Thermal Kinetics of Color Change, Rheology, and Storage Characteristics of Garlic Puree/Paste

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ABSTRACT: Kinetics of color change of garlic puree at selected temperatures and rheological behavior and effects of packaging materials and storage temperatures on color of garlic paste were investigated. Results indicated that color change during thermal processing of garlic puree followed first-order reaction kinetics with an activation energy of 13.78 kJ/mol. Garlic paste behaved as a pseudoplastic material and flow activation energy at 100 rpm equaled 13.30 kJ/mol. Both temperature and duration of storage had effect ($P \leq 0.05$) on total color of garlic paste. Degreening of garlic paste was observed during storage at 25 °C and complete degreening occurred at about 48 to 52 d. Storage of garlic paste at 5 °C enhanced greening.

Key Words: garlic paste, kinetics, rheology, color, storage

Introduction

GARLIC (*ALLIUM SATIVUM* L) IS AN IMPORTANT *ALLIUM* SPEcies, known for its therapeutic uses and as a flavoring agent. It has been recognized as a valuable condiment in the everyday cooking in many cultures. Quality of garlic products is evaluated on the basis of their sensory characteristics, mainly color, flavor, and pungency. Garlic contains allicin, which makes it an antioxidant, antibacterial, and antibiotic (Augusti 1996) and is also responsible for the typical garlic flavor. Allyl-S-cysteine sulfoxide (allin) is converted to diallyl thiosulfinates (allicin) by action of allinase, an enzyme, and degrades to disulfides and thiosulfinates (Carson 1967).

Color is an important attribute because it is usually the 1st property the consumer observes (Saenz and others 1993). Various factors are responsible for the loss of color during processing of food products. These include Maillard and enzymatic browning and process conditions, such as pH, acidity, packaging material, and duration and temperature of storage. Generally, garlic paste should have light tan to cream color but greening of garlic products during preparation and storage has been recognized as a major quality problem (Sano 1950; Lukes 1986; Rejano and others 1997). Change in color during thermal processing could be used as a tool to evaluate the quality of garlic puree/paste. To optimize the process, it is important to determine the kinetic parameters (reaction order, reaction rate constant, activation energy) for color change (Weemaes and others 1999). The color kinetics of food products is a complex phenomenon, and dependable models to predict experimental color change, which can be used in engineering calculations, are scarce. Therefore, experimental studies and application of various simplified models to represent the behavior are required. Several authors studied the color kinetics of food materials during thermal processing in terms of changes in Hunter tristimulus color values *L, a,* and *b* (Shin and Bhowmik 1994; Kajuna and others 1998; Nanke and others 1999; Berry 1998; Weemaes and others 1999; Ahmed and others 2000). Hence, if the kinetics of color change is determined and the order of color change is established, the total color can be used to evaluate quality of food material during thermal processing. No information is available on thermal kinetics of garlic puree.

Knowledge of rheological properties of food puree/paste is essential for the product development and design and evaluation of the process equipment. Although, numerous studies have been conducted on the rheological properties of fruit and vegetable products (Rao 1977), no information is available on garlic paste.

The present study was undertaken to investigate: (1) the kinetics of color change of garlic puree at selected processing temperatures using the Hunter color scale values (*L, a, b*) or a combination of these; (2) physicochemical and rheological characteristics of garlic paste; and (3) the effects of temperature and packaging material on color during storage of garlic paste.

Materials and Methods

Preparation of puree

Fresh garlic bulbs (Variety: Punjab Selection-I) were procured locally after harvesting and stored at 25 ± 1 °C for 1 mo before processing. Garlic bulbs were subjected to mild pressure by hand to separate into cloves. Cloves were dried in a tray drier at 40 ± 1 °C for 30 min to facilitate peeling. Peeling was done manually. After peeling, cloves were blanched at 90 °C for 15 min in hot water followed by grinding in a laboratory size grinder. The ground material was passed through a 14-mesh sieve to obtain the product of uniform consistency.

Thermal treatment of puree

Thermal kinetics of garlic puree was studied by heating it at selected temperatures (70, 80, and 90 °C) for a residence time of 0 to 20 min. Approximately 200 g of puree was weighed and transferred into a 250-mL glass beaker and covered with a lid. The beakers containing puree were placed in a constant temperature water-bath at selected temperatures (± 1 °C) and periodically agitated to ensure uniform temperature throughout the bulk of the sample. The temperature of the sample at its geometric center was monitored using a thermometer. The beakers were heated for 0, 5, 10, 15, and 20 min, respectively, after the puree at its geometric center attained the desired temperature. The samples were transferred to an ice-water bath immediately after the thermal treatment.

Preparation of paste

Paste was characterized as the product obtained after adding salt and organic acid to puree. The paste was prepared by adding sodium chloride at 10% (w/w) to garlic puree to increase its total soluble solids (TSS). Fresh garlic puree had a pH of 5.8, and final pH of the paste was adjusted to 4.1 by adding 30% citric acid (w/v) solution. It is established that an acidified food (pH $<$ 4.6) requires only pasteurization (Garcia and others 1999). The paste was, therefore, thermally processed at 80 °C for 15 min and packaged immediately in selected containers: glass and polyethylene terephthalate (PET) and high-density polyethylene (HDPE) pouches. Storage studies were carried out at 25 $\pm$ 1 °C and 5 $\pm$ 1 °C for 124 d. The samples were analyzed periodically for color, total soluble solids (TSS), pH, and titratable acidity.

Color measurement

Color measurement was carried out using a Hunter colorimeter model D25 optical sensor (Hunter Assoc. Laboratory Inc., Reston, Va., U.S.A.) on the basis of 3 color values, namely *L, a,* and *b*. The instrument (45°/0° geometry, 10° observer) was calibrated against a standard cream reference tile (*L* = 76.74, *a* = -1.25, *b* = 21.58). A glass cell containing the heat treated product was placed above the light source and covered with a white plate and *L, a, b* values were recorded.

Model for computation of change in color

Degradation of color pigments has been shown to follow the first-order reaction kinetics (Huang and von Elbe 1985; Hutchings 1994; Shin and Bhowmik 1994; Toledo 1997; Ahmed and others 2000). Following these evidences, it was reasoned that the color change due to thermal treatment of garlic puree followed first-order reaction kinetics, represented by Equation 1:

$$\ln (C / C_o) = -k.t \qquad (1)$$

The Arrhenius equation to relate the dependence of the rate constant with temperature is represented by Equation 2:

$$k = k_o \exp (-E_c / RT_a) \qquad (2)$$

Rheological behavior of garlic paste

Apparent viscosity of the garlic paste was measured using a rheometer model RVDV-III (Brookfield Engg. Lab. Inc., Stoughton, Mass., U.S.A.) in the temperature range of 50 to 90 °C. The paste was placed in a 500-mL graduated glass beaker with flat bottom. The S-4 spindle was selected for the sample measurement and was used without spindle guard of the viscometer. The viscosity measurements were carried out between 30 and 150 rpm. Thermostatic water bath (TC 500) provided with the instrument was used to regulate the sample temperature ($\pm$1 °C). The activation energy was computed at constant rpm (η_{100}) using Equation 3:

$$\eta_a = \eta_\infty \exp (-E_a / RT_a) \qquad (3)$$

Physicochemical properties

Total soluble solids (°Brix) and pH were determined using a refractometer (Atago, Japan) at 20 °C and a pH meter with glass electrode (Systronics, India), respectively. To determine total solids, paste was dried under vacuum at 70 °C to constant weight (16 to 18 h) (Ranganna 1986). Titratable acidity was measured in terms of citric acid following the method described by Wang and others (1995). Five g paste diluted with 95 mL distilled water making the volume to 100 mL, filtered through Whatman 41 filter paper and titrated against 0.1 N NaOH, using phenolphthalein as an indicator. Sodium chloride was determined by titration with silver nitrate (Ranganna 1986). Water activity (a_w) of the product was determined following the method of Landrock and Proctor (1951). Each experiment was replicated twice, and the average values were used in the analysis.

Table 1—Selected combinations of the Hunter color scale values for garlic paste at 70 °C and the regression coefficients of Equation 1

S. Nr..	Combination	k, per min	Correlation coefficient	Standard error
1	*L*	0.001	0.81	0.0002
2	*-a*	0.009	0.99	0.0003
3	b	0.002	0.59	0.0003
4	*-La*	0.010	0.99	0.0003
5	*Lb*	0.003	0.97	0.0001
6	*-ab*	0.010	0.98	0.0004
7	*-L/a*	0.008	0.97	0.0004
8	*L/b*	0.001	0.48	0.0005
9	*-a/b*	0.007	0.96	0.0040
10	*-Lab*	0.012	0.99	0.0003
11	*-La/b*	0.008	0.95	0.0006
12	*-L/ab*	0.010	0.95	0.0006
13	*-bL/a*	0.006	0.96	0.0004

Statistical analysis

The influence of time and temperature of storage on color was determined by paired samples T-test using the Statistical Package for Social Science Research (SPSS 1996) software. Significance of differences was defined at $P \leq 0.05$.

Results and Discussion

THE PH AND ACIDITY OF GARLIC PASTE WERE 4.1% AND 0.35%, respectively. TSS, total solids, and water activity values were 33 °Brix, 27% and 0.86%, respectively. The paste contained 9.6% sodium chloride. TSS, titratable acidity, and pH of garlic paste did not change ($P \leq 0.05$) during storage. The Hunter color *L, a,* and *b* values of garlic paste were 59.75, -1.95, and 18.54, respectively.

Effect of temperature on the kinetics of color change

Hunter color *L, a,* and *b* values of garlic puree were 69.37, -3.25, and 15.95, respectively. Degreening of garlic puree was observed during thermal treatment at all temperatures. Since the -*a* value in the Hunter color scale indicates the greenness on the chromaticity dimensions, it may be used to describe the degreening of garlic puree during thermal processing. However, as the puree changes color during thermal processing, *L* and *b* values change and should also be included to describe the total color change. Therefore, *L, a, b* and different combinations of these were selected to ascertain their effect on the total color change of garlic puree. These combinations were subjected to linear regression with respect to time as represented by Equation 1, and the coefficients were determined (Table 1). Correlation coefficient and standard error values were used as the basis to select the combination that best described the first-order reaction for the entire temperature range. It was found that $L \times a \times b$ was the most appropriate combination that described closely the first-order reaction kinetics of color change of garlic puree for the temperature range used in this study (Figure 1). The coefficient of correlation values were between 0.991 and 0.994 while the standard error values were less than 0.0004.

Table 2—Values of the coefficients of Equation 4

Packaging material	Storage temp.	k1	k2	Correlation coefficient	Standard error
Glass container	25 °C	-1978.7	1.642	0.97	0.16
	5 °C	-2236.6	-1.626	0.97	0.16
PET container	25 °C	-2149.8	1.681	0.96	0.21
	5 °C	-2156.6	-3.559	1.00	0.02
HDP pouch	25 °C	-2121.3	1.647	0.97	0.16
	5 °C	-2172.5	-2.889	1.00	0.07

While working on thermal processing of pea puree, Shin and Bhowmik (1994) argued that all the 3 parameters should be combined together and found *La/b* as the optimum combination to describe total color degradation. Ahmed and others (2000) reported similar observations while working on thermal processing of green chilli puree.

Effect of temperature on the rate constant is shown in Figure 2. The data indicated that the dependence of the rate constant on temperature obeyed the Arrhenius relationship (Equation 2). Correlation coefficient for the linear regression analysis equaled 0.986. The computed value of activation energy for color change was 13.78 kJ/mol, which is in range with the values reported by Ahmed and others (2000) (11.4 and 16.0 kJ/mol, respectively, for water-blanched and lye-treated green chilli puree).

Rheological behavior of garlic paste

Garlic paste behaved as a non-Newtonian material (Figure 3). Apparent viscosity of garlic paste decreased with increase in rpm of spindle (shear rate is directly proportional to rotational speed of spindle) and temperature. Variation of apparent viscosity with temperature followed the Arrhenius equation (correlation coefficient = 0.982) (Equation 3, Figure 4). The activation energy was estimated to be 13.30 kJ/mol.

Effect of temperature and packaging material on color of garlic paste during storage

Both temperature and storage period had an effect ($P \leq 0.05$) on the total color of garlic paste. Storing paste at 25 °C resulted in gradual degreening where as greenness increased with time at 5 °C (Figure 5). Complete degreening of garlic paste occurred at about 48 to 52 d of storage at 25 °C. Similar observations on degreening of garlic products and bananas with storage period at and above 23 °C has been reported by Lukes (1986), Rejano and others (1997), and Kajuna and others (1998).

Total color as represented by $L \times a \times b$ was used to describe the variation in color of paste. An equation similar to that proposed by Kajuna and others (1998) was used to relate the variation of Hunter $L \times a \times b$ values with temperature and period of storage

$$L \times a \times b = k_1 + k_2 \times T \times D \quad (4)$$

The coefficients of linear regression of Equation 4 are reported in Table 2. It is obvious that Equation 4 described adequately the variation of total color of garlic paste with duration of storage (Figure 5).

Packaging materials did not affect total color ($P > 0.05$) at 25 °C but the effect was significant ($P \leq 0.05$) at 5 °C.

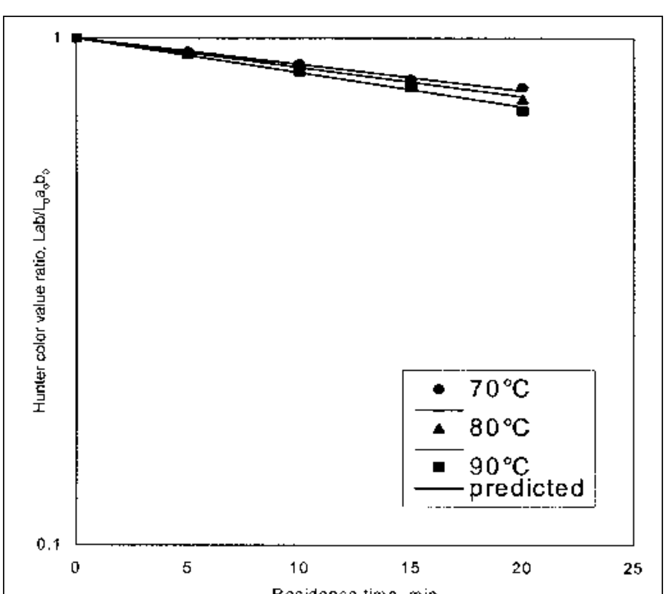

Figure 1—Temporal variations of Hunter color value ratio (*Lab/L$_o$a$_o$b$_o$*) of heat degraded garlic paste at selected temperatures

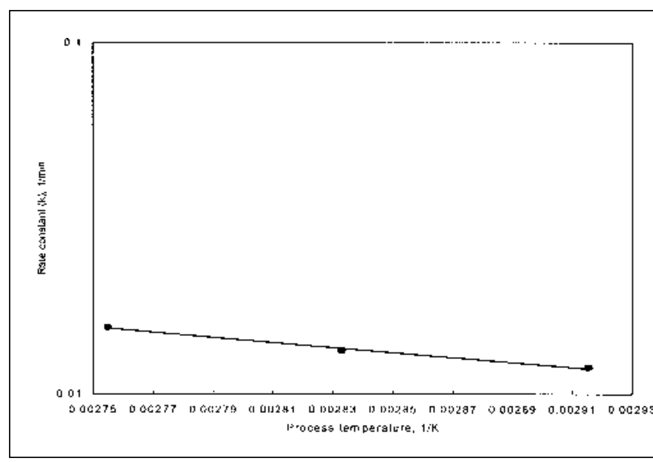

Figure 2—The Arrhenius plot relating rate constant to process temperature

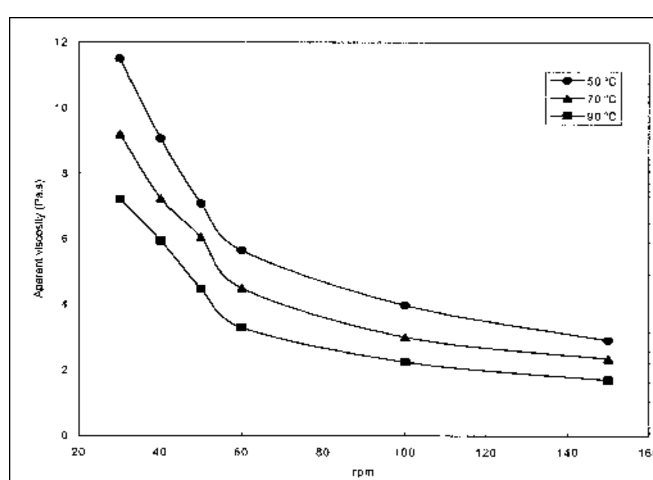

Figure 3—Effect of rotational speed on apparent viscosity of garlic paste at selected temperatures (rotational speed is directly proportional to shear rate)

Samples packed in glass containers showed minimum greening while maximum greening was noticed in PET containers at 5 °C. Glass containers may, therefore, be recommended for storage of garlic paste at 25 °C. Results of this study indicated that garlic paste should be stored at 25 °C and be held for at least 48 to 52 d before reaching the consumer (Figure 5).

Conclusions

THE KINETICS OF COLOR CHANGE OF GARLIC PUREE FOLlowed first-order reaction. The combination $L \times a \times b$ can be used to predict the variation of total color of garlic puree. The rate constant increased with temperature, and the dependence could be described using the Arrhenius equation. Garlic paste exhibited the non-Newtonian behavior, and the apparent viscosity decreased with increased temperature and shear rate. Storage for 48 to 52 d at 25 °C resulted in complete degreening of garlic paste. This study clearly demonstrates the advantage of objective measurement to study color changes of garlic puree/paste.

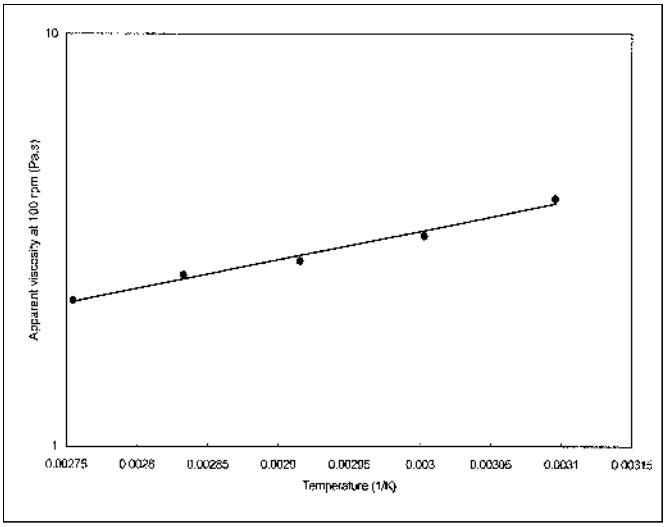

Figure 4—Dependence of apparent viscosity at 100 rpm on temperature of garlic paste

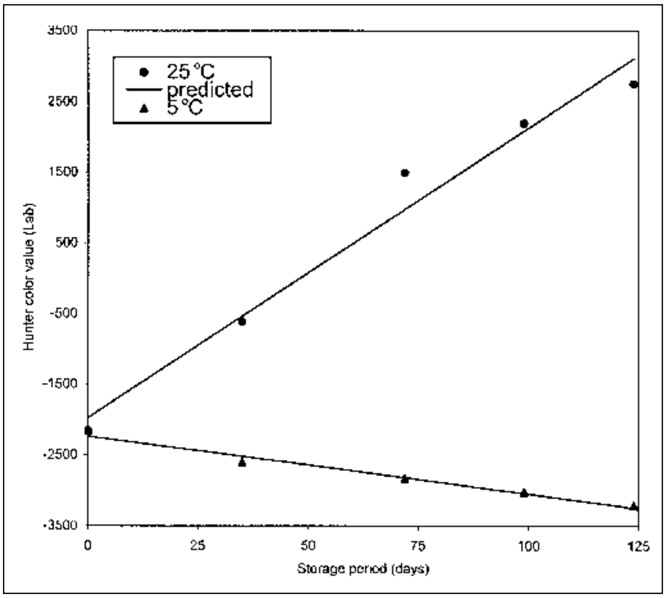

Figure 5—Effect of storage temperature on total color of garlic paste packed in glass container

Nomenclature

a—tristimulus color value
b—tristimulus color value
C—to measured Hunter color value (L, a, b) or a combination of these, dimensionless
C_o—to measured color value(s) at zero time, dimensionless
D—duration of storage (d)
E_a—to activation energy for apparent viscosity at 100 rpm (kJ/mol)
E_c—to activation energy for change in color (kJ/mol)
k—to rate constant (min^{-1})
k_o—to frequency factor (min^{-1})
k_1—to intercept, dimensionless
k_2—to slope-depicting rate of color change at selected temperatures, $(°C.d)^{-1}$
L—to tristimulus color value
η_a—to apparent viscosity (Pa.s)
η_∞—to frequency factor (Pa.s)
η_{100}—to apparent viscosity at 100 rpm (Pa.s)
rpm—to revolution per min of spindle
R—to universal gas constant
t—to heating time (min)
T—to storage temperature (°C)
T_a—absolute temperature (K)

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