Middle-East Journal of Scientific Research 6 (3): 224-229, 2010
ISSN 1990-9233

Application of Arrhenius Kinetics to Evaluate the Stability of Pistachio Nuts at Various Conditions

N. Sedaghat

Department of Food Science, Ferdowsi University of Mashhad (FUM), Mashhad, Iran

Abstract: Pistachio is the edible seed of the pistachio tree (pistacia vera L.) the Ohadee variety of Iranian raw dry pistachio nuts was selected for the experiments. The method of Accelerated Shelf Life Testing (ASLT) used for storage of pistachio. Free Fatty Acid (FFA) of raw dried pistachio nuts were investigated at 21%, 8% & <2% O_2 and different storage temperature (5, 20, 35, 45°C). Samples were experimented at 4, 6, 8, 10, 12 weeks by use of split-plot design. Results showed that FFA formation under each three factors (oxygen percent, temperature and storage time) and the interaction of three factors were significant ($p<0.0000$). The activation energies were 11.01, 3.78 and 0.915 kcal / mol under air (21% O_2), 8% and <2% O_2 storage, respectively. Raw dried pistachio nuts at 21% O_2 was more sensitive to FFA formation to temperature change.

Key words: Pistachio nuts · Rancidity · Free fatty acid · Activation energy

INTRODUCTION

Pistachio nut (*Pistachia vera* L.) is grown mainly in Iran, USA, Syria, Turkey, Greece and Italy It is one of the most popular nuts in the world with its high nutritional value and unique flavour as a snack and a food ingredient. Iran is the first country in pistachio export in recent years and now exports 140,000 tons value over $800 million to 76 countries. Pistachio kernels are a good source of fat (50–60%) and contain unsaturated fatty acids (linoleic, linolenic and oleic acids), essential for human diet [1-2].

Lipid oxidation is of paramount importance to food quality. It may lead to the development of rancid off-flavors, cause changes in color or texture reduce shelf life and/or impair nutritional quality. Although saturated fatty acids can react with oxygen, the susceptibility of lipids to oxidation is significantly greater with higher unsaturation in the fatty acid chains. The lipid oxidation is a complex process in evolving numerous reactions that give rise to numerous chemical and physical changes. Temperature is one of the main environmental factors that influence the rate of quality loss the dependence on temperature of most reactions in food can be expressed more precisely by the Arrhenius model [3-4].

Kenetic data are essential for predicting oxidative stability of oils under various heat processing, storage and distribution conditions. The effective of temperature on the rates of chemical reactions and application of it to the study of food quality losses were studied by Labuza T.P and Riboh D. (1982). The kinetic approach and the Arrhenius relationship that describes the influence of temperature on the reaction rate constants were also promoted by Saguy and Karel [5]. Lai and Heldman [6] developed methods to determine the value of the activation energy of food quality losses from shelf life data at known temperature.

Several investigators have reported on the chemical composition and quality of pistachio nuts but a few dealt with Rafsanjan-grown "Ohadee" nut which represent the largest portion of pistachio production in Iran [7-9]. The objective of this investigation will be shown the effect of factors such as oxygen, temperature and storage time on the quality of pistachio nuts and applying the Arrhenius model in prediction of stability of raw dried pistachio nuts.

MATERIALS AND METHODS

Materials

Reagents: All chemicals used in this study were supplied from Merck Company.

Pistachio Nut Samples: The Ohadee variety of Iranian pistachio nut was used for the experiments. The raw dry pistachio nut samples with an average moisture content

Corresponding Author: Dr. Nasser Sedaghat, Department of Food Science, Ferdowsi University of Mashhad (FUM), Mashhad, Iran

of about 5%(wet basis)initially were supplied from Rafsanjan Pistachio Factory in Iran. Upon receiving, they were placed in sealed plastic bags and held at 0 -1°C for experiments.

Methods

Experimental Design and Storage: One glass container was assigned to each of the combination of three variables studies: (1) Oxygen concentration: 21% (air), 8% and < 2% with nitrogen flushed atmosphere; (2) storage temperature: 5,20,35,45°C; (3) storage time 4,6,8,10,12 weeks. Each glass had two valves and after nitrogen flushing from one valve, air atmosphere go out from another valve and amount of O_2 concentration remained control with Oxygen Analyzer (GFG Company). Total of 600 g of the selected pistachio nuts was placed in each of the 60 jars (4*3*5). Aluminum foil was used to cover all jars to exclude light.

Extraction of Pistachio Nuts Oil: At appropriate time pistachio nuts were removed from storage and 300 g nuts removed their shells and them were chopped to granule by pounder. To accurately report lipid composition, it is important that the lipids be extracted quantitatively without decomposition from the food product. Oil was extracted by 250 ml hexane in a dark place at ambient temperature for PV, FFA analysis, the solvent was evaporated under vacuum at 30°C to dryness.

Chemical Analysis: Free Fatty Acid (FFA) was determined by Titration Method of AOAC (1990) as percent oleic acid. All determinations of Free Fatty acid and Peroxide value were performed in duplicate [10].

Estimate the Arrhenius Parameters: For estimating the Arrhenius parameters used the Two-step Linear Least Squares Method [11].

Statistical Analysis: The results were compared by multifactor analysis of variance (multifactor ANOVA) to test for significant differences. Means of the groups were compared using the least significant difference (LSD) multiple range test by using a Statgraphics statistical packet (Statgraphics plus, 2000). Differences among sample means were reported to be significant when $p<0.05$ and Sigma Plot 8 soft ware used for drawing plots.

RESULTS AND DISCUSSION

Deterioration in the pistachio nuts during storage is also attributable to lipid oxidation Factors influencing lipid oxidation in addition to the nature of the substrate are free fatty acids, oxygen concentration, temperature, water content, physical condition, fatty acid position, exposure to light, exposure to certain metals, pro oxidants and antioxidants. The oxidation of fatty acids in raw dried pistachio nuts leads to off-flavors and it can be developed peroxide value and free fatty acid percent.

Ohadee cultivar, have average composition such, moisture 3.1%, oil 58.4 %, protein 17.8 %, carbohydrate 16.4 % and fatty acid, palmitic 11.2 %, stearic 0.8 %, oleic 59.1 %, linoleic 26.7 % and linolenic 0.3 %. In term of FFA, multiple factor ANOVA results showed that the FFA under each three factors (oxygen percent, temperature and storage time) and the interaction of three factors were significant ($p = 0.0000$) but LSD Multiple Rang Test revealed that there was no significant difference between some levels of treatments (Table 1). The results of interaction three factors (O_2%, temperature and storage time) on FFA showed in Figures 1, 2 and 3.

It is seen from Figure 1 that increase of O_2% and storage temperature the FFA has increased and the minimum amount of FFA was at < 2% O_2 and 5°C treatments and FFA at level < 2% O_2 was less than from

Table 1: The results of LSD multiple range test for raw dried pistachio nuts FFA parameter at $\alpha = 0.05$ level

Factors	Levels	Mean of FFA (% oleic acid)	Homogeneous group[a]
Temperature	5°C	0.357	A
	20°C	0.420	B
	35°C	0.480	C
	45°C	0.504	D
Oxygen percent	21%	0.482	E
	8%	0.437	F
	< 2%	0.403	G
Storage time	4 weeks	0.402	H
	6 weeks	0.415	I
	8 weeks	0.445	G
	10 weeks	0.449	G
	12 weeks	0.492	H

[a]Same letter indicates that difference is not significant at $\alpha = 0.05$ level

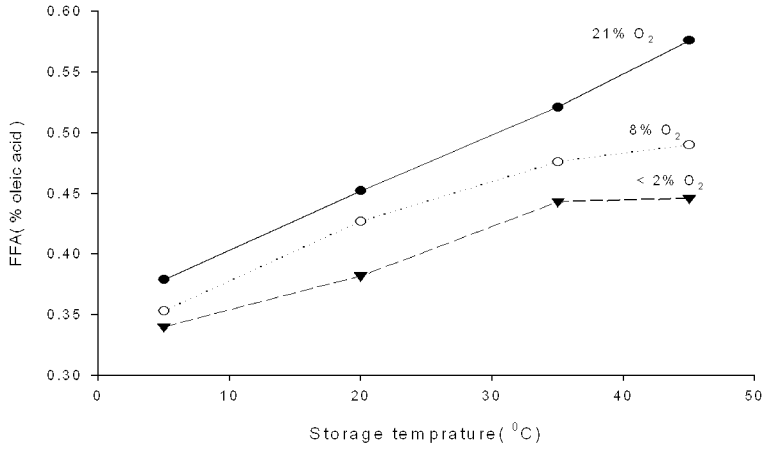

Fig. 1: Multiple Rang Tests for effect of O_2% and storage temperature (°C) on FFA raw dried pistachio nuts, each point indicates LS mean of 10 determinations

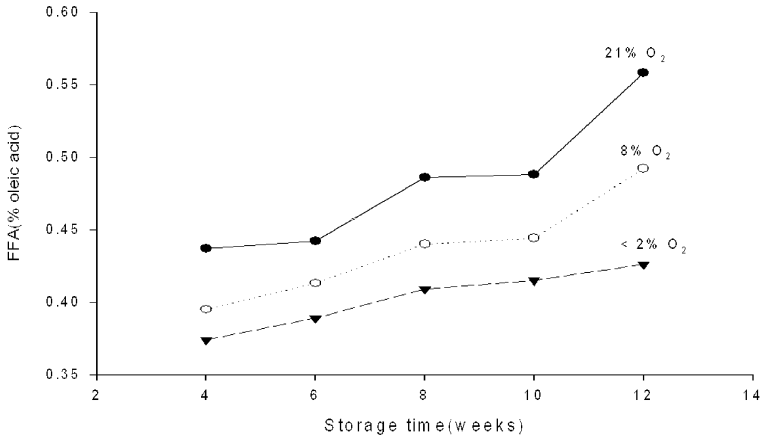

Fig. 2: Multiple Rang Tests for effect of O_2% and storage time (weeks) on FFA raw dried pistachio nuts, each point indicates LS mean of 8 determination

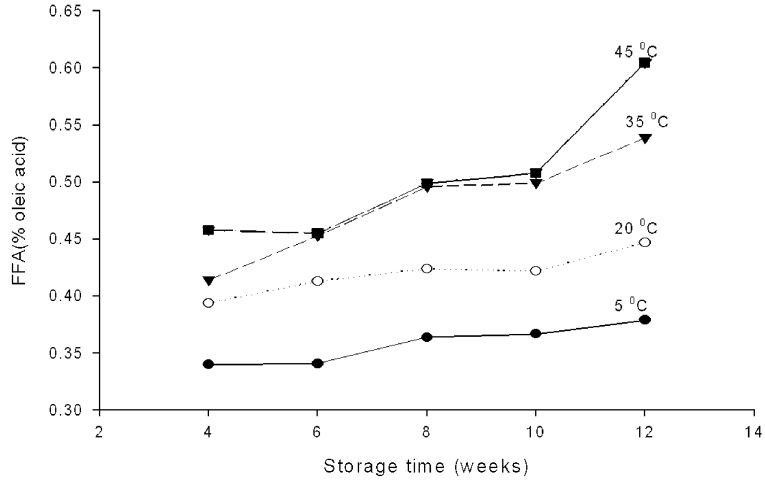

Fig. 3: Multiple Rang Tests for effect of temperature(°C) and storage time (weeks) on FFA raw dried pistachio nuts, each point indicates LS mean of 6 determination

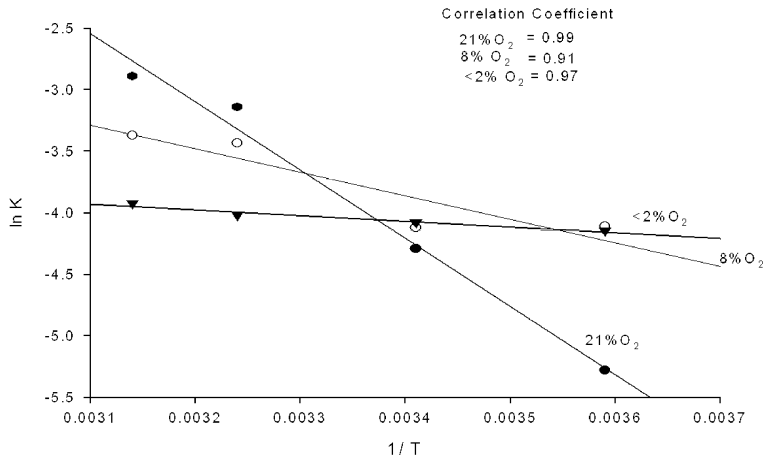

Fig. 4: ln(K) versus 1/T plot for FFA formation on the raw dried pistachio nuts stored at 21%, 8% and <2% O_2

8% and 21 % O_2 ($p < 0.05$). This results was confirmed that quality of pistachio nuts under gas flushing packaging (<2% O_2) with MAP packaging (8% O_2) and air packaging (21% O_2) is significant ($p< 0.05$), Therefore, gas flushing packaging can be useful packaging for raw dried pistachio nuts because it is significant ($p<0.05$) from 21% and 8% O_2, Blakistone [12] reported that flushing with N_2 is currently commonly used to reduce residual O_2 in packs containing cashews, pistachios, mixed nuts and dried fruit, it is being successfully used on raw, fried and roasted nuts.

From Figure 2, it has been resulted increase of storage time and oxygen percent, the FFA has increased. This result was confirmed that quality of pistachio nuts based on FFA under < 2% O_2 is significant from 8% and 21% O_2 ($p<0.05$).

It is seen from Figure 3, the higher of temperature and storage time the higher of FFA and minimum amount of FFA has been at 5°C (cold storage). As a consequence we introduce optimum storage condition for raw dried pistachio nuts can be at 5°C and <2% O_2.

Amount of FFA was maximum 0.755% (% Oleic acid) for treatment of 21 % O_2, 45°C and week 12 (data not shown). Since FFA didn't exceed 5 % which is the recommended maximum level in products for human consumption. Pistachio nuts may be acceptable in terms of FFA, similar results were obtained by Maskan and Karatas [7] during 12 months storage of pistachio nuts under various conditions and evaluation of fatty acid oxidation. He reported that the pistachio nuts had a high stability. A high concentration of oleic acid gave stability to pistachio nuts. Oxidative stability of oleic acid has been studied and reported by many researcher [13, 14].

Estimation of Arrhenius Parameters: The most common method to estimate the Arrhenius parameters is the Classic successive Two-steps ordinary Linear Least Squares Fit. In this method the first regression of C vs. t is done at each temperature, to estimate the rate constant K. The second step is to regress ln (K) vs. 1/T to obtain the estimates of ln (K_0) and Ea / R [11]. The FFA data of raw dried pistachio nuts from all storage condition best fitted. The first order rate kinetics model with correlations coefficient greater than 0.91.The reaction rate values obtained at 5, 20, 30 and 45°C are plotted against reciprocal absolute temperature, T and the result shown in Figure 4. Each set of results was represented by Arrhenius equation. For this a computer package program (Sigma Plot 8) was used. The equation was used as following.

$$\text{Ln } Q = \ln Q_0 - KT \quad (1)$$

$$\text{Ln } K = \ln K_0 - Ea/RT \quad (2)$$

Where; Q is FFA concentration at time t, K is the rate constant ($week^{-1}$), Q_0 and K_0 are pre – exponential factor or frequency factor, Ea is the Activation Energy (kcal/mol), T is the absolute temperature (K) and R is the gas constant (1.98 kcal/mol.K). The K value for each sample was calculated from Eq.(1), with reasonable correlation coefficients are shown in Table 2. Ea and K_0 values were determined from the slopes and intercepts respectively of the line generated by regressing ln (K) versus 1/T by use of least square linear regression (Figure 4). The reaction rate constants for 21%, 8% and <2% O_2 at 5, 20, 35 and 45°C were shown in Table 2.

Table 2: Estimated parameter from first order rate equation on FFA formation of the raw dried pistachio nuts

Temperature	5°C			20°C			35°C			45°C		
Oxygen	21%,	8%,	<2%	21%,	8%,	<2%	21%,	8%,	<2%	21%,	8%,	<2%
Q_0	0.365	0.310	0.307	0.405	0.376	0.392	0.366	0.366	0.314	0.358	0.372	0.384
SE(±)	0.0088	0.0248	0.0240	0.0297	0.0169	0.0161	0.0548	0.042	0.0262	0.1149	0.056	0.0132
K	0.0051	0.0164	0.0158	0.0136	0.0162	0.0169	0.043	0.0324	0.0179	0.0552	0.341	0.0197
SE(±)	0.001	0.0029	0.0028	0.0035	0.002	0.0019	0.0065	0.005	0.0031	0.0135	0.0066	0.0015
r	0.94	0.95	0.95	0.91	0.97	0.98	0.96	0.96	0.95	0.92	0.94	0.99

In Figure 4, the plots gave straight lines with correlation coefficients (r) of 0.99, 0.91, 0.97 for 21%, 8% and <2% O_2. The lines should be parallel but from this figure it is clear that the plots of 21% O_2 (air system), 8% O_2 and <2%O_2 (N_2 system) are not parallel to each other. It may be due to different FFA formation from the air system and N_2 system.

Table 2, lists K values of FFA formation at four temperatures of 21%, 8% and <2% O_2 it was seen that the higher of temperature the higher of K values, but changing the amount of k value at 5 and 20°C are different from 35°C and 45°C for 21%, 8% and <2% O_2. At 20°C even 5°C with decrease of O_2 % K value increased but at 35 and 45°C with decrease of O_2 % K value decreased, so for reducing amount of O_2 used of gas flashing (N_2), this result confirmed that N_2 at high temperature has a protective effect on FFA oxidation but at 20°C and cold storage (5°C) have not. The experimental activation energies have derived from the experimental data, which describe the temperature dependence of reactant loss or product formed under those experimental conditions. The determined activation energy values are 11.01, 3.78 and 0.915 k cal/ mole in 21 %, 8% and <2% O_2. It is obvious from the Figure 4 the graph of 21% O_2 is steeper the slope from 8% and < 2% O_2, it means pistachio nuts at 21% O_2 is more sensitive to FFA formation to temperature change. High activation energy indicates a strong temperature dependence that is to say the reaction will run very slowly at low temperature but very fast at high temperature. So at 21% O_2 with a higher activation energy implies that smaller temperature change is needed to induce a certain change in the rate of FFA formation and pistachio nuts at 21% O_2 is more susceptible to FFA formation at higher temperature than 8% and < 2% O_2 conditions [15, 16].

CONCLUSIONS

According to results, the FFA under each three factors (oxygen percent, temperature and storage time) and the interaction of three factors were significant (p = 0.0000). Moreover, the FFA data of raw dried pistachio nuts from all storage condition was appropriate in first order rate kinetics model (R^2>0.91). The determined activation energy values was 11.01, 3.78 and 0.915 k cal/ mole in 21 %, 8% and <2% O_2 and pistachio nuts at 21% O_2 was more susceptible to FFA formation at higher temperature than 8% and < 2% O_2 conditions.

REFERENCES

1. Gamlı, F. and I. Hayoglu, 2007. The effect of the different packaging and storage conditions on the quality of pistachio nut paste, J. Food Engineering, 78: 443-448.
2. Kashaninejad, M., A. Mortazavi, A. Safekordi and L.G. Tabil, 2006. Some physical properties of Pistachio (*Pistacia vera* L.) nut and its kernel, J. Food Engineering, 72: 30-38.
3. Taub, I. and R.P. Singh, 1997. Food storage stability.CRC press,Washington.D.C.USA., pp: 91-92.
4. VanBoekel, M.A.J.S., 1996. Statistical aspects of kinetic modeling for food science problems, J. Food Sci., 61: 477-485.
5. Tan, C.P., Y.B. Che Man, J. Selamat and M.S.A. Yusoff, 2001. Application of Arrhenius kinetcs to evaluation oxidative stability in vegetable oil by isothermal differential scanning calorimetry , J. AOCS., 78(11): 1133-1138.
6. Lai, D. and D.R. Heldman, 1982. Analysis of kinetics of quality changes in frozen foods, J. Food Process Engineering, 6: 179-200.
7. Maskan, M. and S. Karatas, 1998. Faty acid oxidation of pistachio nuts stored under various atmospheric conditions and different temperatures, J. Sci. Food Agric., 77: 334-340.
8. Hadorn, H., T. Keme, J. Kleinert, M. Messerli and K. Zuercher, 1995. Behaviour of Oil Seeds under Various Storage Condition, Zucker-und-suesswaren Wirtschaft, 33(10): 317-322.
9. Palazoglu, T.K. and M.O. Balaban, 1998. Supercritical CO2 extraction of lipids from roasted pistachio nuts, American Society of Agricultural Engineers, 41(3): 679-684.

10. AOAC, 1990. Official Methods of Analysis (15th ed). Association of Official Analytical Chemists, Washington D.C., USA.
11. Cohen, E. and I. Saguy, 1985. Statistical evaluation of Arrhenius model and its applicability in prediction of food quality losses, J. Food Processing and Preservation, 9: 273-290.
12. Blakiston, B.A., 1998. Principles and applications of Modified Atmosphere Packaging of foods, Blackie Academic and professional, an imprint of Thomson Science, London, UK., pp: 175.
13. Molteberg, E.L., E.M. Magnus, J.M. Bjorge and A. Nilsson, 1996. Sensory and chemical studies of lipid oxidation in raw and heat treated oat flavors, Cereal Chemistry, 73: 579-587.
14. Neff, W.E., T.L. Mount, W.M. Rinsch, H. Konishi and M.A. Agaimy, 1994. Oxidative stability of purified canola oil triacylglycerols with altered fatty acid composition as affected by triacylglycerol composition and structure, J. AOCS., 71: 1101-1109.
15. Labuza, T.P. and D. Riboh, 1982. Theory and Application of Arrhenius kinetics to the prediction of nutrient losses in food, Food Technology, OCT., pp: 66-74.
16. Tijskens, L.M.M., M.L.A.T.M. Hertog and B.M. Nicolai, 2001. Food process modeling, Woodhead Publishing Limited and CRC press LLC, USA., pp: 35-57.