California Almond Shelf Life: Lipid Deterioration During Storage

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Abstract: The effects of storage conditions on the lipid deterioration in California almond nuts and sliced were studied. Natural whole almonds with or without polyethylene (PE) packaging and blanched whole almonds and sliced with PE packaging were stored in 10 different storage conditions which were combinations of different temperatures and relative humidity levels. The peroxide values (PVs), iodine values (IVs), and free fatty acids (FFAs) were monitored during the storage. The PVs in the natural samples did not change noticeably whereas the blanched samples changed greatly, indicating that skins may have played a significant role. The IVs decreased slightly in the 1st 150 d of storage and then leveled off. The slightly faster changes in IVs in the blanched samples coincided with the greater changes in PVs in the blanched samples. The natural samples exhibited much higher FFA levels than the blanched samples after storage. In general, FFA increased with increasing storage time, temperature, and humidity. Highest levels of FFA were observed in the samples stored at high temperature and high humidity.

Keywords: almond, free fatty acids, iodine value, lipase, lipid oxidation

Practical Application: The results reported in this article provide useful information that almond producers and processors could use to develop their storage and transport processes.

Introduction

Fresh almonds are living organs in which respiration and other biochemical processes continue to take place before they are processed or consumed. Respiration is the predominate process for almonds to acquire nutrients and energy to maintain their metabolic activities after they are separated from their parent plants. Too high a respiration rate because of inappropriate control of storage conditions and packaging can cause serious damages to almonds. Furthermore, several processes and conditions may work hand in hand against our goal of keeping almonds fresh. Almonds contain about 49% oil (Maguire and others 2004). Like all dry foods, especially oil rich nuts, almonds' sensory quality can suffer from lipid oxidation (Addis 1986; Allen and Hamilton 1994). Lipid oxidation can result in loss of flavor (because of rancidity), color, nutrient value and functionality, and accumulation of compounds that may be detrimental to health (Addis 1986). Almonds have a very high level of unsaturated fatty acids, making almonds prone to lipid oxidation.

Lipid deterioration in almonds may proceed in 2 ways: (1) enzyme-catalyzed hydrolytic cleavage and (2) atmospheric oxygen driven oxidative lipid cleavage. Enzyme-catalyzed hydrolytic cleavage occurs when the moisture content is elevated above the critical level, at which enzymes are activated resulting in lipid cleavage. The resultant FFAs, if further oxidized, may give rise to rancidity. In addition, FFAs are preferred substrate for respiration. As a result of the accelerated respiration activity, water, heat, and CO_2 are produced. Higher moisture content and self-heating further intensify the enzyme-catalyzed hydrolytic reactions, creating a chain-reaction scenario. Therefore, it is very important to keep the enzymatic activities and respiration rate low by maintaining low-moisture content and low temperature. The atmospheric oxygen driven oxidative lipid cleavage or autooxidation requires presence of oxygen. The oxidation reactions are enhanced by light, heat, and heavy metals. Controlling the atmospheric composition and temperature, and employing packaging are the common techniques for minimizing autooxidation of lipids in nuts (Mate and others 1996; Maskan and Karata 1998; Jensen and others 2003; Mexis and others 2009). Some of these methods were studied on almonds (Senesi and others 1991; Rizzolo and others 1993; Mexis and Kontominas 2010; Mexis and others 2011). Mexis and Kontonminas (2010) studied the effects of oxygen absorber, nitrogen flushing, and active packaging on the quality of almonds stored at 4 and 20 °C, and relative humidity of 75%. The quality parameters examined were mostly lipid oxidation related. They found that the treatment methods employed in their study effectively reduced lipid oxidation, and in particular, the use of oxygen absorber could extended the shelf life of almonds to at least 12 mo irrespective of packaging materials, lighting conditions, and temperatures. However, some of these findings and methods may be impractical for long-distance shipping across oceans, and inland transport, handling of bulk raw almonds. Furthermore, there

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is a lack of studies on the relationships between change in moisture content (loss or gain) and lipid oxidation, and the effect of temperature on lipid oxidation in almonds.

In the 1st part of this research, we investigated the changes in moisture contents, mold growth, and textural properties of almonds under different temperature, humidity, and packaging conditions. This study was focused on the lipid oxidation in almonds stored under the same conditions. Particularly, we examined the correlation between the lipid oxidation and moisture contents of the almonds, and the effect of temperature on the lipid oxidation kinetics. Mathematical modeling of the lipid oxidation data will be presented.

Materials and Methods

Almond samples were provided by the Almond Board of California (ABC). The initial moisture content, oil content, and texture of the samples were determined. Sample type and packaging conditions are listed in Table 1. The storage conditions are listed in Table 2.

Samples were taken periodically for analysis of water content, peroxide value (PV), FFAs content, and iodine value (IV) during the storage. Sampling was more frequent in the early stage than the later stage of the storage study. Some treatments did not last to the end of the study because they spoiled at high temperature and high humidity.

Water content

Weighed almond sample into a clean and dry container with lid, and known weight (W_1). The total weight of the sample and the container with lid was recorded as W_2. The sample and container (with lid removed) were placed into a drying oven operated at 105 to 110 °C. The sample and container with lid were weighed during the drying until they reached a constant weight (W_3).

Table 1–Almond sample labels and descriptions.

Sample label	Type	Form	Raw or blanched	Package
A	Nonpareil	Whole	Raw	1 lb sealed PE bag
B	Nonpareil	Whole	Raw	1 lb carton without PE liner
C	California	Whole	Blanched	1 lb sealed PE bag
D	California	Regular sliced	Blanched	1 lb sealed PE bag

Table 2–Storage conditions.

#	ID RT[a]	Temperature (°C)	*RH* (%)
1	4.4/45	4.4(40 °*F*)	45
2	4.4/75	4.4(40 °*F*)	75
3	4.4/95	4.4(40 °*F*)	95
4	21.1/45	21.1(70 °*F*)	45
5	21.1/70	21.1(70 °*F*)	70
6	21.1/95	21.1(70 °*F*)	95
7	37.8/35	37.8(100 °*F*)	35
8	37.8/65	37.8(100 °*F*)	65
9	37.8/95	37.8(100 °*F*)	95

[a]Ambient condition: in summer, the temperatures ranged from 20 to 35 °C and humidity ranged from 70% to 90%. In winter, the temperatures were in the range of 5 to 15 °C, and humidity was in the range of 60% to 80%.

Water content was calculated according to the following equation:

$$WC\,(\%) = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad (1)$$

Oil extraction

Oil was extracted from almond samples for analysis of PV, FFA, and IV. To extract oil, about 300 g of samples were pressed. Oil extracted was stored in 50 mL iodine flask at 40 °F before analysis. All analyses were completed within 1 d of the oil extraction.

PV

Weigh 5.00 ± 0.05 g of oil sample into a 250 mL Erlenmeyer flask and add 30 mL acetic acid–chloroform (3:2) solution, and 0.5 mL saturated potassium iodide (KI) solution. Allow the solution to stand with occasional swirling for 1 min and then add 30 mL distilled water. Slowly titrate with 0.01-N sodium thiosulfate ($Na_2S_2O_3$). Continue titrating until the color changes to light yellow. Add 0.5 mL of 1% soluble starch indicator. Continue titrating, shaking the flask vigorously near the endpoint which is a faint blue color. Add the sodium thiosulfate ($Na_2S_2O_3$) dropwise until the blue color just disappears. The PV as mEq of peroxide per kg of oil was calculated according to following equation:

$$PV = \frac{V \times C \times 1000}{W}, \quad (2)$$

where V is the volume of $Na_2S_2O_3$ solution in mL, C is the concentration of the $Na_2S_2O_3$ solution in mol/L, and W is the weight of the oil sample taken in g.

IV

The oil sample was filtered through a dry filter paper before analysis. A known amount of extracted oil was transferred into a dry, clean 500-mL flask containing 20 mL of carbon tetrachloride. Twenty-five milliliter of Wijs reagent was pipetted into the flask. Twenty milliliter of potassium iodide test solution and 100 mL of recently boiled and cooled water were added to the flask. The mixture in the flask was titrated with 0.1-N sodium thiosulfate gradually and shaking constantly until the yellow color of the solution almost disappears. Add starch test solution, and continue the titration until the blue color disappears entirely. Toward the end of the titration, stopper the flask and shake it vigorously so that any iodine remaining in solution in the carbon tetrachloride may be taken up by potassium iodide solution. A blank (control) was titrated in the same manner and at the same temperature. The IV was calculated by the following equation:

$$IV = \frac{(B - S) \times 12.69 \times C}{W}, \quad (3)$$

where $(B - S)$ is the difference between volumes (in L) of sodium thiosulfate required for the blank and for the sample, C is normality of the sodium thiosulfate in mol/L, and W is weight of the oil sample in g.

FFAs

Placed known weight (W, approximately 10 g of oil extracted from almond sample into a 200 mL Erlenmeyer flask; added

50 mL ether, 50 mL 95% ethanol, 2 to 3 drops of 1% phenolphthalein indicator; and titrated the mixture with 0.005 mol/L sodium hydroxide ethanol solution until the mixture turns pink for at least 1 min. The volume of the titrant consumed was recorded as V. FFA content was calculated using the following equation:

$$FFA(\%) = \frac{V \times C \times 282}{1000 \times W} \times 100, \quad (4)$$

where C is the calibrated concentration of sodium hydroxide ethanol solution and 282 is oleic acid molar mass in g/mol.

Lipase activity

A 2.00 ± 0.01 g of almond sample, 1 mL of oil, and 5 mL of phosphate buffer were added to a mortar, ground with quartz sand into a fine paste, and carefully transferred to a Erlenmeyer flask. Wash the mortar with 5 mL of water a few times and pooled all liquid into a Erlenmeyer flask and sealed with a stopper. The flask was incubated at 4.4, 21.1, and 37.8 °C for 24 h. Add 50 mL of ethanol and ether mixture to the flask, shake, and allow to stand for 1 to 2 min. Filter the mixture into a 50 mL flask. Pipette 25.0 mL of filtrate to another Erlenmeyer flask, add 3 to 5 drops of phenolphthalein indicator, titrate with 0.05 N KOH solution. Record the volume of consumed KOH solution. The results

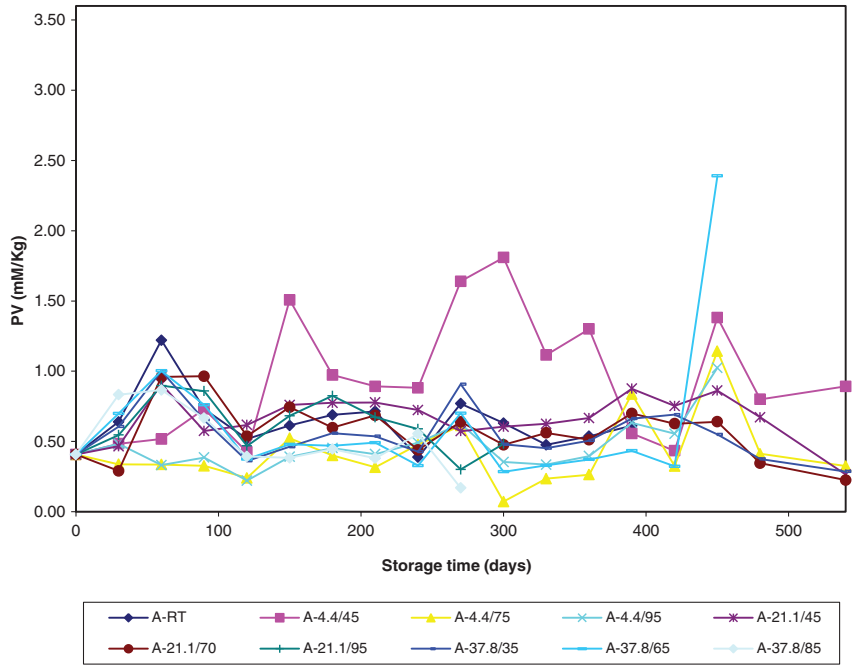


Figure 1–Change in PV content in almond (Sample A) during storage.

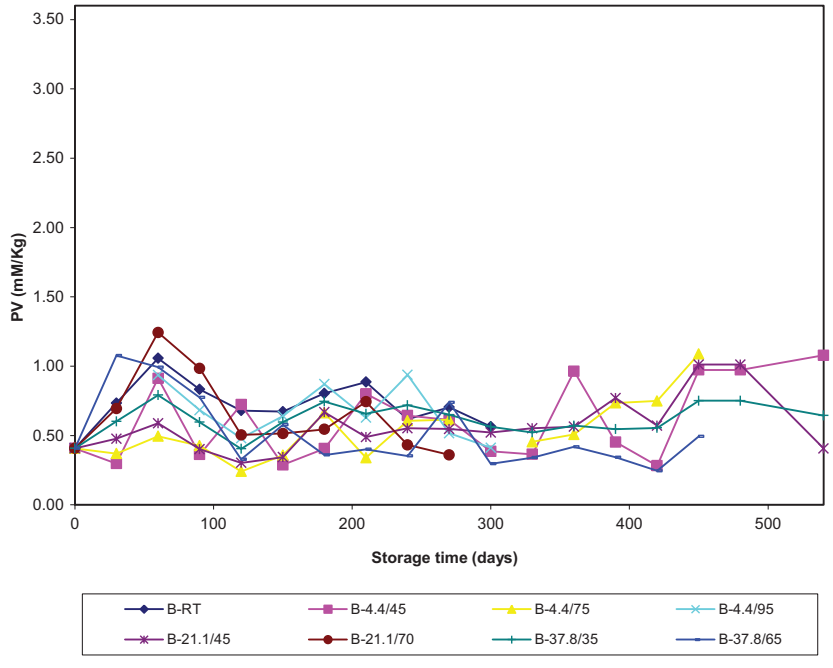


Figure 2–Change in PV content in almond (Sample B) during storage.

for blanks were obtained by going through the same procedure except for the incubation step. The lipase activity was calculated according to the following equation:

$$X = \frac{(V_1 - V_0) \times C \times 56.1}{m \times (100 - M)} \times \frac{60}{25} \times 100, \quad (5)$$

where

X, lipase activity, dry base in mg KOH/g;
V_1, volume of KOH solution consumed (sample) in mL;
V_0, volume of KOH solution consumed (blank) in mL;
C, molar concentration of KOH solution in mol/L;
m, weight of sample in g;
M, water content of sample in %;
56.1 molar weight of KOH in g/mol.

Statistical analysis

Data computation and statistical analysis was performed using Microsoft Excel 2003. All data were the averaged values (mean) of 3 replicates. Standard deviations (SD) and coefficients of variation (CV) were calculated for all data. CV, which is the ratio of the standard deviation to the mean, is unit less and is therefore a good

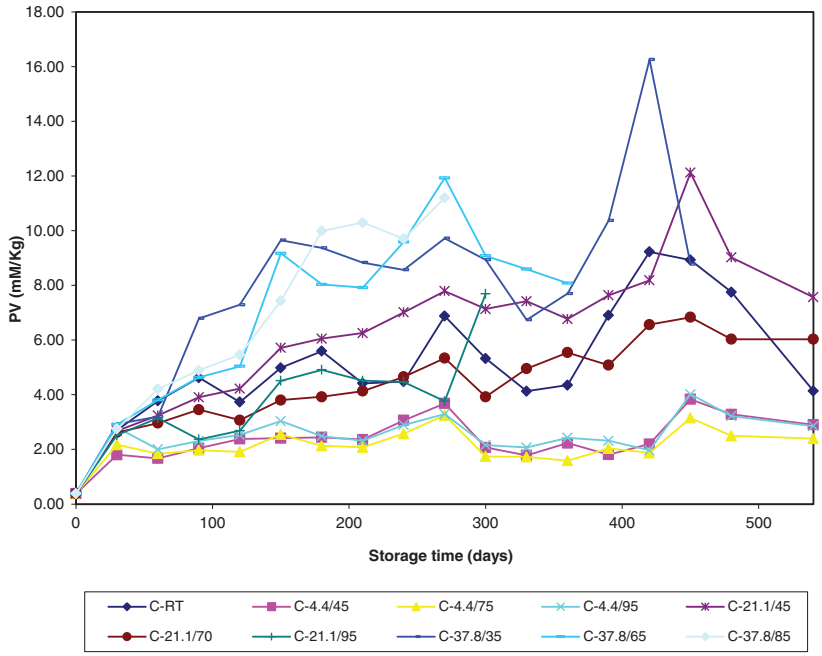


Figure 3–Change in PV content in almond (Sample C) during storage.

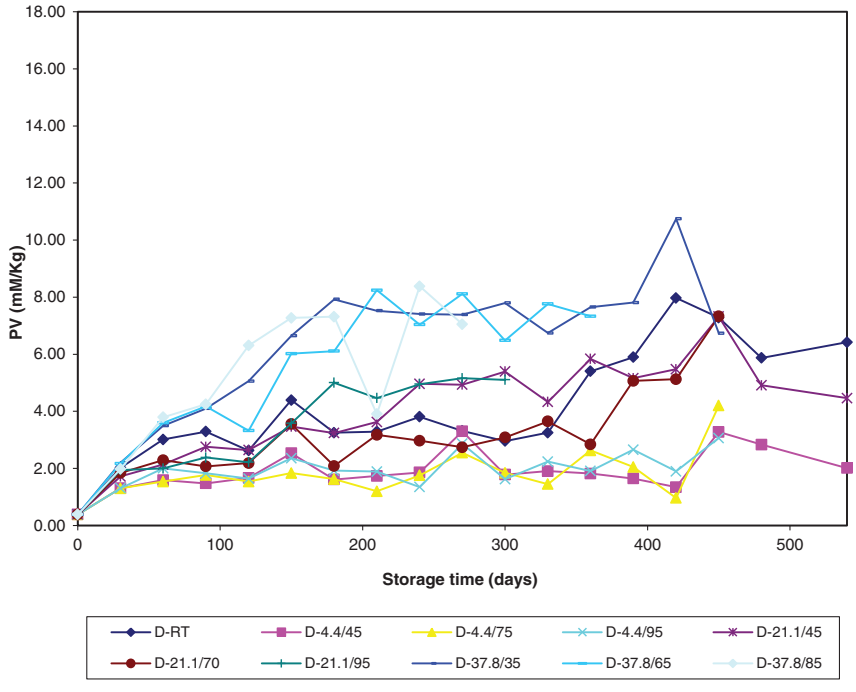


Figure 4–Change in PV content in almond (Sample D) during storage.

indication of dispersion of the data from the mean. We found that the CVs for FFA data were below 5% except for a few data being above 5%. For PV, the CVs were below 3% with a few exceptions. The CVs for IV were mostly below 1% with few exceptions. These low CVs indicate that the data are statistically acceptable. Error bars are not shown in the FFA, PV, and IV figures because adding the error bars to the curves renders the charts difficult to read. Correlation analysis was conducted to produce correlation coefficients for FFA and moisture content. *t*-tests were performed to determine the significance level of the correlation coefficients.

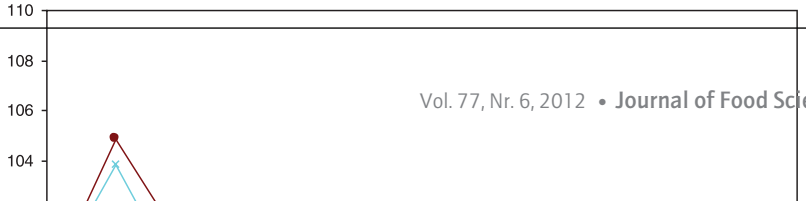
Results and Discussion

PV

The changes in PVs in almonds are shown in Figure 1 to 4. The PVs for the natural samples (A and B) did not change noticeably over the storage time. On the other hand, the blanched samples (C and D) show high PVs and large changes during the storage. Because Samples C and D were blanched, their enzyme activities were much lower than that of Samples A and B, we therefore speculate that production of peroxides may be mainly because of the nonenzymatic oxidation or autooxidation of lipids. The

Figure 5–Change in IV in almond (Sample A) during storage.

Figure 6–Change in IV in almond (Sample B) during storage.



obvious difference in PVs between the raw and blanched samples may be attributed to the protective functions of almond skins. 1st, almond skins are rich in antioxidants that can fight against oxidation. 2nd, almond skins act as an oxygen barrier, which also helps minimize oxidation. The fluctuation shown in all PV curves may be explained by the fact that peroxides are instable and can be further degraded to other compounds such as aldehydes, ketones, and so on, even while new peroxides are produced.

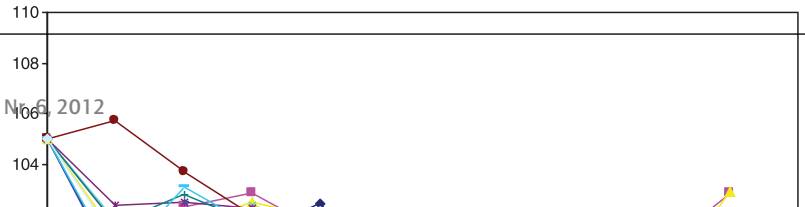
The PVs increased with increasing storage temperature. At the same temperature, the higher the relative humidity is, the lesser the changes in PVs. This suggests that oxidation was promoted by heat but limited by humidity. It is possible that high humidity reduces the exposure of lipids oxygen.

IV

IV indicates the degree of unsaturation in oil, and hence a higher IV is considered a higher potential for oxidation and rancidity. The IVs for all tested samples are shown in Figure 5 to 8. The IV compared with storage time curves fluctuate greatly; however the general trend is that the IVs for all samples decreased

Figure 7–Change in IV in almond (Sample C) during storage.

Figure 8–Change in IV in almond (Sample D) during storage.



slightly up to 150 d of the storage and then leveled off even after 330 d of storage. We therefore decided to terminate the monitoring of IVs. IV seems to decrease faster at higher storage temperature and humidity, and the IVs in the blanched samples decreased faster than the raw samples, which may be because of higher oxidation of unsaturated fatty acids in the blanched samples without skin protection as discussed above.

FFA

The changes in FFA contents during storage are shown in Figure 9 to 12 for the 4 different sample sets. Samples A and B had higher initial FFA content (0.181%) than Samples C (0.091%) and Sample D (0.145%), made from a different variety. The high initial FFA contents in Samples A and B may be because of greater prestorage accumulation of FFA compared with Sample C and D whose enzymatic activities had been inactivated by blanching to certain degree. In general, FFA increased with increasing storage time, temperature, and humidity. Highest levels of FFA were observed in the samples stored at high temperature and high humidity.

For Sample A (Figure 9), at low temperature (4.4 °C), FFA increased only slightly whereas at medium and high temperatures,

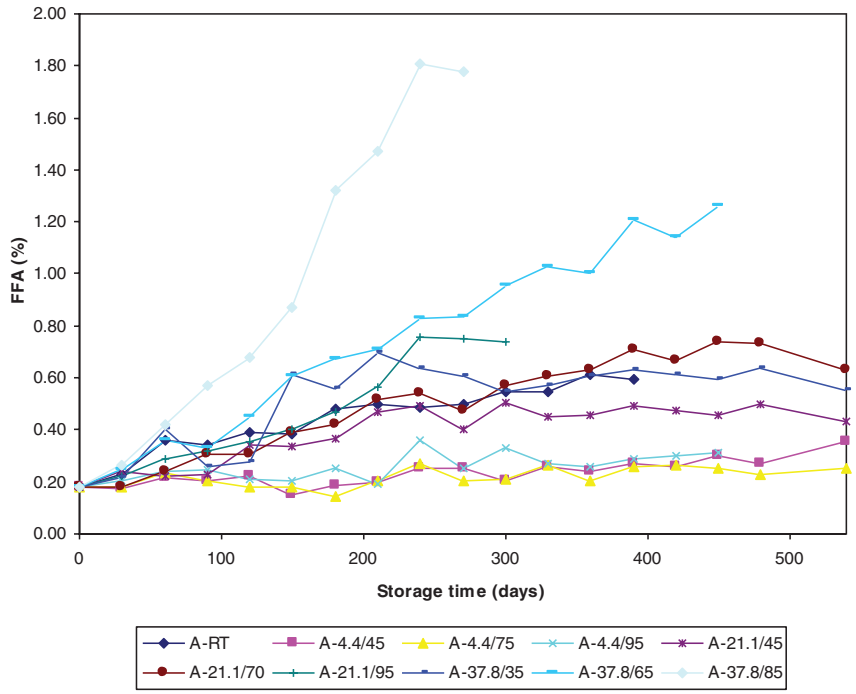


Figure 9–Change in FFA content in almond (Sample A) during storage.

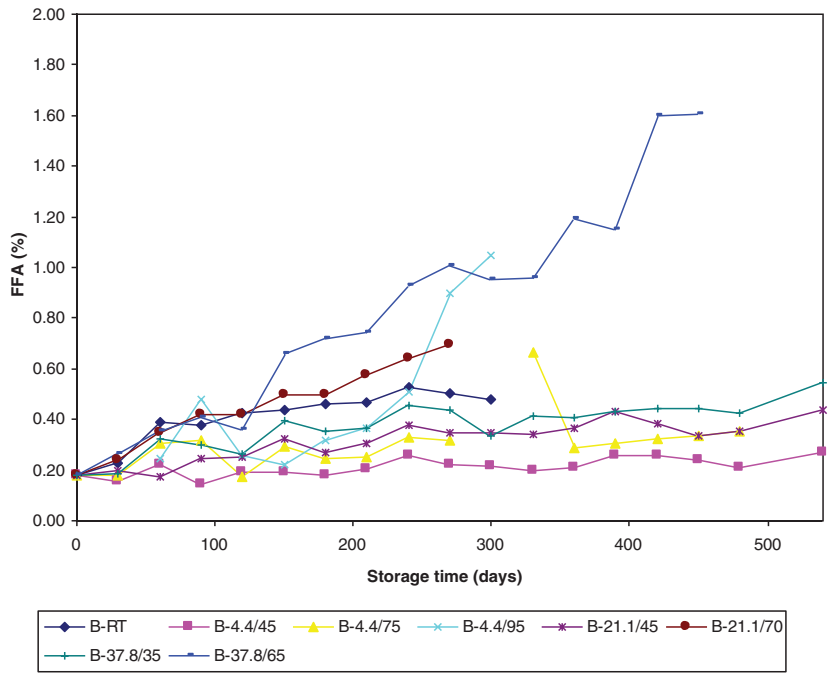


Figure 10–Change in FFA content in almond (Sample B) during storage.

FFA increased dramatically even at low relative humidity, suggesting the importance of temperature. We believe that the high temperature favored the biochemical reactions leading to FFA formation. Figure 13 shows the lipase activity in 3 forms of almonds used in this study at different temperature. For Sample A, the lipase activity doubled when temperature was raised from 4.4 to 21.1 °C, and increased by 20 times at 37.8 °C. At the same temperature, FFA increased with relative humidity. The 1st part of this research showed that the relative humidity during storage dictated the moisture movements and thus the moisture contents of the samples. We conducted a correlation analysis between the FFA contents and moisture contents for all samples and the results are shown in Table 3. Again for Sample A, all except for 2 samples stored at low temperature, show significant correlation between FFA and moisture content. The positive correlations suggest that the increased moisture content favored enzymatic reactions. Interestingly, A-21.1/45 and A-37.8/35 show negative correlation between FFA and moisture contents. A close look at the moisture content compared with storage time curves found that the 2 samples experienced significant loss of moisture during the storage. Despite this loss of moisture content, FFA continued to accumulate as the related reactions occurred at relatively high rates because of high temperatures. However, the FFA contents in these 2 samples began to level off or decline after 300 and 390 d for

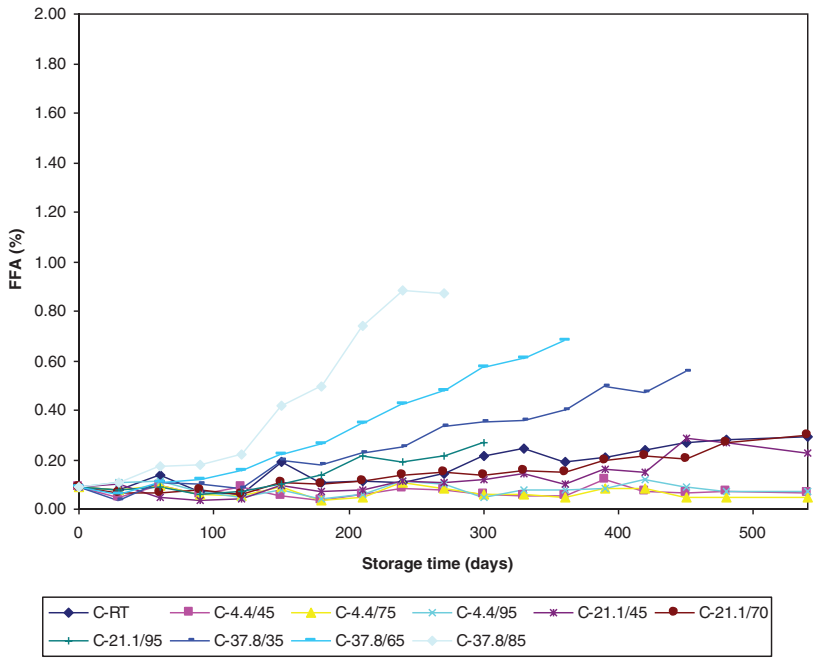


Figure 11–Change in FFA content in almond (Sample C) during storage.

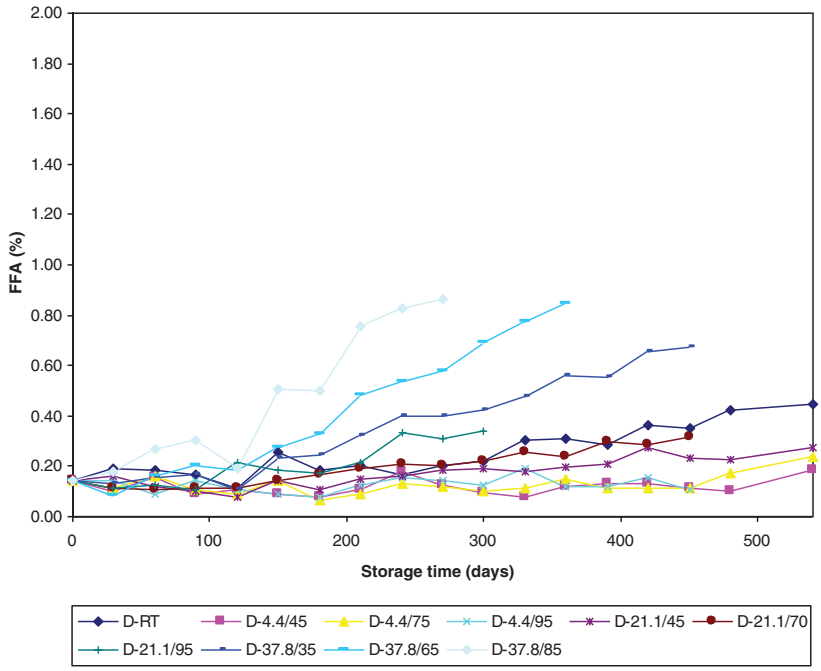


Figure 12–Change in FFA content in almond (Sample D) during storage.

A-21.1/45 and A-37.8/35, respectively, which may be attributed to the reduced enzyme activity when the moisture contents of the samples were lowered to critical values after certain period of storage.

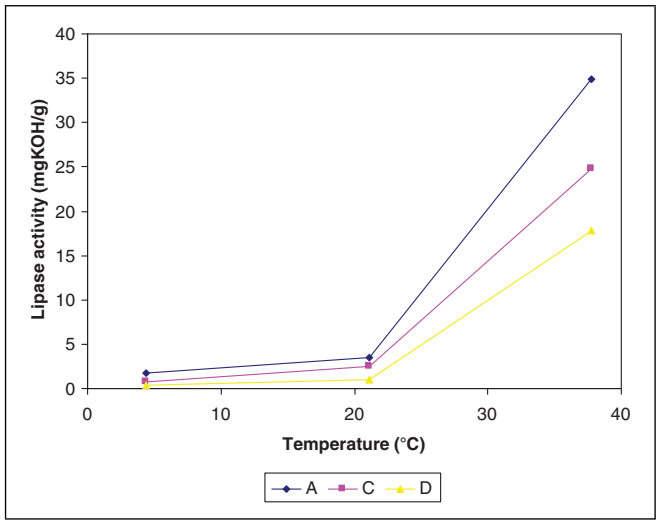


Figure 13–Lipase activity of almonds as a function of temperature (A: raw whole almond, C: blanched whole almond, and D: blanched almond slices).

Sample B behaved similar to Sample A with respect to the effects of storage temperature and relative humidity. We noticed that the FFA in Sample B (Figure 10) was generally higher than Sample A at medium to high relative humidity and lower than Sample A at low-relative humidity and medium to high temperatures. Packaging, which affected moisture absorption, is believed to be responsible for the difference in FFA between the 2 samples. At medium or high relative humidity, unpackaged Sample B absorbed more moisture than Sample A with PE package, whereas at lower relative humidity but medium to high temperatures, Sample B without packaging lost more moisture than Sample A.

FFA formation in Sample C (Figure 11) follows the similar trends observed in Samples A and B but at a lower level, which may be attributed to the lower lipase activity caused by blanching. Figure 6 shows clearly that the lipase was not totally inactivated by blanching, and its activity increased dramatically with increasing temperature. The negative correlations shown in Table 3 were because of significant loss of moisture during the storage at low-relative humidity and medium to high temperatures as discussed above.

Sample D (Figure 12) shows a similar change pattern in FFA to those of Sample C. Sample D had the lowest lipase activity among the 3 forms of almonds used in this study (Figure 6) but its FFA level was generally higher than that of Sample C because its initial FFA was higher than others.

Table 3–Correlation coefficients (*r*) for moisture content and FFA.

Sample ID	*r*	Sample ID	*r*	Sample ID	*r*	Sample ID	*r*
A-RT	0.673[a]	B-RT	0.845[a]	C-RT	0.376	D-RT	0.189
A-4.4/45	0.347	B-4.4/45	0.303	C-4.4/45	−0.046	D-4.4/45	0.173
A-4.4/75	0.151	B-4.4/75	0.495	C-4.4/75	−0.230	D-4.4/75	0.253
A-4.4/95	0.569[a]	B-4.4/95	0.815[a]	C-4.4/95	0.129	D-4.4/95	−0.090
A-21.1/45	−0.644[a]	B-21.1/45	0.035	C-21.1/45	−0.685[a]	D-21.1/45	−0.580[a]
A-21.1/70	0.861[a]	B-21.1/70	0.749[a]	C-21.1/70	0.594[a]	D-21.1/70	0.467
A-21.1/95	0.949[a]	B-37.8/35	−0.223	C-21.1/95	0.801[a]	D-21.1/95	0.799[a]
A-37.8/35	−0.719[a]	B-37.8/65	0.539[a]	C-37.8/35	−0.432	D-37.8/35	−0.160
A-37.8/65	0.786[a]			C-37.8/65	−0.545	D-37.8/65	−0.622[a]
A-37.8/85	0.947[a]			C-37.8/85	0.724[a]	D-37.8/85	0.892[a]

[a]Indicates that the correlation is significant at or above $P_{0.05}$ level.

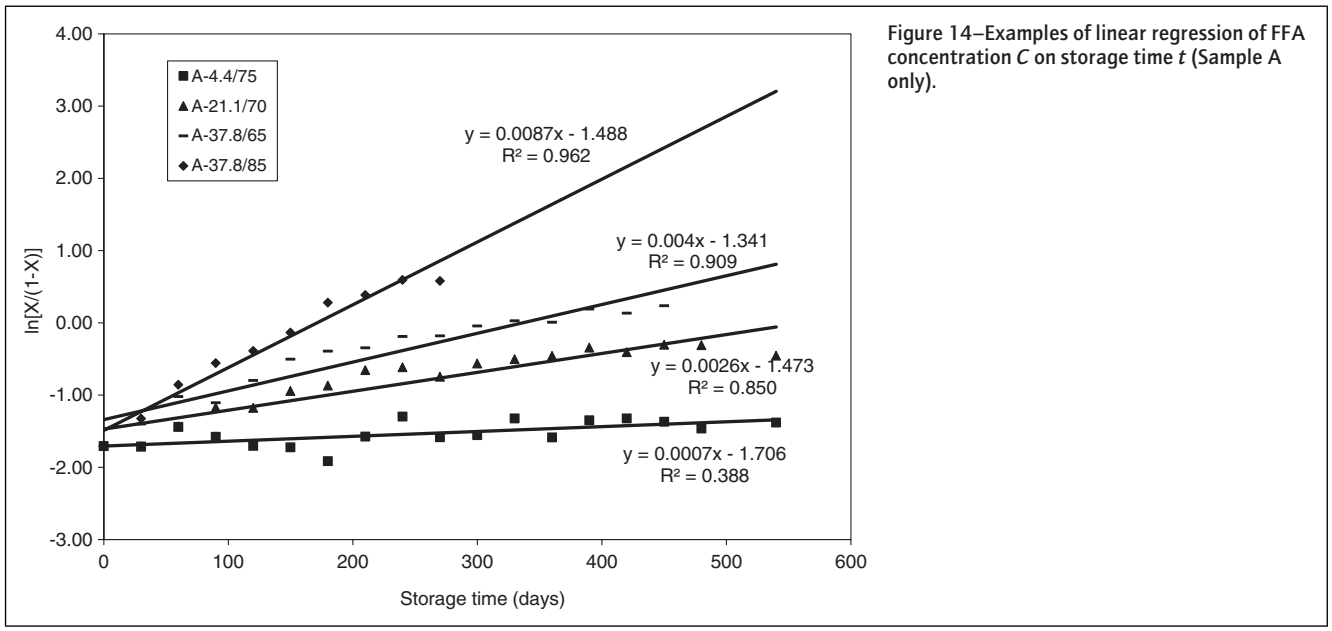


Figure 14–Examples of linear regression of FFA concentration *C* on storage time *t* (Sample A only).

Kinetics of FFA formation

Kinetic studies of lipase hydrolysis of lipids which produce FFA have been traditionally carried out using pure lipase and known substrates and the classic Michaelis–Menten model (Lam and Proctor 2002). In our study, FFA formation in almonds was a result of very complex reversible, consecutive, and multistep reactions, and possibly secondary degradation reactions involving multiple unknown substrates. Therefore, FFA formation is difficult to analyze and predict using theoretical models. When the aim is not to delineate reaction mechanisms, empirical models may be useful for quantitative description of FFA formation kinetics, which provides adequate information on the rate of FFA formation. Lam and Proctor (2002) used an empirical model based on Paolucci-Jeanjean and others' work (2000) to follow the kinetics of FFA formation on the surface of milled rice. Özilgen and Özilgen (1990) and Barreto and others (2003) used the logistic equation to simulate lipid oxidation in foods with reasonable results. The logistic equation seems to be simple empirical approach, which takes the form of

$$\frac{dC}{dt} = kC\left[1 - \frac{C}{C_{\max}}\right], \tag{6}$$

where C is the concentration of the product at time t, $C_{\max}$ is the maximum attainable value of product concentration at the end of the reaction, and k is the reaction rate constant. $C_{\max}$ is unknown in our study. The highest concentration of FFA observed from our study was 1.81% for sample A-37.8/85. By looking at the FFA curves in Figure 2 to 5, the FFA concentration was expected to rise to a much higher level with prolonged storage time. For the sake of simplicity, we assumed that $C << C_{\max}$, and therefore the term $[1 - \frac{C}{C_{\max}}]$ approaches 1 in Eq. (6), and hence Eq. (6) can be rewritten as:

$$\frac{dC}{dt} = kC \tag{7}$$

Eq. (7) is a 1st-order reaction. The integration of Eq. (7) yields:

$$C = C_0 e^{kt}, \tag{8}$$

which is rearranged to a linear equation as follow:

$$\ln C = \ln C_0 + kt. \tag{9}$$

Eq. (8) represents a line of independent variable t (storage time), and dependent variable C (FFA concentration). Running linear regression of ln C on t will allow us to obtain k (slope of the line) and C_0 (the intercept of the line). Figure 14 shows a few examples of the plots of ln C against t with linear fits for Sample A. The model fits better for samples with higher FFA formation rates than for samples with lower FFA formation rates. The numerical values for k, C_0, and regression coefficient r for all samples are listed in Table 4. The t-tests indicate that the regression coefficients are at least $P = 0.05$ significant for all samples except for 6 samples, 3 from each of Samples C and D, which were stored at low temperature. The small increase in FFA in these samples at low storage temperature led to large variations. The values in Table 4 can be used to establish equations based on Eq. 8 or Eq. 9 to predict the FFA concentration for specific storage conditions.

From Table 4, we can see that the FFA formation rates increased with increasing temperature. To establish the relationship between FFA formation rates and temperature, Arrhenius equation (Eq. 10) was used.

$$k = k_0 e^{-Ea/RT}, \tag{10}$$

or its linear form

$$\ln k = \ln k_0 - \frac{Ea}{R}\frac{1}{T}, \tag{11}$$

where k is the FFA formation rate available in Table 4, k_0 is the pre-exponential factor, E_a is activation energy, R is gas constant, and T is absolute temperature (°K). Because 2 subsets of Sample B were discarded in the early stage of the storage because of spoilage and k values for 6 samples from C and D stored at low temperature are not reliable as indicated by the insignificant regression coefficients, we applied Eq. 11 to the FFA formation rates for

Table 4–Numerical values for the parameters in FFA formation model (Eq. 8).

	k	C_0	r
A-RT	2.58×10^{-3}	0.252	0.909[a]
A-4.4/45	1.06×10^{-3}	0.175	0.822[a]
A-4.4/75	6.72×10^{-4}	0.182	0.623[a]
A-4.4/95	1.02×10^{-3}	0.200	0.719[a]
A-21.1/45	1.65×10^{-3}	0.245	0.823[a]
A-21.1/70	2.62×10^{-3}	0.229	0.922[a]
A-21.1/95	4.89×10^{-3}	0.198	0.986[a]
A-37.8/35	1.88×10^{-3}	0.294	0.725[a]
A-37.8/65	3.99×10^{-3}	0.261	0.954[a]
A-37.8/85	8.69×10^{-3}	0.226	0.981[a]
B-RT	2.87×10^{-3}	0.253	0.840[a]
B-4.4/45	7.77×10^{-4}	0.171	0.707[a]
B-4.4/75	1.24×10^{-3}	0.215	0.596[a]
B-4.4/95	5.07×10^{-3}	0.168	0.826[a]
B-21.1/45	1.50×10^{-3}	0.207	0.868[a]
B-21.1/70	4.47×10^{-3}	0.230	0.951[a]
B-37.8/35	1.50×10^{-3}	0.244	0.822[a]
B-37.8/65	4.35×10^{-3}	0.259	0.959[a]
C-RT	2.66×10^{-3}	0.076	0.849[a]
C-4.4/45	8.04×10^{-5}	0.066	0.045
C-4.4/75	-7.54×10^{-4}	0.078	0.386
C-4.4/95	-2.11×10^{-6}	0.077	0.001
C-21.1/45	2.93×10^{-3}	0.050	0.816[a]
C-21.1/70	2.84×10^{-3}	0.062	0.946[a]
C-21.1/95	4.55×10^{-3}	0.061	0.871[a]
C-37.8/35	5.16×10^{-3}	0.065	0.935[a]
C-37.8/65	6.75×10^{-3}	0.072	0.979[a]
C-37.8/85	9.32×10^{-3}	0.088	0.985[a]
D-RT	2.04×10^{-3}	0.138	0.870[a]
D-4.4/45	2.59×10^{-4}	0.107	0.163
D-4.4/75	5.86×10^{-4}	0.104	0.330
D-4.4/95	2.89×10^{-4}	0.115	0.174
D-21.1/45	1.69×10^{-3}	0.106	0.806[a]
D-21.1/70	2.45×10^{-3}	0.105	0.944[a]
D-21.1/95	3.73×10^{-3}	0.108	0.889[a]
D-37.8/35	4.13×10^{-3}	0.118	0.957[a]
D-37.8/65	6.09×10^{-3}	0.109	0.969[a]
D-37.8/85	6.96×10^{-3}	0.147	0.943[a]

[a]Indicates that the regression fit is significant at or above $P_{0.05}$ level.

Table 5–Temperature dependence of FFA formation rates.

	Low *RH*	Medium *RH*	High *RH*
K_0	2.64×10^{-1}	1.75×10^{4}	8.43×10^{5}
E_a (Cal/Mol)	3.01×10^{3}	9.32×10^{3}	1.12×10^{4}

Sample A only, and the resultant data are shown in Table 5. The activation energy values are 3.01×10^3, 9.32×10^3, and 1.12×10^4, for low, medium, and high-relative humidity ranges, respectively. These data indicate that the FFA formation reaction was more temperature dependent and the reaction rate increased faster at higher relative humidity (*RH*) than at lower *RH*. Similar temperature dependence was reported for lipid oxidation in Pistachio nuts when they were stored in different atmospheric environments (Maskan and Karata 1998), and in other foods (Labuza 1982).

To incorporate the temperature (*T*) dependence of FFA in the kinetic model, we combine Eqs. 8 and 10,

$$C = C_0 e^{kt} = C_0 e^{k_0 e^{-Ea/RT} t}, \quad (12)$$

where k_0 and E_a can take the values shown in Table 5. Alternatively, because k_0 and E_a are a function of the relative humidity, they can be computed empirically by establishing $k_0 = f(RH)$ and $E_a = f(RH)$ relationships using experimental data like those shown in Table 5. Therefore, Eq. 12 can be used to predict FFA concentration *C* at any given time *t* at known storage temperature (*T*) and *RH* when initial FFA concentration C_0 is determined experimentally.

Conclusions

The PVs in the raw samples did not change noticeably whereas the blanched samples changed greatly, in which the skins may have played a significant role. The IVs decreased slightly in the 1st 150 d of storage and then leveled off. The slightly faster changes in IVs in the blanched samples coincided with the greater changes in PVs in the blanched samples. Samples A and B had higher initial FFA (0.181%) than Samples C (0.091%) and Sample D (0.145%). The high-initial FFA contents in Samples A and B may be because of greater prestorage accumulation of FFA compared with Sample D whose enzymatic activities had been inactivated by blanching to certain degree. In general, FFA increased with increasing storage time, temperature, and humidity. Highest levels of FFA were observed in the samples stored at high temperature and high humidity. The changes in PV and FFA in our study seem disconnected. The PVs were high in the blanched samples where FFAs were low. The high FFAs in the raw samples did not yield high PVs. Therefore, we believe that FFA contributed little to the peroxides in almonds through FFA oxidation mechanism. Therefore, FFA alone is not a reliable indicator of rancidity (Harris and others 1972). The skins were very effective in preventing FFAs from further oxidation. On the other hand, blanching, which is believed to inactivate enzymes in the almonds, did not provide much protection against autooxidation of lipids.

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