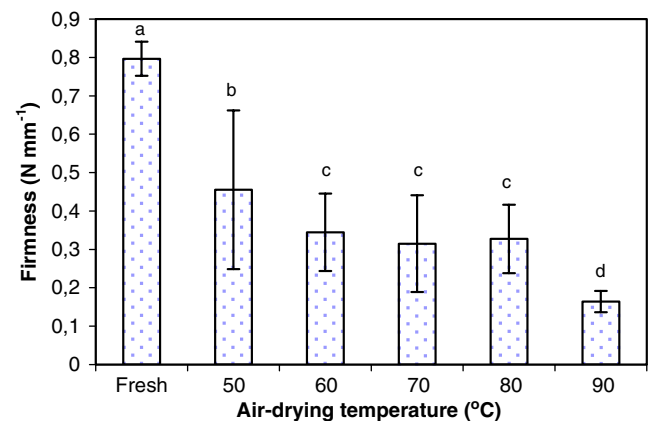
Fig. 4 Effect of air-drying temperature on the firmness of dehydrated blueberries samples. *Identical letters above the bars* indicate no significant difference

maximum loss of 92% of this vitamin was reported when samples were dried at 80°C. Similar vitamin degradation due to irreversible oxidative reactions was reported by other authors (Vega-Gálvez et al. 2009).

The initial phenolic content was 1058.28±16.51 mg gallic acid 100 g^{-1} dry blueberries sample. It can be observed (Fig. 2) that an increase in drying temperature had an important effect on the total phenolic content compared to the fresh sample. Long drying times associated to low process temperatures (e.g., 50, 60 and 70°C) contribute to diminish the protective effect against oxidative damage to cells. Furthermore, an important increase of polyphenols concentration was observed at high temperature (e.g., 90°C) probably due to generation of different antioxidant compounds having a varying degree of antioxidant activity. Ambiguous connections between the content of particular antioxidants and antioxidant activity are difficult to explain only on the basis of quantitative analysis. Some authors suggested that not only the level of antioxidants but also a synergy occurring between them and the other fruit constituents might influence the differences in the antioxidant ability of food extracts (Capecka et al. 2005).

The radical scavenging activity was investigated based on air-drying temperature ($p < 0.05$) as observed in Fig. 3 where dehydration at high temperatures (e.g., 80 and 90°C) shows higher antioxidant activity rather than at low temperatures (e.g., 50, 60 and 70°C). This behaviour could be related to drying process at low temperatures which implies long drying times that may cause a decrease of antioxidant activity (Garau et al. 2007). In this study, the correlation coefficient between TPC and DPPH scavenging activity was found to be weak ($R^2 = 0.624$), indicating that perhaps other phenolic or non-phenolic compounds might be also contributors to the antioxidant activity (Giovanelli and Buratti 2009).

An important modification of blueberries colour was observed during drying at all the working temperatures due to an increase of browning compounds related to NEB reaction ($p < 0.05$). This could be related to an increase in the kinetic reaction with temperature. A maximum NEB value of 0.0406±1.65×10^{-3} Abs g^{-1} dry matter at 90°C compared to 0.0048±6.11×10^{-5} Abs g^{-1} dry matter (80°C), 0.0057±3.54×10^{-5} Abs g^{-1} dry matter (70°C), 0.0021± 3.342×10^{-5} Abs g^{-1} dry matter (60°C), 0.0013±1.087× 10^{-4} Abs g^{-1} dry matter (50°C) was observed (data not shown). Furthermore, Maillard reaction products, especially melanoidins, have been reported to have antioxidant activity through scavenging oxygen radicals or chelating metals (Yilmaz and Toledo 2005).

Regarding to the firmness of blueberries, Fig. 4 shows the effects of air-drying temperature on this physical property ($p < 0.05$). It can be observed that an increase in air-drying temperature has an important influence on this

textural property. In fact, high-drying temperatures (e.g., 90°C) provoked a reduction of this property of 79% compared to the fresh sample. This tissue firmness reduction could be explained due to changes in the plant cell wall that occur during processing at high temperatures causing important decreased of internal pressure (Vega-Gálvez et al. 2008).

Conclusions

In this study, it was demonstrated that Weibull model can simulate the drying curves of blueberries ($R^2 = 0.98$; $\chi^2 < 2.20 \times 10^{-3}$; SSE$<1.97 \times 10^{-3}$). Air-drying temperature influenced the vitamin C content, total phenolic content, as well as the radical scavenging activity in the range of temperatures under study. The decrease in quality was less pronounced at high temperatures (80–90°C) with respect to low temperatures (50–60–70°C) where long process times lead to notable reduction of nutrient property and antioxidant activity. However, at high-drying temperatures, more browning as well as lower fruit tissue firmness was observed. In conclusion, the results of this work indicate the reported quality attributes of the dried fruit together with the drying kinetics of blueberries can be used to optimise the drying operation taking into account nutritional, physical and antioxidant fruit properties. The air-drying temperature could be used as the process control variable.

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