Tr. J. of Engineering and Environmental Sciences
22 (1998) 33-38

Effect of Temperature and pH on Nonenzymic Browning in Minced Dried Pepper During Storage

Fahrettin GÖĞÜŞ, Sami EREN
University of Gaziantep, Food Engineering Deparment, Gaziantep-TURKEY

Received: 25 / 9 / 1996

Abstract: The effect of temperature and pH was investigated on the nonenzymic browning reactions in minced dried paprika. The browning pigments formation was both pH and temperature dependent. Increasing pH in a very narrow range from 3 to 4 affected the rate of nonenzymic browning reactions as function of temperature. Brown pigments formation followed the zero-order reaction kinetics. The temperature dependency was explained by the Arrhenius model in a temperature range from 5 to 35°C. The rate in the increase of brown pigments decreased after 10 weeks of storage at all temperatures and pH values studied.

Key Words: Minced dried pepper, Nonenzymic browning, Temperature, pH.

Kıyılmış Kurutulmuş Biberin Saklanması Esnasında Sıcaklık ve pH'nın Enzimik Olmayan Esmerleşmesine Etkisi

Özet: Kıyılmış ve kurutulmuş biberde sıcaklık ve pH'nın enzimik olmayan esmerleşme reaksiyonu üzerine etkisi incelendi. Kahverengi pigmentlerin oluşumu hem pH hem de sıcaklığa bağlı bulundu. pH değerinin 3'ten 4'e dar bir aralıkta artması sıcaklığın bir fonksiyonu olarak enzimik olmayan esmerleşme reaksiyonlarının hızını etkiledi. Kahverengi pigmentlerin oluşumu sıfırıncı derece reaksiyon kinetiği izledi. Sıcaklık bağımlılığı, 5'den 35°C'e yükselen bir sıcaklık aralığında, Arrhenius modeliyle açıklandı. Kahverengi pigmentlerin artışındaki hız çalışılan tüm sıcaklıklarda ve pH değerlerinde 10 haftalık bir depolama sonrasında azaldı.

Anahtar Sözcükler : Kıyılmış kurutulmuş biber, Enzimik olmayan esmerleşme, Sıcaklık, pH.

Introduction

Garden peppers, Capsicums, include a remarkable range of sizes, shapes and colors of fruits. The members of Capsicums are used primarily as spices. They can be divided into three broad types:

i) Chilli peper which is grown and processed for its flavor

ii) Paprika which is grown and processed for its color

iii) Cayenne pepper and hod red repper which is grown and processed for its pungency.

Before being consumed, it is usually stored in the form of whole pods, or dice or powder for several months after harvest and drying. It can also be stored and consumed in the form of minced and dried products particularly in South East region of Turkey. Nonenzymic browning is considered to be a quality factor because of color deterioration of processed red pepper products during the application of high temperature processess such as drying and evaporation and also during the storage for long time periods. It has been found that increase in the content of browning pigments is the main reason of color change in heated paprika (Ramakrishnan and Francis, 1973). Because pepper is high in content of reducing sugars and amino acids (Holdsworth, 1979), it is a good medium for Maillard reactions during its processing and storage of its products. Daoud and Luh (1967) found that the water soluble brown pigments increased during the storage of freeze dried red bell peppers. It has also been found that the water activity and temperature had a significant effect on the nonenzymic browning reaction rate of dried red peppers during their storage (Lee et al., 1991). However, no study found in the literature related with the effects of the normal storage conditions on the browning rate of red pepper and its products. So, it was decided to seek out the pH and temperature effects on the browning rate of minced pepper and the kinetics of the formation of nonenzymic browning products during the storage.

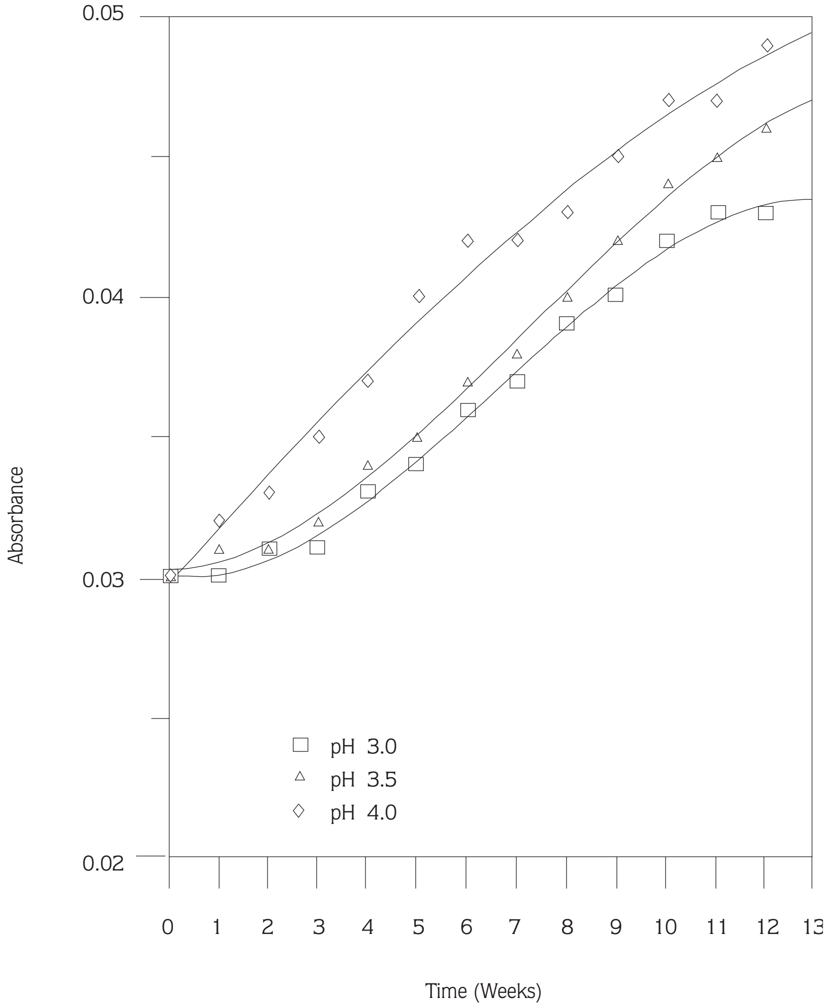

Figure 1. Brown pigment formation in minced dried pepper at 5°C. The solid lines represent polynomial regression.

Materials and Methods

Minced pepper making

The minced pepper was made from a local variety of paprika type red pepper (Bursa, Turkey). The peppers with a moisture content of 91% were processed just after harvesting. Red peppers free from stem and seeds were washed with water. They were sun-dried prior to mincing. The drying took five days to reach a moisture content of 6%. The product obtained had a pH value of 4.0. Sodium chloride (Sigma) (0.35% w/w) was added to the prepared product for inhibition of the microbial activity.

The product was placed into glass tubes without head space. The tubes containing the minced pepper samples were then stored at various temperatures (5, 25, 35°C) and pH (3.0, 3.5, 4.0) for 12 weeks. The pH of samples was adjusted by the addition of lactic acid (Sigma) (1 M). The samples were analysed were performed in duplicate.

Measurement of Browning

Before measurement of brown pigments in minced dried pepper, the samples were diluted with distilled water and stirred continuously with a magnetic stirrer for 15 min in order to extract the color. Then they were filtered with filter paper. Color was determined as absorbance in the samples. The absorbance of the filtrate was read at 420 nm (Spectronic 20 Bausch-Lamb). The value obtained was considered as the non-enzymic browning index (Meydav et al., 1977).

Results and Discussion

Browning pigments formation in minced pepper during storage:

Figures 1 to 3 show the change in absorbance for minced pepper at three different temperatures and at three different pH values for a period of 12 weeks. The temperature and pH values studied were decided

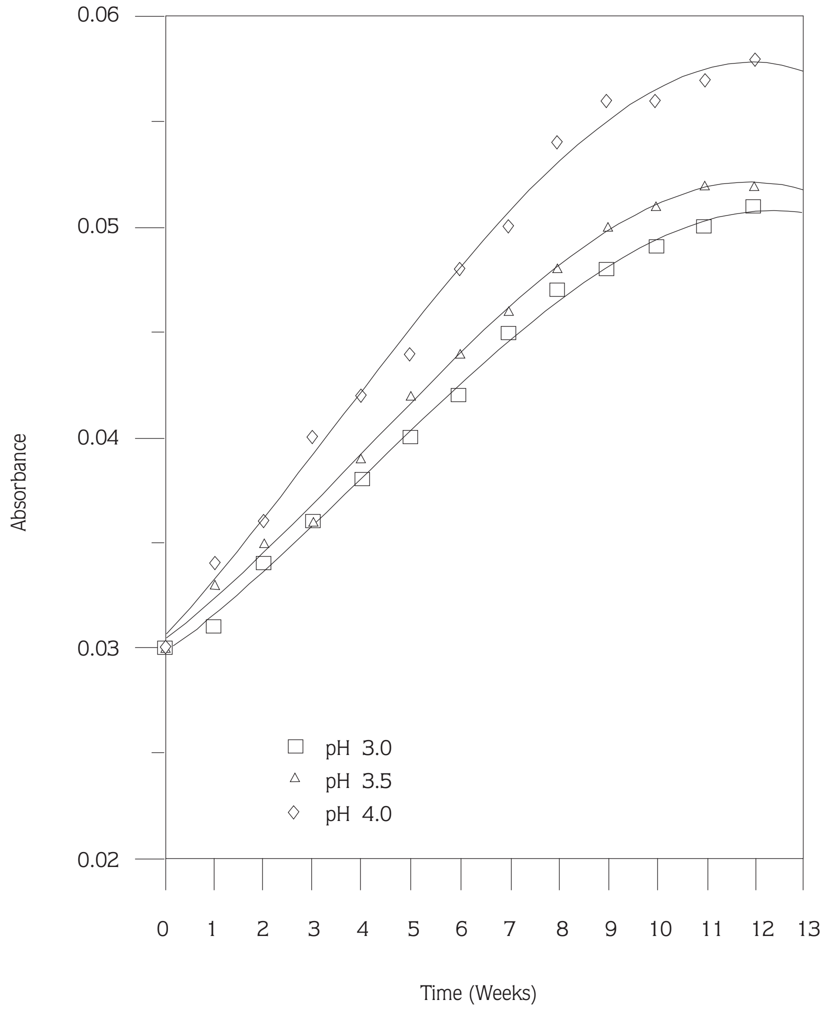

Figure 2. Brown pigment formation in minced dried pepper at 25°C. The solid lines represent polynomial regression.

by considering the actual storage conditions of home made minced pepper.

As it is seen from Figure 1, there is a significant induction period for low pH values (3.0 and 3.5) at 5°C. However, the induction period disappears by increasing pH at the same temperature. The same trend of showing the pH dependency is observed at higher temperatures in Figures 2 and 3. There is only a short induction period for pH 3.0 at 25°C. The induction period disappears for higher pH values at 25°C and for all pH values at 35°C. It can be observed that the rate of browning increases with increasing pH at a given temperature (Figures 1-3). The studies based on the effect of pH on the browning reactions have been carried out at high temperatures in a short time (Ashoor and Zent, 1984; Buera et al., 1987). The lower limit of browning was in a pH range of 4 and 6 in most of these studies. Because of modelling of actual minced pepper in this study, the pH is out of the range compared to the previous studies. However long term storage studies made it possible to observe the change in the browning at such low pH values from 3 to 4. Even if the pH values are lower and the range is narrower compared to the studies in the literature, increase in the browning is apparently higher at higher pH values. It is the natural result of having less amount of unprotonated amino groups at lower pH values. Because the larger the percent of any of the amino acids that are in the unprotonated form means more moles of amino acid can react with reducing sugars (Labuza and Baisier, 1993)

From the Figures 1 to 3, it can be seen that the change of increase of absorbance values in unit time decreases after 10 weeks in all cases of pH and temperatures. It is especially apparent at pH 3.0 that the increase in the brown pigments formation slows down at all temperatures. These results suggest that there is a cease-point for the brown pigments formation at low pH values in a temperature range changing from refrigeration conditions to the normal room tempera-

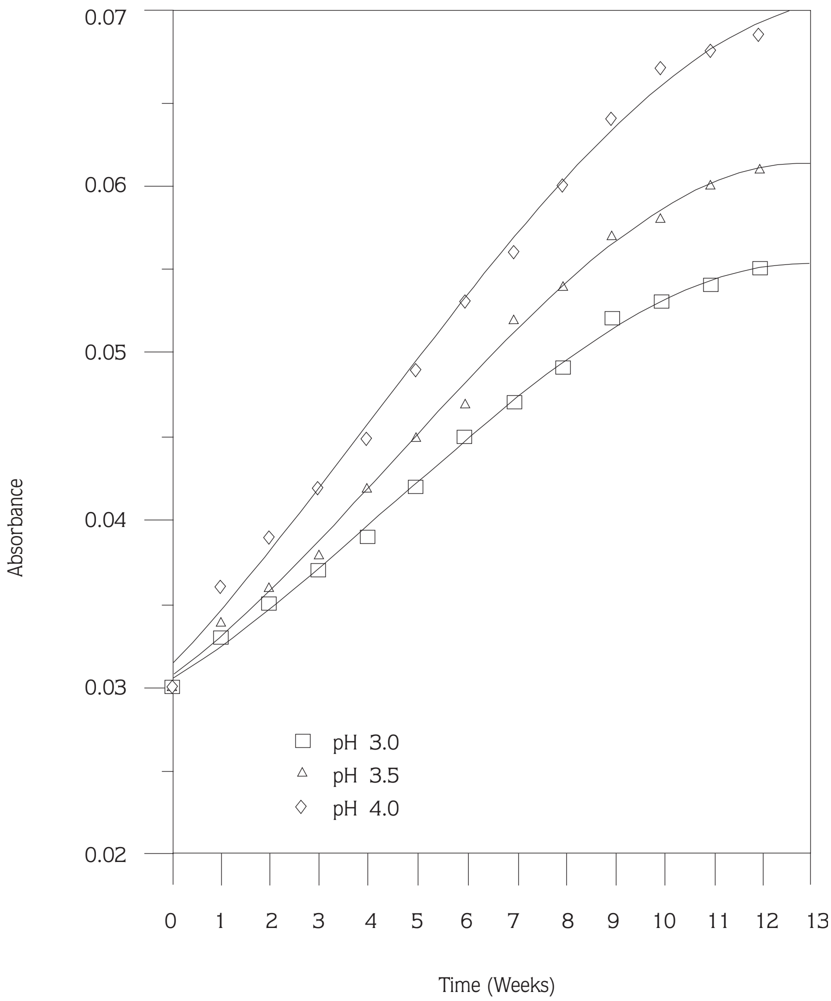

Figure 3. Brown pigment formation in minced dried pepper at 35˚C. The solid lines represent polynomial regression

ture conditions. It may be a direct result of less amount of unprotonated amino groups which are low in minced pepper compared to the model systems based on high concentrations of amino acids and reducing sugars (Labuza and Baisier, 1993).

Kinetics of the nonenzymic browning in minced dried pepper:

A zero order model for the kinetics of browning was used by Mizrahi et al. (1970) for cabbage, Waletzko and Labuza (1976) for a semimoist food, and Rapusos and Driscoll (1995) for onion slices. From the behaviour of plots given in Figures 1 to 3, it was decided to use a zero order kinetics in this study as well. The reaction rate constants (k) found for various pH values and temperatures are given in Table 1 with their regression coefficients.

Except few of them the plots showed no induction period and their linear parts were used to find the reaction rate constants. As it is seen in Table 1, the reaction rate constant increases with increasing pH and temperature. As it is mentioned above this behaviour is in aggreement with previous studies (Ashoor and Zent, 1984; Buera at al., 1987).

Table 1. Rate constants with their ragression coefficients and activation energies at different pH for minced dried pepper during storage.

pH	T (˚C)	k (10^{-3} OD $week^{-1}$)	R^2	E_a (kcal $mole^{-1}$)
3.0	5	1.26	0.998	
3.0	25	2.12	0.990	3.75
3.0	35	2.41	0.998	
3.5	5	1.45	0.998	
3.5	25	2.33	0.992	4.07
3.5	35	2.99	0.988	
4.0	5	1.59	0.989	
4.0	25	2.85	0.991	4.66
4.0	35	3.61	0.987	

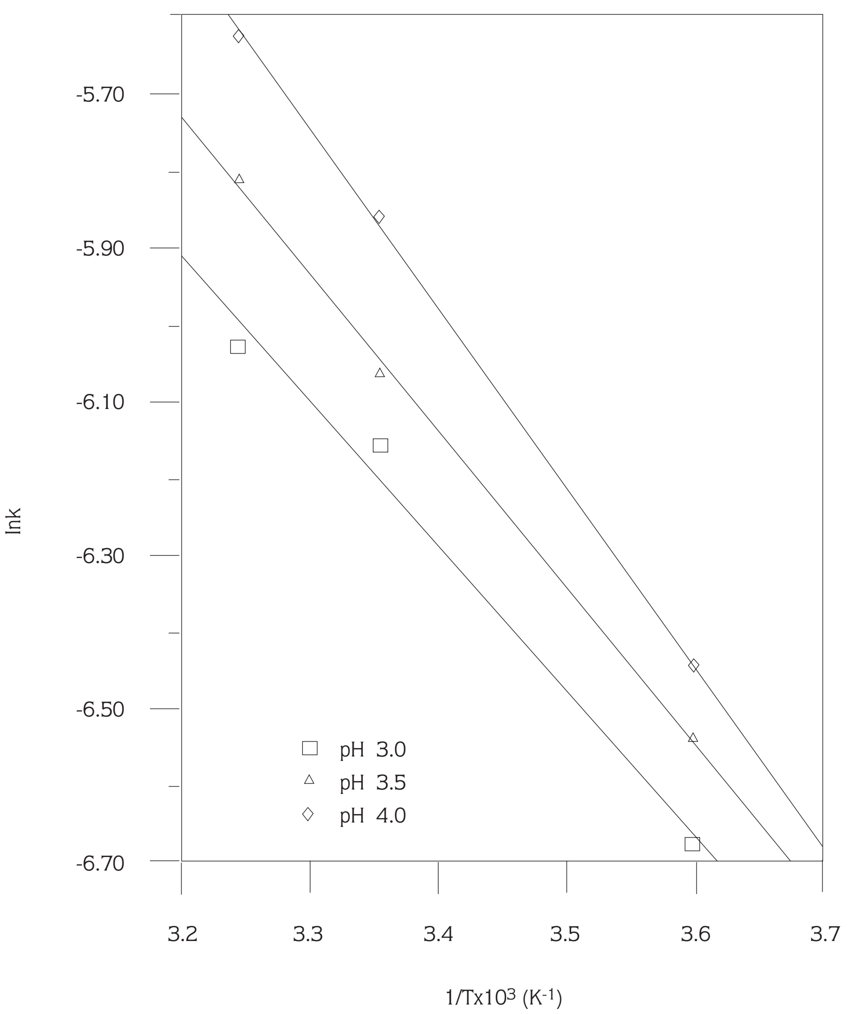

Figure 4. Arrhenius plot for browning of minced dried pepper at three temperatures (5, 25, 35 °C)

As with other chemical reactions, the observed temperature dependence of the nonenzymic browning reaction has been modelled using the Arrhenius concept (Cohen et al., 1994). Arrhenius plots of minced pepper samples were given in Figure 4.

The activation energies (E_a) obtained from the slopes of the plots were given in Table 1 for three different pH values. In minced pepper samples, the activation energy was found to be in the range of 3-5 kcal/mole. The activation energy found in the previous studies is reported to be in the range of 10-24 kcal/mole for pepper products. This may be because of storing the minced pepper at its practically applied very low storage temperature and pH. At these low pH values; even if the browning tends to increase in long term up to a certain level, the reaction rate was found to be slow. The temperature dependency of the system is apparent in the Arrhenius plots. However, the small changes in the reaction rate was found to be slow. The temperature dependency of the reaction rate constants because of very slow reaction rates make the activation energy of the system lower than the expected. If pH is increased to the optimum for the nonenzymic browning reactions, the activation energy most robably would be increased to the levels found in the previous studies (Toribio and Lozano, 1986; Cohen et al., 1994).

As a result, the nonenzymic browning reaction in the minced pepper during its storage is mainly dependent on pH and temperature. The storage time is not that important at the studied low temperature and pH values. First few months of the storage play a crucial role in the formation of brown pigments, however the increase in the brown pigments formation slows down during the further storage of the minced pepper.

References

Ashoor, S.H. and Zent, J.B. Maillard browning of common amino acids and sugars. Journal of Food Science, 49, 1206-1207, 1984.

Buera, M.P., Chirife, J., Resnik, S.L. and Wetzler, G. Nonenzymic browning in liquid model systems of high water activity: Kinetics of color changes due to Maillard's reaction between different single sugars and glycine and comparison with caramelization browning. Journal of Food Science, 52, 1063-1067, 1987.

Cohen, E., Birk, Y., Mannheim, C.H. and Saguy, I.S. Kinetic parameter estimation for quality change during continuous thermal processing of grapefruit juice. Jorunal of Food Science, 59, 155-158, 1994.

Daoud, H.N. and Luh, B.S. Packaging of foods in laminate and aluminum-film combination pouches IV. Freeze dried red bell peppers. Food Technology, 21, 339-343, 1967.

Holdsworth S.D. Vegetables. In: Priestley, R.J. (Ed), Effects of Heating on Foodstuffs, Applied Science Publichesrs Ltd, London, pp 307-351, 1979.

Labuza, T.P. and Baisier, W.M. The kinetics of nonenzymatic browning. In: Schwartzberg, H.G. and Hartel, R.W. (Eds), Physical Chemistry of Foods. Marcel Dekker, Inc. New York, pp. 595-649, 1993.

Lee, D.S., Chung, S.K. and Yaki, K.J. Non-enzymic browning in dried red pepper products. Journal of Food Quality, 14, 153-163, 1991.

Meydav, S., Saguy, I. and Kopelman I.J. Browning determination in citrus products. Journal of Agriculture and Food Chemistry, 25, 602-604, 1977.

Mizrahi, S., Labuza, T.P. and Karel, M. Computer-aided predictions of extent of browning in dehydrated cabbage. Journal of Food Science, 35, 799-803, 1970.

Ramakrishnan, T.V. and Francis, F.J. Color and carotenoid changes in heated paprika. Journal of Food Science, 38, 25-28, 1973.

Rapusas, R.S. and Driscoll, R.H. Kinetics of non-enzymatic browning in onion slices during isothermal heating. Journal of Food Enginerring, 24, 417-429, 1995.

Toribio, J.L. and Lozano, J.E. Heat induced browning of clarified apple juice at high temperatures. Journal of Food Science, 51, 172-175, 179, 1986.

Waletzko, P. and Labuza, T.P. Accelerated shelf-life testing of an intermediate moisture food in air and in an oxygen free atmosphere. Journal of Food Science, 41, 1338-1344, 1976.