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Research paper

Preliminary modeling of the visual quality of broccoli along the cold chain

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ABSTRACT

A simulation approach based on transport phenomena is proposed in this paper, to help manage the logistics of fresh broccoli during cold chain. Indeed, for many varieties of fresh vegetables their shelf-life depends critically on storage temperature progress, affecting the visual quality (VQ) as a consequence of changes in intrinsic quality parameters. Broccoli was chosen as a model food, and average ammonium (NH_{+}^{4}) concentration was adopted as a proper quality parameter associated with residual VQ. Therefore, a mathematical model for predicting the residual VQ is proposed depending on the keeping temperature (among 5 and 20 °C), for a relatively long storage duration (up to 12 days). Model validation is brought over by comparing experimental and computed VQ.

The predictions were affected by maximum errors of about 3%, 13% and 16% for runs at 5, 10 and 20 °C respectively. The effect of temperature fluctuations were then explored. Two non-isothermal scenarios commonly occurring during retail stores in European and US handlers were first analyzed to test the model's ability to predict the visual quality score. Moreover, the model can be easily applied to assess the household or retail shelf-life, or in general the expiration date after a given storage duration.

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1. Introduction

In the fresh produce sector, procedures along the cold chain are needed to ensure product shelf-life assessment and extension. In this framework, new analytical tools could help to reach awareness and prediction of selected parameters, such as the visual quality, whose decrement with time should be prevented. For most fresh produce, storage temperatures as low as 0 °C are recommended to maintain turgidity and slow down the degradation issues such as respiration rate, enzymatic processes, and microbial activities. A proper thermal management is therefore the simplest and easiest way to delay produce deterioration. However, due to imperfect operation of the refrigeration equipment and/or the relatively high energy cost, optimal storage conditions are seldom exercised throughout the entire cold chain, and frequently fresh vegetables are even presented in retail shops at ambient temperatures.

In this paper, fresh broccoli (*Brassica oleracea* L.) is used as a suitable model food: visual quality loss (flowering, yellowing, soft

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rots, dehydration) occurs if no proper refrigerated storage is employed, limiting its commercial value. Then, as for most fresh produce, this item must be cooled at harvest and kept in proper conditions thereafter, even overnight during retail and with continuity throughout the cold chain. The importance of operating conditions and equipment design of cold chain was reviewed by Laguerre et al. (2014) and Dabbene et al. (2008) These conditions, when applied to produce items, concur in changing the sensory visual quality, VQ, which influences consumer perception and therefore affects the level of purchase acceptability (Amodio et al., 2007). Quality indicators for frozen broccoli, subject to realistic cold chain conditions, were already investigated by Gonçalves et al. (2011). Some physical and chemical indicators can be used for objective assessment of VQ (Salinas-Hernández et al., 2015; Barrett et al., 2010). Among these, ammonium (NH_4^+) is a proper parameter or indicator for various vegetables. This is produced during storage as a consequence of senescence in various vegetables (Cefola et al., 2010; Chandra et al., 2006). Generally, ammonium production is associated to protein catabolism, even if a clear relationship has not been found and other biochemical changes are probably involved (Tudela et al., 2013; Baclayon and Matsui, 2008; Chandra et al.,

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Nomenclature pre-exponential term, μ mole (g s)⁻¹ fw Α kinetics parameter, J(mol K)а b kinetics parameter, I mol⁻¹ substrate specific heat, $I (kg K)^{-1}$ c_p Ď substrate diffusion, m²s⁻¹ substrate conductivity, $W(m\ K)^{-1}$ k K rate of production, μ mole (g s)⁻¹ fw E_a activation energy, J mol⁻¹ gas universal constant, J (mol K)⁻¹ R R^2 coefficient of determination VQ visual quality t time, s Т temperature, K Greek storage duration, s ∆t species concentration, μ mole (g s)⁻¹ fw φ density, kg m⁻³ ρ Subscripts

environmental, storage; E experimental; I initial

2008). Recently, this subject was brought up by Pace et al. (2014) who highlighted on a significant relationship between ammonium and VQ in lettuce during cold storage. On these grounds, modeling and correlation of the VQ change with (NH_4^+) can be a suitable tool to help define residual shelf-life. Mathematical models that describe how temperature influences the evolution of various quality indicators for various vegetables have been developed by several authors, as reviewed by Gwanpua et al. (2015). These models generally consist in mathematical equation assemblies describing the processes that drive the degradation of each quality aspects. However, to date, (NH_{Δ}^{+}) was never modeled in a vegetable during cold chain in order to predict its shelf-life. Such opportunity is exploited in the present work, in which VQ and NH₄ were mathematically related in broccoli florets by using a transport phenomena framework, to account for energy transfer and indicator progress with time. Vitalizing the process brings over the advantages of performing a series of "what if" scenarios, such as the evaluation of the residual commercial value of produce (a critically minimum VQ) in a variety of cold chain conditions.

2. Material and methods

The work was divided in two phases: in the first, the following experiments were carried out:

- 1 Assessment of sensory visual quality, VQ;
- 2 Analytical measurement of the average (NH $^{\perp}_4$) content (or concentration), $\overline{\phi}_E$;

Then, the following Computations were performed:

- 1 Building a statistical correlation between VQ and $\overline{\phi}_E$; to obtain a function f;
- 2 Building and validation of a computational model based on differential equations to represent the balances of (NH₄⁺) and heat, to yield for a computed (NH₄⁺) concentration, φ_C ;

3 Conversion of the average computed concentration φ_C into a computed (virtualized) visual quality score VQ_C using the function f established above.

2.1. Experiments

Broccoli (*Brassica oleracea* L.) was cultivated in a local farm in Southern Italy in winter period (medium air temperature 8 °C) and after about 1 h from the harvest quickly transported under refrigerated condition at 4 °C using cold box to laboratory. Individual florets (with smallest stems) were removed from broccoli heads and stored at 5 °C, 10 °C and 20 °C for 12 days in a cold room equipped with a data logger to temperature control, with a precision \pm 0.5 °C. Broccoli florets were analyzed after harvest and 4, 8 and 12 days for visual quality and ammonium content. Measurements were performed in quadruplicates.

A selected group of 10 assessors (made up of 5 females and 5 males, aged between 24 and 50 years old), previously involved as members of the trained descriptive analysis panel for broccoli, was trained to describe the changes in visual quality during storage at various temperatures. Sensory visual quality, VQ, was scored on a 9-1 scale, where 9 refers to excellent and fresh appearance, 7 to good, 5 to fair (limit of marketability), 3 to poor (usable but not saleable), and 1 to unusable. Intermediate numbers were assigned where appropriate (Kader, 2002).

Then, a quantity of 5 g chopped samples was homogenized with 20 mL distilled water for 2 min, centrifuged for 5 min at 12,000 rpm. A quantity of 0.5 mL extract was added with a nitroprusside reagent following heating at 37 °C for 20 min and reading absorbance at 635 nm (Weatherburn, 1967) by means of a spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan). The concentration of NH4⁺ ($\overline{\phi}_E$) was expressed as µmole NH4⁺ 100 g⁻¹ of fresh weight (fw) using ammonium sulfate as standard (0–10 µg mL⁻¹, R² = 0.99).

2.2. Computations

2.2.1. Statistical analysis of experimental data linking NH_4^+ concentration and VQ

Experimental data of $\overline{\phi}_E$; and VQ were statistically analyzed running a multifactor ANOVA for a series of storage temperatures (5, 10 and 20 °C), storage durations (4, 8, 12 days) and their interaction. A Pearson correlation coefficient (r) between $\overline{\phi}_E$ and VQ was calculated on 36 data, and a linear regression was performed by using SigmaPlot 12.0 (SigmaPlot, 2008).

A significant relationship (P < 0.0001) between $\overline{\phi}_E$ and VQ (R² = 0.85) was found, thus $\overline{\phi}_E$ can be considered as an objective parameter to estimate the broccoli VQ and their related shelf-life. The following linear regression was obtained:

$$VQ = f(\overline{\phi}_E) = 9.447 - (1.096 \times \overline{\phi}_E) \tag{1}$$

Equation (1) was used in the computational model in order to predict the broccoli visual quality in various storage conditions.

2.2.2. Formulation of the model

In order to simulate the production and diffusion of NH $_4^+$ in the produce tissues of the selected model food, a transient model of heat and mass transfer is implemented to compute the progress of temperature, T, and ammonium concentration, φ_C . After literature scrutiny, as no information to ammonium-producing protein kinetics was found, it was then assumed that the available proteins do not influence on NH $_4^+$ production. Lying the determination of the ammonium kinetics outside of the work scope, a simple zero-order

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