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FREEZE-DRYING KINETICS FOR DIFFERENT TYPES OF FOOD PRODUCTS

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ABSTRACT. This study presents the experimental data and the analysis of freeze-drying kinetics of three types of frozen food products: leaves of spinach and watercress, yeast suspension and pre-boiled wet rice. The effective diffusion coefficients for each product during dehydration are determined by applying the mass transfer model described by the Fick's second law. The drying rates are obtained as a function of moisture content, and show specific curves of falling rate period.

Keywords: *freeze-drying, moisture ration, Fick's diffusion model, effective diffusion coefficient, drying rate.*

INTRODUCTION

Freeze-drying or lyophilisation is a unit operation which has been used in a number of applications for many years, most commonly in the food and pharmaceutical industries, in the production of products sensitive to heat: vaccines, pharmaceuticals, biotech products, foods and beverages. The freeze-drying technique, characterized by as high drying rate, low drying temperature and oxygen deficient drying environment, ensures the structural integrity and the preservation of most of the initial raw material properties, such as shape, taste, aroma, colour, flavour, texture, biological activity, nutritive values, vitamins and minerals etc. Up to now, it is the most important technique to dry coffee, enzymes, food ingredients and other high-value foods.

Freeze-drying is a dehydration process during which the moisture/water transformed in ice is removed by warming in the drying chamber under vacuum (the tray with the sample is placed between the heating plates), so that the ice sublimes from frozen materials.

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Freeze-drying has three steps: freezing, primary drying and second drying. First the material is frozen completely to convert the moisture into ice, by keeping the conditions of water below those of triple point (4.58 mm Hg, 0 ºC) [1]. Than in the drying chamber, when the pressure is well below the vapour pressure of ice, the ice is transferred from the product to the condenser by *sublimation*, elimination of the frozen water, and the inside bounded unfrozen water is eliminated by *desorption* [2].

During sublimation: a) the heat is transferred from the shelf to the frozen material through the tray and the vial, and conducted to the sublimation front, b) the ice sublimes and the water vapour formed passes through the dried portion of the product to the surface of the sample, c) the water vapour is transferred from the surface of the product through the chamber to the condenser, and d) the water vapour condenses on the condenser.

As ice sublimes, the sublimation interface, which starts on the surface of the material, recedes and a porous shell of dried material remains. Considering the mass transfer mechanism, the vaporized water is transported through the porous layer of the dried material. At the end of sublimation step a porous plug is formed. Its pores correspond to the spaces that were occupied by ice crystals [3].

In the secondary drying step, unfrozen water is removed by desorption from the dried layer of the product. This stage is performed by increasing the temperature and by reducing the vapour pressure in the dryer.

In the contrast with mass transfer, which always flows through the dried layer, the heat transfer can take place by conduction through the dried layer or through the frozen layer [4, 5].

The major disadvantage of freeze-drying is the high cost of operation. Compared to air drying processes, which remove water in a single stage, freeze-drying is an expensive process since it takes large operation times and consumes large amounts of energy to freeze the product, to sublimate the ice, to condense the water vapour, and to maintain the vacuum pressure in the system [6, 7].

In the present work, the experimental data obtained during the freeze-drying process of different food products were analysed considering the mass transfer model. Experiments were carried out for: spinach and watercress leaves, which are rich in antioxidants and during the freeze drying can preserved the content of antioxidants as in fresh samples; yeast suspension, which is sensitive to temperature as other microbial species; and wet rice which has a high quantity of vitamins and minerals and can be rehydrated more easily after a freeze drying process.

The drying parameters: effective diffusion coefficient and mass transfer rate were determined using Fick's diffusion model, which described the mass transfer mechanism [8, 9].

RESULTS AND DISCUSSION

There are two type of models used to analyze the freeze-drying kinetics: diffusion models based on mass transfer mechanism and models which describe simultaneous heat and mass transfer processes for the solids.

Mass transfer model

The diffusion or mass transfer model is widely used in describing the mass transfer mechanism. The evolution of drying was characterised by the drying curve considering the variation of the moisture content (kg water/kg dried material) with the time (min) for spinach and watercress leaves, yeast suspension and wet rise grains (Figure 1).

The sample moisture content M was calculated on a dry basis according to equation (1):

$$M = \frac{m_t - m_f}{m_f} \quad (1)$$

M is moisture content dry basis (kg water/kg dried matter), m_t - sample weight at a specific time (kg), and m_f - finale sample dried weight (kg).

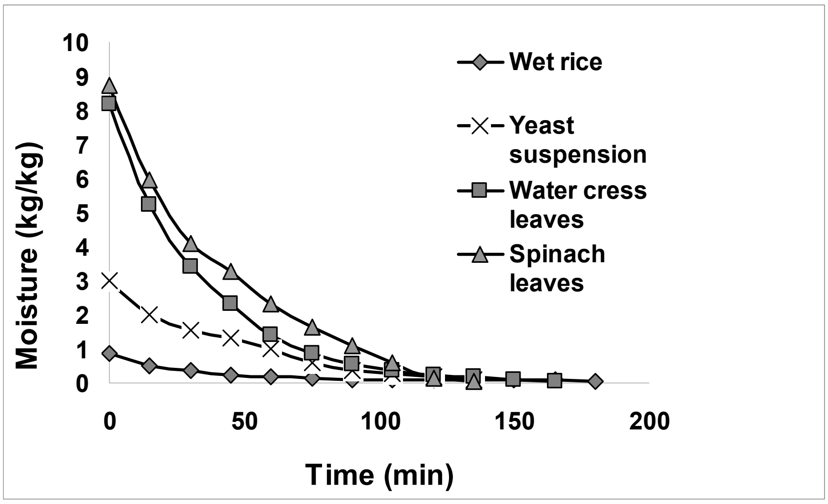

Figure 1. Drying curves.

As the drying curves show, the water loss is higher in the case of leaves than in the case of yeast suspension and than in the case of wet rice, considering the same period of time.

To determine the values of the water loss during the freeze-drying, the moisture ratio (M_R) on wet basis can be expressed in the exponential form of equation (2) [8, 9]:

$$M_R = \frac{M - M_e}{M_0 - M_e} = e^{-kt} \quad (2)$$

k is the drying constant, M, M_0 and M_e – moisture content at each measured time, at the begin and at the end of drying period (kg moisture/kg dried matter).

When the equilibrium moisture content M_e has negligible effect, the equation (2) becomes:

$$M_R = \frac{M}{M_0} = e^{-kt} \quad (3)$$

The moisture reduction was rapid during the initial stage of the drying up to the first hour, and then the moisture reduction is almost constant.

During a drying period of 180 min water cress and spinach lost more than 98 % of the initial moisture, while yeast suspension 96 % and wet rice only 75 %.

From these results, it could be stated that internal resistance to water transfer was greater in wet rice than in yeast suspension and than in leaves of watercress and spinach.

The Fick's second law of unsteady state diffusion was used in order to characterize the freeze-drying of our samples and to calculate the effective moisture diffusivity coefficient D_{eff}, considering constant moisture diffusivity, thin layers and a uniform initial moisture distribution:

$$M_R = \frac{M}{M_0} = Ae^{-\frac{D_{eff}}{L^2}t} \quad (4)$$

L is the thickness of sample.

The dimensionless moisture content (M_R) change during freeze drying is presented in Figure 2.

In order to determine the effective diffusion coefficients (D_{eff}) the experimental drying data in term of ln(M_R) are plotted versus time (Figure 3, a-c). Each straight line obtained has the slope given as equation (5) shows:

$$\text{Slope} = k = \frac{D_{eff}}{L^2} \quad (5)$$

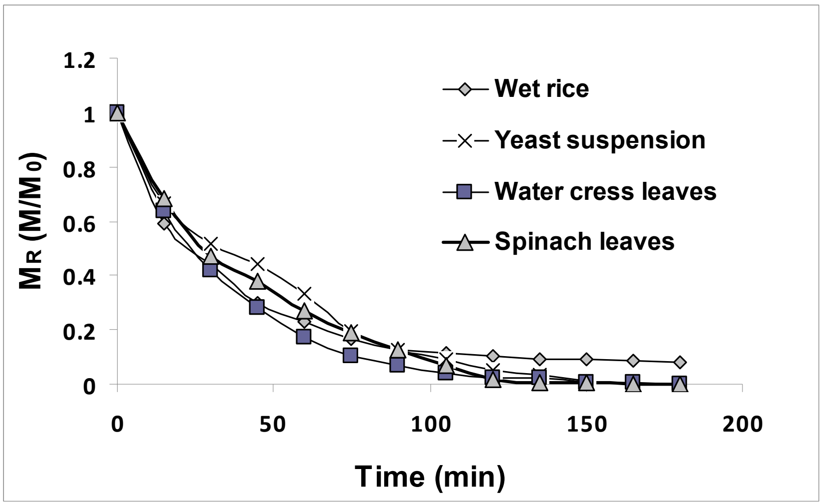

Figure 2. Moisture ratio (M_R) versus freeze drying time.

Diffusion coefficient is a drying constant important in understanding the drying behaviour of the product [10]. The Figure 3 shows for each material two distinct drying stages, with two diffusion coefficients, that can be attributed to the change of drying mechanism or to the change of porosity during freeze drying process.

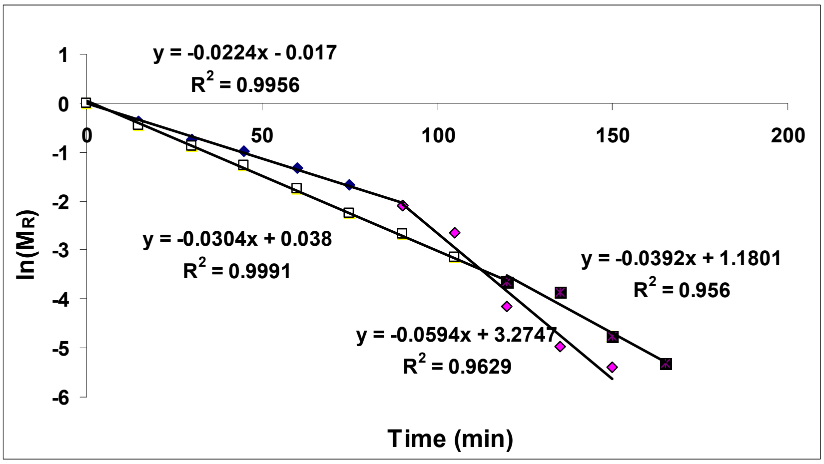

Figure 3. a) Moisture diffusion for freeze drying of spinach (rhomb) and water cress during the time drying (square).

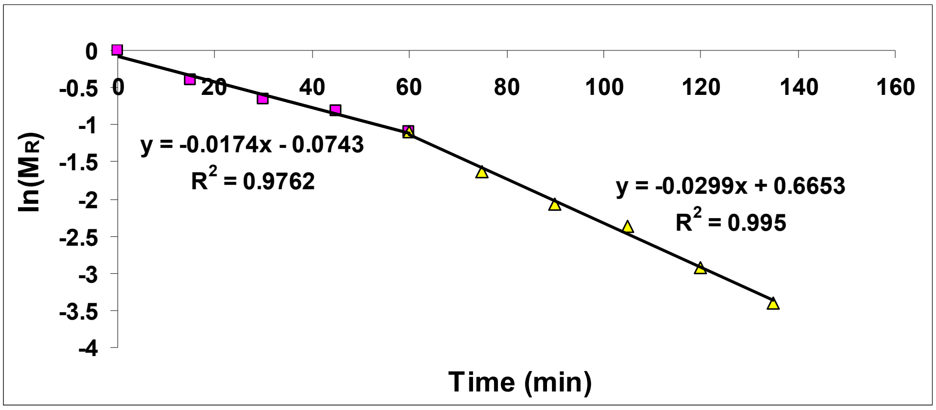

Figure 3. b) Moisture diffusion for freeze drying of yeast suspension during the time drying.

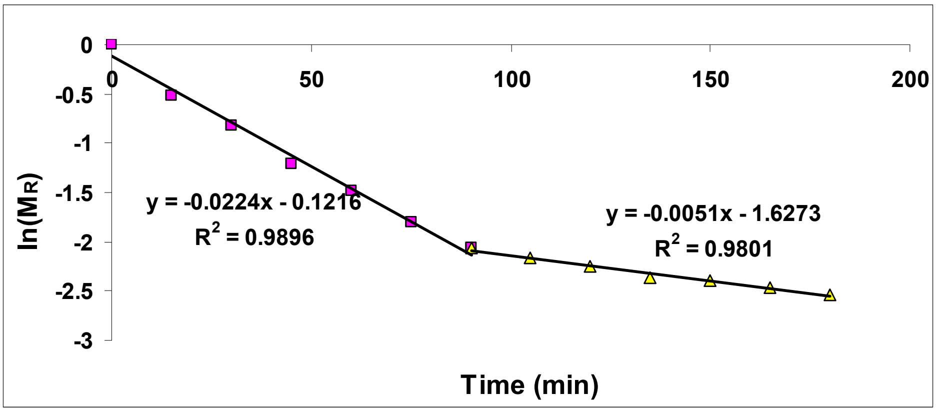

Figure 3. c) Moisture diffusion for freeze drying of wet grains rice in time.

The values of effective diffusivity for spinach are found to vary from $4.973{\cdot}10^{-8}$ m^2/s on the first step to $1.336{\cdot}10^{-7}$ m^2/s on the second step (with an average value of $9.1665{\cdot}10^{-8}$ m^2/s) and for the watercress the obtained values vary from $6.84{\cdot}10^{-8}$ m^2/s on the first step to $8.82{\cdot}10^{-8}$ m^2/s on the second step (with an average value of $7.83{\cdot}10^{-8}$ m^2/s). In the case of yeast suspension, the obtained diffusion coefficient values are $6.96{\cdot}10^{-8}$ m^2/s in the first step and $1.2{\cdot}10^{-7}$ m^2/s in the second step, (with an average value of $9.48\ {\cdot}10^{-8}$ m^2/s), while in the case of wet rice the values are $8.96{\cdot}10^{-8}$ m^2/s in the first step and $2.04{\cdot}10^{-8}$ m^2/s in the second step (with an average value of $5.5{\cdot}10^{-8}$ m^2/s).

The obtained values of diffusion coefficient in the case of leaves and yeast suspension have shown that during freeze-drying the resistance to the mass transfer is higher at initial stage (D_{eff} is lower in first stage) and gradual formation of porous structure improves mass transfer (D_{eff} is higher in the second stage).

In the case of wet rice the value of D_{eff} is higher in the first stage and lower in the second stage, the rice surface being affected by shrinkage, and so the resistance to the mass transfer increases during the experiment.

The drying rates, calculated by equation (6) versus moisture ration are shown in Figure 4.

$$\mathbf{D_R} = \frac{\Delta \mathbf{M}}{\mathbf{A} \cdot \Delta \mathbf{t}} \tag{6}$$

where A is the surface area of the tray where each sample is placed.

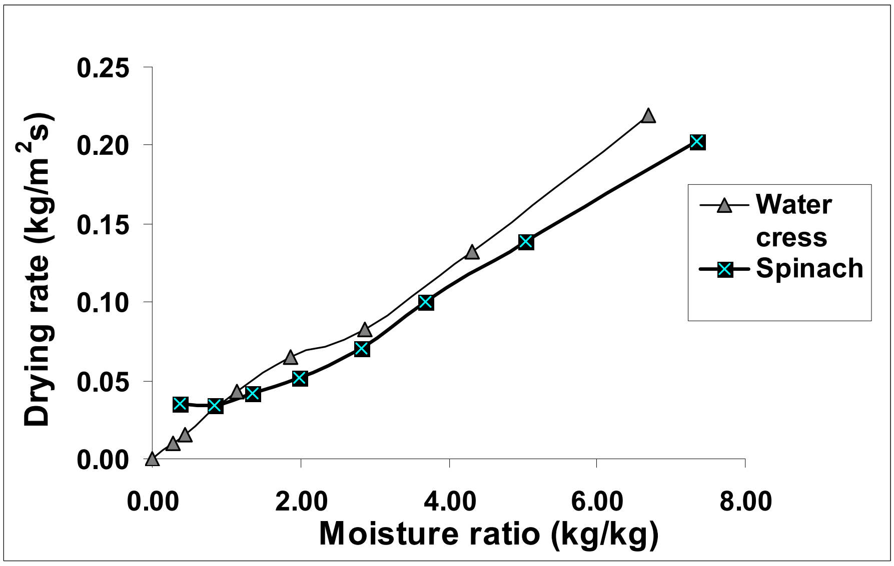

Figure 4. a. Drying rate versus moisture ratio in the case of leaves.

As can be seen in Figure 4, drying rate decreases continuously with the moisture content, which is specific for the falling rate period. This was mainly due to the higher moisture migration from the surface as drying proceeded.

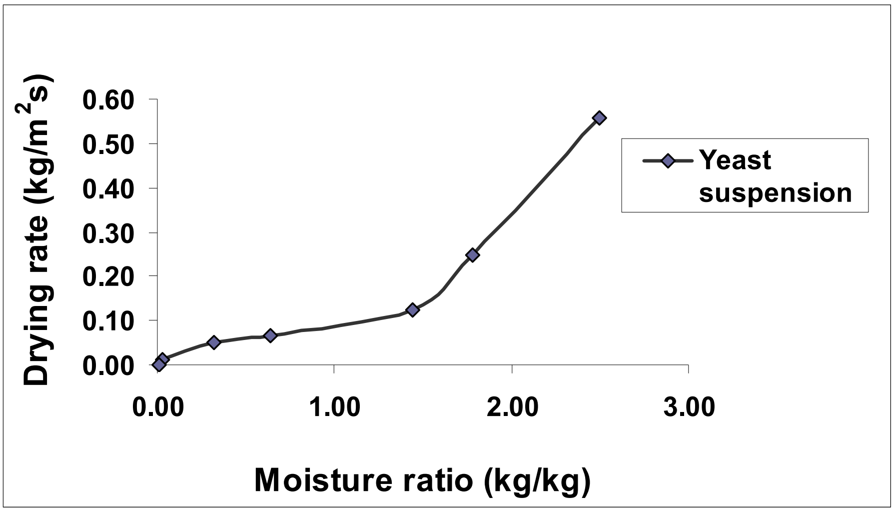

Figure 4. b. Drying rate versus moisture ratio in the case of yeast suspension.

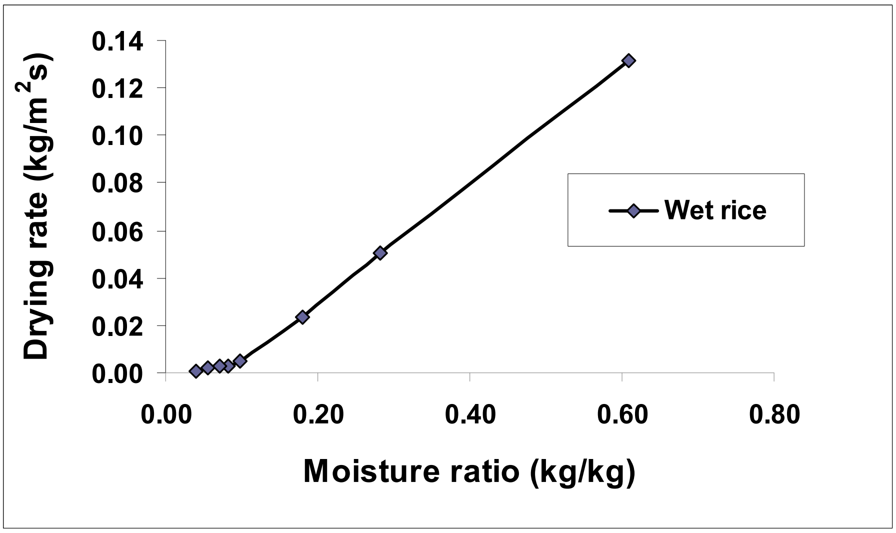

Figure 4. c. Drying rate versus moisture ratio in the case of wet rice.

Higher diffusion rate during freeze drying obtained for the sample containing yeast suspension and leaves of watercress and spinach comparative to wet rice grains can be explained by the better mass transfer in first structures/textures.

In the same time, only in the case of pre-boiled wet rice the diffusion coefficient decreases from the first stage to the second one, which could mean that for this product the second stage of drying involves the decrease of the porosity due to the shrinkage.

CONCLUSIONS

The results obtained by the freeze-drying of spinach, watercress leaves, yeast suspension and pre-boiled wet rice have shown the change of the drying mechanism during the process for each product.

The effective diffusion coefficients were determined by applying the Fick's second law. The values of effective diffusivity were found to vary from $4.973{\cdot}10^{-8}$ m^2/s on the first step to $1.336{\cdot}10^{-7}$ m^2/s on the second step (with an average value of $9.1665{\cdot}10^{-8}$ m^2/s) for spinach, from $6.84{\cdot}10^{-8}$ m^2/s on the first step to $8.82{\cdot}10^{-8}$ m^2/s on the second step (with an average value of $7.83{\cdot}10^{-8}$ m^2/s) for the watercress, from $6.96{\cdot}10^{-8}$ m^2/s in the first step and $1.2{\cdot}10^{-7}$ m^2/s in the second step (with an average value of $9.48\ {\cdot}10^{-8}$ m^2/s) for yeast suspension, and from $8.96{\cdot}10^{-8}$ m^2/s in the first step and $2.04{\cdot}10^{-8}$ m^2/s in the second step (with an average value of $5.5{\cdot}10^{-8}$ m^2/s) for pre-boiled wet rice.

The drying rate has shown for each material continuously decreases with the decrease of moisture content, which is specific for the falling rate period.

EXPERIMENTAL

Each sample with the measured thickness (1.5 mm in the case of leaves, and 2 mm for yeast suspension and wet rice), placed in the tray, was first allowed to freeze for 24 hours at -40 ^{0}C in the freezer and than the frozen sample, was placed inside the freeze dryer (ALPHA 1-2 LD_{Plus}, MARTIN CHRIST Gefriertrocknungsanlagen GmbH Germany) for a period of 3 hours at 0.1 – 0.15 mbar. Before placing the sample inside of the vacuum drying chamber, the temperature of the heating plate was reduced to -40 ^{0}C, the same value as the temperature of the frozen sample. The condenser temperature was kept from - 45 ^{0}C to - 50 ^{0}C.

By connection to the vacuum pump, the material is warmed and so the ice sublimes without melting. The mass variation of the samples has been measured at each 15 minutes during 3 hours. The samples which were taking out from the freeze dryer were transferred to the desiccators for attaining equilibrium. Three replications were done for each case in order to obtain a reasonable average.

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