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Kinetic parameters of surface color degradation of canned fresh green peas sterilized in a rotary retort

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Abstract

The kinetic parameters of surface color degradation of canned fresh green peas sterilized in a rotary retort, using the a* value from a spectrophotometer as the physical parameter and the concept of fractional conversion in conditions of unsteady state were determined in the range of retort temperatures of 120 and 131 °C. Experimental initial a* values fluctuated between −14.4 and −15.7, while final a* values ranged between −0.165 and −4.75. After five iterations performed, solving simultaneously the energy balance of the system, the differential equation of unsteady conduction for spheres and the first-order degradation reaction of surface color by numerical methods, the best values of $k_{100\,^\circ C}$ and E_a determined were $5.48 \times 10^{-4}\,s^{-1}$ and 89.37 kJ/mol respectively, being 5.68% the deviation between experimental and predicted fractional retentions of a* with the determined parameters.

Keywords: Color degradation; Kinetic parameters; Canned green peas; Sterilization

1. Introduction

Accurate kinetic parameters, rate constant and activation energy, are essential to predict quality changes that occur during thermal processing (Steet & Tong, 1996). Heat sterilization of green vegetables results in color change from the natural green to what is described as an olive brown color, being attributed the color change to the conversion of the cholrophyll found in the green plants to pheophytin, through the substitution of the magnesium of the chlorophyll by hydrogen (Hayakawa & Timbers, 1977). These authors studied the influence of heat treatment on changes in visual green color of asparagus, green beans and green peas using the ratio of stimulus value $-a/b$ to evaluate the color changes; they reported a z-value of 39.4 °C for the discoloration of green peas using the mentioned parameter $-a/b$ and assuming first-order reaction kinetics and the D-z model for temperature dependence. Steet and Tong (1996) determined kinetic parameters for the thermal degradation of visual green color in peas using the a-value as the physical parameter, the concept of fractional conversion, and an Arrhenius relationship for temperature dependence, obtaining an activation energy of 76.2 kJ/mol. Smout, Banadda, Van Loey, and Hendrikx (2003) studied color degradation of green peas on a kinetic basis and used the a-value as a measure of color change, obtaining an activation energy of 52.4 kJ/mol. Alcedo, Durán, and Rodrigo (1973) determined that the parameter $L+a$ was the best to define the color changes of canned green peas, meanwhile Garrote, Silva, Bertone, and Roa (2006) studied surface color changes during end over end sterilization of fresh green peas, using the a* value as a measure of green color change.

Isothermal and dynamic thermal approaches have been used to determine kinetic parameters (Lenz & Lund, 1980). In steady-state procedures the thermal lag (heat up or cool

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Nomenclature

a*	value of a* at time t
a^*_o	initial value of a*
a^*_f	value of a* at long times
A_c	surface area of the can, m^2
A_p	surface area of green peas, m^2
C_p	specific heat of brine, kJ/kg°C
E_a	activation energy, kJ/mol
F_R	sterilizing value, minutes at 121.11 °C
h_{fp}	fluid to particle heat transfer coefficient, W/m^2°C
k	specific rate constant, s^{-1}
k_p	thermal conductivity of green peas, W/m°C
m_l	mass of brine, kg
n_p	number of green peas in the can
r	radial coordinate, m
R_g	universal gas constant, kJ/molK
T	temperature, °C or K
T_a	retort temperature, °C
T_{ah}	variable retort temperature during come-up time, °C
T_{ac}	variable retort temperature during come down time, °C
T_{ao}	initial retort temperature, °C
T_c	center temperature of green peas, °C
T_l	brine temperature, °C
T_{ps}	surface temperature of green peas, °C
T_w	cooling medium temperature, °C
T_{wo}	initial temperature of cooling stage, °C
t	time, s
t_t	total time, s
t_h	heating time, s
t_c	cooling time, s
U	overall heat transfer coefficient, W/m^2°C
x_s	surface color retention of green peas

Greek symbols

α_p	thermal diffusivity of green peas, m^2/s
τ_h	retort time constant during heating, s^{-1}
τ_c	retort time constant during cooling, s^{-1}

down) is insignificant compared with overall processing time and degradation reaction is considered to occur at constant temperature. The required data are concentration of the degraded attribute and heating time at constant temperature. In unsteady-state procedures the degradation reaction occurs at a variable temperature and the data required are concentration of the degraded factor or attribute and the temperature profile of the sample during the heating-cooling process (Rodrigo, Mateu, Alvarruiz, Chinesta, & Rodrigo, 1998). The unsteady-state procedure is more flexible and can be applied to uniform and non-uniform heating situations; besides, a food medium, rather than an aqueous buffer solution, is always used for determining kinetic parameters (Welt et al., 1997). Svensson and Eriksson (1974) studied the thermal inactivation of lipoxygenase in green peas, but using kinetic parameters previously determined in green peas press juice. Naveh, Mizrahi, and Kopelman (1982) and Luna, Garrote, and Bressan (1986) studied the thermal destruction of peroxidase in the blanching of corn-on-the cob, considering the corn cob as a finite homogeneous cylinder. Rodrigo et al. (1998) used an unsteady-state method for estimating texture degradation during heating–cooling of green asparagus spears. Garrote, Silva, and Bertone (2001) determined kinetic parameters of lipoxygenase inactivation during blanching of cut green beans using two unsteady-state procedures.

The objective of this work was to determine the kinetics parameters of surface color degradation of canned fresh green peas sterilized in a rotary retort, using the a* value as the physical parameter and the concept of fractional conversion in conditions of unsteady state.

2. Materials and methods

2.1. Materials

Green peas: Green peas (Utrillo XPF 131 variety) were obtained from fields around the city of Santa Fe (Argentina); they were shelled, sized (diameter 10 mm) and immediately processed (Garrote, Bertone, Silva, & Avalle, 2001).

Preparation: Green peas (220 g) were blanched in water at 100 °C during 1 min, drained and immediately placed into a can (inner diameter = 69.8 mm and height = 107 mm); a brine, aqueous solution of NaCl (2 g/100 ml) and sucrose (1.5 g/100 ml) at 95–100 °C was added to the can up to the prescribed headspace; the can was exhausted during 0.5 min at 95–100 °C, closed with a closing machine Paduch (model RTF 20) and cooled in chilled water at 0–4 °C to reach an average temperature of 20 °C; immediately after cooling the reference can was opened, brine was separated from green peas, and surface color in green peas was determined (see corresponding section). For each sterilizing run three cans were prepared as previously described; in one of the cans a thermocouple was placed into the center of a nylon sphere (diameter 10 mm) and this placed in the center of the can; another was placed into the retort processing water. The three cans were placed inside the retort basket, at its center and along its shaft. Six cans, filled with water, were placed at both sides (10 cm) of the three cans with the green peas. The dimensions of the nine cans were identical to the previously mentioned reference can. Thermocouples Ellab Type T were used in every case and a Fluke Data Logger, model 2625 A, was used for the recording of temperature–time relationships.

Processing: Green peas were sterilized in a pilot plant rotary retort designed by the working group and locally constructed. The equipment consists of a cylindrical process vessel (45 liters), a cylindrical storage vessel (600 liters), recirculating and cooling water pumps, a water-steam heat exchanger, a digital thermo-regulator, temperature recording and control elements. Thermal treatment of canned foods can be done either with saturated live steam (highest working pressure 5 kg/cm^2) or (immersion or sprayed) hot water recirculated through a water-steam heat exchanger to keep the maximum temperature (160 °C). Inside the process vessel, the basket can rotate at 0–60 rpm. All runs were carried out to give an end-over-end rotation to the samples while in process, accordingly to conditions presented in Table 1. The temperature of the process water in the storage vessel was initially heated to 15 °C above the operating temperatures and was quickly transferred to the process vessel so that a come-up time of less than 2 min was achieved. At the end of heating, the product was cooled by rapidly replacing the sterilizing water with cold water while maintaining a constant working pressure (Lekwauwa & Hayakawa, 1986). The temperature responses of the samples were collected at intervals of 0.5 min at 120 °C and of 0.25 min at 130 °C. Heating step was finished when the sterilizing value at reference temperature of 121.11 °C in the center of the nylon sphere was 5 min; cooling time was equal to heating time.

2.2. Methods

To determine the kinetic parameters for green color loss using the a* value as the physical parameter, the concept of fractional conversion was applied; fractional conversion is a convenient variable often used in place of concentration. In many instances it may be useful to determine a physical property that can be directly and easily measured by an instrument, instead of concentration, to monitor the extent of a chemical reaction (Steet & Tong, 1996).

For determining kinetic parameters of surface color degradation, a set of kinetic data (rate constants vs temperatures of a first-order reaction) must be assumed; from this assumed model the surface color fractional retention is calculated as

$$(x_{\text{surface}})_{\text{calc.}} = \exp\left\{-k_{\text{ref.}}\left\{\int_0^{t_t} \exp\left[-\frac{E_a}{R_g}\left(\frac{1}{T_{\text{ps}}}-\frac{1}{T_{\text{ref.}}}\right)\right] \mathrm{d}t\right\}\right\}, \tag{1}$$

where $x_{\text{surface}} = (a^* - a_f^*)/(a_o^* - a_f^*)$.

When x_{surface} was obtained a new value for the rate constant could be calculated by

$$k_{i+1} = \ln(x_{\text{surface}})_{\text{calc.}}\, k_i / \ln(x_{\text{surface}})_{\text{exp.}}. \tag{2}$$

These new rate constants were used to obtain by regression a new E_a; calculations were repeated in successive iterations until the calculated fractional retentions were equal or proximate to the experimental fractional retentions.

In order to obtain x_{surface}, T_{ps} as a functions of time must be known; the following equations must be solved simultaneously for heating and cooling stages, by numerical methods (Chandarana & Gavin, 1989; Sastry, 1986).

2.2.1. Heating stage

(a) Energy balance,

$$UA_c(T_{\text{ah}} - T_l) = m_l C_{\text{pl}} \mathrm{d}T_l/\mathrm{d}t + h_{\text{fp}} n_p A_p (T_l - T_{\text{ps}}). \tag{3}$$

(b) Governing equation during unsteady conduction during heating in a sphere,

$$\partial T/\partial t = \alpha_p(\partial^2 T/\partial r^2 + 2/r\partial T/\partial r) \tag{4}$$

$$\text{Initial condition}: \quad T(r,0) = T_0. \tag{5}$$

$$\text{Simmetry condition}: \quad \partial T(0,t)/\partial r = 0. \tag{6}$$

$$\text{Boundary condition}: \quad k_p \partial T(R,t)/\partial r = h_{\text{fp}}(T_l - T_{\text{ps}}). \tag{7}$$

(c) Exponential variation of heating medium temperature in the retort

$$T_{\text{ah}} = T_{\text{ret.}} - (T_{\text{ret.}} - T_{\text{ret.o}})\exp(-\tau_{\text{hret.}} t). \tag{8}$$

Table 1
Experimental conditions used and heat transfer coefficients assumed during sterilization of canned green peas

Run	Rotation speed, rpm	Headspace, mm	Retort temperature, °C	Initial temperature, °C	Heating time[a], s	U, W/m^2 °C	h_{fp}, W/m^2 °C
1	10	8	120.57	21.9	621.9	740	1323
2	5	4	120.52	20.5	709.7	523	655
3	5	12	120.64	19.4	682.6	579	800
4	15	4	120.47	24.2	695.1	552	750
5	15	12	120.74	23.8	558.9	851	1632
6	10	12	130.86	23.6	269.9	905	1950
7	10	4	130.86	24.6	290.8	701	1124
8	15	8	129.21	24.3	321.9	871	1805

[a]Cooling time = heating time.

(d) Sterilizing value at the center of the particle

$$(F_R)_{heating} = \int_0^{t_h} 10^{(T-121.11/10)} dt. \quad (9)$$

2.2.2. Cooling stage

(e) Energy balance

$$h_{fp} n_p A_p (T_{ps} - T_l) + m_l C_{pl} dT_l/dt = U A_c (T_l - T_{ac}). \quad (10)$$

(f) Governing equation during unsteady conduction during cooling in a sphere,

$$\partial T/\partial t = \alpha_p (\partial^2 T/\partial r^2 + 2/r \partial T/\partial r). \quad (11)$$

$$\text{Initial condition :} \quad T(r,0) = f(r). \quad (12)$$

$$\text{Simmetry condition :} \quad \partial T(0,t)/\partial r = 0. \quad (13)$$

$$\text{Boundary condition :} \quad k_p \partial T(R,t)/\partial r = h_{fp}(T_{ps} - T_l). \quad (14)$$

(g) Exponential variation of cooling medium temperature in the retort

$$T_{ac} = T_w + (T_{wo} - T_w) \exp(-\tau_{cret.} t). \quad (15)$$

(h) Sterilizing value at the center of the particle

$$(F_R)_{cooling} = \int_{t_h}^{t_c} 10^{(T-121.11/10)} dt. \quad (16)$$

Differential equation for unsteady conduction in a sphere was solved using a finite difference method with explicit scheme, being $\Delta r = 0.0005$ m and $\Delta t = 0.2$ s. Thermal diffusivity and thermal conductivity of green peas were assumed to be 1.54×10^{-7} m^2/s and 0.5 W/m K respectively (Holdsworth, 1997). Green peas experimental density was 1062 kg/m^3; with the density and the weight of green peas the number of particles could be calculated. Measured surface area of the can, A_c, was 0.0317 m^2. Brine heat capacity was estimated from its composition at an average temperature between retort temperature and initial temperature (Heldman & Lund, 1992). U and h_{fp} were taken from Garrote, Silva, Roa, and Bertone (2006). τ_h and τ_c were determined by nonlinear regression from experimental heating and cooling retort temperature accordingly to Eqs. (8) and (15), using the program Statgraphic (Statistical Graphic System Plus for Windows 3.0). a_f^* was determined at 110 °C after a processing time of 3 h. T_w was 20 °C.

Per cent deviation between experimental and predicted fractional retentions obtained with the kinetics parameters determined, was calculated as

$$\%\ \text{deviation} = \sqrt{\frac{\sum((x_{pred.} - x_{exp.})/x_{exp.})^2}{n-1}} \times 100, \quad (17)$$

where $n = 8$.

Determination of surface color in green peas. Surface color of green peas of the reference can and the sterilized cans were determined using a spectrophotometer Minolta CR-508d (Minolta Corp., Ramsey, NJ, USA). Color was recorded using a CIE – a* uniform color space where a* indicates chromaticity on a green (−) to red (+) (Rocha & Morais, 2003). Green peas were drained and surface dried with absorbent paper and placed in an excavated wood plate in order to fix its position before recording the color. The focusing of green peas with the measuring opening of the colorimeter was practically individual, performing the readings in at least 10 green peas, and taking an average of a* values. Tests concerning the mean difference of two independent normal distributions with equal but unknown variances were performed to compare the averages of a_o^* and a* values.

3. Results and discussion

Table 1 shows rotation speeds, headspaces, retort temperatures, initial temperatures and heating times to obtain a sterilizing value of 5 min, used in the different experimental runs performed; it also shows the heat transfer coefficients assumed for the predictions necessary for the determination of the kinetic parameters of color degradation (Garrote, Silva, Roa et al., 2006); cooling times were equal to heating times. Table 2 shows the time constants of retort during heating and cooling ($R^2 > 0.99$), theoretical center temperatures of green peas at the end of heating and total sterilizing values, and average experimental values of a_o^* and a*, determined for all the runs. Deviation between experimental and theoretical total sterilizing values was 3.40%; this very good agreement shows that temperatures of green peas were predicted satisfactorily.

At long times, more than three hours at 110 °C, the average value of a_f^* obtained was 4.53. Although for all the runs the sterilizing value at heating was of 5 min, total sterilizing values at a retort temperature of 130 °C almost doubled the total sterilizing values at 120 °C, but surface color was greater at 130 °C, because heating and cooling times were lower (means of a* values at 130 °C were statistically different to those at 120 °C); better color quality of green peas may be obtained working at higher temperatures-shorter times during end-over-end sterilization (Garrote, Silva, Bertone, et al., 2006).

In order to determine the kinetic parameters, it was necessary to assume a pair of values of $k_{100\,°C}$ and E_a to start with the iterations; the values of $k_{100\,°C} = 8.57 \times 10^{-4}$ s^{-1} and $E_a = 52.4$ kJ mol^{-1} given by Smout et al. (2003) for **a** value were adopted. Table 3 shows the

Table 2
Retort time constants, theoretical center temperatures of green peas at the end of heating and total sterilizing values, and average experimental a_o* and a* values obtained during the runs performed

Run	τ_h, ($\times 10^2\,s^{-1}$)	τ_c, ($\times 10^3\,s^{-1}$)	T_c, at the end of heating, °C	$(F_R)_{total}$, min.	a_o*	a*
1	4.2	4.98	120.56	5.67	−15.70[a] (1.307)	−1.44[a] (0.544)
2	10	5.02	120.47	5.77	−14.89[a] (0.532)	−0.458[b] (0.554)
3	2.9	5.01	120.61	5.72	−14.89[a] (0.532)	−0.165[b] (0.555)
4	10	5	120.43	5.75	−15,57[a] (0.694)	−0.733[a,b] (0.891)
5	7.6	5	120.73	5.66	−15.57[a] (0.694)	−1.798[a,c] (0.827)
6	3.2	5	128.86	10.70	−15.66[a] (0.368)	−4.75[d] (1.208)
7	9	5.03	128.32	10.81	−14.40[a] (1.437)	−3.155[e] (1.094)
8	2.4	4.97	127.72	9.34	−14.40[a] (1.437)	−3.190[e] (1.122)

a_f* = 4.53. Means with different superscripts in the same column are significantly different ($P<0.05$). Standard deviations are shown between parenthesis ($n = 10$).

Table 3
Experimental and theoretical fractional retentions of surface color of green peas for the iterations performed

Run	Experimental fractional retention of surface color	Theoretical fractional retention of surface color				
		$k_{100\,°C} = 6.78\times10^{-4}\,s^{-1}$ $E_a = 69.09$ kJ/mol $R^2 = 0.9756$	$k_{100\,°C} = 6.05\times10^{-4}\,s^{-1}$ $E_a = 79.78$ kJ/mol $R^2 = 0.9783$	$k_{100\,°C} = 5.74\times10^{-4}\,s^{-1}$ $E_a = 85.20$ kJ/mol $R^2 = 0.9816$	$k_{100\,°C} = 5.55\times10^{-4}\,s^{-1}$ $E_a = 88.05$ kJ/mol $R^2 = 0.9822$	$k_{100\,°C} = 5.48\times10^{-4}\,s^{-1}$ $E_a = 89.37$ kJ/mol $R^2 = 0.9824$
1	0.2951	0.3107	0.2984	0.2897	0.2871	0.2847
2	0.2568	0.2766	0.2665	0.2589	0.2569	0.2549
3	0.2418	0.2957	0.2846	0.2764	0.2741	0.2719
4	0.2618	0.2801	0.2697	0.262	0.2599	0.2578
5	0.3148	0.3299	0.3164	0.3070	0.3041	0.3016
6	0.4596	0.4968	0.4717	0.4558	0.4493	0.4451
7	0.4060	0.4613	0.437	0.4216	0.4150	0.4113
8	0.4078	0.4748	0.4526	0.4381	0.4324	0.4285
	% Deviation	12.97	8.65	6.39	5.91	5.68

For each iteration the successive $k_{100\,°C}$ and E_a are shown.

results obtained for the iterations performed; the last iteration gave the minimum deviation between the experimental and theoretical fractional retentions of surface color, 5.68%, being the kinetic parameters obtained, $k_{100\,°C} = 5.48\times10^{-4}\,s^{-1}$ and $E_a = 89.37\,kJ\,mol^{-1}$. Steet and Tong (1996) obtained an activation energy of $76.2\,kJ\,mol^{-1}$ and $k_{100\,°C} = 6.09\times10^{-4}\,s^{-1}$ for green peas color degradation measured in terms of the **a** value, also using the fractional conversion concept but using a steady state method; their results were similar to those obtained in this work, using an unsteady state methodology (see Table 3, iteration with a deviation of 8.65%). The mentioned authors determined that the kinetic parameters for loss of greenness fell between those of chlorophyll *a* and *b* indicating that green color loss was a consequence of losing both chlorophyll *a* and *b*; the activation energies determined were, for the range 70–90 °C, $81.6\,kJ\,mol^{-1}$ for chlorophyll *a* and $71.6\,kJ\,mol^{-1}$ for chlorophyll *b*; Lenz and Lund (1977) obtained for the degradation of chlorophyll in green peas puree in the range 115.55–137.77 °C, an activation energy of $92\,kJ\,mol^{-1}$; kinetic parameters

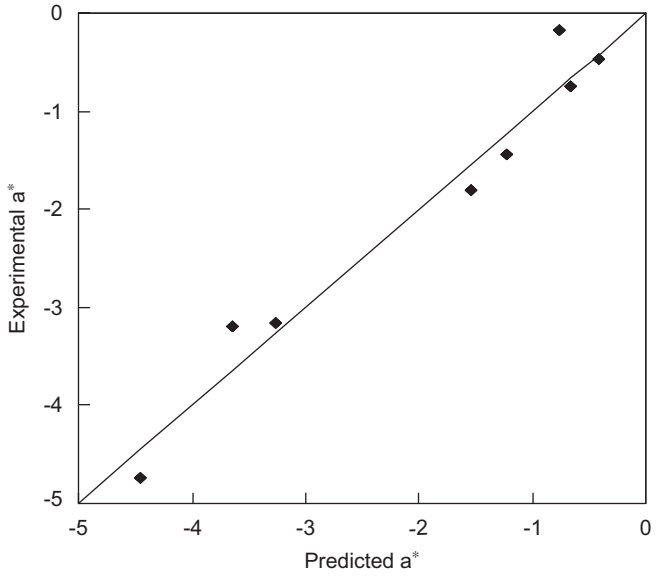

Fig. 1. Comparison of experimental and predicted a* values obtained with the kinetic parameters determined: __ predicted values, ◆ experimental values.

determined in our work were very close to those obtained by the last mentioned authors, probably because the range of temperatures used in both cases were very similar.

Fig. 1 compares experimental and predicted a* values obtained using the kinetic parameters determined, being the agreement very satisfactory. Determined kinetic parameters may be used to optimize the end-over-end sterilization of canned green peas in order to obtain maximum retention of surface green color.

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