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A model-based study of rehydration kinetics in freeze-dried tomatoes

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Abstract

Characterising rehydration kinetics is key to understand the effect of microstructure on the quality of rehydrated products. Well-connected porous networks, like the ones created by freeze-drying processes, can enhance water absorption and transport, leading to higher final quality rehydrated products. Such products present the basis for a novel distribution scenario for (freeze-)dried products that are rehydrated closer to the consumption point. In this work, fresh tomatoes were first freeze-dried and subsequently rehydrated at different temperatures. Four rehydration models were fitted to the experimental data using regression analysis. The goodness-of-fit was evaluated according to (i) Root Mean Squared Error (ii) adjusted R-square (iii) Akaike Information Criterion (iv) Bayesian Information Criterion. The Exponential and Weibull models provided the most accurate descriptions of the rehydration kinetics. The effect of temperature on rehydration kinetics was also evaluated, with rehydration capacities and equilibrium moisture contents of the rehydrated tomatoes increasing with temperature. In addition, activation energy values for rehydration, which were in accordance with the existing literature values, were also obtained from the fitted rehydration rate parameters.

Keywords: Rehydration kinetics; Freeze-drying; Model discrimination

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Nomenclature

		w	sample weight
E_a	Activation energy	w_0	initial sample weight
k_i	kinetic constant	w_d	dried sample weight
MR	moisture ratio	X	moisture content (d.b)
RC	rehydration capacity	X_0	initial moisture content (d.b)
t	time	X_{eq}	equilibrium moisture content (d.b)
T	temperature	α	scale parameter
w	sample weight	β	shape factor

1. Introduction

Ensuring a fast rehydration and the preservation of the food organoleptic properties, especially in the case of vegetables and fruits, is key for the design, development and optimisation of convenience and ready-to-eat foods, which represent the main application of dried foods [1] and also a growing market. Typically, freeze-dried fruits and vegetables present shorter rehydration times and higher rehydration capacities than products dried using any other drying technique [2,3]. In addition, flavour retention in rehydrated freeze-dried vegetables and fruits is comparable to that of fresh boiled ones [4], and the loss of vitamin and nutrients is minimised due to the low processing temperature employed. Therefore, from a quality perspective, freeze-dried rehydrated foods represent the best option to satisfy increasing consumers' demand of healthier convenience/ready-to-eat foods.

Besides quality, consumers are demanding also more sustainable food products. Minimisation of the environmental impact of food production is focused mainly on two stages of the food chain: processing and distribution. As foods are mainly consisting of water, phase changes involved during freeze-drying (i.e. solidification, sublimation and vaporisation/condensation) [5] will represent the main contribution to the total process energy demand. Freeze-drying energy demand can be reduced either by optimal process design [6,7] or by the combination with other drying techniques [8,9]. On the other hand, as the impact of transportation mostly depends on kg of product shipped and miles travelled, the reduced weight of dried products alongside a reduction on the *food miles* [10] can contribute to decrease the total environmental burden. In this framework, a distributive manufacturing model [11], where only valuable ingredients are shipped and any other additive or component (as can be water) is added later at the local level could represent an interesting alternative: processing plants would source freeze-dried foodstuff to a local and smaller network formed by multiple rehydration points closer to the consumer, leading to a more efficient and sustainable scenario for the supply of high quality foods. Thus, the characterisation of rehydration kinetics is key to understand the effect of freeze-dried microstructure on the quality of rehydrated products.

Rehydration kinetics studies typically focus on the effect that prior drying processes and temperature of the rehydration medium (water) have on the restitution capacity of the foodstuff. Both empirical models (e.g. Peleg, Weibull) and theoretical expressions (e.g. capillarity, First-order kinetics) are used to describe water uptake kinetics [4,12,13]. Despite the relevance of fresh tomatoes for human health [14] and also their significance in the global market (global production of approx. 170 Mt in 2014 of which 17Mt were produced in the EU [15]) works on rehydration of tomatoes after freeze-drying processes are scarce and present a limited modelling approach (i.e. reduced number of kinetic models considered and/or lack of model discrimination). In [4] rehydration kinetics of freeze-dried tomato (among other vegetables) were characterised using a first-order kinetic law, while in [12] the Peleg's model was employed.

This work presents a comprehensive study on rehydration kinetics of freeze-dried tomatoes that combines both experimental and modelling approaches. Fresh tomatoes have been freeze-dried and rehydration tests have been performed under different temperature conditions. These empirical results have been employed to fit rehydration kinetics of the freeze-dried products to four different models: Peleg, Exponential, First-Order and Weibull. Information theory methods (Akaike and Bayesian Information Criteria) have been employed to discriminate the models both by its accuracy and number of parameters involved, thus taking complexity of the models into account. The effect of the medium temperature on the rehydration capacity and kinetics of freeze-dried tomatoes has also been investigated, and the corresponding activation energies for rehydration estimated. Overall, this study: (i) characterises the behaviour of cellular freeze-dried microstructures on rehydration kinetics and (ii) reveals the potential of an alternative supply scenario based on distributive manufacturing principles.

2. Materials and Methods

2.1. Experimental procedure

Fresh tomatoes were purchased in a local supermarket and stored at 5 °C. After washing, draining and removing the external impurities, the tomato pericarp was cut into pieces of 1 cm x 1 cm x 2 cm (height x width x length). The fresh samples were frozen at -20 °C and then dried under vacuum (condenser temperature of -110 °C, chamber pressure of 0.1 mbar) using a bench top Freeze Dryer (SCANVAC Coolsafe^{TM}, model 110-4, Denmark) for 48h.

These freeze-dried samples were then used in a series of rehydration experiments. A weighed amount of dried tomato samples was immersed into distilled water at three different temperatures (i.e. 20 °C, 40 °C and 50 °C) and removed at regular intervals, blotted with paper to eliminate the surface water and then reweighed. Rehydration capacities (RC %) for each temperature were measured for all the samples [2]:

$$RC = 100 \times \frac{\left(w(t) - w_d\right)}{\left(w_0 - w_d\right)} \tag{1}$$

where *w(t)* is the sample weight in grams at time *t*, w_d (g) is the dried sample weight w_0 (g) is the sample initial weight.

2.2. Rehydration kinetics modelling

Four empirical models have been employed to describe the rehydration kinetics of freeze-dried tomatoes: Peleg, first-order kinetics, exponential and Weibull. The Peleg model [16] defines the moisture content (d.b.) of the sample as:

$$X(t) = X_0 + \frac{t}{k_1 + k_2 t} \tag{2}$$

where *t* (in minutes) reads for time, X_0 is the initial moisture content (d.b), k_1 is the Peleg rate constant - a kinetic parameter - and k_2 is Peleg capacity constant, which is related to the equilibrium moisture content X_{eq} as follows:

$$X_{eq} = X_0 + \frac{1}{k_2} \tag{3}$$

The exponential model takes the following form [1]:

$$MR = \exp\left(-k_3 t^{k_4}\right); \quad MR = \frac{X(t) - X_{eq}}{X_0 - X_{eq}} \tag{4}$$

For values of $k_4 = 1$, the exponential model leads to a first order kinetic expression. Finally, the Weibull distribution function is described by two parameters: the scale parameter α, which is related to the reciprocal of the rate process, and the shape factor β [1].

$$\frac{X(t)}{X_{eq}} = 1 - \exp\left[-\left(\frac{t}{\alpha}\right)^{\beta}\right] \tag{5}$$

2.3. Parameter estimation and model discrimination

The model parameters were estimated by minimising the error, *e*, between experimental (θ) and predicted (i.e. fitted) values ($\bar{\theta}$):

$$J = \sum_{i}^{N} e_i^2 = \sum_{i}^{N} \left(\theta_i - \overline{\theta}_i\right)^2 \tag{6}$$

where N is the number of measurements in the experimental data set. The Least Squares method was employed in all cases, and it was implemented using the function *lsqcurvefit* in Matlab with a tolerance of 10^{-10}.

The goodness-of-fit of each fitted model was evaluated using three different measures [17]: adjusted R^2 (R^2_{adj}), corrected Akaike Information Criterion (*AICC*) and the Bayesian Information Criterion (*BIC*), all of which consider the number of parameters p employed by each model.

$$R^2_{adj} = 1 - \frac{N-1}{N-p}\left(1 - R^2\right) \tag{7}$$

$$AICC = AIC + \frac{2p\left(p+1\right)}{N-p-1} \tag{8}$$

$$BIC = p\ln\left(N\right) - 2\ln\left(L\right) \tag{9}$$

In Equations (7)-(9), R^2 is the regression coefficient of determination, *AIC* is the Akaike Information Criterion [18,19] and L is the maximum log-likelihood of the estimated model [17]. The model with best performance will be defined by the higher R^2_{adj} and lower *AICC* and *BIC* values [20].

3. Results and Discussion

3.1. Rehydration kinetics

Figure 1 shows the rehydration curves corresponding to tests performed at 20°C, 40°C and 50 °C. These curves reveal characteristic trends of a diffusion-controlled process [21,16]: for all the rehydration temperatures investigated, freeze-dried tomato samples exhibited an initial high rate of water absorption followed by a slower rehydration stage that lead to equilibrium moisture values - asymptotic behaviour in the curves - approx. after 50 minutes. This is four times faster than the rehydration processes (range of temperature of 25°C to 85°C) of hot air dried tomatoes reported by [22,23], and six times faster than rehydration (at 20°C) of infrared (IR) dried tomatoes in [24].

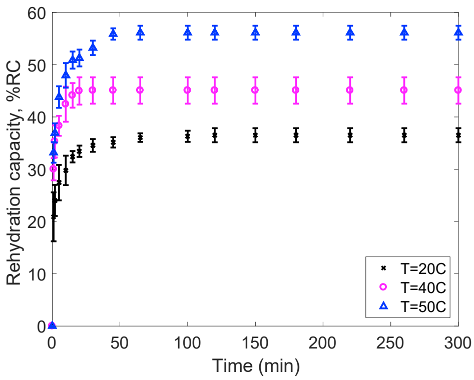


Fig. 1. Rehydration curves corresponding to medium temperatures of 20 ºC (crosses), 40 ºC (circles) and 50 ºC (triangles). Higher temperature resulted in higher rehydration capacities.

Higher rehydration capacities, and therefore higher final equilibrium moisture contents, resulted from increasing the temperature of the rehydration medium: 52% *RC* was achieved at 50 °C opposed to only 37% *RC* at 20 °C. However, none of the rehydrated samples reached the moisture content of the fresh tomatoes, which indicates an irreversible drying process [4]. This effect of the rehydration medium temperature during rehydration is in agreement with the positive effect of temperature reported by [25] for rehydration of hot-air dried tomatoes. Higher temperatures lead to higher degrees of swelling and also enhance diffusion through cell walls of non-interconnected pores. Overall, rehydration capacities of freeze-dried tomatoes presented in this work are higher (up to 58% at 50 ºC) than those found for hot-air dried tomatoes - around 30%, for a rehydration medium at 25 ºC to 80 ºC according to [23].

3.2. Estimation of rehydration constants and rehydration models discrimination

Rehydration parameters corresponding to the four empirical models considered in this work - Peleg, First-order kinetics, Exponential and Weibull – are shown in Table 1. The estimated values of the Weibull's shape factor β ($\sim$0.4) for freeze-dried tomatoes do not match expected values for either Fickian ($\sim$0.8) or non-Fickian diffusion mechanisms ($\sim$0.6), suggesting that capillary flow may exist, as reported for freeze-dried carrots by [26].

Table 1. Regression and goodness-of-fit results for rehydration kinetics

Model	Temperature	Parameters	RMSE	R^2_{adj}	AICC	BIC
Peleg						
	20 ºC	k_1=0.231; k_2=0.179	*0.232*	*0.976*	*1.268*	*2.077*
	40 ºC	k_1=0.090; k_2=0.141	*0.117*	*0.996*	*-22.111*	*-21.302*
	50 ºC	k_1=0.095; k_2=0.110	*0.290*	*0.985*	*8.898*	*9.708*
Exponential						
	20 ºC	k_3=0.704; k_4=0.380	*0.064*	*0.998*	*-42.738*	*-41.929*
	40 ºC	k_3=1.003; k_4=0.442	*0.068*	*0.999*	*-40.431*	*-39.622*
	50 ºC	k_3=0.885; k_4=0.367	*0.093*	*0.998*	*-29.701*	*-28.892*
First order						
	20 ºC	k_5=0.442	*0.516*	*0.880*	*26.971*	*27.538*
	40 ºC	k_5=0.824	*0.324*	*0.967*	*11.114*	*11.681*
	50 ºC	k_5=0.645	*0.660*	*0.920*	*35.364*	*35.931*
Weibull						
	20 ºC	α=2.417; β=0.376	*0.068*	*0.998*	*-40.591*	*-39.782*
	40 ºC	α=0.968; β=0.439	*0.072*	*0.999*	*-38.723*	*-37.914*
	50 ºC	α=1.365; β=0.364	*0.096*	*0.998*	*-28.642*	*-27.833*

Further evidence for this is that the times corresponding to the fast initial water absorption stage observed during the tomato rehydration tests (5-10 seconds, see Figure 1) are in agreement with the capillary suction time-scale (approx. 6 seconds) predicted by [27] during the rehydration of freeze-dried foods.

The corresponding values of $RMSE$, R^2_{adj}, $AICC$ and BIC are also presented in Table 1, while the predicted moisture contents are plotted against the experimental data in Figure 2. The lowest R^2_{adj} corresponds to the First-order model (Figure 2c), showing that a single kinetic constant is not sufficient to describe the initial fast absorption rate and the subsequent relaxation of the system accurately. On the other hand, the Exponential model (p = 2), with the highest R^2_{adj} and the lowest $AICC$ and BIC values, constitutes the most accurate option to describe the rehydration kinetics of freeze-dried tomatoes, closely followed by the Weibull model. The accuracy of these two models is also revealed in Figure 2(b) and Figure 2(d) (Exponential and Weibull, respectively) with most of the points lying on the correlation line.

3.3. Effect of temperature on rehydration kinetics

The effect of temperature on the equilibrium moisture content of the rehydrated samples is reflected on the values of the Peleg's capacity constant k_2. This constant is inversely related to the water absorption capacity of the samples [28], thus decreasing values for rising temperatures, as those reported in Table 1 for the freeze-dried tomato samples, are attributed to higher equilibrium moisture contents in the rehydrated samples (see Figure 1).

Both the Peleg's rate constant k_1 and Weibull's scale parameter α are related to the water absorption rate of the system: the terms $1/k_1$ and $1/\alpha$ are higher in those systems with faster initial rates. For the system under study, both

Peleg and Weibull rate parameters show the same trend, with the fastest initial absorption rate corresponding to medium temperatures of 40ºC; the slowest rate corresponds to rehydration at 20 ºC.

To evaluate the overall effect of temperature on the rehydration kinetics, the inverse of the temperature $1/T$ was plotted against the natural logarithmic of both the Peleg and Weibull rate constants (Figure 3(a) and 3(b), respectively). These Arrhenius plots reveal a very similar system behaviour at the higher temperatures investigated, i.e. 40ºC and 50ºC, with corresponding points very close for both Peleg and Weibull model predictions. The activation energy E_a (kJ/mol) of the rehydration process was also calculated from these plots as the slope of the best linear fitting to the data. Again, similar values were obtained from both Peleg and Weibull constants (i.e. E_{a_Peleg} = 25.5 kJ/mol and $E_{a\_Weibull}$ = 18.3 kJ/mol. These values are in accordance with literature results for rehydrated tomato [29] and other vegetables [30,31,32].

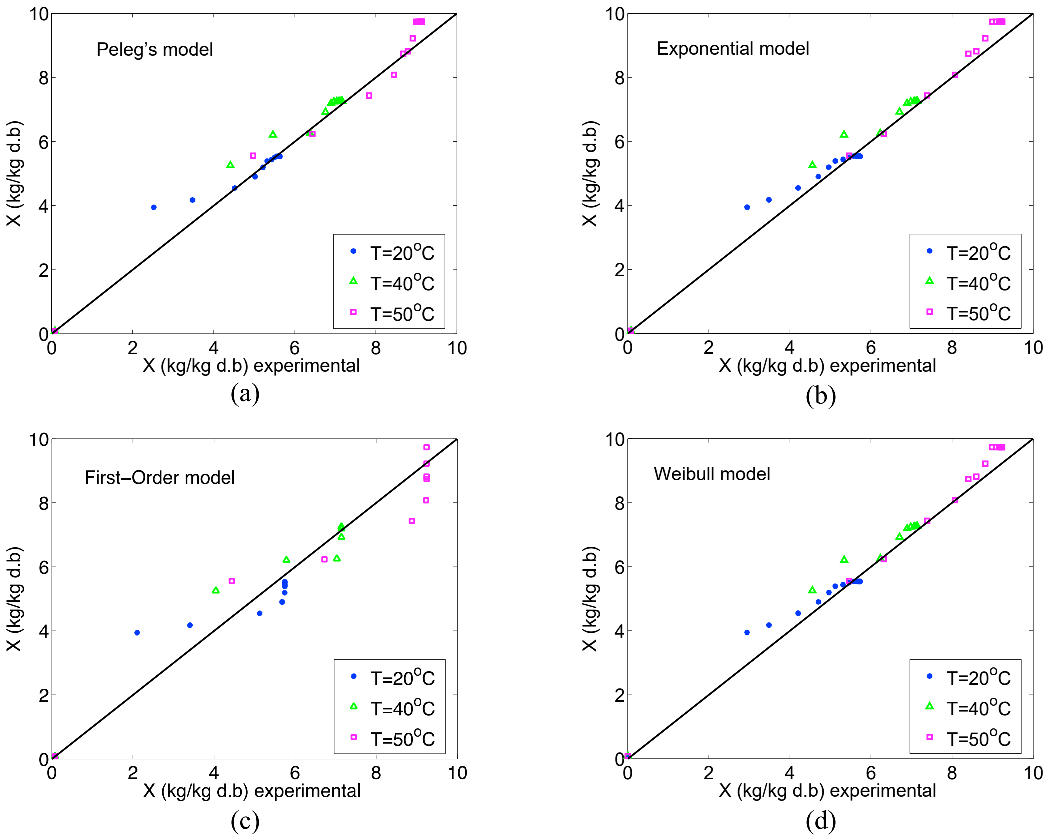
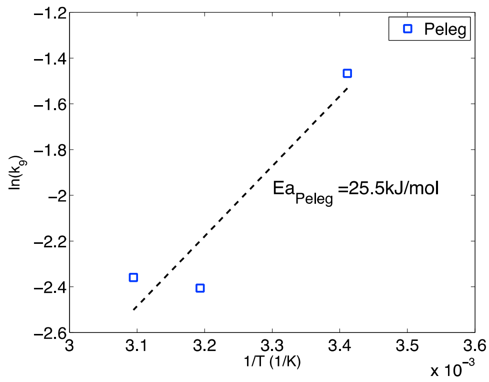
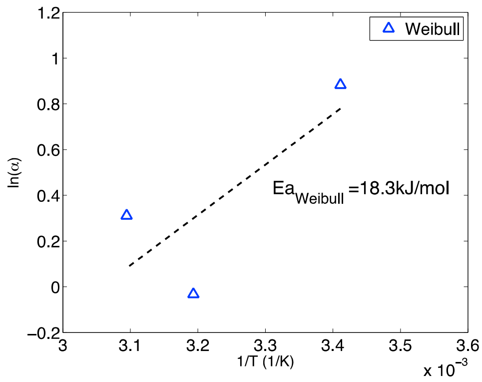


Fig 2. Correlation between predicted and experimental moisture contents (d.b.) for: (a) Peleg's model (Eq. 2), (b) Exponential model (Eq. 3), (c) First-Order model (Eq. 4 and k_{12}=1) and (d) Weibull model (Eq. 5).



(a)



(b)

Fig. 3. Effect of temperature rehydration on the rehydration rate according to (a) Peleg's model (b) Weibull model alongside estimated activation energy values for the system.

4. Conclusions

Rehydration kinetics of freeze - dried tomatoes have been experimentally investigated and modelled in this work. According to the selected discrimination criteria - i.e. minimal *RMSE*, higher R^2_{adj} and lower *AICC* and *BIC* values - the Exponential and Weibull models will reliably predict the fast initial water absorption rates and subsequent relaxation that characterises the rehydration of the freeze-dried tomato system studied.

The effect of temperature on rehydration kinetics has been also investigated. Increasing temperature of the rehydration medium (20 ºC, 40 ºC and 50 ºC) has resulted in higher rehydration capacities and equilibrium moisture contents, as indicated by the experimental rehydration curves and the estimated Peleg capacity constant. The energy activation of the rehydration process has also been calculated via the estimated Peleg's and Weibull's rate constants, with values in accordance with the existing literature. In addition, the estimated values of Weibull's shape parameter suggest the existence of a capillary flow contribution to water absorption in the initial times of the rehydration process, which could also explain the fast initial absorption rates observed.

Overall this comprehensive model-based study characterises the effect of a highly interconnected porous microstructure on the rehydration kinetics of dried tomatoes, revealing also the potential of an alternative supply scenario based on distributive manufacturing principles, where dried foods/powders could be first distributed and then rehydrated closer to the consumption point.

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