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Carotenoid Destruction and Nonenzymatic Browning during Red Pepper Drying as Functions of Average Moisture Content and Temperature

Dong-Sun Lee*, Hyun-Ku Kim
*Dept. of Food Engineering, Kyungnam University, Masan
Korea Food Research Institute, Banweol, Hwasung-Kun

고추 건조과정에 있어서 평균 수분함량 및 온도에 따른 Carotenoid 파괴 및 비효소적 갈변

이동선*·김현구
*경남대학교 식품공학과, 한국식품개발연구원

Abstract

Functional relationships of carotenoid destruction and nonenzymatic browning during red pepper drying were established by the dynamic test using the moisture-temperature-quality history curve in actual drying experiments. The dependence of the rate constants on temperature and moisture content was established and analysed assuming that carotenoid destruction and nonenzymatic browning are the first order and the zero order reaction, respectively. Carotenoid destruction rate constant was high at high moisture and high temperature, and had a minimum value at some intermediate moisture content. As dependence of rate constant on temperature, activation energy of carotenoid decolorization ranged from 7.7 to 27.4 kcal/mol, showing higher value at higher moisture content. Nonenzymatic browning showed higher rate at higher temperature and higher moisture content. Activation energy of browning was in the range of 7.5-20.2 kcal/mol with higher value at higher moisture level.

Key words: red pepper drying, kinetics, carotenoids, browning

Introduction

Carotenoid destruction and nonenzymatic browning are two main reactions affecting the color deterioration of red pepper during drying⁽¹⁾. For the color retention of dried red pepper low temperature drying was proven to be desirable⁽²⁾. The quantitative relationship between these quality changes and process variables such as moisture content and food temperature is needed for the proper optimization and control of red pepper drying. Average moisture content and food temperature are important process variables which represent the state of drying and can be easily measured during drying. Therefore we attempted to establish kinetic models of carotenoid destruction and nonenzymatic browning as functions of average moisture content and temperature.

Materials and Methods

Dynamic test was conducted using drying conditions which can be experienced in actual red pepper drying⁽³⁾. Drying temperature was dynamically changed stepwise throughout the drying period. Four sets of drying were undertaken under widely different conditions in order to represent the possible various drying schedules. Fresh red pepper purchased from the local market was throughflow dried in the cabinet drier. 200 g of red pepper was spread on the 20 × 20cm tray. In each set of experiment, 7 trays of red pepper were dried. One sample tray was randomly withdrawn from the dryer at selected sampling times. Removed tray was weighed for moisture estimation, freezed in

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Corresponding author: Dong-Sun Lee, Department of Food Engineering, Kyungnam University, 449, Weolyoung-dong, Masan, Kyungnam-do, 630-701

-20 °C, freeze-dried at plateau temperature of 25 °C, sealed in aluminium laminated pouch, and stored at -20 °C up to the quality evaluation. Through the whole drying period food temperature was monitored by copper-constantan thermocouple inserted in the center of assorted samples.

Quality was evaluated for the pericarp of the freeze-dried sample because the quality of dried red pepper mainly depends on the color of this fraction. The separated pericarps were sliced into fine particles. About 0.1g sample was extracted with 100m*l* distilled water at 30 °C for 2 hours and filtered through Toyo No.2 filter paper. Absorbance of the filterate was read at 420nm against the blank of distilled water in order to determine the browning level. The data were presented in optical density per 0.1g dry solid basis by compensating moisture content factor. The residue was throughly washed with distilled water and extracted in 90m*l* acetone at 30 °C for 2 hours with a little shaking (60 strokes/min.) for carotenoid determination. The extract was filtered through Toyo No.2 filter paper into 100m*l* volumetric flask and the residue was washed with acetone to make up to 100m*l* solution. The optical density of the extracted solution was measured at 455nm against blank of pure acetone. The absorbance was converted into the concentration of total carotenoids using extinction coefficient of beta-carotene $F_{1cm}^{1\%} = 2500$. Moisture content was determined by measuring weight before and after drying at 60 °C in the vacuum for 40 hours.

For the kinetic model determination, carotenoid destruction and nonenzymatic browning were assumed to be the first order and zero order reaction, respectively(4,5). The moisture and temperature dependence of these two quality changes was described as equations (1)-(8). Arrhenius equation was applied in analysing the temperature effect on the reactions. The activation energy and frequency factor were formulated as functions of moisture content.

For carotenoid destruction;

$$\frac{dC}{dt} = -kC \tag{1}$$

$$k = k_0 \exp(-E_{ac}/RT_a) \tag{2}$$

$$\ln k_0 = P_1 + P_2 M + P_3 M^2 \tag{3}$$

$$E_{ac} = P_4 + P_5 M + P_6 M^2 \tag{4}$$

For nonenzymatic browning;

$$\frac{dB}{dt} = k_b \tag{5}$$

$$k_b = k_{b0} \exp(-E_{ab}/RT_a) \tag{6}$$

$$\ln k_{b0} = P_{b1} + P_{b2} M + P_{b3} M^2 \tag{7}$$

$$E_{ab} = P_{b4} + P_{b5} M + P_{b6} M^2 \tag{8}$$

The parameters P_1 - P_6, P_{b1} - P_{b6} were determined by the iteration method used by Lee *et al.*(3), which utilized the moisture-temperature-quality history of the drying experiment. The computation was done by TeleVideo TS 2605 personal computer. Other functional forms were also tested, but the models described above were chosen with respect to fittness and simplicity.

Results and Discussion

Carotenoid destructuction

The parameters in equation (3) and (4) which describe the moisture and temperature dependence of the carotenoid destruction are presented in Table 1. The simulated carotenoid retentions using this parameter model showed very good agreements with experimental data and no consistent pattern of residuals. Fig. 1 shows the estimated rate constant as a function of average moisture content and food temperature. The carotenoid destruction is fast at high temperature and high moisture. Moisture effect on the rate is great at higher temperature. The rate constant has a minimum value at some intermediate moisture content. These minimum points are about 0.8g water/g dry solid at 80 °C, about moisture 1.0 at 60 °C, and about moisture 1.8 at 45 °C. The rate constant increases a little as the moisture content decreases below this moisture level. The temperature dependence is higher at higher average moisture content. The activation energy is in the range of 7.7 - 27.4 kcal/mol with higher value at higher moisture content. Our rate constants and activation energy at moisture 0 are similar to those of

Table 1. Parameters describing the functional relationships of carotenoid destruction and nonenzymatic browning in red pepper drying

Quality change	Equation No.	Parameters					
		P_1 or P_{b1}	P_2 or P_{b2}	P_3 or P_{b4}	P_4 or P_{b4}	P_5 or P_{b5}	P_6 or P_{b6}
Carotenoid destruction	Equations (3) and (4)	4.1879	-1.9466	3.2619	7698.3	-692.58	1911.2
Nonenzymatic browning	Equations (7) and (8)	1.6492	5.5260	0.1713	7459.2	3736.5	2.9828

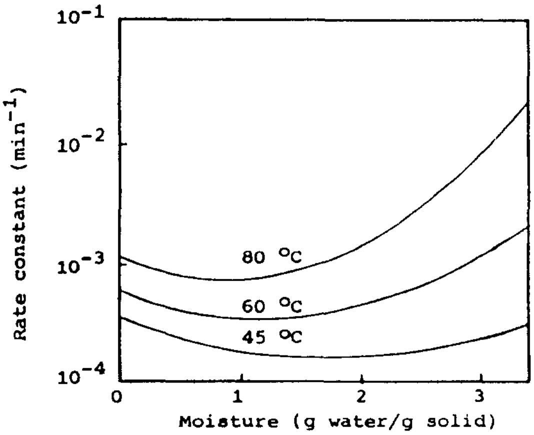

Fig. 1. Estimated first order rate constant of carotenoid destruction in red pepper drying as a function of average moisture content and temperature.

beta-carotene at dry conditions in food systems reported by Stefanovich *et al.*(6).

Carotenoids in some model foods and vegetable were reported to be most stable at some intermediate water activity(7-9), which coincides with our results at low temperature. Carotenoid destruction rate at high moisture content may be high because of solubilization and mobilization of catalysts. Copper and peroxidase-like water soluble protein in red pepper enhance the carotenoid oxidation rate as catalysts. Ascorbic acid content is also known to influence the stability of carotenoids(10). Ascorbic acid in low concentration shows prooxidant effect, but in high concentration gives antioxidant effect with or without copper ion when some moisture exists. In the course of red pepper drying, ascorbic acid concentration is low and catalysts have high mobilities at the initial stage because of high moisture content. Therefore all these conditions combined accelerate carotenoid destruction. But with further moisture removal, ascorbic acid concentration increases due to the concentration of the soluble portion, the increased viscosity decreases mobility of catalysts, and therefore carotenoid oxidation rate begins to decrease. At very low moisture content ascorbic acid effect stops, the peroxidase activity acts continuously, and then carotenoid destruction rate increases with dryness. In this low moisture range water protects carotenoids, which may be explained by hydration of metal catalysts and bonding with peroxide produced in this free radical reaction. Goldman *et al.*(11) discussed the mechanism of the carotenoid decolorization and the water effect. Even though average moisture content was used as an independent variable for the carotenoid deterioration, moisture effect in red pepper drying seems to follow general pattern in the dried foods.

Nonenzymatic browning

The parameters of browning in equation (7) and (8) are also tabulated in Table 1. This functional relationship could explain our dynamic experimental data quite well. Fig. 2 shows the browning rate as a function of food temperature and moisture content. Generally the browning rate is high at higher temperature and higher moisture. Activation energy indicating temperature dependence is higher at higher moisture content and in the range of 7.5 - 20.2 kcal/mol which is somewhat lower than that of usual nonenzymatic browning(12). Moisture dependence of rate constant shows smooth increase of rate with moisture.

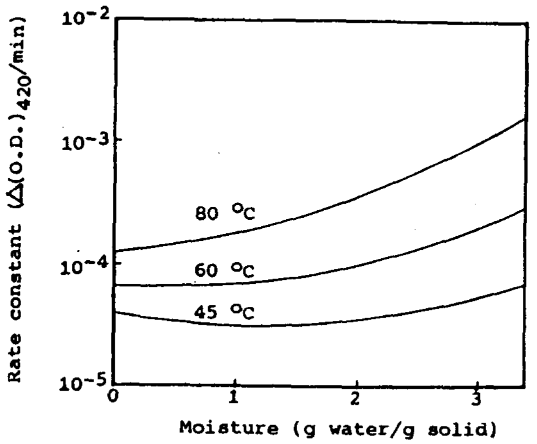

Fig. 2. Estimated zero order rate constnt of nonenzymatic browning in red pepper drying as a function of average moisture content and temperature.

At lower temperature, moisture affects little on browning rate.

This pattern of reaction rate is somewhat unique when compared with general moisture dependence of browning. Usually browning rate increases with water content up to a maximum and decreases again as the water content increases⁽¹³⁾. The maximum point usually locates around water activity of 0.7, but depends on specific conditions. In our model maximum point does not appear. This difference can be elucidated by the course of the dynamic test. In our dynamic test experiment, quality evaluation was conducted for the pericarp of red pepper, but moisture content was the mass average value. This comes from unusual characteristics of red pepper, i.e. its quality is governed by the color of the pericarp of surface while the completeness of drying is determined by average moisture content decrease. Though food temperature is nearly uniform throughout the sample, moisture distribution shows sharp gradient within food during dehydration⁽¹⁴⁾. Real local moisture content in the pericarp would be somewhat different from average moisture content. From initial drying the surface of red pepper would have low local moisture content favorable for browning while average moisture content is high. Therefore the usual pattern of low browning rate at high moisture side may be hidden or mixed with that of high rate at lower intermediate moisture when expressed as a function of average moisture content. This results in high rate of browning at high average moisture. This phenomenon would be more prominant in the drying of red pepper which consists dominantly of falling rate period and has a main mass transfer resistance in the pericarp⁽¹⁵⁾. For the carotenoid destruction above mentioned this effect might also appear, but the different dependence of this decolorization on water activity or moisture seems not to interfere the overall trend. Therefore the established functional relationship must be understood in the limitation of the dynamic test. But for the practical optimization of drying which has similar pattern of moisture distribution, the results obtained would be very useful considering the limitation of the static kinetic study and complexity of the actual food drying operation. Lee *et al.*⁽³⁾ discussed these points. Conclusively these models are thought to be useful considering the model formulation problems in the optimization study⁽¹⁶⁾.

Nomenclature

B : Browning level (O.D. at 420nm)

C : Carotenoid concentration (mg/100g dry solid)

E_{ac} : Activation energy of carotenoid destruction (cal/mol)

E_{ab} : Activation energy of nonenzymatic browning (cal/mol)

k : Rate constant of carotenoid destruction (min^{-1})

k_0 : Frequency factor in carotenoid destruction (min^{-1})

k_b : Rate constant of browning (ΔO.D. at 420 nm/min)

k_{b0} : Frequency factor of browning (ΔO.D. at 420 nm/min)

M : Moisture content (g water/g dry solid)

P_1 - P_6: Parameters of carotenoid destruction

P_{b1} - P_{b6} : Parameters of browning

R : Gas constant, 1.987 cal/mol.K

t : Time(min)

T_S : Food temperature (K)

요 약

고추의 건조 중 중요한 품질요소인 carotenoid 파괴 및 비효소적 갈변의 kinetics를 건조 중 품질측정을 이용한 dynamic test에 의하여 평균 수분함량과 온도의 함수관계를 결정하였다. 1차반응으로 가정된 carotenoid 파괴 속도상수는 고온 고수분에서 높았으며 수분의존성에 있어서 건조중간의 어떤 수분함량에서 최소치를 보여주고 있었다. 온도의존성에 있어서 활성화에너지는 7.7-27.4 kcal/mol로 나타났고 수분함량이 높을수록 높았다. 0차반응으로 분석된 비효소적 갈변은 온도와 수분함량이 높을수록 쉽게 일어났으며 활성화에너지는 7.5-20.2 kcal/mol로서 수분함량이 높을수록 높았다.

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