Postharvest operations of pistachio nuts

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Abstract The most important postharvest operations of pistachio nuts including handling, transportation, green hull removal, dehydration, bulk storage and packaging of pistachios were studied. Results showed that air temperature had pronounced effect on drying time and air velocity didn't any significant effect on drying time. The entire drying process occurred in falling rate period and constant rate period was not observed. The optimum conditions for bulk storage of pistachio nuts were between 0 and 10 °C and relative humidity (RH) of 65–70 % or kept at higher than 10 °C (e.g. 15 °C) and less than 32 % RH, and monolayer moisture content had the longest shelf life due to the minimum changes in its lipid quality factors. The higher temperatures and longer storage times will accelerated deteriorative reactions in pistachio nuts especially on fat component and nylon under vacuum is the best packages for pistachio nuts among other packaging materials were studied in this research.

Keywords Pistachio · Postharvest technology · Sorption isotherm · Drying · Storage · Packaging

Introduction

Pistachio nut (*Pistacia vera* L.) is one of the major agricultural products in Iran, mainly in Kerman, Khorasan, Semnan and Pars provinces. The world pistachio exports in 2010 was 320,000 t out of which 160,000 t (50 % of the world's exports) was produced in Iran. Iran is considered to be the most important pistachio exporter in the world (Tavakolipour and Mokhtarian 2012). Pistachio is consumed worldwide both in

raw and toasted form, and as ingredient in fermented meats, ice cream, bread, sauces, puddings, halva, baklava and other traditional Persian food. Pistachio composition varies depending on cultivar, maturity at harvest and moisture content. The compositional analysis of Persian pistachio kernels (Table 1) indicates that pistachio is a high nutritional nut. It is very rich in unsaturated fatty acids (89.1 % of the total fatty acids), and 30 % of this proportion is polyunsaturated. Pistachio nut has a high lipid content and very rich in unsaturated fatty acids and this makes the pistachio nut a very sensitive product to rancidity and mold contamination.

According to recent studies, pistachios have many health benefits, since they regulate cholesterol levels, have a positive effect on cardiovascular diseases, and for their antioxidant concentrations specially Polyphenols and Tocopherols (Tsantili et al. 2011).

Proper harvesting and postharvest handling are two key activities in achieving maximum yield of good quality of pistachio nuts, which effect marketability and profit. Proper handling after harvest is very important unit operation. The qualities of dried nuts are greatly influenced by the drying and storage operations (Kashaninejad et al. 2010). Harvest usually begins in early September and continues for 4–6 weeks. Pistachios are mechanically shaken from the tree or by hand and fall directly onto a catching frames. High moisture content, 40 to 50 % on a fresh weight basis, split shell pistachios, tender outer green hull all contribute to susceptibility of nuts to mechanical damage and contamination once they drop on the orchard floor. It is because *Aspergillus flavus* is present on the wet orchard soil and has the potential to infest pistachios that contact the soil (Thompson et al. 1997).

During various postharvest processes such as drying, storage and packaging, water adsorption and desorption processes play an important role on deteriorative factors such as, external and internal browning, lipid oxidation and microbial growth of nut and shell (Tavakolipour and Kalbasi-Ashtari 2008). Because a_w is the most important parameter for the

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Table 1 Composition and fatty acid profile of pistachio nuts

Chemical composition	(%)
Moisture ^a	2.5–4.1
Protein ^a	15–21.2
Fat ^a	55.2–60.5
Carbohydrate ^a	14.9–17.7
Fiber ^a	1.7–2
Ash (minerals) ^a	2.2–2.5
Fatty acids profile	(%)
Palmitic Acid ^b	10.24–11.20
Stearic Acid ^b	0.7–0.9
Palmitoleic Acid ^b	0.6–0.7
Oleic Acid ^b	51.0–52.0
Linoleic Acid ^b	26.7–27.1
Linolenic Acid ^b	0.3–0.5

^a Kamangar and Farsam (1977), ^b Tsantili et al. (2010) and Satil et al. (2003)

stability of raw and processed agricultural products, the sorption isotherms can be used to estimate optimum residual moisture content as a result of drying process (Wang and Brennan 1991). Sorption isotherms can also be used to design their suitable packaging and storage conditions (Saravacos et al. 1986), and to select proper ingredients for preparation of a formulated intermediate moisture food (Mir and Nath 1995). However, very limited data are available on sorption isotherms of different pistachio varieties (Chayjan and Esna-Ashari 2011; Zomorodian and Tavakoli 2007). Tavakolipour and Kalbasi-Ashtari (2008) determined the sorption characteristics of whole pistachio nuts, kernel and powder at 15, 25, 35 and 40 °C and developed sorption equations for the obtained data.

Drying pistachio nuts is one of the most important unit operations in any pistachio processing plant. The improper operation of pistachio drying may cause severe damage to the nut both qualitatively and quantitatively. Drying temperature affects the sensory attributes of pistachio nuts and its roasted flavor increases during high drying temperatures (116–138°C). Tavakolipour (2011) studied the pistachio drying in cross flow convective dryer. He determined effective diffusivity (D_{eff}) by using Fick's second law in the range of 7.061×10^{-10} to 2.105×10^{-9} m²/s over temperature range of 40–70 °C. Also, some researches conducted on modeling of thin layer drying kinetics of pistachio nuts (Chayjan and Esna-Ashari 2011; Kouchaczadeh and Shafeei 2010; Tavakolipour 2011). Application of modern and combined technology (such as ultrasound assisted sun drying) for pistachio drying resulted lower power consumption and greater economic saving (Kouchaczadeh 2013).

It is well known that many factors, such as prolonged storage under air and/or at a relatively high temperature and humidity have negative effects on various nut quality attributes. In comparison with other food products, studies on the storage

stability of pistachio nuts are very limited. Tavakolipour et al. (2010) evaluated the storage stability of whole split pistachio nut (Kerman cultivar), stored at 5, 15, 25 and 35 °C and relative humidity of 11 to 87 %. Tsantili et al. (2011) investigated the effects of cultivar, drying and storage conditions on total phenolics (TP), total flavonoids (TF) and total antioxidant capacity (TAC) of fresh in-shell kernels of pistachios. They stored dried nuts in packaging atmosphere of dry air or N₂ at 1 °C or 20 °C for 6 or 12 months prior to quality control experiments. Leufven et al. (2007) studied on packaging of pistachio nuts in multilayer plastic pouches (PS/EVOH/PE) at varying conditions (atmospheres, partial vacuum and by using oxygen scavenger) at the temperature of 20, 35 and 50 °C. Bellomo et al. (2009) worked on stability of pigment and oil in pistachio kernel packaged using two films (nylon and ethylene vinyl alcohol) with and without oxygen scavengers at three different temperatures after 14 months. Raei et al. (2010) investigated the effects of different packaging materials including five layers of compound film, modified polypropylene and metalized plastic, and packaging atmosphere on the quality of roasted pistachio nuts. Results showed that packaging pistachio nut in metalized film and five-layer films with gases N₂/CO₂ and vacuum conditions kept the quality of pistachio better and extended shelf-life. Raei and Jafari (2011) studied the effect of four packaging materials including cellophane, two and three layers plastic pouches, and metal cans on quality attributes of pistachio nuts were stored in two temperatures (ambient and 40 °C) for 1 year. Results indicated that two and three layer plastic pouches resulted in higher quality attributes for the stored pistachios. Shakerardekani and Karim (2012) evaluated the effect of different type of flexible packaging films (LDPE, PVC, LDPE/PA, PA/PP and PET) on the moisture and aflatoxin contents of whole pistachio nuts during storage at ambient temperature (22–28 °C) and relative humidity of 85–100 %. The aims of this research are find the best models for prediction of water sorption isotherms which useful for pistachio storage and packaging, optimum drying temperatures and dehydration kinetic model for retention of nutrients and antioxidant to final dried product and find optimum storage conditions such as temperature and relative humidity and packaging materials for extension of pistachio shelf life and aflatoxin growth prevention.

Materials and methods

Materials

For drying experiments, the pistachio nuts immediately transported to laboratory, were dehulled and sorted for selection of uniform size and split pistachio and kept in darkness at a temperature of 5 °C until drying experiments. Average moisture content of Pistachio found to be 47 % (wet basis).

For sorption isotherms, storage and packaging experiments raw and dried Kerman variety pistachio nuts were purchased from a local market. They were sorted and separated as split and non split samples. Medium-sized and split pistachio nuts with a moisture content of 4.5 % (d.b.) were selected for the tests and stored at 5 °C. Various saturated salt solutions including LiCl, CH₃COOK, MgCl₂, K₂CO₃, Mg(NO₃)₂, NaNO₂, NaCl, and KCl were used to maintain constant relative humidity.

For bulk storage experiments, four saturated salt solutions including LiCl, MgCl₂, NaNO₂ and KCl were used to obtain constant relative humidity. Packaging materials including cellophane, nylon and metal cans were used in pistachio packaging.

Methods

Moisture sorption isotherm

Sorption isotherms of pistachio nuts were determined by a static gravimetric method at 15 and 35 °C according to Tavakolipour and Kalbasi-Ashtari (2008).

Dehydration process

Drying experiments carried out in pilot plant with the help of cross flow drier at air temperatures of 40, 50, 60, and 70 °C. Heated air was forced through the product by a centrifugal fan. The ambient temperature and drying temperature exactly below and over the drying bed were measured by high precision thermometer (accuracy ± 0.1 °C, model LM 35, USA), relative humidity by capacitance sensors (accuracy ± 2 %, model capacitive, Philips, UK), and air velocity by a hot wire anemometer (accuracy ± 3 %, model 405-V1, Testo, UK) and the weight loss by a digital balance (accuracy ± 1 g, model GF2000, A & D, Japan) at regular intervals of 10 min. All measurements were done by using a data logger connected to a computer.

Bulk storage

Pistachio nuts stored at different temperatures (5, 15, 25 and 35 °C) and relative humidity range of 11–87 %. Saturated salt solutions were prepared to provide a range of 0.11, 0.36, 0.62 and 0.88 a_w values ($a_w = ERH/100$). The glass jars were kept in incubators at 5, 15, 25 and 35 °C in darkness and the temperature was maintained to an accuracy of ± 0.3 °C during the storage period. Approximately 120 g pistachio samples was weighed, put into Petri dishes and placed over the saturated salt solutions in triplicate in glass jars. Initial quality parameters of pistachios such as moisture content, free fatty acids, and peroxide value were determined initially and then in 15 days intervals during storage period. In each

sampling 15–17 g nuts randomly peaked, packed in cellophane bags, sealed and stored in dark and cold place prior to chemical and sensory analysis (Tavakolipour et al. 2010). Nut oil extraction and its quality factor determination has been explained in packaging section.

Packaging

After drying of pistachio nuts, three packaging materials including cellophane, nylon and metal cans were used for product packaging under ambient and vacuum conditions at different temperatures (25 and 40 °C) for 3 months storage period. Then, 250 g of pistachio nut sample was placed in each packages. The samples were filled in cellophane films packaged under common conditions. Pistachios are divided in two samples, half of them were filled in the nylon and metal cans under ambient conditions and another half were packaged under vacuum conditions. Adequate number of every type packages stored at two temperatures, ambient temperature (about 25 °C) and 40 °C. Every month, one of each type of packages was selected, and then samples were dehulled and ground. The moisture content of the samples was determined by drying of ground samples in a vacuum oven at 60 °C until a

Fig. 1 Effects of water activity and isotherm temperatures on moisture sorption of pistachio nuts during (a) adsorption and (b) desorption

Table 2 Drying time in optimum drying conditions

Temperature (C)	Bed thickness	Air velocity (m/s)	Drying time (min)
50	monolayer	1	275
50	monolayer	2	250
60	monolayer	1	170
70	monolayer	1	130
70	monolayer	2	120

constant weight was reached (AOAC 1990). For determination of pistachio oil attributes, ground samples were extracted by chloroform-methanol solvents (by a ratio of 2:1 v/v) for 4 h in darkness at ambient temperature. The solvent was evaporated under vacuum at 30 °C (Maskan and Karatas 1998). The Peroxide value of pistachio kernel oils was measured by the iodometric titration method (BS 1987) and free fatty acids were determined by titration method based on oleic acid percent (AOAC 1990).

Mathematical modeling

Moisture sorption data were fitted to six mathematical equations including BET, GAB, Smith, Oswin, Halsey and Henderson. Experimental drying data were fitted to the seven well-known drying models i.e. the Newton, Page, Modified Page, Henderson and Pabis, Logarithmic, Diffusion and Thomson. The peroxide value data of pistachio nuts stored at different conditions versus storage time were best fitted with first order chemical reaction.

Results and discussion

Moisture sorption isotherm

The equilibrium moisture content of pistachio samples (related to their adsorption and desorption isotherms) were decreased whenever the temperature increased and water activity was constant (Fig. 1). When the pistachio's storage temperature increased, its hysteresis reached to the highest value for water activity in range of 0.2–0.7, and it reached to the lowest when a_w dropped below 0.2 or jumped above 0.7. Among different suggestive models for fitness of desorption data, Smith model was the best sorption model. Venkatachalam and Sathe (2006) used two widely models of BET and GAB to see the fitness of equilibrium moisture sorption data for the pistachio nut that stored within 4 weeks of storage at 25°C in different relative humidities (a_w in range of 0.082–0.97). Chayjan and Esna-Ashari (2011) claimed that the ANN model was better than the Oswin and Guggenheim–Anderson–de Boer (GAB) models. Zomorodian and Tavakoli (2007) found Halsey model is the most proper equation for adsorption processes for two varieties (Ohadi and Kaleghochi), whereas the Oswin and Smith models were most appropriate for desorption processes at constant temperature of 50 °C.

Dehydration process

Drying air temperature is the most important factor in drying of pistachio nuts. With increasing temperature from 40 to 70 °C, drying time for thin layer position decreased from 275 min at 40°C to 120 min at 70 °C that shown time is decreased about

Fig. 2 Observed versus predicted moisture ratio for Modified Page's model at 70 °C

Fig. 3 Peroxide value variation during storage period at 35 °C (ERH = 11–82 %)

50 %. Air velocity doesn't have any significant effect on the drying time, because drying of pistachio nut occurred in falling rate period. Statistical analysis of drying data and scoring of treatments among all treatments result the five treatments acquired the most scores as shown at Table 2. Between these treatments, two treatments involved 70 °C, 1 and 2 m/s and monolayer thickness. Other treatments involving 50 and 60 °C, 1 and 2 m/s and thin layer thickness.

By using statistical parameters of R^2 , P and RMSE, Modified Page model may assume to represent the thin layer drying behavior of Pistachio nuts among above mentioned drying kinetic models. Several models have been proposed for different pistachio varieties for example two term model for drying of Ohadi cultivar (Chayjan and Esna-Ashari 2011), page model for Khany and Abasali cultivars in microwave-convective drying (Kouchaczadeh and Shafeei 2010). As an example, predicted values of moisture ratio ($MR = \frac{X - X_e}{X_i - X_e}$) against experimental values for air tempera-

ture 70 °C shown in Fig. 2, as seen there are high correlation between two data sets (Tavakolipour 2011).

Bulk storage

Moisture content of pistachio nuts decreased with increasing relative humidity and temperature during storage time. When storage temperature rose from 5 to 35 °C, the peroxide value increased considerably due to the temperature effects on rate of lipid oxidation. High storage temperature (more than 10 °C) and relative humidity (more than 70 %) had a synergic effect on increasing rate of peroxide formation. When relative humidity and temperature of environment are respectively less than 32 % and 10 °C, the inside pistachio moisture content is lower than outside monolayer moisture content. As a sample, peroxide value versus storage time at 35 °C showed in Fig. 3. In addition, increasing temperature and relative humidity both had synergic effects on lipolysis reaction and rate of free fatty

Fig. 4 Moisture content (% wet basis) variation of pistachio nuts stored at ambient temperature and various packaging materials

Fig. 5 Peroxide value (PV) variation of pistachio nuts stored at ambient temperature and various packaging materials

acid production (Tavakolipour et al. 2010). Temperatures between 0 and 10 °C are recommended for pistachios depending upon expected storage duration; the lower the temperature, the longer the storage life. Tsantili et al. (2011) results showed that low temperature and packaging atmosphere with N₂ prevented additively the losses of some pistachio nutrient components. In particular, losses were advanced by storage time, were prominent in air at 20 °C, but best prevented in N₂ at 1 °C. Low oxygen atmospheres (<0.5 %) aid in maintenance of flavor quality.

Packaging

Moisture content of pistachio nuts in different packaging materials was statistically significant so samples packed in metal cans indicated the lowest change in moisture content whereas samples packed in cellophane films indicated the highest changes in moisture content in comparison to other packaging materials as showed in Fig. 4.

Pistachios packaged in cellophane were behaved like bulk storage and easily affected by the environment and lost their moisture content due to weak moisture barrier properties of cellophane film. Samples stored at ambient conditions had higher moisture content which could be due to a lower water vapor transfer rate at room temperatures. In other words, by increasing temperature from 25 to 40 °C, moisture is evaporating faster and will be removed from the product. Raei et al. (2010) reported that by decreasing moisture content crispness and tenderness of the pistachio nut will be influenced significantly. Figure 5 showed peroxide value in various packages at ambient temperature during storage period. Peroxide is the first chemical compound which is produced after oxidation of fats and oils. When peroxide value reaches to a certain limit, different reactions occurred. Results showed that peroxide formation was higher at 40 °C compared to room temperature which is in agreement with previous results since at higher temperatures, rate of chemical reactions will be increased.

As showed in Fig. 5, the pistachio nut samples packaged in cellophane indicated the highest increase in peroxide value and the samples packaged in vacuum nylon showed the lowest increase in peroxide value. The higher increase of peroxide value in pistachio nut samples packaged in cellophane film than other packages can refer to higher permeability of cellophane film to gases such as O₂ and more access to oxygen in comparison with vacuum packaging. Surprisingly, pistachios packaged in metal cans had also higher peroxide value which showed they are not good barriers to oxygen and even water vapor. Some researchers have used other packages, for example packaging pistachio nut in metalized film and five-layer films with gases N₂/CO₂ and vacuum conditions kept the quality of pistachio better and extended shelf-life. In another research, their results revealed that two and three layer

plastic pouches resulted in higher quality attributes for the stored pistachios (Raei et al. 2010; Raei and Jafari 2011).

Conclusions

In this investigation, the most important postharvest operation of pistachio nuts which includes: dehydration, bulk storage and packaging of pistachios were studied. The moisture sorption isotherms and binding energy between water and pistachio have major roles on design of pistachio dryer and determination of optimum storage conditions. The plots of sorption isotherms were determined for pistachio nut at temperature of 15 and 35 °C. Hysteresis was the highest value, when a_w was in range of 0.2–0.7 and it reduced when it was less or more than 0.2 and 0.7, respectively. Among different suggestive models for fitness of sorption data, Smith model was the best sorption model. The effect of temperature on drying of whole pistachio nut in a cross flow drier was investigated. Increase in drying temperature from 50 to 70 °C in monolayer decreased drying time from 275 to 120 min. Air velocity didn't any significant effect on drying time. The entire drying process occurred in falling rate period and constant rate period was not observed. The Modified Page model was found to be the best model for describing the drying behavior of the Kerman pistachio cultivar.

Pistachio nuts bulk stored at less than 10 °C (e.g. 5 °C) and RH(relative humidity) of 65–70 % or kept at higher than 10 °C (e.g. 15 °C) and less than 32 % RH, and gained enough moisture content in monolayer had the longest shelf life due to the minimum changes in its lipid quality indicators. The effects of various packaging on quality of pistachio nuts indicated that different packages and conditions had a significant effect on the quality attributes of pistachio nuts. It was found that nylon under vacuum is the best packages for pistachio nuts. Also, results showed that higher temperatures and longer storage times will accelerated deteriorative reactions in pistachio nuts especially on fat component.

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