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Kinetics of textural and color changes in green asparagus during thermal treatments

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Abstract

The textural and green color degradation of asparagus were determined after heat treatments at temperatures between 70°C and 98°C for selected time intervals. Maximum shear stress required to cut through green asparagus and the hue angle of the spear surface color were selected to represent the textural and color changes in thermally treated asparagus. Thermal softening of asparagus followed a first order kinetic reaction. The activation energies for softening of asparagus were 24.0 ± 0.5 kcal/mol and kinetic reaction rates ($k_{84°C}$) ranged from 0.016 min^{-1} at the butt segment to 0.027 min^{-1} at the bud segment of the spears. Green color changes of asparagus spear surface followed a first order reaction. The activation energies for green color degradation of asparagus were 13.1 ± 0.2 kcal/mol and kinetic reaction rates at 84°C were 0.0066 ± 0.0002 min^{-1}. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Asparagus; Texture; Color; Kinetics; Pasteurization

1. Introduction

Fresh asparagus is gaining popularity due to its unique texture and flavor. The color and texture of asparagus are, however, sensitive to thermal treatments such as cooking, blanching, or pasteurization. Vegetables softening during those treatments follows first order kinetics (Loh & Breene, 1981; Nicholas & Pflug, 1962; Paulus & Saguy, 1980). Lengthy heating of vegetables in canning results in additional softening described by a second simultaneous first order kinetics (Huang & Bourne, 1983). Rodrigo, Rodrigo, Fiszman and Sanchez (1997) studied the kinetics of thermal softening of asparagus texture after heating between 70°C and 100°C using Kramer cell and wire cell tests. They used the two-component first order kinetic model to describe textural softening of asparagus. The activation energies for the textural softening of asparagus determined by Rodrigo et al. (1997) ranged from 9.56 to 23.41 kcal/mol.

Prolonged cooking of asparagus has an olive green color compared to the bright green color of mild heat treated asparagus. Color changes in green vegetables during thermal processing are the result of the conversion of chlorophyll to pheophytin, through the magnesium substitution of the chlorophyll by hydrogen (Woolfe, 1979). The conversion of chlorophyll to pheophytin follows first order reaction kinetics (Schwartz & Von Elbe, 1983). Many studies used chromatography method to quantify the conversion of chlorophyll to pheophytin to represent the color degradation of green vegetables (Canjura, Schwartz & Nunes, 1991; Steet & Tong, 1996). More than 50% conversion of the chlorophyll to pheophytin must occur before a change of color from bright green is observed (Mackinney & Joslyn, 1941; Woolfe, 1979). A chromatography method to quantify the conversion of chlorophyll to pheophytin might not be suited in the measurement of the color intensity on the surface of thermally treated green vegetables. In those cases, a direct measurement of color changes may be more appropriate. Hayakawa and Timbers (1977) reported that the color change from the natural green to an olive brown of asparagus puree followed first order reaction kinetics and the activation energy for the color changes was 18.08 kcal/mol. Since asparagus is often served as a spear, examination of the change in the spear surface color is desired. No reports are available assessing color changes of asparagus spear surface. The objective of this study was to develop

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Nomenclature

S_m	maximum shear stress (Pa)	t	time (min)
F_m	maximum shear force (N)	k	rate constant (min^{-1})
D	diameter (m)	n	order of reaction
$\pm L$	lightness-darkness	k_A	Arrhenius equation constant (min^{-1})
$\pm a$	red-green	E_A	activation energy (kcal/mol)
$\pm b$	yellow-blue	R	universal gas constant (1.987 kcal/mol K)
$\tan^{-1}(b/a)$	hue angle	T	temperature (K)
P	food property	θ	hue angle (°)

kinetic models to describe the textural and color changes of green asparagus spears during heating in the temperature range applicable to short time cooking, blanching and pasteurization.

2. Materials and methods

2.1. Thermal treatments

Fresh asparagus (*Asparagus officinalis* L. var. Mary Washington) was obtained from a local grocery store (Pullman, WA). The spears were washed with tap water and drained. Twenty-five asparagus spears were placed in distilled water baths set at 70°C, 80°C, 90°C or 98°C. Five spears were removed at the time intervals listed in Table 1 and immediately cooled in running water at 17°C.

2.2. Instrumental analysis of texture

A standard method for quantifying asparagus texture is not yet available. Textural measurements based on shearing through asparagus spears reported by Rodrigo et al. (1997) may be appropriate. Large variations in the textural measurements may, however, result from inherent variation in the diameter of asparagus spears when maximum force necessary to cut through the spears is used as a measure of texture. Based on preliminary studies comparing selected test methods to evaluate the spears, the maximum shear stress (shear force/cross-sectional area) appeared to be a more consistent indicator for evaluation of the asparagus texture. In this study, maximum shear stress was used to measure the textural changes of green asparagus during thermal treatments.

Table 1
Heating time and temperature for fresh asparagus

Temperature (°C)	Heating time (min)			
70 ± 0.2	30	60	90	120
80 ± 0.2	20	40	60	80
90 ± 0.2	15	30	45	60
98 ± 0.2	5	10	20	30

Prior to the textural measurements, asparagus spears at room temperature were cut into three segments as shown in Fig. 1. The mean diameter of each segment was measured and the cross-sectional area was calculated. Maximum force required to cut through sample was determined with a TA.XT2 Texture Analyzer (Texture Technologies, Scarsdale, NY/Stable Micro Systems, Godalming, Surrey, UK) interfaced with a personal computer. The TA.XT2 Texture Analyzer was fitted with a single blade (10 cm × 0.3 cm) and a test cell (8.8 cm × 10 cm) (Texture Technologies, Scarsdale, NY/Stable Micro Systems, Godalming, Surrey, UK). Each shear test was performed at a cross-head speed of 3.0 mm/s. The maximum shear stresses were determined using the following equation:

$$S_m = \frac{F_m}{2(\pi D^2/4)}, \tag{1}$$

where S_m is the maximum shear stress (Pa), F_m the measured maximum force (N) that cut through the specimen and D is the diameter (m) of the test segment of a asparagus spear. The kinetic experiments for textural degradation of green asparagus were carried out in five replicates.

2.3. Color measurements

A Minolta colorimeter (Minolta Spectrophotometer CM-2002, Minolta Camera, Japan) was used to determine the 'L', 'a' and 'b' values for the surface of thermally treated asparagus samples. Ten spear readings of the bud and butt segments of the asparagus spears were

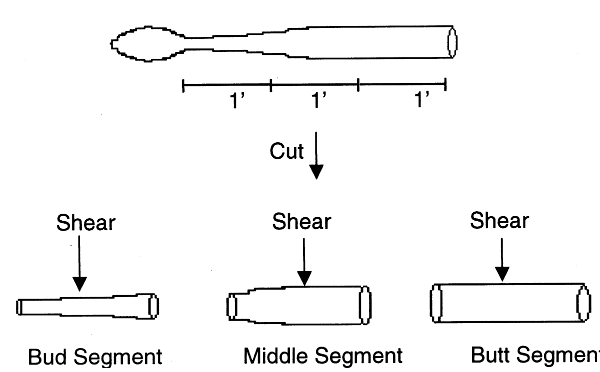

Fig. 1. Specimens for measuring maximum shear stresses.

taken for the color measurement, respectively. Mazza and Oomah (1994) indicated that for whole peas, tristimulus color values (L, a and b) were poorly correlated with chlorophyll contents. The chromatic function of hue, however, correlated well with chlorophyll contents and can be used to predict the psychosensorial evaluation of color in whole dry green peas. The color changes of asparagus due to thermal treatments were interpreted by calculating the hue angle. The hue angle, which describes the hue (the attribute by which a color is identified as green, yellow, red, etc.), was obtained by calculating $\tan^{-1}$ 'b'/'a' (Little, 1975).

2.4. Kinetic modeling of textural and color degradation

The reaction order of the textural and color degradation of green asparagus was determined by a graphical method described in Swinbourne (1971). A linear regression analysis was performed on the plot of shear stress versus time for the zero order, half order, first order and second order of reactions. The best fitted line was decided by examining the coefficient of determination (r^2) (Hill & Grieger-Block, 1980).

The rate of change in food properties during heating can be modeled as

$$\frac{dP}{dt} = \pm kP^n, \tag{2}$$

where P is the food property, t the time, k the rate constant and n is the kinetic order of the reaction (Labuza & Riboh, 1982). The rate constant is temperature dependent and often follows the Arrhenius relationship (Taoukis, Labuza & Saguy, 1997):

$$k = k_{\text{ref}} \exp\left(-\frac{E_A}{R} \left[\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right] \right), \tag{3}$$

where k_A is the reaction rate constant (min^{-1}), E_A the activation energy (kcal/mol K), R the universal gas constant (1.987 cal/mol K), T the absolute temperature (K) and k_{ref} is the reaction rate constant (min^{-1}) at the reference temperature (T_{ref}). The reference temperature selected for this study was 84°C, the mean temperature of 70°C and 98°C.

3. Results and discussion

3.1. Textural changes

Fig. 2 presents typical results on the changes of maximum shear stress to cut through asparagus spears as treatment time increased at each temperature. The shear stress to cut asparagus decreased with an increase in heating time and temperature. The reduction of asparagus shear stress may be attributed to the loss of mechanical strength as well as the adhesion of cell walls (Van Buren, 1979).

The results from graphical determination of reaction order are summarized in Table 2. The r^2 values indicated a first order reaction of the thermal degradation of asparagus texture. The reaction rate constant was calculated from the slope of Ln (shear stress) versus time using linear regression analysis (Fig. 2). The reaction rate constants for the butt, middle and bud segments were 0.016, 0.023 and 0.027 min^{-1}, respectively. The differences in rate constant might have resulted from the increase in the amount of fiber content from the bud to the butt segments of asparagus. Hayakawa and Timbers (1977) also observed that the hardness of asparagus gradually increased from the tip to the base of the asparagus spears.

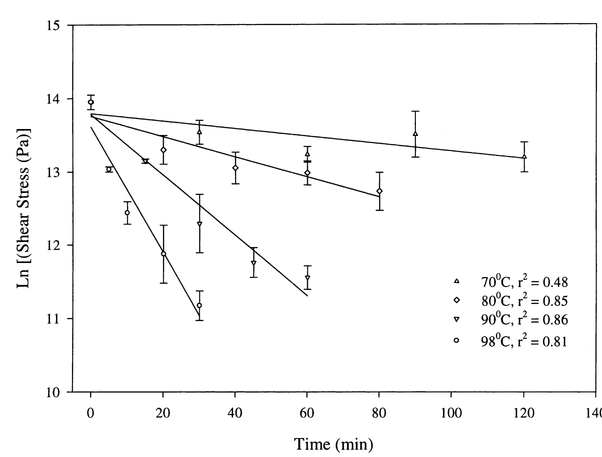

Fig. 2. Maximum shear stress (Pa) for middle segment of asparagus spears.

Table 2
Estimation of the order of textural degradation of green asparagus by examining the r^2 from plots of zero, half, first and second order reactions

Temperature (°C)	0 order, S_m vs time	1/2 order, $S_m^{0.5}$ vs time	1st order, $\ln S_m$ vs time	2nd order, $1/S_m$ vs time
70	0.45	0.46	0.48	0.49
80	0.76	0.82	0.85	0.77
90	0.67	0.78	0.86	0.82
98	0.54	0.67	0.81	0.91

Table 3
Kinetics information for textural degradation of green asparagus due to thermal treatments

Reaction rate and activation energy	Butt segment	Middle segment	Bud segment
$k_{70°C}$ (min^{-1})	0.0034 ± 0.0013	0.0050 ± 0.0012	0.0060 ± 0.0013
$k_{80°C}$ (min^{-1})	0.0104 ± 0.0015	0.0137 ± 0.0018	0.0191 ± 0.0017
$k_{90°C}$ (min^{-1})	0.0271 ± 0.0028	0.0419 ± 0.0030	0.0493 ± 0.0041
$k_{98°C}$ (min^{-1})	0.0618 ± 0.0054	0.0859 ± 0.0061	0.0983 ± 0.010
k_{ref} (min^{-1})[a]	0.0160 ± 0.0005	0.0228 ± 0.0018	0.0270 ± 0.0023
E_a (kcal/mol K)	24.5 ± 0.7	24.5 ± 1.2	23.5 ± 1.7

[a] Reference temperature was 84°C.

3.2. Activation energy for textural degradation

The activation energy (E_A) of the thermally induced textural degradation in asparagus was calculated based on the Arrhenius relationship described by Eq. (3). The activation energies for the butt, middle and bud segments of asparagus were 24.5, 24.5, and 23.5 kcal/mole, respectively (Table 3). These values fall in the range of the reported activation energies (19.5–28.0 kcal/mol) for softening of whole corn, peas, beans and potatoes (Rao & Lund, 1986).

Although the rate constant for texture softening of the asparagus bud segment was larger than the butt segment, the activation energies for butt, middle and bud segments of asparagus were not significantly different ($P > 0.05$) (Fig. 3). Lund (1986) concluded that reaction rates of fruits and vegetables at a reference temperature are sample-specific and strongly depended on the pH, oxygen, and presence of other constituents. Environmental factors have, however, less influence on the Arrhenius activation energies of fruits and vegetables compared to reaction rates. For plant tissues, the activation energies are in the range associated with chemical reactions such as hydrolysis of cell wall constituents, swelling due to expansion of gasses, and heat induced changes in water holding capacity that can affect the plant tissues (Lund, 1986). Since the fiber content in three longitudinal regions of asparagus spears has little influence on Arrhenius activation energy, the softening mechanism of asparagus tissue may be identical throughout the spears.

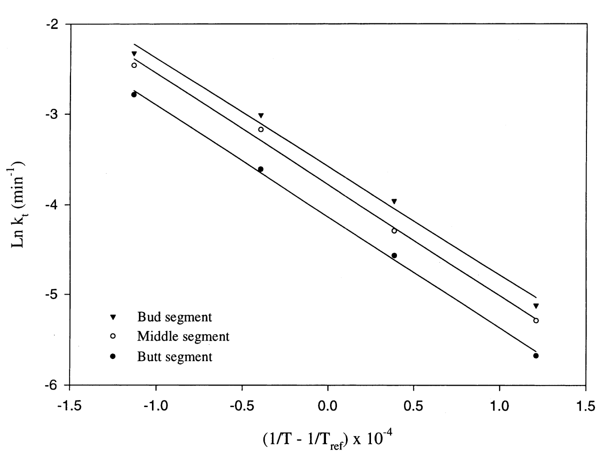

Fig. 3. Arrhenius plot for textural changes in three different segments of asparagus spears.

Rodrigo et al. (1997) reported activation energies of 20.43 and 18.32 kcal/mol (using Kramer cells) and 9.56 and 23.41 kcal/mol (using cutting wire) for a two-component first order kinetic model for the thermal degradation of green asparagus. Those activation energies are smaller than the activation energies measured in this study. The difference might have been resulted from different method used in sample preparation and textural measurements. The two-component kinetic models are applicable to the thermal softening of vegetables at high temperatures over long processing times (Huang & Bourne, 1983). In this study, the one-component kinetic model was adequate to describe the textural changes of asparagus in the tested temperature range.

3.3. Color changes

An initial brightening of the green color is observed during the early heating of asparagus. The bright green color is attributed to removal of air around the fine hairs on the surface of asparagus spears and the expulsion of air between the cells that lead to a change in the surface reflecting properties (Woolfe, 1979). Further heating caused the color of asparagus spears to change from bright green to olive-brown which is attributed to the pheophytinization (Francis, 1985).

Hue angle of the butt and bud segments decreased from 140° to 90° with increase in heating times (Fig. 4 for middle segment). The reduction in hue angle corresponds to a decrease in the intensity of greenness and an increase in yellowness (Little, 1975). The reduction in hue angle from this study agrees with the results reported by Woolfe (1979) that prolonged heating of green vegetables caused deterioration of the chlorophyll pigments that led to a color change from green to olive green, and eventually to yellow.

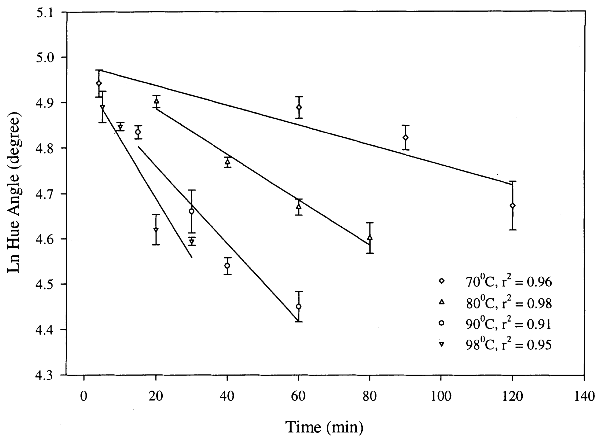

Fig. 4. Hue angle of thermally treated asparagus (butt segment).

The change of the hue angle can be described by a general kinetic reaction:

$$\frac{d\theta}{dt} = \pm k\theta^n, \quad (4)$$

where θ is the hue angle (degree), t the time (min), k the rate of color changes due to thermal treatment (min^{-1}) and n is the order of reaction. Results from graphical determination of reaction order for color changes of green asparagus are summarized in Table 4. The values of r^2 from the graphical determination indicated a first order reaction for color changes of asparagus due to thermal treatment. Other studies conclude that color degradation, obtained by the color reflectance of green vegetables, followed a first order kinetic model (Hayakawa & Timbers, 1977; Shin & Bhowmik, 1995). The reaction rate constants for color changes on the surface of bud segments of the asparagus spears were smaller than that for the butt segment (Table 5).

Table 4
Estimation of the order of color changes of green asparagus by examining the r^2 from plots of zero, half, first and second order reactions

Temperature (°C)	0 order, θ vs time	1/2 order, $\theta^{0.5}$ vs time	1st order, $\ln\theta$ vs time	2nd order, $1/\theta$ vs time
70	0.97	0.97	0.96	0.77
80	0.85	0.97	0.98	0.91
90	0.89	0.89	0.91	0.74
98	0.93	0.95	0.95	0.99

Table 5
Kinetics information for color changes of green asparagus due to thermal treatments

Reaction rate and activation energy	Bud segment	Butt segment
$k_{70°C}$ (min^{-1})	0.0029 ± 0.0002	0.0032 ± 0.0002
$k_{80°C}$ (min^{-1})	0.0050 ± 0.0002	0.0054 ± 0.0004
$k_{90°C}$ (min^{-1})	0.0087 ± 0.0005	0.0069 ± 0.0006
$k_{98°C}$ (min^{-1})	0.0130 ± 0.0010	0.0167 ± 0.0010
k_{ref} (min^{-1})[a]	0.0064 ± 0.0001	0.0068 ± 0.0007
E_a (kcal/mol K)	12.9 ± 0.4	13.2 ± 2.3

[a] Reference temperature was 84°C.

3.4. Activation energy for color changes

The activation energies for color changes of asparagus obtained from the slope of the Arrhenius plots were 12.9 kcal/mol for the bud segment and 13.2 kcal/mol for the butt segment, respectively (Table 5). These values were not significantly different ($P > 0.05$). The activation energies for color changes in green asparagus were smaller than the activation energy of asparagus color changes (18.08 kcal/mol) reported by Hayakawa and Timbers (1977). The results from this study, however, agree with reported activation energies (15.2 and 7.6 kcal/mol) for thermal degradation of chlorophyll a and b in spinach puree (Gupte, El-Bisi & Francis, 1964).

4. Conclusions

Maximum shear stress obtained by cutting through the spears using a TA.XT2 Texture Analyzer was used to determine textural softening during the thermal process of green asparagus. The thermal softening of green asparagus spears at temperatures between 70°C and 98°C followed a first order reaction, with an activation energy of 24.0 ± 0.5 kcal/mol. The reaction rate constants for texture softening at butt, middle, and bud segments at 84°C were 0.0160, 0.0228, and 0.0270 min^{-1}, respectively. Asparagus surface color changes (from green to olive-green) followed a first order Arrhenius reaction kinetics. The activation energy was estimated to be 13.1 ± 0.2 kcal/mol. The kinetics data for textural and color degradation of asparagus spears should be useful for designing mild heat treatments, such as blanching, cooking and pasteurization.

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