



XVIIth World Congress of the International Commission of Agricultural and Biosystems Engineering (CIGR)

Hosted by the Canadian Society for Bioengineering (CSBE/SCGAB)
Québec City, Canada June 13-17, 2010



BROWNING KINETICS EVALUATION USING IMAGE PROCESSING TECHNIQUES

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CSBE101092 – Presented at Section VI: Postharvest Technology, Food and Process Engineering Conference

ABSTRACT Colour changes in peach ‘Extra’ jam owing to thermal treatment at different temperatures (80°C, 85°C, 90°C and 95°C) were investigated. Browning kinetics were assessed on jam samples brought just after concentration phase in order to determine the effect of the thermal treatments, subsequent to this step, that take place during the production process (hot bottling, final pasteurization). Colour measurements were performed applying image processing techniques on images acquired through a flatbed scanner as well as by traditional measurements with colorimeter. CIELAB colour space was considered using lightness (L^*), colour difference (ΔE) and a^* parameters to describe browning evolution with time at the considered temperatures. A first order kinetic model was applied to L^* changes. A kinetic model based on a two-stage mechanism was employed to describe a^* evolution. Colour difference was modeled with both kinetics even if the two-stage model better describe the evolution of this parameter. Experimental data strongly fit with the adopted models except for the treatment at 80°C in which colour changes resulted almost negligible.

Keywords: ‘Extra’ jam, browning kinetics, flatbed scanner, image processing.

INTRODUCTION Computer vision employing image processing techniques is becoming a more and more diffused technique for quality evaluation in food products. This technique can be applied to evaluate and characterize a number of properties (colour, texture, size and shape) of a food product reducing operating time respect to the traditional assessment methods (Du and Sun, 2004). Concerning colour, different sorting and quality control systems has been based on colorimetric measurements (Mac Dougall, 2000). However most food matrixes have a heterogeneous nature and many commercial colorimeter only provide average values detected on a small area (some square millimetres) of the sample surface. For these reasons, in many cases, food samples have to be homogenised, using blender or grinder, to achieve uniform colour (Yam and Papadakis, 2004). Another strategy consists in to carry out an high number of measurements. In both cases colour measurements of a heterogeneous media are rather difficult and time-consuming. Colour measurement through computer vision system, on the contrary, allows to analyse a large portion or the entire sample surface, avoiding homogenization operations. However the employment of image processing for food

quality requires the development of appropriate image acquisition methods and image processing algorithms for each specific kind of product.

In 'Extra jam' production processes quality alterations are a noticeable problem because can cause a significant number of rejected lots. During the process, jam undergoes to several thermal treatments that modify its physical and sensorial properties. Prolonging these treatments beyond the optimal levels can compromise the overall quality of the product, making it unpleasant to the consumers even if the bioactive compounds may not have been affected. This condition can be caused by machinery breakdowns, anomalies in the plant or wrong set up of plant parameters. Colour changes are the most evident effect of an excessive heating.

Browning kinetics due to thermal treatments were already studied for the case of the concentration of fruit purees (Lozano & Ibarz, 1997, Garza et al., 1999, Ibarz et al., 2000). Unfortunately only few data can be found on the behaviour of jam when subjected to post-concentration thermal treatments. Concentrated product, in fact, undergoes to heating processes during bottling and final pasteurisation, which can activate further browning mechanisms.

Aim of this work is to assess and identify browning kinetics, due to thermal treatments, in 'Extra jams' by means of colour analysis, comparing image processing and traditional colorimetric technique. The knowledge of browning kinetics can help manufactures to improve products quality looking for the best trade off between technological requirements (e.g. process times and temperatures profiles, logistics), essential into the production processes, and organoleptic characteristics of final products.

MATERIALS AND METHODS Thermal treatments at four different temperatures (80°C, 85°C, 90°C and 95°C) were carried out in laboratory on a high quality peach 'Extra jam'. Jam samples, about 10 kg, were brought in a factory (Agrimontana s.p.a., Borgo San Dalmazzo -CN- Italy) immediately after the concentration phase, during a standard production cycle. Collected samples were water-cooled and stored at +4°C until they are used for the experimentation.

Thermal treatment of jam samples was carried out in glass flask (25 mm diameter x 150 mm high), sealed with a tin foil and a rubber band, dipped into a thermostatic baths at the four considered temperatures, with treatment times up to 420 minutes (7 hours). After the target temperature of the jam bulk was achieved, three flasks were extracted from each bath and immediately cooled in a melting ice bath to stop browning reactions. This procedure was repeated every 60 minutes and every 30 minutes, during the first two hours, for the thermal treatments at 90°C and 93°C. Temperature of jam bulk was monitored in two separated flasks by a stainless steel probe (Onset Computer – TMC6-HC) fixed on flasks cork and connected to a datalogger (Onset Computer – HOBO U12). After flasks cooling, their content was analyzed, together untreated jam, as following described.

Colour Analysis Colour measurement was carried out with two different techniques: by colour image analysis of the pictures acquired by a professional flatbed scanner (Microtek ScanMaker i900) and by colorimeter (Konica Minolta CR-400). The results obtained by the two techniques were compared. In both cases, jam samples were putted in

a white polyethylene (PE) template consisting of a grid of 3x5 holes of 50 mm diameter and 10 mm thick. Images acquisition with flatbed scanner was performed arranging the template over a borosilicate glass plate placed on scanner glass. To ensure a homogeneous background, a white PE plate (10 mm thick) was then placed over the template filled with jam samples. Finally, a black box covered the entire system as shown in Figure 1. Scanner colour calibration was carried out placing a Kodak Q-60 colour target over the borosilicate glass and generating the ICC profile by the scanner calibration software. In this way the effect of additional glass was reduced. A picture of each template hole containing jam was acquired at 600 dpi resolution.



Figure 1. Template filling with jam samples (left), white PE plate placed over the template (centre) and the black box that covers the system (right).

CIELAB (L^*, a^*, b^*) colour space was considered to evaluate the colour change in jam following the heat treatment. Colour coordinates of pixels on acquired images were determined by Adobe Photoshop[®], following a procedure similar to the one described in Yam and Papadakis (2004). In particular, colour coordinates (L^*, a^*, b^*) were measured inside of an entire hole of the template selecting it with the circular mask tool and evaluating the coordinate mean value by the software Histogram Window. Colorimeter (D75 light source and 10° observer) measurements were performed putting the same borosilicate glass plate on the template filled with jam samples. Fifteen measurement for each hole were carried out avoiding the regions with air bubbles.

Colour changes in jam samples were described through kinetics models applied to lightness (L^*), colour difference (ΔE) and a^* colour parameters as discussed in the following section. Experimental data were fitted with these models applying a non-linear regression on SPSS 14[®] statistical software in order to obtain kinetic parameters.

RESULTS Browning kinetic assessment in jams by image processing resulted to be a very fast, functional and reliable technique, because the whole surface of a number of samples can be analyzed at once. In this case, obtained colour coordinates (L^*, a^*, b^*) are averaged on the set of all pixels included within the circular mask, therefore the technique is undoubtedly suitable for heterogeneous food matrixes as 'Extra' jams. A good correspondence was found among the experimental data obtained with colorimeter and flatbed scanner, thus only the results about image processing techniques will be considered here after.

Lightness (L^*) decreased with treatment time for all considered temperature, even if colour changes were negligible at 80°C. The falling of this parameter in heat-treated samples indicates that they are turning darker, therefore it can be taken as a measurement of browning (Lozano and Ibarz, 1999; Ibarz et al., 2000). Furthermore, as can be noted in Fig. 2, lightness decrease was more intense at increasing treatment temperature.

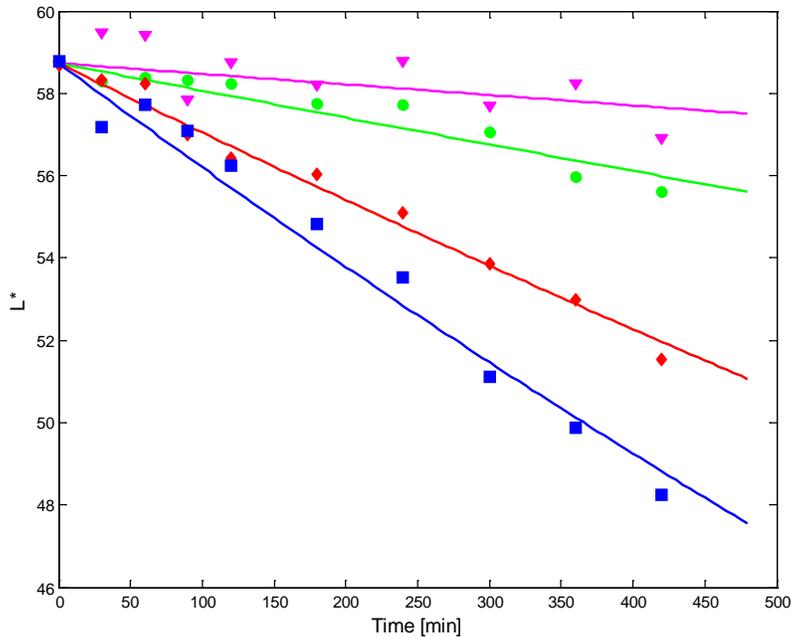


Figure 2. Evolution of lightness during heating of peach jam at different temperatures: 80°C (▼); 85°C (●); 90°C (◇); 95°C (■).

Experimental data concerning L^* was fitted with the following first order kinetic model

$$L^* = L_0^* e^{-k_1 \cdot t} \quad (1)$$

where L_0^* is the lightness values of the untreated samples, k_1 the kinetic constant (min^{-1}) and t the heating time. Fitted parameters of Eqn (1) and the correspondent regression coefficients for the considered temperatures are reported in Table 1. Kinetic constant (k_1) increases with treatment temperature indicating a more intense browning phenomena at highest temperature levels. It has to be noted that the obtained regression coefficients show a strong fitting with the adopted model, excluding the data concerning 80°C for which regression is not significant.

Table 1. Kinetic parameters relating to L^* evolution at different temperatures

Temperature [°C]	L_0^*	k_1 [min^{-1}]	R^2
80	58.73	0.000044	0.503
85	58.73	0.0001139	0.907
90	58.73	0.0002913	0.985
93	58.73	0.000440	0.976

Colour difference (ΔE) increases with time and treatment temperature as reported in Fig 3. Two different kinetic models were adopted and compared to describe colour difference evolution with heating time: a first order and a combined model. The first order model for ΔE can be written as

$$\Delta E = \Delta E_{\infty} (1 - e^{-k_1 \cdot t}) \quad (2)$$

in which is ΔE_{∞} the maximum value of colour difference achieved at each treatment temperature during the heating time. Sometime, a first order kinetic model (Eqn 2) does not adequately describes browning phenomenon (Garza et al., 1999; Ibarz et al., 1999), in particular at lowest treatment temperatures as found by Ricauda et al. (2009) in the case of jams. For this reason a combined kinetic has been developed, in which the browning reactions are considered to consist of two stages. A first phase of coloured compound formation that follows a zero order kinetics and a second one, characterized by the destruction of the natural pigments, which can be described with a first order kinetic (Garza et al., 1999; Ibarz et al., 1999). In the case of colour difference parameter the combined kinetics model can be expressed with the following exponential relation

$$\Delta E = \frac{k_1}{k_0} (1 - e^{-k_1 t}) \quad (3)$$

where k_0 and k_1 are the zero order and first order kinetic constant respectively.

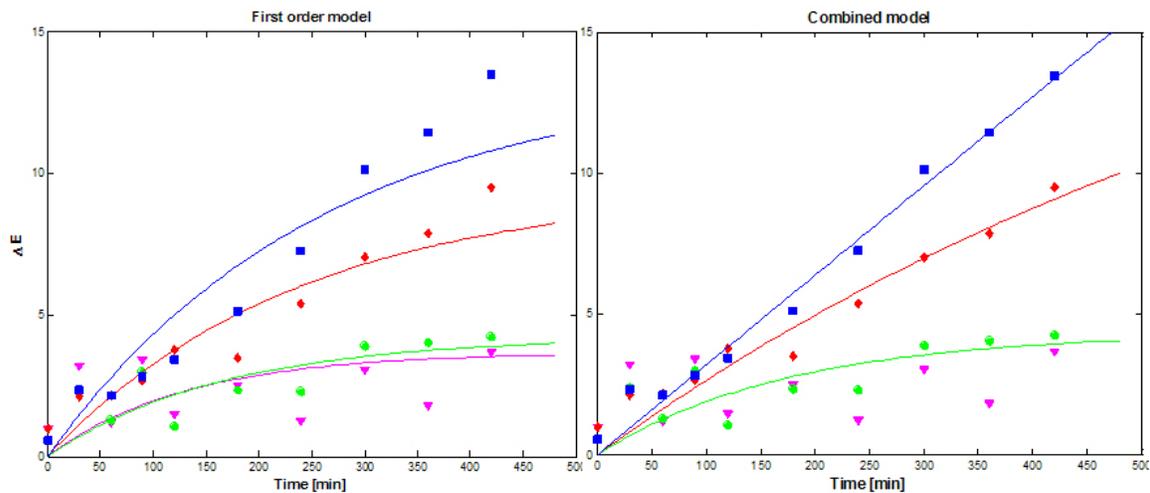


Figure 3. Evolution of colour difference during heating, described with a first order kinetic (left) and the combined model (right), at different temperatures: 80°C (\blacktriangledown); 85°C (\bullet); 90°C (\diamond); 95°C (\blacksquare).

Regression parameters obtained with the two kinetic model are reported in Table 2. A decrease of the kinetic constant with heating temperature was observed about first order kinetic, indicating a more rapid colour change at the highest temperatures (90°C and 93°C). In the case of composite kinetic, both zero order and first order kinetic constants increased with temperature, excluding at 80°C in which the model does not fit adequately with experimental data. It has to be noted that composite model better describes ΔE evolution during heating, since the regression coefficients are higher than those obtained with the first order model.

Table 2. Kinetic parameters relating to ΔE evolution at different temperatures obtained applying first order and composite kinetic models.

Temperature [°C]	First order kinetic			Composite kinetic		
	ΔE_{∞}	k_1 [min ⁻¹]	R^2	k_0 [min ⁻¹]	k_1 [min ⁻¹]	R^2
80	3.67	0.0076343	0.597	0.068490	0.050749	0.664
85	4.22	0.006031	0.902	0.008131	-0.000354	0.981
90	9.48	0.0041977	0.915	0.014153	0.000230	0.97
93	13.45	0.0038587	0.903	0.024116	0.000550	0.994

Colour coordinates a^* and b^* show an opposite trend with the treatment time (Fig. 4). In particular, to an increase of a^* corresponds a decrease of b^* . The a^* parameter expresses the variation in the green-red ($-a^*$, $+a^*$) axis and the b^* parameter, the variation in the blue-yellow ($-b^*$, $+b^*$) axis. Therefore the monitored behaviour of a^* and b^* colour coordinates, as function of treatment time, indicates an overall colour change from yellow hues towards reddish-brownish ones. A more intense colour change, as predictable, was pointed up at 90°C and 93°C respect to 80°C and 85°C.

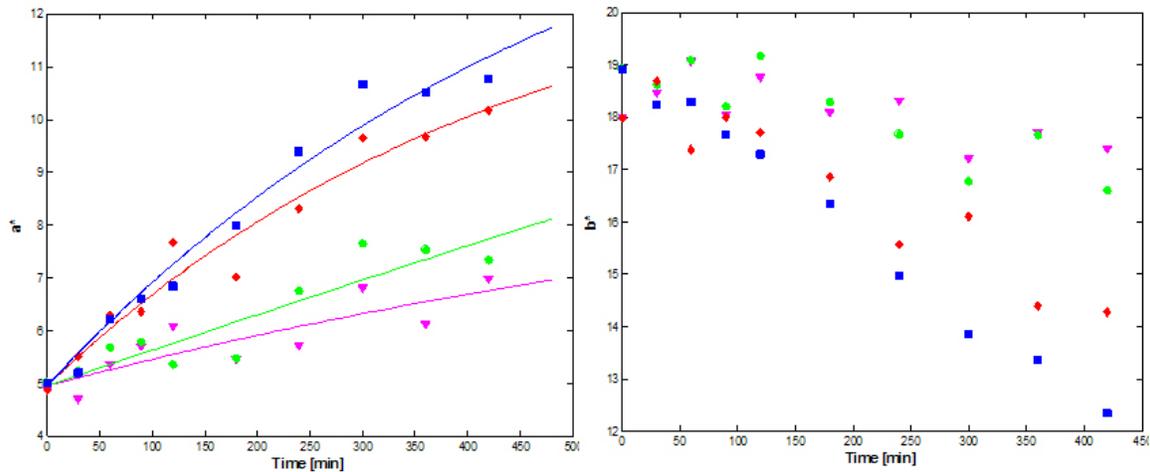


Figure 4. Evolution of a^* (left) and b^* (right) colour parameters during heating at different temperatures: 80°C (▼); 85°C (●); 90°C (◇); 95°C (■).

Only the evolution of a^* was fitted with a kinetic model. In particular the combined model was considered fitting the experimental data with the following expression:

$$a^* = \frac{k_0}{k_1} - \left(\frac{k_0}{k_1} - a_0^* \right) \cdot e^{-k_1 t} \quad (4)$$

where a_0^* is the mean value of a^* for the untreated samples, whereas k_0 and k_1 are the zero order and first order kinetic constants. Regression coefficients show a good fitting between trials results and combined model (Table 3), in particular at 90°C and 95°C, even if less strong than in the case of ΔE parameter. Observing the evolution of the

experimental data concerning to a^* , reported in left side of Fig. 4, an asymptotic behaviour appears after 300 min with a significant less increase of the parameter at all considered treatment temperatures.

Table 3. Kinetic parameters relating to a^* evolution at different temperatures obtained applying the composite kinetic model.

Temperature [°C]	a_0^*	k_0 [min ⁻¹]	k_1 [min ⁻¹]	R ²
80	4.94	0.010438	0.001034	0.706
85	4.94	0.007653	0.000159	0.827
90	4.94	0.030279	0.002224	0.951
93	4.94	0.030853	0.001886	0.973

CONCLUSION Colour image analysis resulted to be a reliable and suitable technique for measuring colour in the case of heterogeneous food media such as jam. Browning kinetic, due to thermal treatment, of peach ‘Extra’ jam was assessed by this technique obtaining a good correspondence with colorimetric measurements, but strongly reducing the operating time. Jam browning kinetics can be described by lightness, colour difference (ΔE) and a^* evolution during heating at different treatment temperatures. Lightness follows a first order kinetic model. Colour difference trend is better described by a two-stage (composite) kinetic model that take in account a colour formation phase (zero order kinetic) followed by a pigment destruction stage (first order kinetic). Even in the case of a^* colour parameter composite model well fit with experimental data. Colour changes resulted negligible in the thermal treatment at 80°C, for this reason no models adopted adequately described colour parameters evolution at this temperature.

Acknowledgements. Authors would like to thanks Andrea Perciballi and Davide Gullino for their work during their graduation thesis; dr. Alessandro Occelli and Agrimontana s.p.a. for the collaboration.

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