LECTURE

INFLUENCE OF TEMPERATURE ON THE QUALITY FACTORS OF SHREDDED CARROTS

EFFETTO DELLA TEMPERATURE SULLA QUALITÀ
DELLE CAROTE ALLA JULIEN

E. TORRIERI[1,2*], M. J. SOUSA-GALLAGHER[1], P. MASI[2], J. KERRY[3] and F.A.R. OLIVEIRA[1]

[1] Department of Process Engineering, University College Cork - National University of Ireland - Cork - Ireland

[2] Department of Food Science, Food Technology and nutrition University College Cork - National University of Ireland - Cork - Ireland

[3] Department of "Scienza degli Alimenti" - Università di Napoli "Federico II" Parco Gussone - 80055 Portici - Na - Italy

*corresponding Author: etorrier@unina.it

ABSTRACT

A mathematical model was developed in order to describe the effect of temperature on the degradation process of shredded carrots. Shredded carrots were stored in an air flux system in the range of temperature 0°-20°C. Storage time varied with temperature to observe the complete decay of pH and colour over time. The experimental data collected at 10°C were used to validate the model. The evolution of the pH over time was reasonably well describes by a Weibull equation, while a first order equation described the colour change. The rate constants of both models varied with temperature according to an Arrhenius - type relationship with activation energy equal to 71±2 KJ/mol for the pH, and 89±5 KJ/mol for the colour.

RIASSUNTO

Un modello matematico è stato sviluppato per descrivere l'effetto della temperatura sui processi di degradazione delle carote tagliate alla julien. Il prodotto è stato condizionato in un sistema a flusso continuo di aria in un range di temperatura

- Key word: kinetics model, shredded carrots, temperature -

0°-20°. Il tempo di conservazione è stato stabilito in funzione della temperatura in modo da osservare il completo decadimento dei parametri pH e colore. Il modello è stato validato a 10°C. Il modello di Waibull descrive bene la variazione del pH nel tempo, mentre la variazione del colore segue una cinetica del primo ordine. Le constanti cinetiche di entrambi i modelli variano con la temperatura secondo una relazione di Arrhenius con una energia di attivazione di 71±2 KJ/mol per il pH e 89±5 KJ/mol per il colore.

INTRODUCTION

Consumer demand for freshness and convenience food has led to the development of many novel products and in particular fresh pre-cut fruits and vegetables. The main concern with these novel products is the detrimental effect on the product quality, exerted by minimally processing operation, i.e. washing, peeling and shredding. Fresh-cut produce in fact is highly perishable with a shelf-life shorter than intact products (BARRY-RYAN & O'BEIRNE, 1999, ZHU *et al.*, 2002, FONSECA *et al.*, 1999). The major objective of scientists and technologist working in this area is to extend the shelf-life of these products while maintaining high quality standards. Refrigeration during storage is essential for preserving the overall quality of minimally-processed food and vegetables since microbiological growth and physical phenomena, which affect the visual appearance of processed vegetables, are very sensitive to storage temperature and temperature fluctuation which may occur along the distribution chain (JACXSENS *et al.*, 2002). Knowledge of the time-temperature history experienced by a ready-to-eat vegetable in the cold chain is of fundamental importance to predict the quality loss and thus the shelf-life of these products. Temperature abuse, such as storage at ambient temperature or improper cooling (T>7°C) has been identified as the major factor in outbreaks of food-borne diseases. In order to predict minimally processed food shelf-life or design the most convenient package for these products, adequate mathematical models are necessary to assess the impact of different parameters and variables, such as temperature and gas composition inside the package, on the quality decay of the product. In fact the decay of the global quality of a commodity is the function of several ambient factors and it is the result of several mechanisms of deterioration. Due to the nature of food systems, describing the evolution of their quality during the storage period is a quite complex task which involves defining one or more appropriate indices directly correlated to the food quality perception. These indices can be derived from sensory evaluation, and chemical or physical measurements (ZOBOLI, 1999, PRZYBYLSKI & ZAMBIAZI, 2000). According to Horta and co-workers the most appropriate characteristics of shredded carrots which can be used to study the effect of the temperature are pH and colour, since other possible characteristics vary significantly during shelf-life or their variability from sample to sample is too high. Moreover there is experimental evidence that both can be correlated to the quality evolution of the carrots during shelf-life (AMANATIDOU *et al.*, 2000; GARCIA-GIMENO, & ZURERA-COSANO, 1997, TALCOTT *et al.*, 2001).

Quality food deterioration is commonly described by a mathematical equation of the type:

$$-\frac{dQ}{dt} = kQ^n \tag{1}$$

where: Q is an appropriate quality index, t is the time, K the rate constant of the quality index decay and n is the pseudo-order of the reaction.

A negative sign is used if the deterioration leads to a decrease of Q and a positive sign for an increase of the index. Usually, quality deterioration processes of foods stored under controlled environmental condition can be described with zero order or first order decay equations. In fact food quality loss at room temperature proceeds quite slowly and moreover many food products become unacceptable as soon as quality diminishes 20-30% with respect to the initial value, thus the quality decay to an unacceptability threshold can be even described by a simple zero order model (LABUZA, 1984). However, there are situations where this approach is too simplistic. Some microbial, enzymatic and chemical degradation kinetics require a more accurate description such as the one provided by the Weibull distribution equation (CARDELLI & LABUZA, 2001; FERNANDEZ *et al.*, 2002; CHUNA *et al.*, 1998). The Weibull distribution probability hypothesized a density function given by (HAHN & SHAPIRO, 1967):

$$f(t) = \frac{\beta}{\tau}^{\beta-1} * \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \quad t>0 \tag{2}$$

With $\tau>0$ and $\beta>0$, whose cumulative distribution is:

$$F(t) = \int f(t)dt = 1 - \exp\left(-\left(\frac{t}{\tau}\right)^{\beta}\right) \tag{3}$$

τ is a scale parameter and $1/\tau$ has the same meaning as the reaction rate constant in eq. 1 while the shape parameter β acts as a behaviour index.

Equation 1-3 can predict the quality evolution on time of packaged commodities provided an estimate of the parameters and their dependence on temperature. Kinetics constant variation with temperature frequently follows an Arrhenius-type equation:

$$K = Ko \exp\left(-\frac{Eatt}{R}\left(\frac{1}{T} - \frac{1}{Tref}\right)\right) \tag{4}$$

Where Ko is the rate constant at a reference temperature, Eatt, the activation energy in KJ/mol, R, the ideal gas constant in KJ/mol K, and Tref, an absolute reference temperature in K. When the package experiences a given time-temperature history T(t), the value which the quality function, F(Q)t, assumes at the time t, can be found according to the equation 1 or 2 by integrating K(T(t)) dt or $1/\tau$ (T(t)) dt from 0 to time t. If the Tref is taken as storage constant temperature to which correspond after time t the same quality F(Q)t, which the packaged food possess after the time-temperature history T(t), then the response function will be in both cases given by:

$$F(Q)t = \int K(f(T))dt \tag{5}$$

where K(f(T)) is the time-temperature dependence of quality loss rate constant. The aim of this paper was the validation of the proposed mathematical model in the cases of pH and colour of shredded carrots.

MATERIAL AND METHOD

Carrots were purchased at the local market. Each set of experiments was performed by using a fresh lot. The carrots were peeled, washed with tap water and shredded. The excess of water was removed with a vegetable centrifuge. Samples of shredded carrots were stored in an air flux system at 0°, 4°, 8°, 10°, 12°, 16° and 20°C. A schematic drawing of the experimental equipment is shown in Fig. 1. It consists of a pump (50 L/h) (A) which conveys ambient air into a humidification chamber (B), provided with four outlets each connected to a plastic box (C). Each box is provided with tight inlets and outlets for standard compressed air tubing through which humidification air enters and comes out continuously. 200 g of shredded carrots were packed in each box. Storage time was a function of the temperature and was chosen in order to observe the complete deterioration of the sample based on previous results (HORTA *et al.*, 2002). At each temperature sampling time was selected in order to get a sufficient number of points to represent the deteriorative process (Table 1). Three replicates were performed at each temperature.

Colour measurement

The colour of the shredded carrots was measured with a tristimulus colorimeter (Minolta Colour Meter CR-300). The diameter of the measurement area was equal to 8 mm. Before performing the colour measurement, the colorimeter was calibrated using a white standard plate (L=100). The colour measurements were performed on the surface of 200 g of shredded carrots

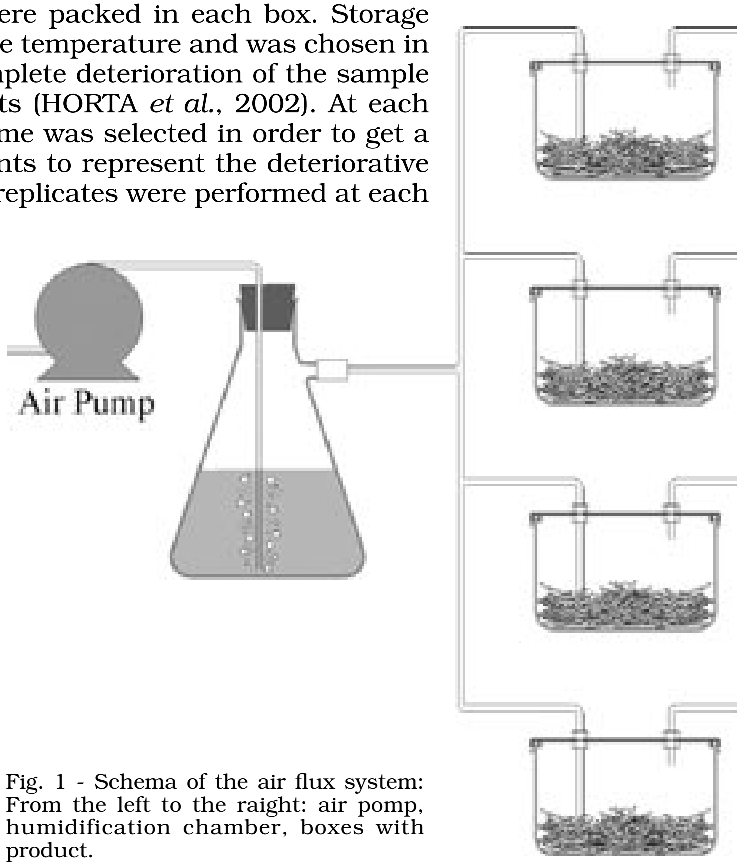

Fig. 1 - Schema of the air flux system: From the left to the raight: air pomp, humidification chamber, boxes with product.

Table 1 - Experimental storage time and sample time to measure the pH and colour of shredded carrots.

Temperature (°C)	Time (days)	Sampling time (days)
0	30	0, 3, 6, 9, 11, 15, 22, 25, 27, 30
4	12	0, 1, 2, 3, 4, 5, 6, 8, 10, 12, 14
8	10	0,1, 2, 3, 4, 5, 6, 8, 10
12	6	0, 1, 2, 3, 4, 5, 6
16	6	0, 0.5, 1, 1.5, 2, 2.5, 3, 4, 5, 6
20	3	0, 0.5, 1, 1.5, 2, 2.5, 3

placed inside the box. The colour were measured in five different positions: two measurements were performed in each position and the shredded carrots were mixed after the first ten measurements and ten extra measurements were done. Twenty readings were taken for each sample and the figures reported are the arithmetic mean of the various measurements.

pH measurement

Aliquots of 25 g of shredded carrots were homogenized with an equal volume of distilled water. The pH of the homogenate was determined with a standard pH meter (Jenway 3310) equipped with a Schott electrode that was previously calibrated by using buffers solution (pH 4 and pH 7) at 20°C. The pH value was expressed as the average of four independent measurements. Two samples were analysed from each box and two measurements were carried out from each sample.

Data Analysis

Data were submitted to ANOVA analysis ($p<0.05$) (Microsoft Excel) to find out the effect of the storage time and temperature on the main quality indices. Experimental data were fitted to the models by least-squares procedure. As the models were not linear the best fittings were achieved by non linear regression, performed by means of the package STATISTICA (release 5.1, 97 edition, Statsoft, Tulsa, OK, USA). The iterative procedure started from a set of parameters given by the operator. The validity of the solution found by statistical procedure was checked by examining statistical figures.

RESULT AND DISCUSSION

Mathematical modelling of colour variation

During storage shredded carrots lose their typical orange colour and when stored at relatively high temperature, browning of the surface becomes evident. According to the CEI system, several parameters derived from instrumental measurement can be used to represent the colour variation such as the coordinate a*, b*, and L*. The “a*” coordinate of the CEI system was chosen because it was the one which best described the colour change of the shredded carrots during storage at different temperatures. A first order decay equation of the form:

$$\frac{a^*}{a^*_0} = \frac{a^*_{inf}}{a^*_0} + \left(1 - \frac{a^*_{inf}}{a^*_0}\right)\exp(-kt) \tag{6}$$

was used to describe the variation of a* through time. To account for the natural variability of the raw material, the actual value of the coordinate “a*” was normalized by dividing it by the corresponding value at time zero. In equation 6, K is the rate constant while a^*_{inf}/a^*_0 is a second parameter which in principle may vary with temperature. At first, experimental data were fitted with eq. 6 by considering both K and a^*_{inf}/a^*_0 adjustable parameters. Fig. 2 shows the influence of temperature on these parameters. From (Fig. 2a) it can be noticed that the a^*_{inf}/a^*_0 values at various temperature are randomly scattered around a constant value (~0,6). Therefore a second fitting procedure was performed by keeping the term a^*_{inf}/a^*_0 constant and equal to 0,6 considering only K as an adjustable parameter. Fig. 2b shows the result of this second procedure. The rate constant K was plotted against the reciprocal of the absolute temperature and a reasonably good linear correlation was obtained, thus K(T) can be described by an Arrhenius-type equation. According to the experimental findings, the colour variation of shredded carrots with varying time and temperature is fully described by the set of equations formed by eq. 4, 6 and:

$$\frac{a^*}{a^*_0} = const \tag{7}$$

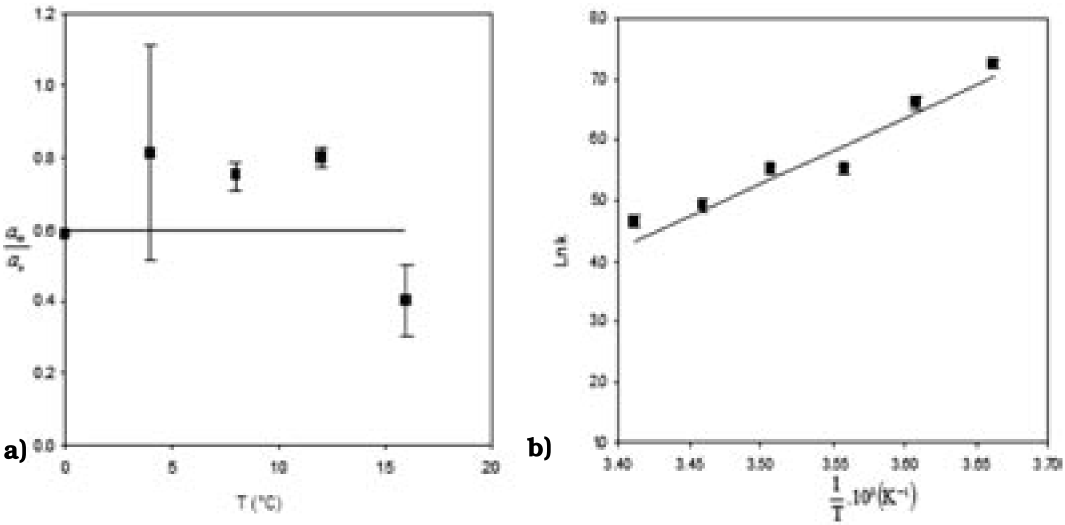

Fig. 2 - Dependence of the first order model parameters from the temperature.

Table 2 - Parameter estimates of the mathematical model in eq. 8 and in eq.11 and relevant statistical data.

Model constant	Estimates±SE	Correlation matrix of parameters		
		$\frac{a^*_{inf}}{a^*_o}$	1/ko	
$\frac{a^*_{inf}}{a^*_o}$ (dimensionless)	0.60±0.06			
ko (1/h)	0.003±0.001	0.96		
Eatt (kJ/mol)	89±5	0.097	-0.089	
R^2_{adj} %	75.5			
		$\frac{pH_{inf}}{pH_o}$	β	1/τ o
$\frac{pH_{inf}}{pH_o}$	0.55±0.01			
β (dimensionless)	2.8±0.3	0.27		
1/τo (1/h)	0.0123±0.0006	0.59	0.22	
Eatt (kJ/mol)	73±4	0.04	0.06	0.18
R^2_{adj} %	88.3			

to get *an estimate* of the parameters which characterise the Arrhenius equation Ko and Eatt, eq. 4 and 7 were incorporated in eq. 6 providing the following relationship:

$$\frac{a^*}{a^*_o} = \frac{a^*inf}{a^*_o} + \left(1 - \frac{a^*inf}{a^*_o}\right)\exp\left(-\left(ko\exp\left(-\frac{Eatt}{R}\right)*\left(\frac{1}{T} - \frac{1}{Tref}\right)\right)t\right) \quad (8)$$

which was fitted to the experimental result by using a non-linear regression procedure. This one–step analysis offers the advantage of a great precision because it avoids the statistical error of the estimation of the intermediate parameters K. The parameters evaluated according to this procedure are listed in Table 2. The proposed mathematical model provides a good fit of the experimental data (Fig. 3), a R^2_{adj} is equal to 75.5% and the residuals are randomly distributed around an average value equal to zero (Fig. 4). By considering the high variability of the raw material this result can be considered quite satisfactory.

Mathematical modelling of the pH variation

Fig. 5 shows the variation of pH of shredded carrots stored under air. pH data collected at different times follow a sigmoidal curve, passing from a value equal to 6.4±0.3, corresponding to fresh carrots, to a value which appears to be independent of temperature and is equal to 3.6±0.2.

ANOVA analysis indicated that time has a significant effect on the pH of shredded carrots with a 95% confidence (P0.05<<0.001). By considering the shape of the pH curves vs time at all temperatures one can conclude that a

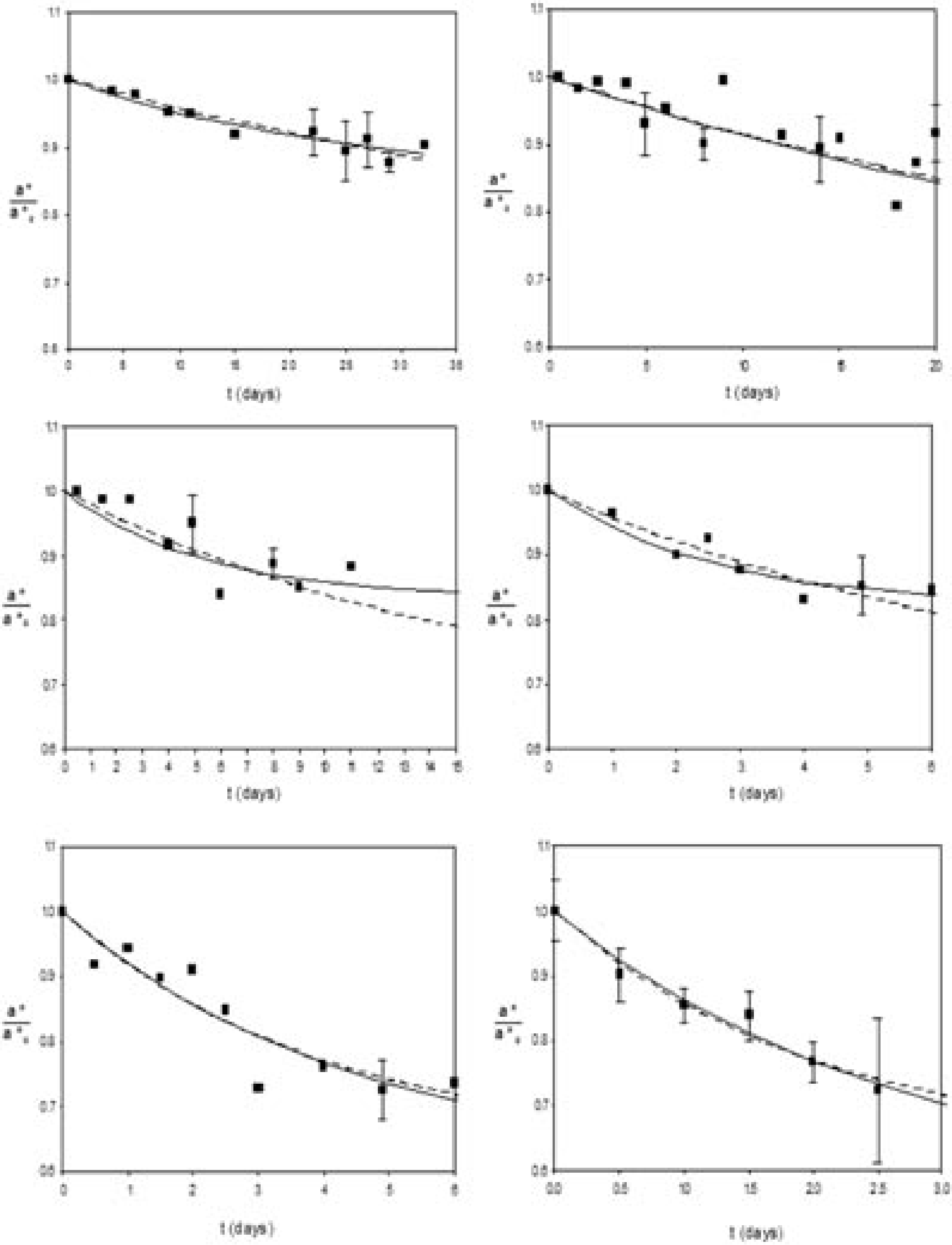

Fig. 3 - Change of the colour (a^*/a^*_o) of the shredded carrots stored in air-flux system over time in a range of temperature 0°-20°C. The dots represent experimental data with the standard deviation, the continous line shows the fit of the first order model to the experimental data at each temperature; the broken line shows the fit of the global model.

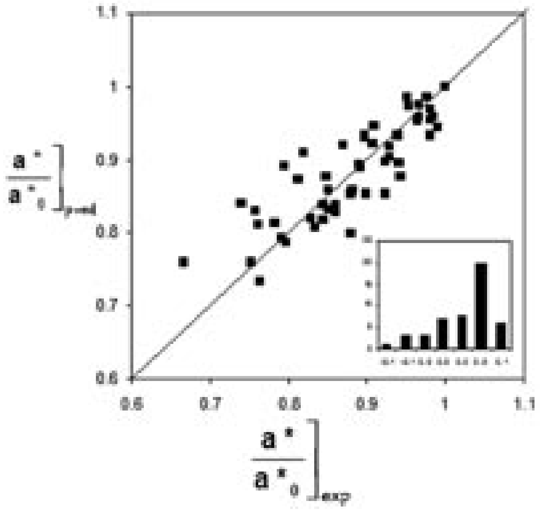

Fig. 4 - Relationship between experimental and predicted values of the colour (a^*/a_o^*) measured during storage of shredded carrots in air flux system in a range of temperature 0°-20°C. Enclosed figure: Frequency distribution of the residual.

first order decay equation is not appropriate to describe the pH evolution on time of shredded carrots. By contrast a Weibull equation of the form:

$$\frac{pH}{pHo} = \frac{pH}{pHo} + \left(1 - \frac{pH}{pHo}\right)\exp\left(-\left(\frac{t}{\tau}\right)^{\beta}\right) \tag{9}$$

where pHo and pHinf are the initial and the steady state values which pH assume respectively, appears to be more adequate. In eq. 9, the term $1/\tau$ has the same meaning as the reaction constant (k) and β is a slope factor (CHUNA *et al.*, 1998). Table 5 summarises the relevant statistical figures which support the hypothesis that Weibull equation is an adequate model to describe the pH variation of shredded carrots with varying time. Again a preliminary investigation was made to assess the influence of temperature on the parameters of eq. 9. Fig. 6 shows the values of pH_{inf}/pH_o, β and $1/\tau$ estimated by non-linear regression of experimental data by using equation 9 at a given temperature. The results plotted in Fig. 6 suggested that pH_{inf}/pH_o as well as β do not vary with temperature, as already reported in the literature (Chuna *et al.*, 1998). Instead $1/\tau$ increases almost linearly with the reciprocal absolute temperature. Hence, an Arrhenius-type equation:

$$\frac{1}{\tau} = \frac{1}{\tau o}\exp\left(-\frac{Eatt}{R}\left(\frac{1}{T} - \frac{1}{Tref}\right)\right) \tag{10}$$

can be used to predict the reaction rate with varying temperature once the parameters Eatt and $1/\tau$ are known. Following the procedure outlined before to define the model relative to the colour of shredded carrots, eq. 10 was incorporated into eq. 9 obtaining:

$$\frac{pH}{pHo} = \frac{pH\,\text{inf}}{pHo} + \left(1 - \frac{pH\,\text{inf}}{pHo}\right)\exp\left(-\left(1/\tau o\exp\left(-\frac{Eatt}{R}\right)*\left(\frac{1}{T} - \frac{1}{Tref}\right)\right)^{t}\right) \tag{11}$$

setting pH_{inf}/pH_o and β equal to a constant and experimental data were fitted to the resulting equation by using a non-linear regression analysis. Tab 6 lists the estimated parameters and the relevant statistical figures. The agreement between the mathematical model and the experimental data is shown in Fig. 5. R^2_{adj} was equal to 89.2% and residual distributed and following a normal distribution with an average equal to zero (Fig. 7 a-b).

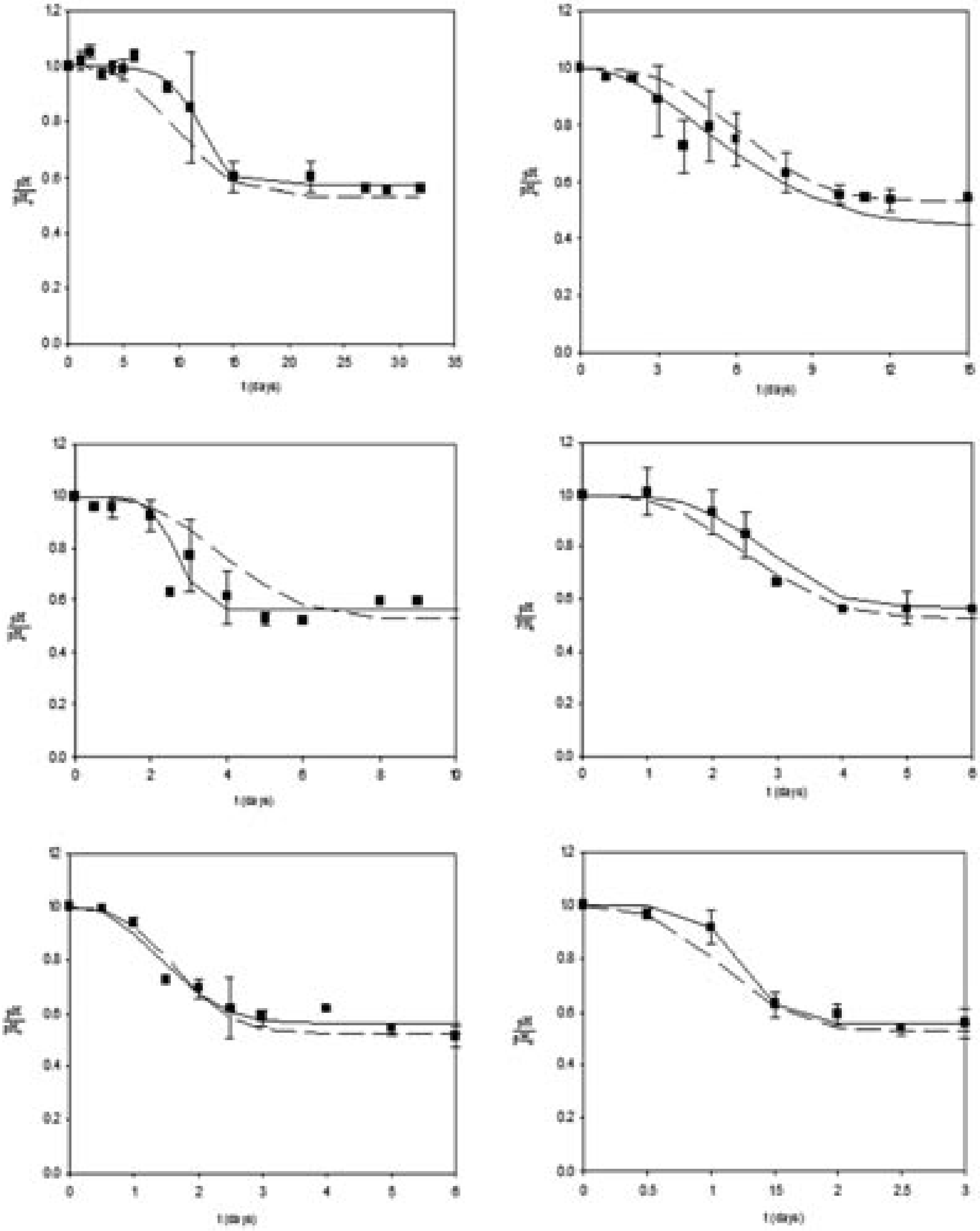

Fig. 5 - Change of the pH/pH_0 of the shredded carrots stored in air-flux system over time in a range of temperature 0°-20°C. The dots represent experimental data with the standard deviation, the continous line shows the fit of the Weibul model to the experimental data at each temperature; the break line shows the fit of the global model.

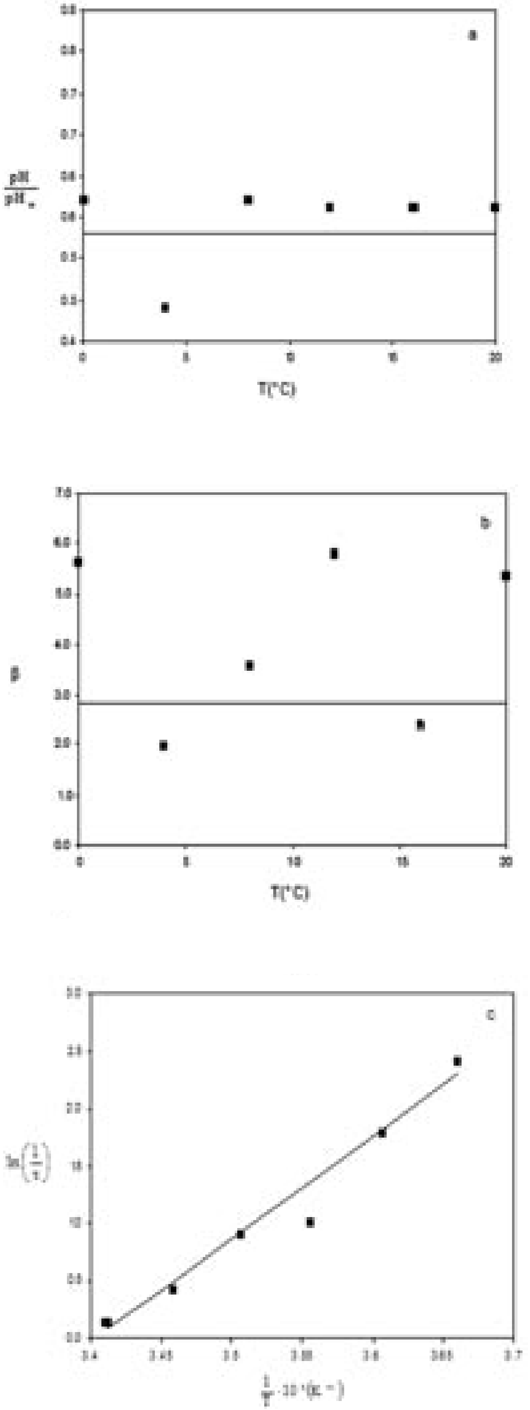

Fig. 6 - Dependence of the Weibull model parameters from the temperature.

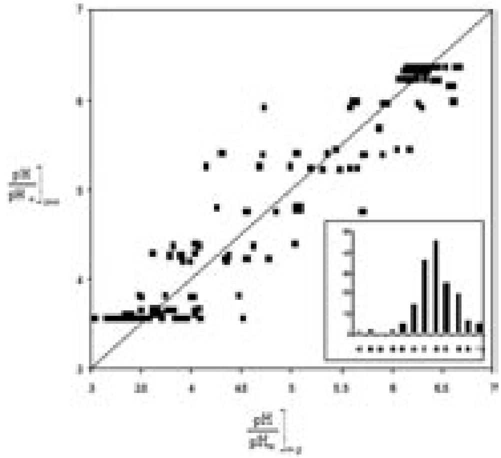

Fig. 7 - Relationship between experimental and predicted values of the pH/pHo measured during storage of shredded carrots in air flux system in a range of temperature 0°-20°C. Enclosed figure: Frequency distribution of the residual.

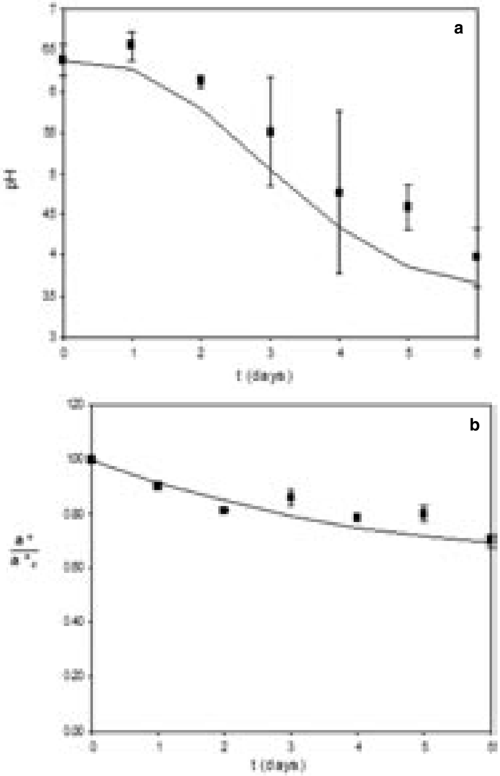

Fig. 8 - Prediction ability of the Weibull model (a) and first order model (b): the dots represent the experimental data at 10°C (a-pH, b-a^*/a^*_0) and the line the values predicted by the models.

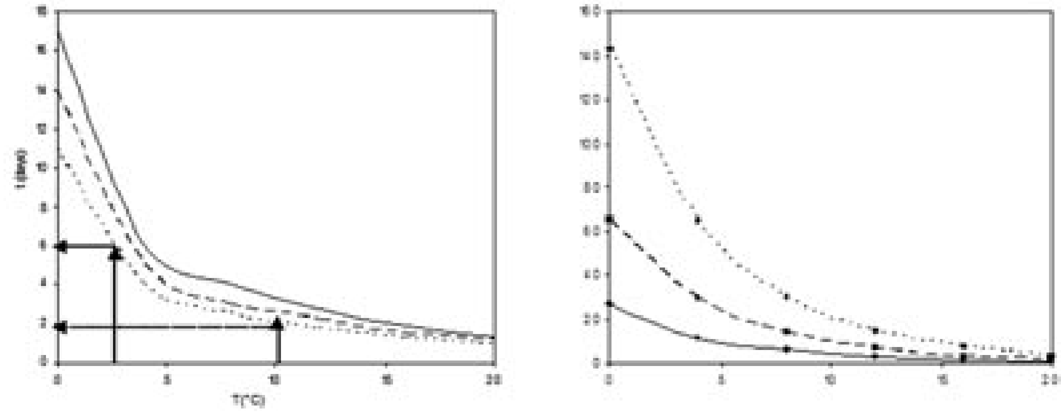

Fig. 9 - Shelf-life prediction - the different lines show different threshold levels (a; pH = —— 5,5 ----- 4.5. b; a* = —— 0.7, ---- 0.9).

CONCLUSION

The results of this investigation showed that a Weibull model, with a rate constant increasing with temperature according to an Arrhenius-type relationship, describe reasonably well the change of pH over time in the range of temperature tested. Among the Lab coordinate system for colour evaluation, a* had the highest sensitivity for the time and temperature changes. A first order model well described the change of colour over time. The reaction kinetics variation on temperature was predicted in a satisfactory manner by an Arrhenius-type equation. To assess the validity of the proposed model, Eq. 8 and Eq. 11 were used to predict colour and pH variation on time of shredded carrots stored in air at 10°C. The agreement between experimental data and model prediction (Fig. 8 a, b) is very good proving the prediction capability of our model. Once defined, the model can be used to predict the shelf-life of shredded carrots at any given temperature. An example is given in Fig. 9 where by way of example the threshold level for pH and colour (a*) values are equal to 4.5 and 0.9, respectively. Accordingly, the predicted shelf-life will be 6 days if the carrots are stored at 4°C and 2 days when stored at 10°C.

REFERENCES

Amanatidou A., Slump R.A., Gorris L.G.M. and Smid E.J (2000). High Oxygen and High Carbon Dioxide Modified Atmospheres for shelf-life extension of minimally processed carrots. Journal of food science. Vol. 65(1) pp. 61-66.

Barry-Ryan C. and O'Beirne D. (1999). Ascorbic Acid retention in shredded iceberg lettuce as affected by minimally processing. Journal of food science. Vol. 64(3) pp. 498-500.

Cardelli C., Labuza T.P. (2001). Application of Weibull Hazard analysis to the determination of the shelf-life of roasted and ground coffee. Lebensmittel-Wissenschaft und-Technologie/ FST. Vol. 34, pp. 273-278.

Chuna L.M., Oliveira F.A.R., Oliveira J.C. (1998). Optimal experimental design for estimating the kinetics parameters of processes described by Weibull probability distribution function. Journal of food Eng. Vol. 37, pp. 175-191.

Fernandez A., Collado J., Chuna L.M., Ocio M.J., Martinez A., (2002). Empirical model building based on Weibull distribution to describe the joint effect of pH and temperature on the thermal resistance of *Bacillus cereus* in vegetable substrate. International journal of food microbiology. Vol. 77. pp. 147-153.

Fonseca S.C., Oliveira F.A.R., Frias J.M., Brecht J.K. and Khe V. Chau (2002). Modelling respiration rate of shredded galega kale for development of modified atmosphere packaging. Journal of food Eng. Vol. 54, pp. 299-307.

Garcia-Gimeno R.M., Zurera-Cosano G. (1997). Determination of ready-to-eat vegetable salad shelf-life. International Journal of Food Microbiology. Vol. 36 pp. 31-38.
Hahn G.J., Shapiro S.S. (1967). Statistical Models in Engineering, Wiley, NewYork.
Horta A., Sousa M.J., Torrieri E., Masi P., Kerry J.P. and Oliveira F.A.R. (2002). Study of the influence of temperature on the quality factors of shredded carrots, 32nd Food Science and Technology Research Conference, University College Cork, Cork, Ireland, September 12-13th, in Programme and Abstracts, (P 80), pp. 158.
Jacxsens L., Devlieghere F. and Debevere J. (1999). Validation of a Systematic approach to design equilibrium modified atmosphere packages for fresh-cut produce. Lebensm.-Wiss. U. – Technology vol. 32 pp. 425-432.
Labuza T.B., (1984). Application of chemical kinetics to deterioration of foods. Journal of chemical education. Vol. 61(4) pp. 348-357.
Pagliarini E., Zanoni B., Giovannelli G. (2000). Predictive study on Tuscan Extra Virgin oil stability under several commercial conditions. J. Agric. Food Chem. Vol. 48 pp. 1345-1351.
Przybylski R., Zambiazi R.C., (2000). Predicting oxidative stability of vegetable oils using neural network system and endogenous oil components. J. of the American oil Chem Soc. Vol. 77(9) pp. 925-931. (28).
Talcott S.T., Howart L.R., Brenes C.H. (2001). Factors contributing to taste and quality of commercially processed strained carrots. Food Research International. Vol. 34. p. 31-38.
Zhu M., Chu C.L., Wang S.L., Lencki R.W. (2002). Predicting oxygen and carbon dioxide partial pressures within modified atmosphere packages of cut rutabaga. Journal of food science Vol. 67(2) pp. 714-720.
Zoboli G. (1999). Gli indicatori di shelf-life. Atti del convegno 4° Trends, Cernobbio. Chiriotti Editori, Pinerolo (To).