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INTERNATIONAL ADVANCED RESEARCHES and ENGINEERING JOURNAL

Journal homepage: www.dergipark.gov.tr/iarej

e-ISSN: 2618-575X

International Open Access

Volume 02
Issue 03

December, 2018

*Research Article*

# A comparative study of raspberry dehydration by lyophilisation or conventional drying

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ARTICLE INFO

*Article history:*
Received 08 May 2018
Revised 18 June 2018
Accepted 26 June 2018

*Keywords:*
Blanching
Drying kinetics
Lyophilisation
Raspberry

ABSTRACT

Dehydration is a food preservation process that allows to increase the availability of products on the market, as well as the introduction of new products. The objective of this work was to perform a comparative study of processes of dehydration of raspberry by freeze-drying (lyophilisation) or conventional drying. Raspberry is a perishable fruit, with about 85% (w/w) water content, and there is a need for preservation processes that generate new products with long term availability. Raw materials were subjected, or not, to blanching pre-treatments. It was analysed the effect of these treatments on physical parameters, such as water activity, colour and moisture content as well in the drying kinetics. It was found that conventional drying allowed to reduce water content to 20.7 to 35.8% while lyophilisation permitted to achieve values from 11.6 to 14%. It was also observed that lyophilisation process correspond to higher colour difference indexes, ranging from 5.30 to 11.8 values.



## 1. Introduction

Dehydration is a food preservation process that allows to increase the availability of the products in the market, as well as the introduction of new products. In 2015 it was estimated that the production of raspberry in Portugal reached the 7500 tons, being 90% for exportation. The raspberry is the second most exported fruit in Portugal, with sales of about 64 M€. Besides conventional drying, lyophilisation is an alternative way to remove excess water from food [1-3]. It is a drying process based on water sublimation from the material caused by application of low pressure on frozen material. This technique results in high-quality dehydrated products [4-6]. Also freeze drying processing of this fruit permits the extraction of oils that can be used as by-products reducing losses and increasing the development of new products [7]. It was also been proofed that even after long-term storage and despite exposure to atmospheric oxygen, freeze dried berries retain the antioxidant properties of the raw material to a very high degree [8]. Physical and chemical pre-treatments are also of great importance, as they allow to improve the quality of products or change their nutritional characteristics [9,10]. In this work a study of the physical parameters and the drying kinetics of untreated and pre-treated samples of raspberry, a different raw material from the previously studied in cited literature, was performed, using lyophilisation or conventional drying.

## 2. Materials and methods

### *2.1 Raw materials and pre-treatments*

The selection of the raw material is of great importance as it will interfere with the dehydration process. Raspberries are classified as fruits with high respiratory rate, that is, the higher the respiratory rate of the fruit, the lower its lifespan and the lower their ability to be conserved. Therefore the importance in developing alternative ways of fruit conservation [11]. The fruit must have good quality and with a state of maturity that allows a good quality of the final product because those aspects will influence the step of freezing and the drying kinetics [12]. Raw materials were bought from local producers and washed with deionized water. Samples were dried either untreated or subjected to blanching processes with

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sodium hydroxide (NaOH), calcium chloride ($CaCl_2$) and ascorbic acid ($C_6H_8O_6$). For blanching with NaOH it was used an aqueous solution with 10 to 20 g/L of boiling water that was finally neutralized with ascorbic acid. For the blanching process with $CaCl_2$ it was used a 0.5% concentration aqueous solution at 95 °C. Finally for the blanching process with ascorbic acid, to inactivate the enzymatic activity [13], it was used a solution of 10 g/L. At the end of each pre-treatment the samples were passed through a cryogenic solution and finally closed in a plastic bag.

***2.2. Dehydration processes***

Both blanched and untreated samples were subjected to dehydration processes either by freeze drying (lyophilisation) or conventional drying. The equipment for the lyophilisation process was a Labconco liophylizer, model Freezone 6 Plus. The drying chamber has bottles where the raw material is hermetically closed under vacuum. The operating conditions were $p$ = 0.14 mbar and $T$ = - 89 °C. During freeze-drying weightings of samples were made in an analytical balance, with an accuracy of 0.0001 g, in order to assess the loss of mass. For the conventional drying it was utilized an industrial oven, from Zanussi, Italy, with programmed temperature at $T$ = 40 °C. At this temperature the blanching can have significant effect on drying kinetics [14]. Once again, samples were periodically weighted to access the loss of mass.

***2.3. Analytical methods***

Water activity, $aw$, was measured at 25 ºC using a water activity meter (Aqualab Series meter 4TE), with an accuracy of ± 0.003, by detecting the dew point of the samples. At least three iterations were made for each sample.

Water content (%) was measured by weighing the samples, in an analytical balance with accuracy of 0.0001g, before and after the drying processes. At least three repetitions were made for each type of samples.

Colour measurement is very important to the consumer, at first impact with the product, and could lead him to accept or reject it [15]. The measurement of the colour was made with a Konica Minolta colorimeter. The parameters that were evaluated, accordingly with the l*, a*, b* system, are the lightness coefficient, l*, the red colour coefficient, a* and the yellow colour coefficient, b*. Then the relative colour difference index, $\Delta E$, is calculated from the following equation

$$\Delta E = \left[\left(l^{*,0} - l^{*}\right)^2 + \left(a^{*,0} - a^{*}\right)^2 + \left(b^{*,0} - b^{*}\right)^2\right]^{1/2} \quad (1)$$

where the superscripts *,0 refers to the colour coefficients of raw (undried) materials. For $\Delta E < 2.3$ samples are equal in terms of colour and if $\Delta E > 2.3$ then samples are different in colour [16].

***2.4. Statistical analysis***

The statistical analysis of the results of dryings was made with the statistical software Action (Software Action. http://www.portalaction.com.br/), integrated in the Microsoft Excel 2010. The Tukey test was used for multiple comparisons tests to study the magnitude of differences between two means of parameters at a significance level of 5% (or 0.05). If we have means followed by equal letters the difference between the two means do not differ significantly by the Tukey test, otherwise they will be statistically significant.

## 3. Results and Discussion

### *3.1. Influence of the pre-treatments in evaluated parameters*

In table 1, there are summarized the results obtained for the evaluated parameters, and described in the previous section, for freeze-drying and conventional drying. Control samples correspond to the undried raw materials. Comparing the two control samples they are a little different due to the fact that we have used for both tests different batches of raspberry. An observation of the results for the water activity parameter shows that there is a clear reduction of $aw$ from conventional drying to freeze-drying, being more pronounced for the samples with pre-treatment with $CaCl_2$. For the water content parameter there are also differences between the control samples and the remaining samples, with a decrease of water content from conventional drying to freeze drying. The lyophilised samples with blanching pre-treatment have shown the lower values. The analysis of the relative colour difference index shows that conventional drying presents less colour change than freeze-drying. The sample of conventional drying with ascorbic acid pre-treatment has a $\Delta E \leq 2.3$ so the difference is not significant. In freeze-drying the sample with the pre-treatment of ascorbic acid have shown the lower colour change as for the conventional drying.

***3.2. Analysis of the drying kinetics***

There are several methods for modelling the drying kinetics, including theoretical, empirical and semi-empirical models. The theoretical models consider the external conditions as the process unfolds and the internal mechanisms of transfer of energy and mass. Empirical models are based on experimental data and the dimensionless analysis. These models follow a relationship between the average moisture content and drying time [17]. They omit the basics of drying process and the parameters have no physical meaning. Semi-empirical models based on the Newton's law of cooling or Fick's second law for diffusion include the Henderson and Pabis model, Lewis model and the Page model [18-20].

Table 1. Obtained parameters for the lyophilization or conventional drying of raspberry. Samples with different letters in the same column are significantly different.

| Drying Process | Sample | Water activity | Water content (%) | ΔE |
|---|---|---|---|---|
| Lyophilisation | Control | 0.9882 [a] | 87.6 [a] | - |
| | Without treatment | 0.2376 [de] | 14.0 [d] | 8.10 |
| | Blanching NaOH | 0.2915 [d] | 11.7 [d] | 6.50 |
| | Blanching $CaCl_2$ | 0.0958 [e] | 11.6 [d] | 11.8 |
| | Blanching ascorbic acid | 0.2750 [d] | 11.8 [d] | 5.30 |
| Conventional Drying | Control | 0.9949 [a] | 85.5 [a] | - |
| | Without treatment | 0.7027 [b] | 35.8 [b] | 5.12 |
| | Blanching NaOH | 0.4839 [c] | 21.1 [cd] | 3.82 |
| | Blanching $CaCl_2$ | 0.5997 [bc] | 20.7 [cd] | 2.42 |
| | Blanching ascorbic acid | 0.6151 [bc] | 27.4 [bc] | 2.07 |

In this work, and due to its simplicity, the experimental drying curves were modelled with the Page model, given by the equation:

$$MR = \frac{x - x_e}{x_i - x_e} = \exp(-kt^n) \qquad (2)$$

where $MR$ represents the moisture ratio (dimensionless), $x$ is the moisture content at any time, $x_i$ the initial moisture content, $x_e$ the equilibrium moisture content, $k$ is the drying rate constant and $n$ it's a constant (dimensionless). Experimental data was adjusted to equation 2. Data is summarized in table 2.

Figures 1 and 2 show the modelled curves for the drying kinetics of raspberry samples by lyophilisation or conventional drying, respectively. Figure 3 summarises all the curves in order to compare the different behaviours. Analysing the kinetics of freeze-drying of raspberry (Figure 1), we can see that the pre-treatments influence the drying curves. In the case of drying pre-treatments with NaOH and ascorbic acid they follow the same drying kinetic. The drying with pre-treatment with $CaCl_2$ is more efficient. For the oven-drying kinetics (Figure 2), initially all samples with pre-treatment have the same behaviour and are more efficient than the drying without pre-treatment. Once again, raspberry drying is faster with pre-treatment with $CaCl_2$.

Table 2. Parameters of the Page model (equation 2) for the drying processes, and correspondent correlation coefficient, $r^2$.

| Drying Process | $k$/h$^{-1}$ | $n$ | $r^2$ |
|---|---|---|---|
| Lyophilisation, without treat. | 0.08083 | 1.0380 | 0.9995 |
| Lyophilisation, NaOH | 0.10651 | 1.0002 | 0.9993 |
| Lyophilisation, $CaCl_2$ | 0.09256 | 1.0880 | 0.9995 |
| Lyophilisation, Ascorbic acid | 0.09731 | 1.0276 | 0.9993 |
| Conventional, without treat. | 0.14769 | 0.68852 | 0.9664 |
| Conventional, NaOH | 0.35358 | 0.56435 | 0.9852 |
| Conventional, $CaCl_2$ | 0.37479 | 0.54676 | 0.9790 |
| Conventional, Ascorbic acid | 0.26842 | 0.57730 | 0.9766 |

Comparing the drying kinetics for freeze-drying and conventional drying (Figure 3) for all the pre-treatments, it is noted that initially the sample curves for conventional drying with $CaCl_2$ and NaOH pre-treatments are the fastest. In general, conventional drying is faster at the beginning but over time freeze-drying reaches higher levels of dehydration.

## 4. Conclusions

Experimental dryings of raspberry samples by conventional drying in oven at $T$ = 40 ºC and by lyophilisation at $p$ = 0.14 mbar and $T$ = - 89 ºC were performed. Several pre–treatments were applied, in order to evaluate the effect in the final product physicochemical characteristics. It can be concluded that the pre-treatments affect the final product characteristics in terms of the evaluated parameters. The pre-treatments with NaOH and $CaCl_2$ of freeze-drying are the most efficient in lowering the humidity of raspberry. The dryings that change less the colour of samples are the conventional ones without treatment and with pre-treatment with NaOH. With the results obtained along the dryings, data was mathematical adjusted to the experimental data with the Page model to describe the kinetics of drying. The

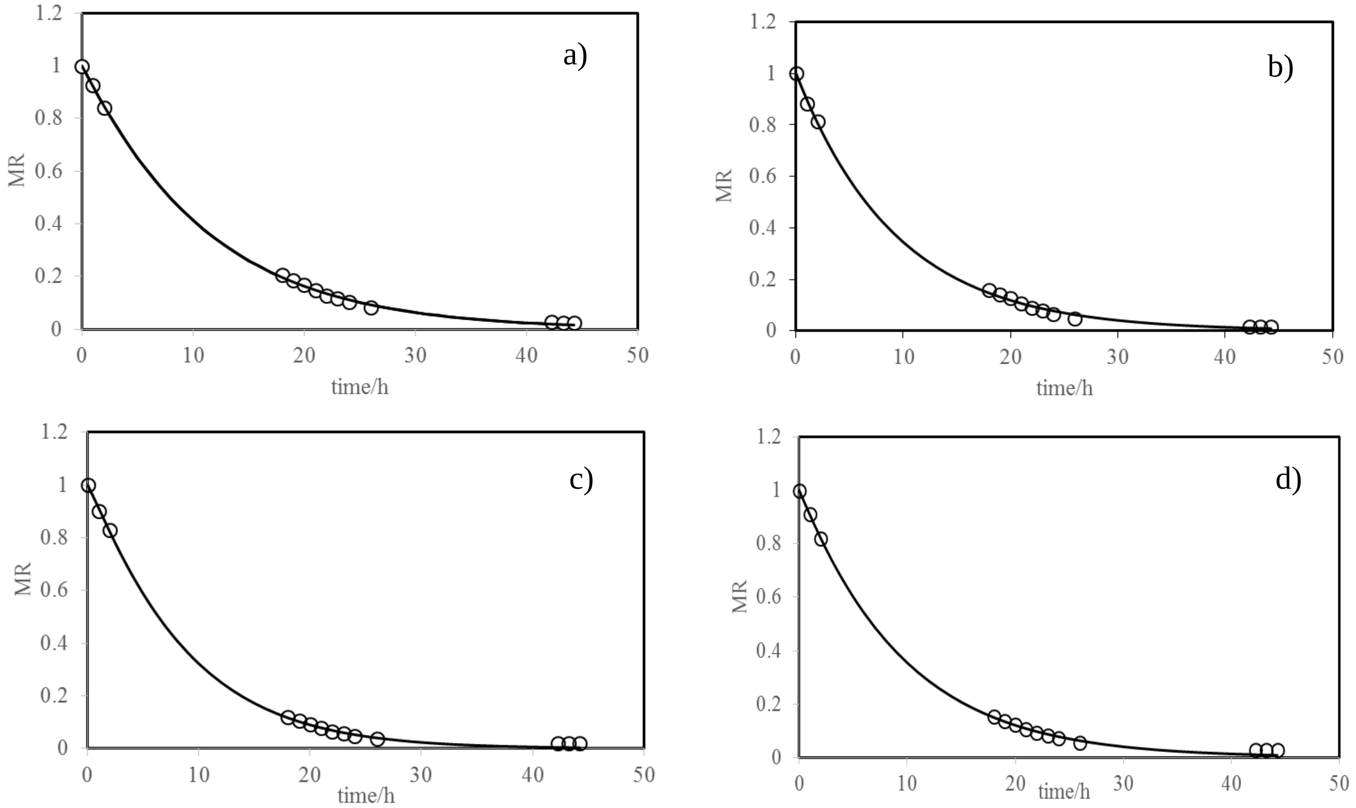


Figure 1. Drying kinetics for freeze drying: ○ exp.; ▬ Page model. a) without treatment; b) blanching with NaOH; c) blanching with $CaCl_2$; d) blanching with ascorbic acid

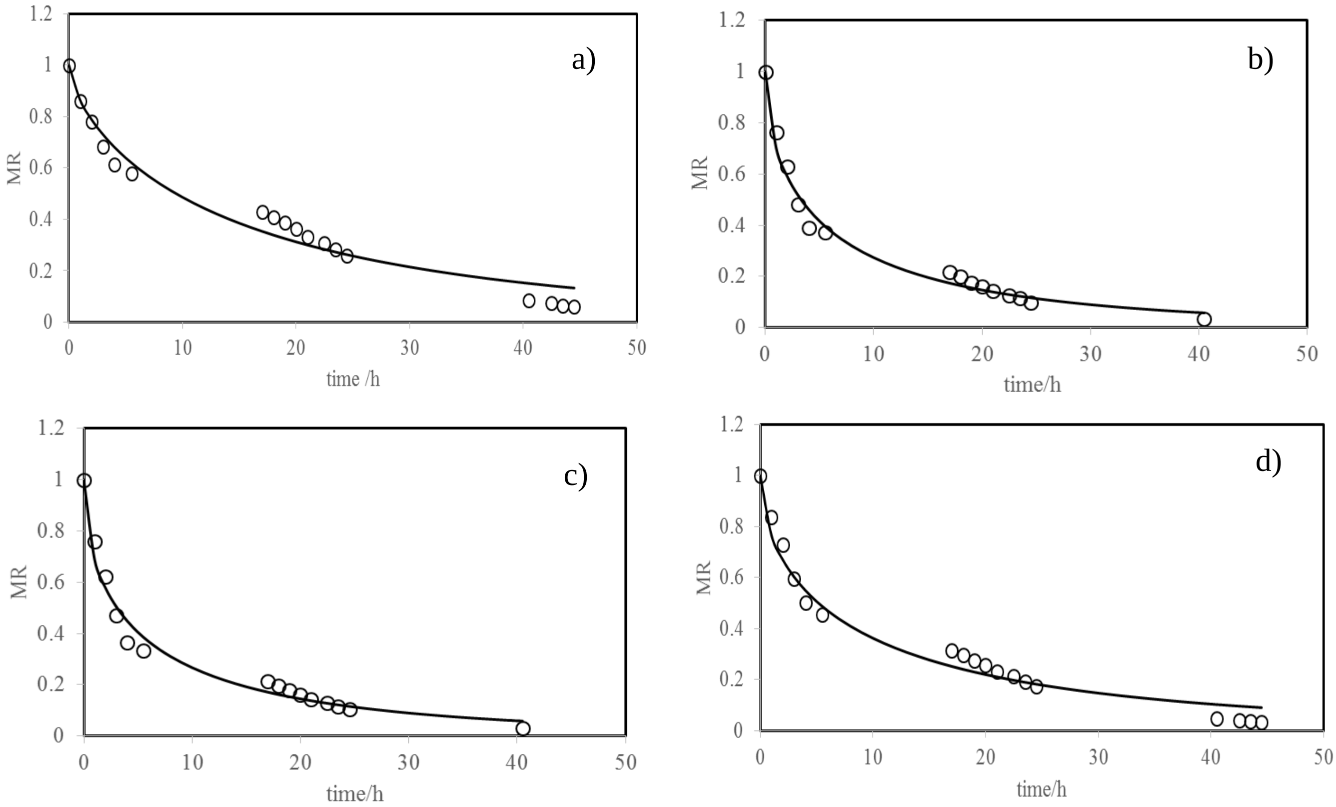


Figure 2. Drying kinetics for conventional drying: ○ exp; ▬ Page model. a) without treatment; b) blanching with NaOH; c) blanching with $CaCl_2$; d) blanching with ascorbic acid

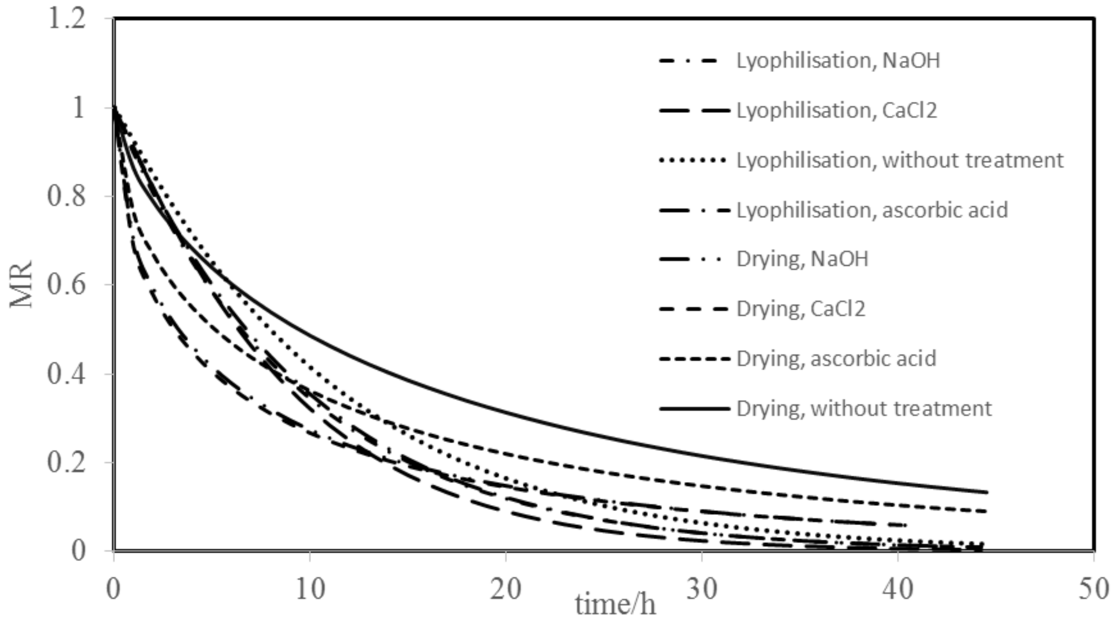


Figure 3. Comparison between the different curves for the drying kinetics

drying kinetics of raspberry for freeze-drying and conventional drying show that the samples with $CaCl_2$ pre-treatment improve the drying rate. Comparing the two technologies, freeze-drying and conventional drying, it was noted that conventional drying is faster initially although the freeze-drying allows achieving higher levels of dehydration. The water contents for conventional drying ranged from 20.7 to 35.8% while for lyophilization values from 11.6 and 14.0% were obtained. Drying kinetics are very different what is reflected in the kinetic parameters. The *k* parameters of the Page model change from 0.08083 to 0.10651 $h^{-1}$ for lyophilisation and from 0.14769 to 0.37479 $h^{-1}$ for conventional drying, while the *n* parameters are much higher for lyophilization ranging from 1.0002 to 1.0880 values. Since there are other factor that are also important, like the difference colour indexes, the choice of technology and pre-treatments applied to the raw material should be chosen accordingly with the final purpose for market application. This work showed that the dehydration processes are effective for long term storage of this fruit, what is very important for the producer's economy.

## Nomenclature

| | |
|---|---|
| *a** | : red colour coefficient |
| *aw* | : water activity |
| *b** | : yellow colour coefficient |
| *k* | : drying rate constant (Page model) |
| *l** | : lightness coefficient |
| *MR* | : moisture ratio |
| *n* | : dimensionless constant of the page model |
| *p* | : pressure |
| *t* | : time |
| *T* | : temperature |
| *ΔE* | : relative colour difference index |

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