Lipid deterioration during storage of Almond kernels (Shalimar var.)

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ABSTRACT

Almond is one of the most valuable nuts in the world. Due to the high presence of these unsaturated fatty acids almonds are highly susceptible to immediate lipid oxidation which impairs their nutritive as well as sensory quality. The aim of the research was to determine the best storage conditions for almond kernels. Almonds of uniform size were manually decorticated and extracted kernels were mechanically dried at 40 ^{0}C to a final moisture content of 4.20% after antioxidant treatment (0.015% BHA + 0.015% BHT). Both treated and untreated samples were packed in LDPE and Laminates (under vacuum) to monitor the changes in quality attributes under ambient (19^{0}C±2^{0}C, RH 22%) and accelerated (35 ^{0}C±1^{0}C, RH 60-70%) storage conditions for a period of 270 days. Antioxidant treated samples packed in vacuum laminates and stored under ambient conditions proved significantly superior by exhibiting minimum free fatty acid value (0.75 mg/g) and minimum peroxide value (109.99 meq/100g) compared to untreated kernels packed in LDPE under accelerated conditions throughout the storage period. The peroxide value and fatty acid value in the treated samples did not change noticeably whereas the untreated samples changed greatly, indicating that antioxidant treatment and packaging have played a significant role. Higher free fatty acid levels than the blanched samples after storage. In general, free fatty acids increased with increasing storage time, temperature, and humidity. Highest levels of free fatty acids were observed in the untreated samples stored at high temperature and high humidity.

Key words: Almond kernels, Antioxidants, Packaging materials, Storage conditions.

1. INTRODUCTION

Almonds (*Prunus dulcis*) are native to Mediterranean region and are considered as one of the oldest tree nuts in the world. According to United States Department of Agriculture foreign agricultural service the average production of almond in India during the year 2016 was 72,000 MT (a 16% increase over last year's production) grown under an area of 17000 hectares. The almond production in India is expanding as like other fruits in the nation. Almond was introduced in Kashmir during 16th century by Persian settlers. Average

production of the almond in Jammu and Kashmir is 7030 MT over an area of 7132 hectares (Anonymous, 2016). Almonds are low in saturated fats and high in many other protective nutrients which help in preventing cardiovascular, cancer diseases and in reducing heart attack risks. Almonds are low in saturated fats and high in many other protective nutrients which help in preventing cardiovascular, cancer diseases and in reducing heart attack risks. On an average 100g of almond contain total fat 949g, monounsaturated fat 31g, total Omega-3 fatty acid 6mg, total Omega-6 fatty acid 12065 mg.

Due to the high presence of these unsaturated fatty acids almonds are highly susceptible to immediate lipid oxidation which impairs their nutritive as well as sensory quality (Maguire *et al.,* 2004). Lipid deterioration in almonds may proceed in two ways; one is enzyme-catalyzed hydrolytic cleavage and second 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 oxidation. The resultant free fatty acids, if further oxidized, may give rise to rancidity. In addition, free fatty acids are preferred substrate for respiration. As a result of the accelerated respiration activity, water, heat and CO_2 are produced leading to 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 autoxidation 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 some of the common techniques for minimizing autoxidation of lipids in almonds (Mexis *et al.*, 2009).

The aim of the research was to determine the best storage conditions for almond kernels. Almonds of uniform size were manually decorticated and extracted kernels were mechanically dried at 40 ^{0}C to a final moisture content of 4.20% after antioxidant treatment (0.015% BHA + 0.015% BHT). Both treated and untreated samples were packed in LDPE and Laminates (under vaccum) to monitor the changes in quality attributes under ambient (19^{0}C±2^{0}C, RH 22%) and accelerated (35 ^{0}C±1^{0}C, RH 60-70%) storage conditions for a period of 270 days.

2. Materials and Methods

The Almonds were procured from Centeral Institute of Temperate Horticulture, srinagar and the study was carried out at Division of Food Science and Technology, Sher-e-Kashmir University of Agricultural Science and Technology of Kashmir (SKUAST-K), Shalimar.

Samples were taken periodically for analysis of free fatty acids (FFAs) content and peroxide value (PV) 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.

2.1 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.

2.2 Free fatty acid (%)

Standard AOAC procedure (2005) was followed for determination of free fatty acid. 5 g sample was taken in a flask and 50 ml benzene was added and kept for 30 minutes for extraction of free fatty acids. After extraction, 5 ml extract, 5 ml benzene, 10 ml alcohol and phenolphthalein as indicator was taken in a flask and titrated against 0.02 N KOH till pink colour disappeared.

$$\%\text{FFA (as oleic acid)} = \frac{282\times 0.02\ \text{NKOH}\times \text{ml of alkali}\times \text{D.F}}{1000\times \text{weight of sample (g)}} \times 100$$

2.3 Peroxide value (meq/kg)

The peroxide value of the crude fat extracted from all the treatment samples was estimated as per Association of American Chemists (AOAC) 1995. 5.0 gram of sample from each treatment was taken in triplicate in a stopper flask. To this 25 ml of solvent (2 volumes of glacial acetic acid and one volume of chloroform) and 1 ml of saturated potassium iodide solution was added. The flask was allowed to stand for one minute, followed by addition of 35 ml of distilled water. The solution was titrated against 0.1 N sodium thio-sulphate using starch as indicator. During the titration the flask was kept shaking to remove the last traces of iodine from the chloroform layer. Blank titration was carried out simultaneously. The peroxide value was calculated as milli equivalent of peroxide/kg of sample.

$$\text{Peroxide value} = \frac{(\text{Sample titre-blank titre})\times \text{Normality of } Na_2S_2O_3\ (\text{meq/kg})}{\text{Weight of sample taken in gram}} \times 1000$$

3. Result and Discussion

- **Free fatty acids**

The data reveals that the antioxidant treated (T_2) almond kernels samples had significantly low value of

free fatty acid content (0.86%) compared to the value of 0.91 per cent recorded in untreated (T_1) samples. A significantly lower mean free fatty acid content of 0.79 per cent was recorded in laminated (P_2) samples under vacuum as compared to the value of 0.97per cent recorded in samples from LDPE packaging (P_1). The significantly higher free fatty acid content was recorded in samples stored under accelerated temperatures (C_2) (0.94%) as compared to value of 0.82per cent recorded in samples stored under ambient temperatures (C_1). With the advancement of storage periods there was increase in free fatty acid content of almond kernels with lowest (0.64%) at o days and highest (1.10%) at 270 days of storage.

Interaction effect of the antioxidant treatment and packaging materials (T×P), antioxidant treatment and storage temperatures (T×C), packaging materials and storage temperatures (P×C), packaging materials and storage periods (P×D), storage temperatures and storage periods (C×D), antioxidant treatment storage temperature and storage periods (T×C×D) and storage temperature, packaging and storage periods (T×C×P×D) were significant but no significant effects of interaction among various treatments on mean variations in free fatty acid value like antioxidant treatment, packaging materials and storage temperatures (T×P×C), packaging materials (C×P), treatment,) antioxidant treatment and storage periods (T×D), antioxidant treatment, packaging materials, and storage periods (T×P×D), packaging materials, storage temperatures and storage periods (P×C×D) were found.

However, minimum and maximum fall was observed in antioxidant treated samples (T_2) from laminate vacuum packaging (P_2) stored under ambient temperatures (C_1) and from untreated (T_1) samples under accelerated temperatures (C_2) in LDPE (P_1) packaging at 270 days of evaluation as indicated by mean free fatty acid value of 0.84 per cent and 1.55 per cent respectively from an initial value of 0.64 per cent recorded at 0 days of storage.

Free fatty acids are the resultant products of lipid oxidation which gives rise to rancidity. Production of FFA is due to hydrolysis of triglycerides by lipase or due to non-enzymatic reaction at high temperature (Camire *et al.,* 2007). According to Indian Standards, FFA concentration should remain under 10% as this limit is acceptable for human consumption (Amin *et al.,* 2016). Antioxidant treated and vacuum packaged samples showed significantly low value of free fatty acids as compared to untreated and LDPE packed samples. The study confirmed previous reports that unshelled almonds maintained at ambient temperatures do not show significant chemical and biochemical changes for one year (Senesi *et al.*, 1996). Among the two storage conditions the higher free fatty acid value was recorded in stored under accelerated temperatures (0.94%) as compared to value of 0.82per cent recorded in samples stored under ambient temperatures. Nogala and Gogolewski (2000) reported that the oxidation of fats and the rate of rancidity development are highly dependent on the temperatures. In the way, the higher the temperature the higher is the rate of rancidity.

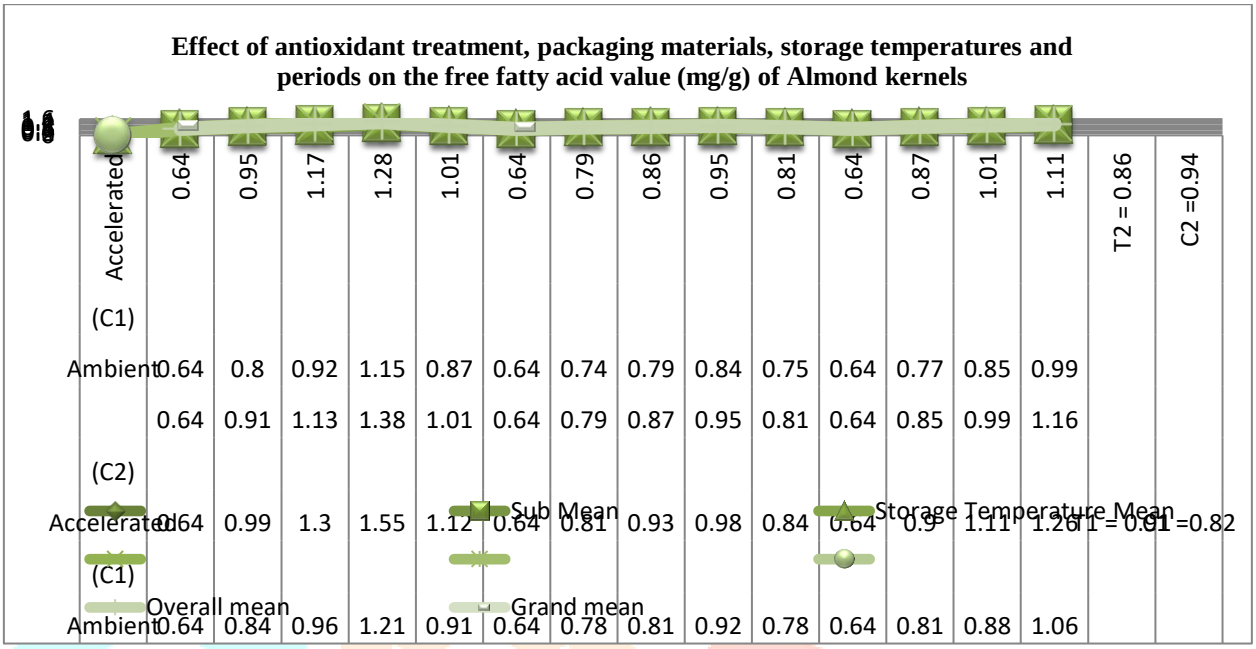

Figure 1: Change in free fatty acid content in Almond kernel Samples during storage.

- **Peroxide value**

Analysis of the data revealed a significant difference in peroxide value of the kernels with respect to the treatments used. Antioxidant treated (T_2) samples recorded significantly lower peroxide value of 1.69meq/100g compared to value 1.74 meq/100g recorded in untreated (T_1) samples. Minimum increase in peroxide (1.65 meq/100g) value was recorded in kernels packed in laminates (P_1) under vacuum as compared to value of 1.76 meq/100g observed in LDPE (P_1) packed samples. Significantly higher peroxide value 1.75 meg/100g was recorded in samples stored under at accelerated temperatures (C_2) as compared to value of 1.68meq/100g recorded in samples stored under ambient temperatures (C_1). Amongst all the packaging materials and antioxidant, no significant increase in peroxide value of the samples was observed at 90 days of ambient storage. The value of 1.52 meq/100g at 0 days and 1.69 meq/100g at 90 days of storages was recorded. However, significantly higher value of 1.89meq/100g was recorded at 270 days of storage.

Perusal of the data further indicated that antioxidant treatment and packaging materials (T×P), antioxidant treatment and storage temperatures (T×C), antioxidant treatment and packaging materials and storage temperatures (T×P×C), packaging materials and storage periods (P×D), antioxidant treatment, packaging materials and storage periods (T×P×D), storage temperature and storage periods (C×D) and antioxidant treatment, storage temperatures, packaging materials and storage periods (T×C×P×D) had

significant effect on the peroxide value of almond kernels but no significant effects of interaction among various treatments on mean variations in peroxide value like that antioxidant treatment and storage temperatures (T×C), packaging materials and storage temperatures (P×C), antioxidant treatment and storage periods (T×D), antioxidant treatment, storage temperatures and storage periods (T×C×D) and packaging materials, storage temperatures and storage periods (P×C×D) was found.

However the minimum peroxide value of 1.52 meq/100g was observed at 0 days of storage amongst all the treatment combinations and a maximum of 1.84 meq/100g was recorded in untreated (T_1) samples packed in LDPE (P_1) stored under accelerated conditions at 270 days of storage.

Antioxidant treated almond kernels significantly reduced the free radical release in kernels in comparison to untreated samples. Efficacy of antioxidant improves because of the reinforcing mechanism wherein primary antioxidant concentration is continuously replenished over extended periods of storage. This means that a significantly low antioxidant, free radical molecule ratio is maintained in the substrate thus helping to keep peroxide value down (Fennema, 1996). The antioxidant treated samples had lower peroxide value 1.69 than the value of 1.74 recorded in untreated samples. The results are in conformity to Sophia (2004) who reported that addition of TBHQ had a significant effect on autoxidation of walnut oils as lesser value of 2.79 was recorded in samples of oils treated with antioxidant compared to higher value of 2.97 in untreated samples. Build up of peroxides was significantly lower in laminates under vacuum packaged samples (1.65) in comparison to the value 1.76 recorded in LDPE packaged samples. LDPE (at times is fairly permeable to oxygen ingress due to development of cracks during long storage and defective sealing), thus allowing autoxidation, which takes place at an accelerated rate that is reflected by higher peroxide value. Finally the initial peroxide content of vacuum packaged almond kernels stored at ambient conditions did not appreciate significantly throughout the 270 days of storage. The results were in conformity to Gracia *et al.* (2002). Senesi *et al.* (1991) studied, in almonds, the effect of a long storage period (224 days) using different temperatures (4 ^{o}C, 20 ^{o}C) and atmospheres (vacuum, nitrogen) and obtained a higher peroxide level when 20 ^{o}C was used.

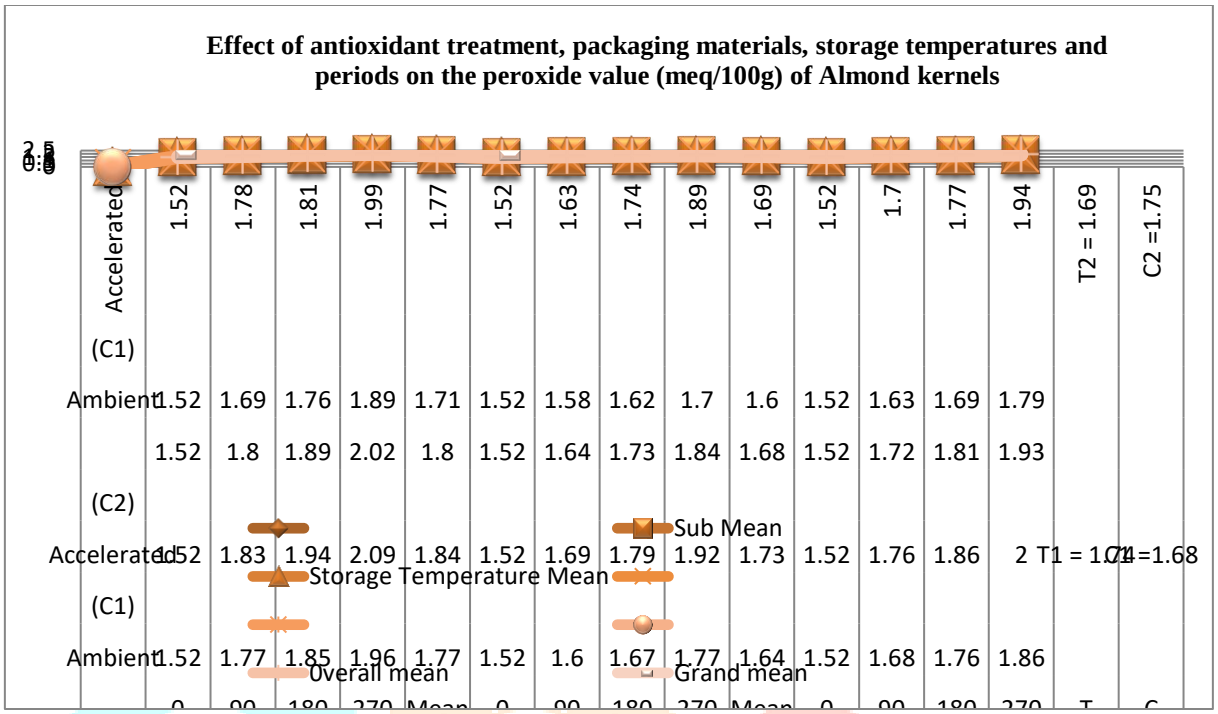

Figure 2: Change in PV content in Almond kernel Samples during storage.

LITERATURE CITED

Amin, T., Bashir, A., Dar, B. N. and Naik, H. R. 2016. Development of high protein and sugar free cookies fortifid with Pea (*Pisum sativum* L.) flour, soibean (*Glycine max* L.) Flour and oat (*Avenus sativa* L.) flakes. *International Food Research Journal* **23**(1): 72-76.

Anonymous, 2016. Physical progress report. Department of Horticulture (Kashmir), Government of Jammu and Kashmir.

AOAC (1995). Official method of analysis of the Association of official Analytical Chemist, 7th ad. AOAC Press, Arlington, Virginia, USA.

AOAC. 2005. Official method of Analysis of the Association of Official Analytical chemists. 10th Ed., Washington DC. USA.

Camire, M. E., Doughtery, M. P. and Briggs, J. L. 2007. Functionality of fruit powders in extruded corn breakfast cereals. *Food Chemistry* **101**(2): 765-770.

Fennema, O. R. 1996. *Food chemistry*. Third edition. Marcel Dekker, Inc., New York pp. 157-430.

Gracia-Pascual, P., Mateos, M., Carbonell, V. and Salazar, D. M. 2002. Influence of storage conditions on the quality of shelled and roasted almonds. *Biosystem Engineering* **84**(2): 201-209.

Maguire, L., O'Sullivan, S., Galvin, K., O'connor, T. and O'Brien, N. 2004. Fatty acid profile, tocopherol, squalene and phytosterol content of walnuts, almonds, peanuts, hazelnuts and the macadamianut. *International Journal of Food Science and Nutrition* **55**(3): 171-78.

Mexis, S. F., Badeka, A. V., Riganakos, K. A., Karakostas, K. X. and Kontominas, M. G. 2009. Effect of packaging and storage conditions on quality of shelled walnuts. *Food Control* **20**: 743-751.

Nogala, K. M. and Gogolewski, M. 2000. Alteration of free fatty acid composition, tocopherol content and peroxide value in margarine during storage at various temperatures. *Nahrung Food* **44**(6): 431-433.

Senesi, E., Rizzolo, A., Colombo, C. and Testoni, A. 1996. Influence of pre-processing storage conditions on peeled almond quality. *Italian Journal of Food Science* **2**: 115–125

Sophia-Devi, L. 2004. *S*tudies on extraction and evaluation of oil from walnuts. M. Sc. Thesis submitted to Dr. Y. S. Parmar University of Horticulture and Forestry, Nauni, Solon (H. P.) pp. 61.