UNIVERSITY OF GAZİANTEP
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CHANGES IN CHEMICAL AND PHYSICAL PROPERTIES OF WILD APRICOT 'ZERDALI' DURING DRYING

M.Sc. THESIS
IN
FOOD ENGINEERING

By
ESRA BAŞARICI ÜNLÜ
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Changes in chemical and physical properties of wild apricot ‘zerdali’ during drying

M.Sc. Thesis

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Supervisor

Assoc. Prof. Dr. Çiğdem SOYSAL

by

Esra BAŞARICI ÜNLÜ

April 2015

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Name of the thesis: Changes in chemical and physical properties of wild apricot 'zerdali' during drying

Name of the student: Esra BAŞARICI ÜNLÜ

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Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Metin BEDİR

Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Ali Rıza TEKİN

Head of Department

This is to certify that we have read this thesis and that in our consensus/majority opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Assoc. Prof. Dr. Çiğdem SOYSAL

Supervisor

Examining Committee Members	Signature
Prof. Dr. Hüseyin BOZKURT (Chairman)	.....
Assoc. Prof. Dr. Çiğdem SOYSAL	.....
Assist. Prof. Dr. A. Levent İNANÇ	.....

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Esra BAŞARICI ÜNLÜ

ABSTRACT

CHANGES IN CHEMICAL AND PHYSICAL PROPERTIES OF WILD APRICOT 'ZERDALI' DURING DRYING

BAŞARICI ÜNLÜ, Esra
M.Sc. in Food Engeering
Supervisor: Assoc. Prof. Dr. Çiğdem SOYSAL
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In this study zerdali was dried by hot air and microwave pretreated hot air drying and their effects on some physical and chemical parameters were evaluated. First of all salicylic acid (SA) treatment was applied to fresh zerdali samples to determine the effectiveness of SA on postharvest life of zerdali. In the second part of the thesis frozen and thawed zerdali was dried. For comparison, apricot was also dried in the same conditions.

Fruits were dried in a pilot plant tray drier with a constant air velocity of 0.5 m/s at 60°C. 1 minute microwave preheating at 350 W was applied before tray drying for microwave + hot air drying. Drying curves showed only a falling rate period. Diffusion coefficients (D_{eff}) were determined ranging between 2.03×10^{-8} and 1.81×10^{-7} m^2/s. High D_{eff} values may be result of the structure change during freezing and thawing operations. The fit quality of 6 thin-layer drying models was also evaluated and the best fit results were obtained with the Logarithmic and Two Term models.

Effects of drying on fruit quality were determined by using the pH, brix, color, total phenolics and total carotenoid analyses. After drying, all color values were decreased as predicted. Sample type and drying method found significantly effective and SA treatment provide little change on color values. Also zerdali found more conservative than apricot on color values. Total phenolic content of zerdali determined significantly higher than apricot before and after drying. Total carotenoid contents were decreased in all samples by drying.

Key Words: Zerdali, apricot, salicylic acid, drying, drying kinetics

ÖZET

ZERDALİDE KURUTMAYA BAĞLI KİMYASAL VE FİZİKSEL DEĞİŞİKLİKLER

BAŞARICI ÜNLÜ, Esra
Yüksek LisansTezi, Gıda Mühendisliği Bölümü
Tez Yöneticisi: Doç. Dr. Çiğdem SOYSAL
Nisan 2015, 65 sayfa

Bu çalışmada zerdali sıcak hava ve mikrodalga destekli sıcak hava sistemiyle kurutulmuş ve kurutmanın bazı fiziksel ve kimyasal parametrelere olan etkileri incelenmiştir. İlk olarak taze zerdalinin hasat sonrası ömrüne etkisini incelemek için salisilik asit (SA) uygulaması yapılmıştır. İkinci bölümde dondurulmuş ve çözünmüş zerdali kurutulmuştur. Karşılaştırma için, kayısıda aynı şartlarda kurutulmuştur.

Meyveler pilot ölçekli tepsili kurutucuda 0,5 m/s sabit hava hızı ve 60°C'de kurutulmuştur. Mikrodalga destekli sıcak havada kurutma için sıcak havayla kurutma öncesi 1 dakika 350 W güçte mikrodalga ön işlemi uygulanmıştır. Kurutma eğrilerinde sadece düşen hız periyodu gözlenmiştir. Difüzyon katsayıları (D_{eff}) 2.03×10^{-8} ve 1.81×10^{-7} m^2/s değerleri arasında bulunmuştur. Yüksek D_{eff} değerleri, kurutma öncesi örneklerin dondurulup çözünmeleri sırasındaki yapı değişikliği sonucu olabilir. 6 ince tabaka kurutma denkleminin uygunluğu incelenmiş ve en uygun sonuçlar Logaritmik ve Two Term modelleriyle sağlanmıştır.

Kurutmanın meyve kalitesine olan etkisi pH, brix, renk, toplam fenolik madde ve toplam karotenoid analizleriyle incelenmiştir. Kurutma sonrası renk değerlerinde beklendiği gibi bir azalma gözlenmiştir. Renk değerlerinde örnek türünün ve kurutma şeklinin istatistiksel olarak anlamlı olduğu ve SA uygulamasının daha az renk değişimine neden olduğu bulunmuştur. Ayrıca renk değerlerinin korunmasında zerdali örneklerinin kayısıdan daha iyi olduğu bulunmuştur. Zerdalideki toplam fenolik içerik kurutma öncesinde ve sonrasında kayısıdan istatistiki olarak yüksek bulunmuştur. Toplam karotenoid değerleri kurutmayla tüm örneklerde azalmıştır.

Anahtar Kelimeler: Zerdali, kayısı, salisilik asit, kurutma, kurutma kinetiği

To My Family...

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CHAPTER I

INTRODUCTION

1.1. Apricot and Wild Apricot (Zerdali)

Apricot is highly appreciated temperate fruit with taste, smell, visual and nutritional properties. It has been widely consumed for over years by various cultures. Apricot is a general name of many types of Apricot fruit. Hasanbey, Kabaaşı, Soğancı, Hacıhaliloğlu, Çataloğlu, Çoloğlu and Zerdali are the example of the local names of apricot cultivars in Turkey.

Zerdali is a wild type of apricot and apricot is cultivated from zerdali by inoculation. Their homeland is China and then via Iran and Mesopotamia they were reached firstly Anatolia and to Greece, Italia and America respectively. The Turkish name of wild apricot "Zerdali" is come from the Persian language "zerd-alü". "Zerd" means "yellow" and "alü" means "plum" in the Persian language. Apricot botanically named as *Prunus armeniaca L.*. Botanic classification of Apricot basically shown in Table 1.1. Prunus is come from the Greek word "prumnon" which means "tree". (Huang et al., 2013)

Table 1.1. Botanical classification of Apricot

Group	*Rosales*
Family	*Rosaceae*
Subfamily	*Prunaidea*
Species	*Prunus*
Name	*Prunus armeniaca L.*

Apricot has an important place in human nutrition because of not only the attractive color and taste but also the rich mineral and vitamin contents and antioxidant properties. Apricot fruits are mostly consumed as fresh but because of their

perishable nature and short storage opportunity they are generally dried. That is well known, the apricot fruit is also used to produce, marmalade, jelly, jam, nectar, juice,

frozen apricot, pulp, extrusion products etc. Furthermore, kernels of apricot are used in the production of cosmetics, aroma perfume, oils, benzaldehyde, and active carbon.

1.2. Properties of Apricot and Zerdali

Apricot fruit basically has two parts as edible fruit part and kernel. Edible part of fruit has bright yellow color because of its carotenoid content. Kernel cover is strong and mostly the inner part of kernel can be edible as snack. Zerdali has mostly same properties with apricot unlike the color which is orangish yellow and the kernel which is bitter as no edible. Apricot and Zerdali fruit parts are shown in Figure 1.1. Zerdali is little smaller then apricot and also has spots on cover. Zerdali has more intense taste than apricot. The differences are due to differences in the chemical composition of the types. Studies showed that the color differences result from the carotenoid content. Generally the carotenoid content was found higher in zerdali than apricot which effect the visual properties (color) and also nutritional properties. Hacıseferoğulları et al. (2007) have studied on mineral contents of apricot fruit varieties and found that all types have remarkable amount of minerals and also zerdali type has excess quantity of aluminum, calcium, magnesium and phosphorus.

a) Zerdali

b) Apricot

Figure 1.1. Appearance of Apricot and Zerdali

1.3. Chemical Composition of Apricot

Apricots are important essential nutrient sources for human such as minerals, vitamins like A, C, riboflavin, niacin, thiamine and pantothenic acid; fibers, bioactive phytochemicals, organic acids, phenolic compounds and carbohydrates (Orsat et al., 2007). Apricot has health benefit properties due to presence of bioactive compounds. Carotenoids, phenolics and antioxidants are important phytochemicals for their biological value. Throughout the ripening period of fruits a series of complex biochemical reactions occur and may cause the production of carotenoids, phenolic compounds and the formation of volatile compounds. Functional and nutritional properties and also taste and color of apricot is highly affected from these contents. Therefore many of study in literature were focused on the composition of apricot (Ali et al., 2011; Hacıseferoğulları et al., 2007; Saracoglu et al., 2009).

Munzuroğlu et al. (2003) studied the chemical composition of apricot and they reported that 100 g of dried apricot contained 66.5 g carbohydrate, 5 g of protein, 0.5 g fat, 979 mg potassium, 108 mg phosphorus, and 12 mg vitamin C.

Mineral contents of different types of apricot fruits are reported by Hacıseferoğulları et al. (2007) aluminum, calcium, iron, potassium, magnesium, sodium and phosphorous were determined as dominant minerals of the apricot fruits. The potassium levels of fruits changed between 20791 ppm (Hasanbey) and 33364 ppm (Zerdali). The highest amounts were found in potassium and phosphorus followed by sodium, calcium, magnesium and iron. Mineral content of zerdali were found to be higher than that of other varieties. Phosphorus content was measured as 2157.41 ppm for zerdali. Also, calcium content of the zerdali was found as 1896.53 ppm. The potassium, sodium, calcium, phosphorus and magnesium levels are adequate. Many enzymes require these elements as cofactors, so that their importance must be taken into account.

In the later years, interest in carotenoids and polyphenols of apricots has increasing for their antioxidant properties and ability to scramble towards chronic disease. The protection effect from oxidative damage in organisms of dietary antioxidants has been demonstrated (Rahman, 2007).

The antioxidant and anticarcinogenic features of vitamins E, C, A, β-carotene and the essential element of selenium are proportionately newly known. Vitamins E, C, carotenoids and selenium might treat independently or in combination as cardioprotective or anti-cancer agents by a variety of mechanisms. One of this mechanism, attributed to carotenoids, vitamin E and C is radical-scavenging (antioxidant) activity. Vitamin C is recognised as the most important vitamin in fruits and vegetables for human. Selenium, functioning as part of glutathione (Munzuroğlu et al., 2003).

Apricot not only has nutritional value in human, but also has some pharmacological importance due to having high amounts of antioxidant. Apricot has mild antiseptic, laxative, ophthalmic, antipyretic and emetic properties and also used as cleansing agent. Daily consumption of apricots has an restrictively effect on chronic atrophic gastritis (CAG) progressions in individuals with Helicobacter pylori infection and mucosal inflammation of the stomach. The apricot seed is also contemplated as antispasmodic, anti-asthamic, analgesic, pectoral sedative and used in the production of chemical materials such as cosmetics, oils, active carbon, benzaldehyde and aroma compounds (Ali et al., 2011).

1.3.1.Carotenoids

Carotenoids are found naturally in big quantities and most widely distributed pigment group. Carotenoids are a large group of fat soluble plant pigments that are synthesized by photosynthetic microorganisms and plants (Lauro and Francis, 2000). Carotenoids structure can be a linear, acyclic, cyclic and shortened.

The carotenoids are known by their structural diversity and various functions. Chemically carotenoids are polyisoprenoid compounds and their structure is characteristic with conjugated double bond system, cause characteristic UV and visible absorption spectra with maximum absorption in the 400-500 nm interval. We can divide carotenoids into two main groups. First group carotenoids composed of only carbon and hydrogen atoms and be named as carotens or hydrocarbon carotenoids. The second group is oxygenated hydrocarbon derivatives, these group contain at least one oxygen function group such as keto (as inconthaxanthin), epoxy (as in violaxanthin), hydroxy (as in β-cryptoxanthin), metoxy or carboxylic acid,

these group be named as xanthophylls (Rodríguez-Bernaldo de Quirós and Costa, 2006).

Carotenoids are found in many birds, insects, marine animals, many flowers and fruits and responsible for the attractive red, yellow and orange colors. These pigments are not produced in the animal body just synthesized by plants and many microorganisms so animals have to obtain carotenoids from plants as food (Rodríguez-Bernaldo de Quirós and Costa, 2006).

Nearly 700 carotenoids have been recognized in the nature. Alpha-, beta- and gamma-carotene, lutein, lycopene, betacryptoxanthin are major types of caroten most abundantly exist in vegetables and fruits (Meléndez-Martínez et al., 2007).

Apricot contains high amount of carotenoids which contribute to fruit color, taste and nutritive value. Nearly 250g fresh apricot or 30g dried apricot supply the daily recommended provitamin A carotenoid level (Huang et al., 2013). In apricot 60-70% of the total carotenoids is represented as β-carotene (Sass-Kiss et al., 2005). Additionally, apricot and its products include little amounts of α-carotene, γ-carotene, lutein and zeoxantin (Dragovic-Uzelac et al., 2007).

Many studies have represented that carotenoids have important functions for human health (Meléndez-Martínez et al., 2015; Rodriguez-Amaya, 2015; Woodside et al., 2015). Carotenoids help to prevent the development of degenerative diseases such as cardiovascular diseases, some types of cancer (e.g. prostate), macular degeneration and age-related cataracts. Carotenoids are free radical scavengers and singlet oxygen quenchers due to their structures contain many double bonds. Also carotenoids have beneficial health effect, with the provitamin A activity. The active form of vitamin A (retinol) and provitamin A is formed by the conversion of alpha- and beta-caroten and beta-cryptoxanthin in the body. Related with vitamin A consumption in the diet eye, skin and dental diseases are decreased (Meléndez-Martínez et al., 2010).

1.3.2. Phenolic Compounds

The term of phenolic compounds refers to a wide range of compounds, which have aromatic ring with hydroxyl group including functional derivations. Phenolics in animal body or non-plant materials are based on consumption of vegetable foods.

Basic phenols are formed by decarboxylation of phenolic carboxylic acid derivatives, thermal deformation of lignin or microbial activity. A few food phenolics dissolve in water and organic solvents. Most abundant phenolics in fruit and vegetables are phenolic acids such as hydroxybenzoic acid and hydroxycinnamic acid and flavanoids such as catechin, flavanol, flavanon, anthocyanidin and chalcones (Akbulut, 2001).

Apricots are important source of phenolic compounds. They have antioxidant potential and act as anti-allergic, anti-microbial, anti-carcinogenic, anti-flammatory and anti-mutagenic role. Most abundant phenolic compounds are rutin, (+)-catechin, (-)-epicatechin, chlorogenic and neo chlorogenic acids in apricot. These compounds protect against regenerative disease related to oxidative stres and alleviate chronic diseases. These protections may cause by the preventive effect of phenolic compounds on the cells (Huang et al., 2013; Hussein et al., 2013).

Phenolic compounds are present in fruits and vegetables at different levels and they have a dominating role in taste formation and they contribute to bitterness and astringency in horticultural crops. Apricot fruits contain varying levels of phytochemicals such as polyphenols, vitamins and carotenoids. That components are the determinants of taste, colour and nutritive values of the fruits (Kan et al., 2014).The apricot fruits belongs to different cultivars contain different levels of polyphenols. Dominant phenolic compound is the chlorogenic acid in apricots. Caffeic acid, neochlorogenic acid, p-coumaric acid, (+)-catechin, (-)-epicatechin, ferulic acid and their esters are also determined phenolic compounds in apricot fruits and their products. Flavonols in apricots exist mostly as glucosides and rutinosides of quercetin and of kaempferol, however, quercetin 3-rutinoside (rutin) predominates.

Phenolics prevent the platelet aggregation, damage of red blood cells and oxidation of LDL lipoprotein. In that context dried apricot can be considered as a good source of bioactive compounds particularly phenolics, carotenoids and vitamin C, in addition to its high calorific value (Hussein et al., 2013). Concentrations and composition of these phytochemicals might differ according to variety, fruit maturity, climatic factors and region of cultivation (Campbell and Padilla-Zakour, 2013).

1.4. Color of Apricot

The consumer correlates the food color with quality, safety and as indicator of good processing. In dehydrated foods, color is a dominant quality parameter. Through drying, discoloration and browning can occur because of biochemical or chemical reactions. Enzimatic oxidation, ascorbic acid browning, caramelization and Maillard reactions are some of the chemical reactions that may occur through drying and storage.

The characteristic color of apricot is changing between golden yellow and orange. Color is one of the most important factor on the consumer attribution like all foods. Color also act as a quality parameter (Özkan et al., 2003).

There are a lot of system for instrumental color measurements such as CIE system, Chroma Cosmos 5000, Natural Color system and Munsell system and etc. The CIE (Commission Internationale de I'Eclairage) was developed by International Comission on Illumination. This system is depend on the premise that three elements (object, source of light and observer) in color evaluation. The main objective of the CIE system is to achieve results valid for normal trichromats (people with normal color vision). The 1931 CIE L, a, b system was designated. The lightness signal is represented by the luminosity (L); L could take values in the range between 0 to 100, 0 refer to black, and 100 is produced by a excellent white. One of the hue signals it can be represented as a single number, usually called (a),describes the redness or greenness. A positive (a) value represents red, on the other hand negative is green. The other hue describes in the same way, with the yellowness or blueness, represented by (b); positive (b) is yellow and negative (b) is blue. The CIE L,a, b 1931system was modified by MacAdam in 1973. This modification was officially recommended in 1976 and its known as "1976 CIE L*, a*, b* space" with the official abbreviation CIELAB. Generally in literature the color of apricot samples were measured on the surface (ground skin color) and were displayed in L*, a*, and b* values which represents light–dark spectrum vary between 0 (black) and 100 (white), the green–red spectrum differ from -60 (green) to +60 (red), and the blue–yellow spectrum differ from -60 (blue) to +60 (yellow) dimensions, respectively (Karabulut et al., 2007). The L*a*b* color system is a three-dimensional coordinate

system with an L*-axis (lightness) and two orthogonal axes namely, an a*-axis (red-green) and b*-axis (yellow-blue), representing chromaticity (Takiwaki, 1998).

1.5. Drying

Drying is apparently one of the oldest methods in food preservation technique, used by human and commonly used for preservation of fruits and vegetables (Lewicki, 2006).

Fresh fruits and vegetables are classified as highly perishable commodities because of the moisture content is more than 80%. Moisture in the foods is one of the important factor in microbiological deterioration and chemical and physical changes. Therefore decreasing the water activity in foods is one of the most important research area in food science (Lewicki and Jakubczyk, 2004). Water activity (a_w) and relative humidity (RH) of a material are related to each other. Water activity or a_w is a property of solutions and can be calculated with the ratio of vapour pressure of the solution to that of vapour pressure of pure water at the same temperature.

$$a_w = \frac{P}{P_0} \qquad \text{(Eq. 1)}$$

where; P_0 is the vapor pressure of pure solvent (usually water) and P is the vapor pressure of the solution.

Water activity of a food is ranged between 0.00 and 1.00 and the equilibrium relative humidity above the food is ranged between 0 and 100%. The relation between equilibrium relative humidity and a_w is given in Eq. (2) as;

$$\%\ \text{Equilibrium Relative Humidity (ERH)} = a_w \times 100 \qquad \text{(Eq. 2)}$$

Water activity is an amount of unbound, free water which available to support chemical and biological reactions in a system. The aim of dehydration of foods is to lower the product's a_w to reach an equilibrium between product shelf life and product quality (Orsat et. al., 2007).

It is absulately known that for growth of microorganisms there is critical a_w. Under that value microorganism cannot grow (Fig. 1.2). For instance, minimum a_w level for most bacteria, yeasts and moulds are nearly 0.9, 0.8 and 0.6 respectively. Moulds and yeasts are more tolerant then bacteria. Additionally there is extreme microorganisms such as halophilic bacteria, osmophilic yeasts have tolerant up to a_w 0.60 level. The

foods which have a_w values between 0.65-0.90 is so-called intermediate moisture foods (IMF) (Erkmen and Bozoğlu, 2008).

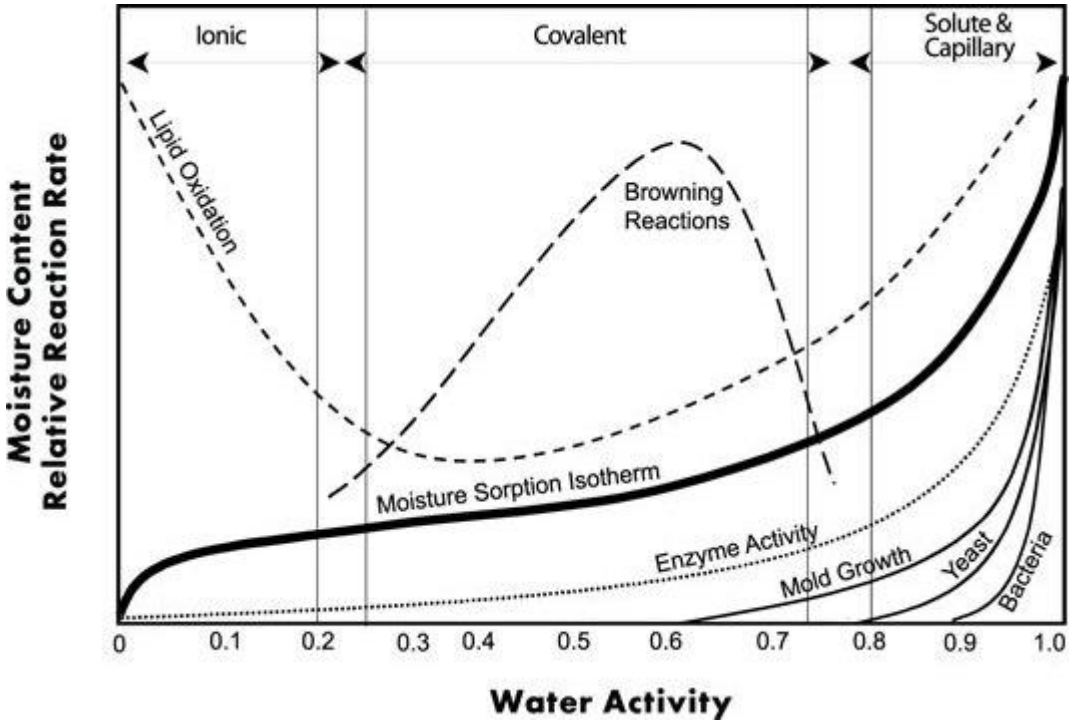

Figure 1.2. Water activity – stability diagram.

The drying of fruits and vegetables is not only provide the increase of shelf life but also increasing bioavailability of nutritional components, safe and easy storage, increasing desirable taste and aroma and to reduce transport and packaging cost by reducing volume and weight (Lewicki, 2006).

Drying in earlier times depends on the sun, which is stil one of the most widely used method but also so many types of drying systems and dryers have been developed to increase quality and energy efficiency (Doymaz, 2004; Hammouda and Mihoubi, 2014). In most drying process water loss performed by convective evaporation, in that necessary heat is supplied by hot air. Hot air drying is the simplest and economical method when comparing other methods in the other hand these technique has some disadvantages such as requires considerable amounth of energy and long drying times.

As climacteric fruit, apricot presents a challange in postharvest storage, has limiting time for storage. Processing, especially drying for apricot, serves as a means to add

value, extend fruit shelf life and enable to availability through year (Campbell and Padilla-Zakour, 2013). Nearly 4 million tons of apricot produced yearly in the world and approximately 750 000 tons of that production is supplied by Turkey. Turkey is the first producer in the world with having nearly the 20% portion of total production. Nearly 100 000 tons of apricot is dried and exported which is the most important part of produced apricot in Turkey. 84% of dried apricots in the World bazaar is supplied by Turkey (Ministry of Food, Agriculture and Livestock, 2014; Ünal, 2010).

1.5.1. Effect of Drying

Some important quality factors of the products such as colour, texture and chemical struture can be changed with drying. The high temperature in the drying process is an major reason for quality loss. Increasing the temperature, cause to increase the change in color (Kone et al., 2013). Reducing the drying temperature is a good way for improving the quality of dried products, obtaining less changes in flavour and nutrients and little shrinkage (Orsat et. al., 2007).

Reduction of volume, which is often called shrinkage is one of the most important physical change in food samples, through the drying process. Shrinkage can be explained by the structural collapse with food molecules which occur due to the loss of water. The most important changes connected with shrinkage are the loss of rehydration capacity, alterations in size, shape, surface cracking and hardening of food materials. In addition, changes in porosity through drying is affected by shrinkage. Porosity and bulk density are important physical properties which have an important role in rehydration of dried materials also their packaging and handling. Dehydrated foods are preserved longer because of their water activity level is lower enough where deteriorative biochemical and chemical reaction rates are reduced to a minimum and where microbiological activity can not occur (Ratti, 2009).

Most of nutritional compounds in foods such as vitamins, essential fatty acids and antioxidants (carotenoids and phenolic compounds) recently become the subject of many studies with increasing interest because of their possible role in the prevention of human diseases, including heart disease and cancer. In the human diet, fruits and vegetables have essential importance. Dietary experts recommend increased intake of fruits and vegetables, because of they contain high levels of fiber, vitamins and

minerals and low levels of fat. In addition, fruits and vegetables is believed as a rich source of antioxidants. Consumption of fruits and vegetables provide many health benefits. On the other hand nutritional quality can be affected by handling, procesing and packaging. Drying not only cause physical and chemical changes, but also can cause loss of nutritional value. The major losses of vitamin and other substances can take place because of oxygen and heat sensitivity, enzymatic oxidation, solubility in water and metal ion catalysis during processing. Additionally amine-sugar interactions (Maillard reaction) can occur among drying and storage and can cause loss of nutrients. Pretreatments, new and innovative drying methods, selection of proper drying methods and optimization of drying conditions can be reduces these nutritional losses (Ratti, 2009).

1.5.2. Drying systems

Over the years, a number of new and innovative drying methods have been developed. In drying generally heat is applied as conduction, convection or radiation to force water to vaporize. For the dehydration of foods and bio-materials, there is a lot of processing technique. Each drying technique has specific effect on product by means of product functionality and quality. The choice of processing method depends on the intended end product charecteristics and its market value. Each process might have adverse effect on a certain product, with a significant reduction of their bioactive components level. The bioactivity and product degradation mechanisms are related to the processing conditions, principally temperature and time and also control of these parameters (Orsat et. al., 2007).

In Turkey, the most common drying method for apricots is open air sun drying, required low capital, simple equipment and low energy input. Hot air drying has gained importance because it has many advantages over sun drying, such as reduced microbial contamination, controllable drying parameters which give more uniform product with less quality degradation, least negative effect of whether conditions, shorter drying times and lower labor costs (Karabulut et al., 2007). Additionally, in literature there is a lot of different drying systems have been studied on apricot such as electron beam irradiation by Wei et al. (2014), gamma irradiation by Hussein et al. (2013), infrared and microwave drying by Karataş and Kamışlı (2007), sun, hot air

and microwave drying by Göğüş et al. (2007), microwave drying by Igual et al. (2012) and etc.

1.5.2.1. Tray Drying

Tray drying systems use trays to expose the food product to heated air in an enclosed space. The trays holding the product inside a drying system (Figure 1.3). Hot air moves over the product surface and heat and mass transfer are proceed. Humidity, temperature, product characteristics, thickness and geometry, air distribution pattern, air velocity and air exchange are the factors which affect the drying rate. Sample is usually placed on trays as one layer for better air circulation over the product. In general increasing air velocity and temperature and decreasing air humidity cause faster drying. A dryer must expel air to dispose of moisture, thereby allowing new, lower humidity air to enter the system. Nevertheless changing the air causes loss of heat from the dryer. Tray dryer is operated as batch systems (Singh and Heldman, 2001).

Tray drying have a lot of advantages such as, sample place as one layer and it provide better contact between air and sample, air flow can be controlled easily so air circulation and drying efficiency is increased. Also tray dryers can be designed for continuous, semi-continuous and batch operations. Temperature can controllable and the size of cabinet and number of tray can be designed with the requirement. Also there are some disadvantages of tray dryers. If using batch tray drier that limits the capacity. For increasing drying rate the air in the system can expel after contact with sample but this cause the necessity of heating new, lower humidity air.

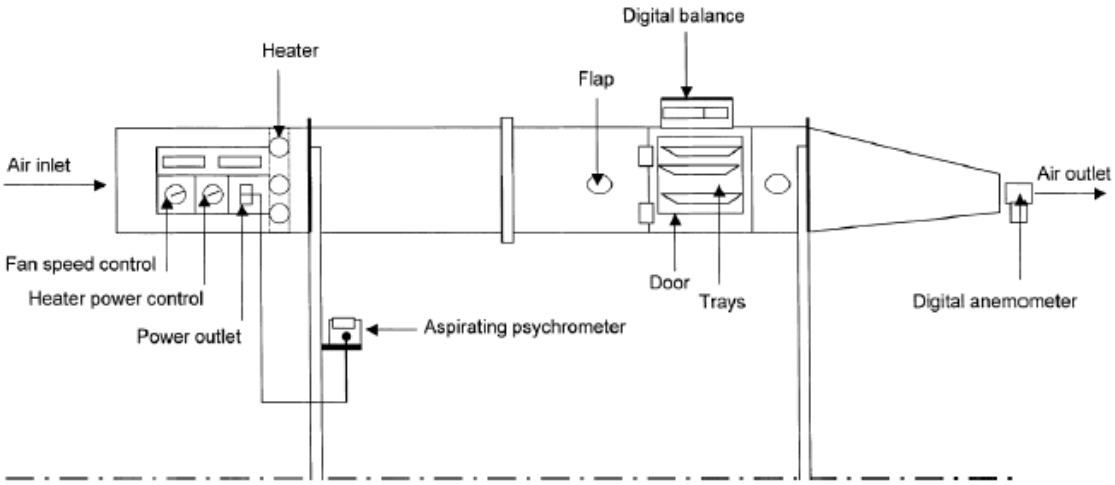

Figure 1.3. Shematic diagram of Tray Drier

1.5.2.2. Microwave Drying

Electromagnetic energy with the frequency between 300 MHz and 300 GHz is used in microwave drying. Mostly used frequency is 2450 MHz. Microwaves are generated inside a cavity by stepping up the alternating current from domestic power lines up to 2450 MHz (Orsat et al., 2005). It is demonstrated that using microwave energy for drying reduce the energy consumption. The microwave energy is an attractive thermal energy source by the reasons of reduced processing time and volumetric heating. For fully complete drying process microwave is recommended to combine with other drying techniques likely vacuum and forced air drying, rather that using alone for increase the process efficiency. Heat in microwave drying is generated inside of the product with molecular excitation caused by alternating electromagnetic field. There is two mechanism exist in the sample and microwave interaction: ionic conduction and dipolar rotation. In ionic conduction, electric fields cause the ions are accelerated and move towards the opposite direction to their own polarity. The ion movement cause collisions between the molecules of the material. A disordered kinetic energy is created and in consequence heat is generated throughout. The rotational energy level of polar molecules are similar to the microwaves energy level. In classical hot air drying the convective heat transfer mechanism exists in which heat are transferred from the surface of material to the inner part, instead of that in microwave system the heat generates from the friction among the fast rotating molecules. It is important to know that the dielectric

properties are related to materials' properties and it is specific only for a given frequency. The dielectric properties can change with frequency, moisture and temperature. Accordingly, the drying process uniformity govern by drying temperature and moisture uniformity. In microwave drying of food products, microwave power density is an important factor to be considered in the processing. Additionally, microwave power density could influence the product drying behavior such as the drying kinetic, the drying speed, drying efficiency and the drying time (Kone et. al., 2013). Use of microwaves can increase rate of drying, enhance final product quality and improve energy consumption (Zhang et al., 2006). The quality of microwave dried commodities is often between air-dried. The rapidity of the process often yields better color and retention of aroma (Orsat et. al., 2007).

1.5.2.3. Combined Drying Systems

Drying method may adversely affect the quality of the food product (Lewicki et al., 2002). More effective and faster drying processes, such as microwave application can be used in food drying to reduce this problem (Contreras et al., 2008). In recent years many of studies have been focused on the effect of drying on retention or loss of nutritional quality. For this aim new technologies were used together with conventional drying and also pretreatments are often used to improve certain quality attributes of the final dried product and to accelerate the drying process (Ratti, 2009).

There is a lot of drying technique and drying equipment developed by thousands of years of experience and trial and error methods as well as resulted from research done during the last hundred years. The process will be used for the final product and expected quality attributes of the product are two important factors must be taken into account when designing a dehydration process. These factors are interrelated with each other since the way the product is used defines its quality indices in many cases (Lewicki, 2006).

In addition to that many different pretreatments and different system combinations were searched by different studies. Wei et al (2014) studied about applying electron beam radiation with sun drying system on apricots. Doymaz (2004) apply pretreatments with using potassium metabisulphide and alkaline ethyl oleate on apricot before drying. Mahmutoğlu et al (1996) used solar drier and pretreated with

SO_2 gas and sodium-meta-bisulphite. Osmotic dehydration was also used as pretreatment of apricot drying (Forni et al., 1997; Riva et al., 2005)

In conventional hot air drying, temperature and the processing time are generally high and long. Hot air drying effect on food quality is well recognized but the dewatering processes and its adverse effect on material properties have limited understanding. This is because of water evaporation at high temperature causes biological, physical and chemical changes in food. These changes can occur in sequence or simultaneously (Lewicki, 2006). The antioxidants are exposed to direct contact with air when material's natural protective layer is destroyed. In that case rapid lipid oxidation can occur in which anti-oxidants functionality destroys. Oxidation of lipid and losses of antioxidant can be reduced by low temperatures, low pressures and short drying times. Through combined microwave and air drying processes there are several model have been shown for mass and heat transfer. The conventional kinetic trend, which observed in hot air drying, significantly changes when microwaves are applied (Contreras et al., 2008).

Mathematical modelling can play an important role in design of the drying process and control of process parameters during drying. With the aim of optimization of the drying process, simulations of accurate kinetic models can be used. These process models validated by experiments provide information about the energy efficiency of different combinations in drying processes and predict the effect of most relevant parameters on drying time.

1.5.3. Drying kinetics

In the drying of various types of samples from one moisture content to another, it is usually desired to estimate the optimum dryer and drying conditions. For instance humidity and temperature for the air used, the time needed to perform the amount of drying required and the size of dryer needed. The drying process of foods depends on understanding the relationship between the water present in the drying medium, which is generally air and the water contained in a foodstuff. The moisture contents are the driving force for dehydration process because of the moisture contents are directly related to the chemical potentials of materials. Food dehydration is a complex phenomenon in shrinking and a hygroscopic system involving simultaneous energy and mass transport. The rate of dehydration is governed by the rate of these

mass and energy transport. Heat transfer from the drying medium to the wet food material can occur with the help of conduction, convection or radiation effects and also in some cases there is a combination of these mechanisms. Heat transfer through drying is generally controlled externally because of the internal heat transfer is usually very rapid than the external heat transfer. In contrast, mass transfer depends on either the movement of water vapor from the solid surface to the bulk medium or the movement of moisture within the solid. Water removal from food can be limited by either mass or heat transfer or by the combine effect of these two transport mechanisms depending on the specific drying process. It is generally approved that the principal rate-limiting step in drying is internal mass transfer. There is no theory to explain exactly the mechanism of internal moisture movement in sample during drying because of the complexity of the process.

The drying kinetics of the product are the most important data required for the design and simulation of dryers and estimate the drying time. Determining the thermal and physical properties of food products, such as the mass and heat transfer, moisture diffusion coefficient, activation energy and suitable drying equations are useful to estimate the ideal conditions. They represent the ease with which a product dehydrates under specific drying conditions. Drying kinetics are affected by the chemical and physical structure of the food and the external conditions of the medium. In the most general case, drying a food under constant conditions is considered in order to obtain the kinetics curve.

Equilibrium moisture contents of various materials cannot be predicted and must be determined experimentally. Similarly, the basic mechanism of rates of drying is quite incomplete, it is necessary in most cases to obtain some experimental measurements of drying rates.

To determine the rate of drying experimentally for a given material, a sample is usually placed on tray. When the tray fill with solid material, drying air stream have an impact only the top surface of the material. By entegrated a balance to the tray drying cabinet, the loss in weight of moisture during drying can be determined at any desired intervals without suspended the operation.

Data to compose to rate of drying curve by experimentally are usually obtained with the results of batch-drying experiment. Total weight (W) data of the wet solid (moisture plus dry solid) at different times (t) during the drying period is acquired. Moisture content, drying rate and moisture diffusity coefficient can be calculated by using these datas. Moisture content (X) values can be calculated with the Eq. 3. Where Ws is the weight of the dry solid in kg and W is the total weight of the water plus dry solid in kg,

$$X_t = \frac{\mathrm{W-Ws}}{\mathrm{Ws}} \frac{(kg\ total\ water)}{(kg\ dry\ solid)} \qquad \text{(Eq. 3)}$$

Equilibrium moisture content of food can be explained as the conditions when there is no water movement between the food and its surrounding air. That is obtaining by the food moisture content reaches in equilibrium value with its surrounding air under a constant water vapour pressure of the surrounding air.

The relative humidity of the air in equilibrium with the food versus moisture content of food graph and also the equilibrium vapour pressure versus moisture content of food graph can be plotted. The equilibrium moisture content X^* can be determined as kg equilibrium moisture per kg dry solid for the given constant. After that the free moisture content X can be calculated in kg free water per kg dry solid for each value of X_t.

$$X = X_t - X^* \qquad \text{(Eq. 4)}$$

Using the data calculated from this equation the free moisture content graph as in Figure 1.4 can be drawn by plotting of free moisture content versus time.

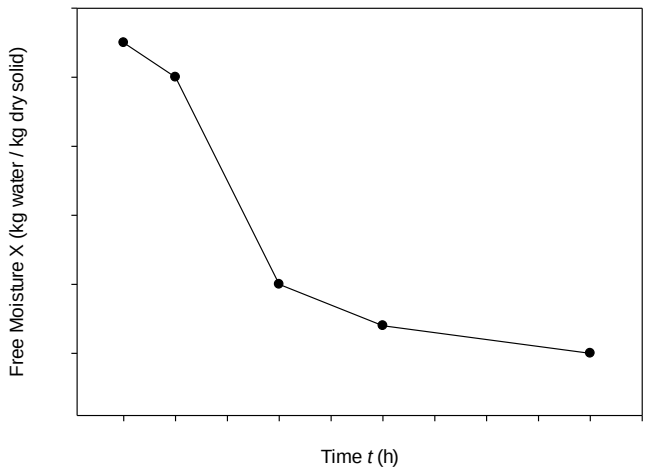

Figure 1.4. General graph for moisture content versus time

To obtain the rate of drying curve from moisture content versus time plot, the slopes of the tangents drawn to the curve can be measured, which give values of dX/dt at given values of time. The rate R is calculated for each point by

$$R = -\frac{Ls}{A}\frac{dX}{dt} \qquad \text{(Eq. 5)}$$

Where R is the drying rate in kg H_2O/h.m^2, Ls is the kg of dry solid used and A is the exposed surface area for drying in m^2. The drying rate curve can be drawn versus time and also versus the moisture content. The calculation of the derivative $\frac{dX}{dt}$ may cause some problems in the overall determination of the drying rate. The easiest way of estimating the numerical temporal derivate is by calculating the difference in water content at two drying times.

The drying process under constant conditions, can be explained in a number of steps which defined by different dehydration rates (Figure 1.5). First part (number 1) is initial part of drying. This period is unsteady-state because sample temperature is different than the drying temperature. This period is usually quite short and it can be ignored for calculating the drying time.

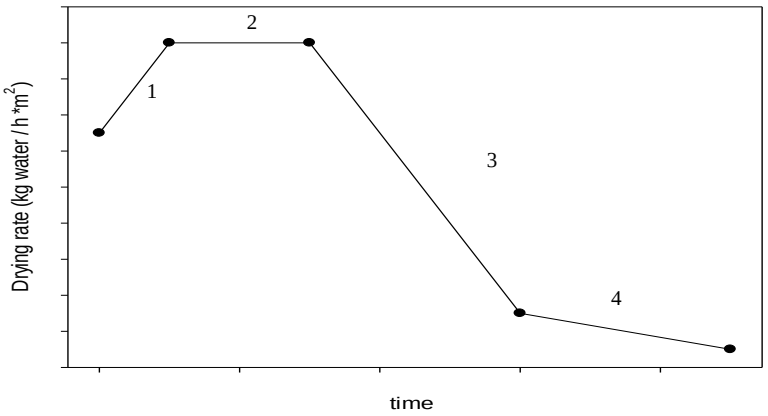

Figure 1.5. General graph for drying rate versus time

Two dehydration periods usually occur: a constant rate period (number 2) during which drying occurs as if pure water is evaporated, the rate graph is straight line and hence rate is constant. Also one or several falling rate periods (number 3 and 4). In third period (number 3) drying rate starts to decrease. For this period the rate graph is often linear. In last period (number 4), the drying rate falls rapidly and finally reach to the equilibrium point. moisture movement in falling rate periods are controlled by combined external-internal resistances or by purely internal resistances (Ratti, 2009; Geankoplis, 2003).

1.5.4. Moisture Diffusivity

The moisture transport process during drying is very complex and often involves one or more transport mechanisms such as liquid diffusion, vapour diffusion, surface diffusion, and hydrostatic pressure differences. As a result of equilibrium concentration of the water vapour on the surface of the materials at low air velocity and at higher temperature, the drying rate increases because of the air has a better contact with sample surface that leads to an increase in the moisture diffusivity. Knudsen flow, capillary flow, surface diffusion mechanisms, molecular diffusion and hydrodynamic flow can occur for the migration from solid to the surface.

The difficulties applying of moisture diffusivity phenomena theory to food processes are due to the different composition and the complex physical structure of foods. Shrinkage or the volume reduction which occur simultaneously within moisture diffusion in drying process is one of the undesirable changes in drying. The diffusion coefficient of the materials can be effected from mass and heat exchange area and modifying physical properties. Generally, shrinkage observed as a result of volume

reduction due to the moisture evaporation from food. The cellular structure of the food is effected from stress caused by heating and loss of water, so that decrease in dimensions and changes in shape can occur in food samples. During the drying of fruits and vegetables unavoidable alterations observed to their original form which cause significant shrinkage because of the high initial moisture contents (80–90%) of them. The whole drying phenomenon especially the drying kinetics can be analyzed with the quantification of this phenomenon. Also the moisture diffusivity which is an another important parameter in drying could be affected by shrinkage.

In optimization and simulation of the drying process of foods, moisture diffusivity have essential role because of moisture diffusion from food to the outer surface controls the transfer rate of inside the materials. Accordingly the water vapour concentration on the material outer surface decreases close to the equilibrium values.

Drying behaviour of agricultural products can be characterized by certainly depending on the thermal and physical properties of the materials, such as moisture diffusion, activation energy and mass and heat transfer. These factors also required for the ideal dryer design of foods (Mırzaee et al., 2009; Touil et al., 2014).

Moisture Ratios (MR) can be determined by Eq.6;

$$\mathrm{MR} = \frac{X - X_e}{X_0 - X_e} \qquad \text{(Eq. 6)}$$

Where X, X_0 and X_e represent the instantaneous, initial and equilibrium dry basis moisture contents (kg water / kg dry solids) respectively. Because equilibrium moisture content (X_e) of samples is relatively small compared to X or X_0, MR equation can be simplified to Eq. 7 (Ghatrehsamanı et al., 2012; Mırzaee et al., 2009 and Chayjan and Alaei, 2013).

$$\mathrm{MR} = \frac{X}{X_0} \qquad \text{(Eq. 7)}$$

Moisture Diffusity for an infinite slab can be calculated from Ficks second law (Eq. 8);

$$MR = \frac{M}{Mo} = \frac{8}{n^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp\left(-\frac{(2n-1)^2 \pi^2 \mathrm{Dt}}{4L2}\right) \qquad \text{(Eq. 8)}$$

where:

MR: moisture ratio

M: moisture content at any time (kg water/kg dry mater)

M_0: initial moisture content (kg water/kg dry mater)

n: 1, 2, 3, . . . the number of terms taken into consideration

t: time of drying in seconds

D: effective moisture diffusivity in m^2/s

L: half thickness of the slice (m)

Only the first term of Eq. 8 is used for a long drying time drying (Mırzaee et al., 2009). Hence:

$$MR = \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 Dt}{4L^2}\right) \quad \text{(Eq. 9)}$$

From Eq (9) a plot of ln (MR) versus time gives a straight line with a negative slope of k_0 (Eq. 10) in which D_{eff} value can be estimated.

$$k_0 = -\frac{\pi^2 D}{4L^2} \quad \text{(Eq. 10)}$$

Linear regression analyses can be used to fit the equation to the experimental data to obtain the coefficient of determination (R^2) (Mırzaee et al., 2009).

1.5.5. Model systems

Thin layer drying equations are used to estimate the drying time for several products and also to generalise the drying curves. The moisture diffusion and activation energy in the thin layer drying of various agricultural products, such as seedless grape, plums, grapes, candle nuts, potato slices, hazelnuts, beriberi fruit, and onion slices have been studied by some research (Mırzaee et al., 2009).

Thin layer drying models can be classified as empirical, semi-theoretical and theoretical. Theoretical models can be applied to all process conditions. However, due to their practical inconvenience, empirical and semi-theoretical models are widely preferred in drying studies.

Theoretical models are derived from the Fick's second law. Semi-theoretical models are derived from the Fick's law as well as the Newton's cooling law. The application

of the semi theoretical models are easy and need less assumption for using the experimental datas but this models are only valid for the application conditions. Empirical models have nearly same properties with semi-theoretical models and give restricted information about drying behaviour of the samples. In food drying studies semi-theoretical and empirical models are widely used (Table 1.2) (Kutlu et. al., 2015).

Table 1.2. Thin layer models in food drying

Model Name	**Model**
Newton	$MR = \exp(-kt)$
Page	$MR = \exp(-kt^n)$
Henderson and pabis	$MR = a \exp(-kt)$
Logarithmic	$MR = a \exp(-kt) + c$
Two term	$MR = a \exp(-k_0t) + b \exp(-k_1t)$
Wang and Sing	$MR = 1 + at + bt^2$

1.6. Aim of the Thesis

Fruits, vegetables and their products play important role in human nutrition because of their health benefits with vitamin, mineral and antioxidant content. There are many processing technique and different product type in food technology however that is well known every food process can cause some changes in food material and can decrease nutritional quality. The consumer appreciation to healthy foods is increasing year over year. Thus food research about natural foods and also design of minimum effective process conditions must increase. Zerdali is a wild type of apricot. Zerdali is a very important traditional summer fruit and has important properties such as color, taste, smell and also rich in vitamin, mineral, carotenoid and phenolic content. Despite that the knowledge about zerdali and the producers interest towards zerdali get less and less in recent years and it become nearly impossible to find fresh zerdali in local markets as well as processed zerdali.

In this study; 1) in order to make the fresh fruit long standing the salicylic acid (SA) treatment was tried, 2) zerdali and apricot were dried by hot air and microwave pretreated hot air drying systems to determine the drying kinetics and effects on some physical and chemical parameters. Resultantly general target of this thesis is to obtain information about fresh and dried zerdali and also increase the consumer appreciation towards this healthy traditional fruit as in old times.

CHAPTER II

MATERIALS AND METHODS

2.1. Materials

Zerdali and apricot samples were obtained from traditional bazaar in Gaziantep. Zerdali and apricot fruits were selected of nearly uniform size and maturity, free from diseases. All samples were brought to laboratory immediately and washed with distilled water for removal of dust and other pollutants. After washing, the excess water was dried on the drying paper.

2.2. Methods

2.2.1. SA Treatment

Salicylic acid treatment was applied only for zerdali samples. Zerdali fruits were divided into two parts; one group was dipped in to 2,0 mmol/L of salicylic acid solution for 5 minutes (Treated Zerdali) while the other part was dipped in to distilled water (Untreated Zerdali) and served as control.

Samples were kept in refrigerator and the following parameters were measured for 12 days with intervals of 3 days. Changes in fresh fruit color by storage time were recorded including parameters L*, a* and b* by Hunter lab colorimeter. The soluble solid content was measured with the help of refractometer and expressed as °brix. Hydrogen-ion concentration was determined with the help of pH meter.

2.2.2. Hot Air Drying

The drying of zerdali and apricot has been performed in a pilot plant tray drier (VOP 8 Tray Dryer, Armfield, UK). Apricot and zerdali (treated and untreated) seeds were taken and all samples were cut into small pieces, and stored at -40°C. Samples stored at -40°C freezer were weighted nearly 200 g and placed to refrigerator for thawing.

After 5 hours, samples put into special aluminium dish for tray dryer as a thin layer and replaced in the driers middle shelf. The drying was performed at a constant air velocity of 0,5 m/s and temperature of 60°C. Hot air flows parallel to the drying surface of the sample. Weight loss was recorded at 15 minutes interval by a digital balance connected to the dryer. Drying was continued until the moisture content of samples fall under 25%.

2.2.3. Microwave Pretreated Hot Air Drying

A programmable domestic microwave oven (Arçelik ARMD 580, TURKEY) with maximum output of 700 W at 2450 MHz was used. Frozen samples were thawed in refrigerator and nearly 200 g sample was put into squared glass dish and MW was applied for 1 minute at 350 W power intensity. After MW pretreatment, samples were dried in tray dryer in the same conditions with other samples, which dried only in hot air drying. Weight loss was recorded at 15 minutes interval by a digital balance connected to the dryer. Drying was continued until the moisture content of samples fall under 25%.

2.2. 4. Analyses

2.2.4.1. Preperation of Samples for Analyses

Samples were used directly as a small pieces for color analysis. For the other analyses samples were homogenized with juice extractor. 5 g homogenized sample was separated for carotenoid analysis. Another 5 g homogenized sample was taken and diluted with 50 ml water and used for other analysis.

2.2.4.2. Color Determination

Color measurement of the samples were performed by HunterLab color measurement device according to CIELAB system. L* (whiteness or brihtness / darkness), a* (redness / greenness), b* (yellowness / blueness) and YI (yellowness index) values were measured from surface of samples. The equipment was calibrated with a black and white ceramic plate standards. For each sample, three measurements were taken.

The results were expressed as total color difference (ΔE) between the initial sample and dried ones to the equation:

$$\Delta E = \sqrt{(L^*_{initial} - L^*_{dried})^2 + (a^*_{initial} - a^*_{dried})^2 + (b^*_{initial} - b^*_{dried})^2}$$

Browning index (BI) values were calculated by using the equation:

$$\text{BI} = \frac{[100*(x - 0.31)]}{0.17} \qquad \text{where x} = \frac{(a^* + 1.75*L^*)}{(5.645*L^* + a^* - 3.012*b^*)}$$

2.2.4.3. Determination of pH

pH values of non-dried, tray dried and microwave and tray dried samples were measured by pH meter (HANNA HI 8314 membrane pH meter, Romania).

2.2.4.4. Determination of Total Soluble Solids

Total soluble solid as °Brix of non-dried, tray dried and microwave and tray dried samples were measured by refractometer (Comecta NR 151 Digital Refractometer, Barcelona).

2.2.4.5. Determination of Total Phenolics

Folin-Ciocalteu method was used for determination of total phenolics (Akın et al., 2008). Diluted sample was taken and clarified by centrifugation at 10000 rpm for 15 minutes at 25°C by Eppendorf Centrifuge 5810R. The extract was filtered through 0,45µm filter. 0.5 mL filtrate, 0.5 ml Folin-Ciocalteu reagent and 4 ml of 7.5% sodium carbonate solution were added to a 25 ml flask and made up with distilled water. Flask was stand for 5-10 minutes at 50°C and then the absorbance was measured in spectrophotometer at 765 nm. Total phenolic content was found by using calibration curve which obtained from known gallic acid concentrations measurements. Resuts were given as mg of gallic acid equivalents (GAE) per 100 g of dry weight.

2.2.4.6. Determination of Total Carotenoid Content

Total carotenoids were extracted according to the method of Akin et al. (2008). 5 g of homogenized sample was taken and extracted with 100 ml of methanol/petroleum ether (1:9, v/v). Then mixture was transferred to a seperating funnel. Lower phase was poured and upper (petroleum ether) phase was added to the 100 ml volumetric flask after filtered through sodium sulfate and volume was made up with petroleum ether. Total carotenoid content was measured with these prepared solution by

spectrophotometer at 450 nm. 2500 was used as extinction coefficient and the results were expressed as milligrams β-carotene equivalents per 100 g of dry weight.

2.3. Modelling of Drying Data

Six empirical and semi-theoretical models (Table 1.2) were tested to fit the moisture ratio versus time. Model parameters were determined by Sigma Plot and the suitability of the fit was evaluated by the R^2 and RMSE parameters.

$$\text{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(MR_{exp.i} - MR_{pred.i})^2}$$

2.4. Statistical Analyses

All data were analyzed by one-way analysis of variance (one-way ANOVA) to test for significant differences. Means of the groups were compared using Duncans‘ multiple range test by using IBM SPSS Statistics 21. Differences among sample means were reported to be significant when $p<0.05$.

CHAPTER III

RESULTS AND DISCUSSION

3.1. Wild Apricot (Zerdali)

Fresh wild apricot was analysed with respect to pH, brix and color. All analysis were made at least in triplicate runs. Values of pH and brix were found as 3.00 and 17.87 respectively. Color of wild apricot was measured by Hunter Colorimeter and L*, a* and b* values are 41.56, 24.96 and 44.42 respectively.

3.2. Salicylic Acid Treatment

Salicylic acid (SA), is a natural phenolic acid, has been reported to enhance postharvest quality of fruits by inhibiting ethylene biosynthesis (Ali et al., 2013), and increasing the bioactive components of fruits (Wang et al., 2015). After harvesting, Zerdali ripens rapidly, undergo softening and deteriorates easily. So it has limited storage period at room or refrigerated storage. Effectiveness of SA on storage life of zerdali was determined by treating Zerdali fruits with 0.2 mM salicylic acid. Zerdali fruits with and without SA treatment were stored at 4°C for 12 days and changes in pH, brix and color of samples were determined during refrigerated storage.

Change in the pH values of Zerdali was given in Figure 3.1. pH values of samples remain nearly same during 12 days of storage. pH of SA treated zerdali show increasing trend during the refrigerated storage, but pH of untreated zerdali increased for first 6 days and then decreased.

Soluble solid contents of treated and untreated zerdali increased with time as shown in Figure 3.2. At the end of the storage period brix value of treated Zerdali was higher than the untreated Zerdali.

Color values of treated and untreated zerdali throughout 12 days storage were given in Figures 3.3, 3.4 and 3.5 as brightness, redness-greenness and yellowness-blueness, respectively. Both SA treated and untreated zerdali samples show similar trend in color measurements. a* and b* values increase to the same value for treated and untreated samples whereas L* value of treated zerdali gets higher at the 12th day.

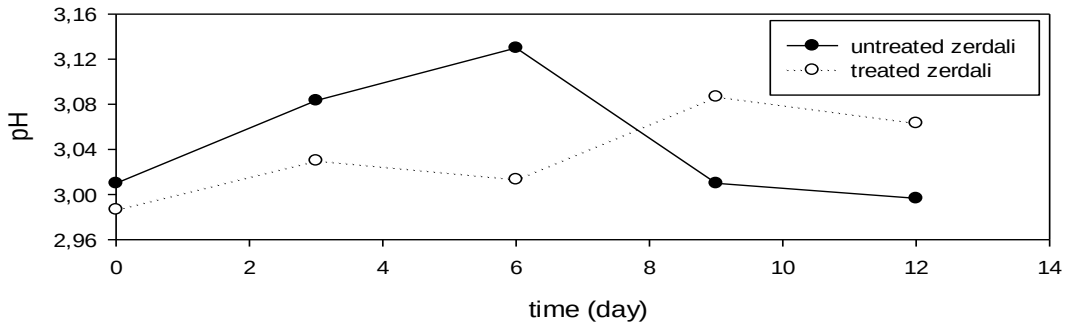

Figure 3.1. Changes of pH by time for treated and untreated fresh zerdali samples

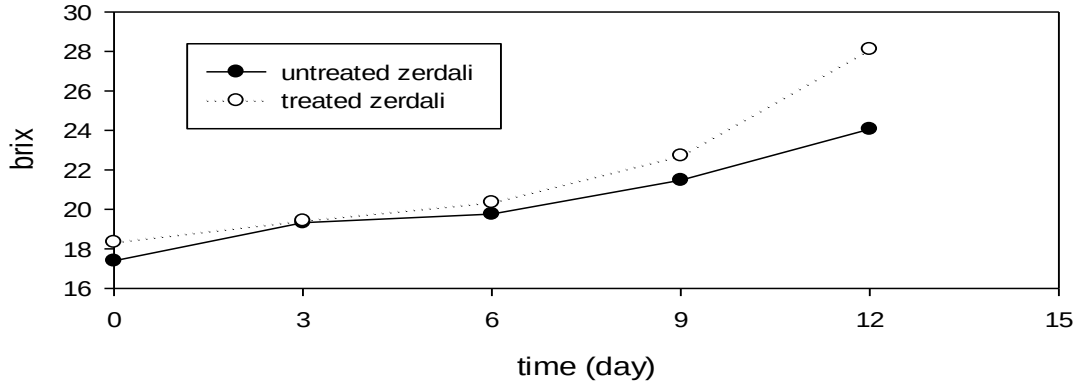

Figure 3.2. Changes of brix by time for treated and untreated fresh zerdali samples

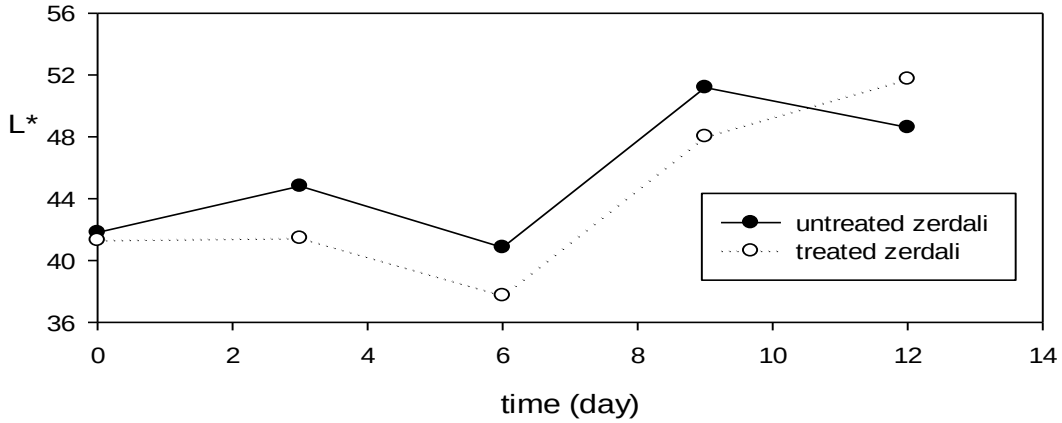

Figure 3.3. Changes of brightness by time for treated and untreated fresh zerdali samples

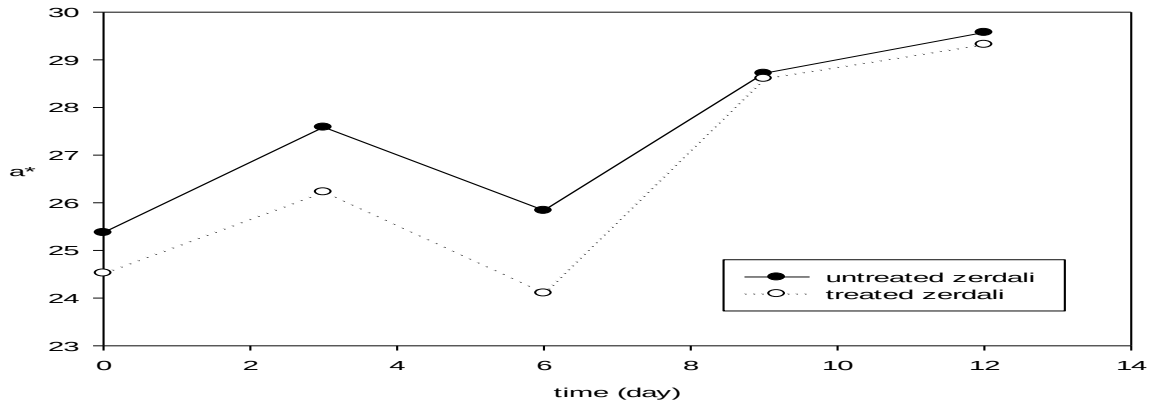

Figure 3.4. Changes of redness-greenness by time for treated and untreated fresh zerdali samples

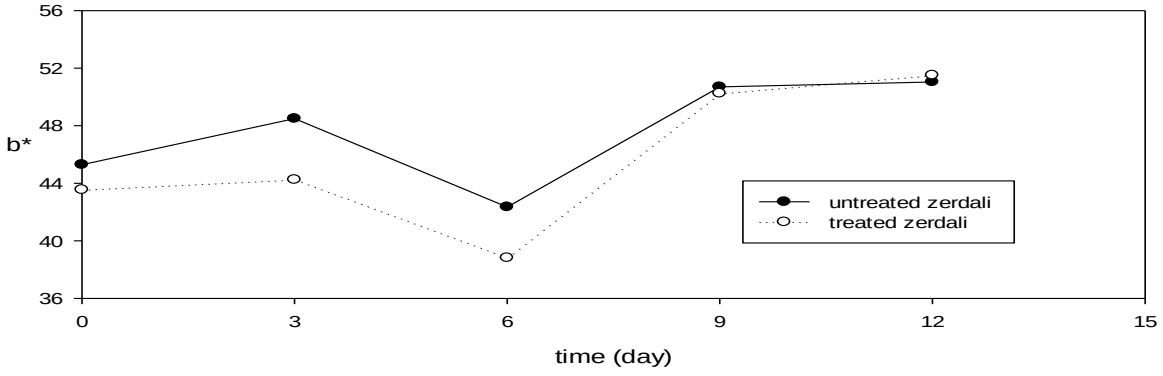

Figure 3.5. Changes of yellowness-blueness by time for treated and untreated fresh zerdali samples

Salicylic acid used to be applied to enhance the local and systemic resistance in fruits against pathogens, for inhibiting the production of ethylene, respiration and senescance and promoting the quality. Fruits treated with SA exhibited significantly higher total phenols, flavanoids, anthocyanins and ascorbic acid contents. Results from literature suggested that SA treatment might be a powerful strategy to enhange antioxidant capacity. The results from literature are more significant than ours which is because of the studying concentrations are higher than ours. They showed that use of SA could retart the ripening process and promote the postharvest quality of apricot fruit (Dokhanieh et al., 2013; Wang et al., 2015).

3.3. Drying of Zerdali and Apricot

Zerdali treated with SA, untreated zerdali and apricot were frozen at -40°C until drying and subsequent analysis. Frozen samples were thawed in refrigerator and then dried in tray drier. Effect of microwave pretreated tray drying was also examined.

3.3.1. Drying Kinetics

The initial moisture contents of apricot and zerdali were about 85 and 81 % (wet basis), respectively. Drying of samples continued until the final moisture contents of about 25 % (by wet basis). Variations of the moisture contents of apricot and zerdali samples with drying time in tray drying are given in Figure 3.6. Moisture contents of all samples decreased with similar trends. Drying curves of samples undergoing microwave + tray drying are given in Figure 3.7. Moisture content trends for both tray and microwave pretreated tray drying was the same, because of the studying constant temperature, as normal and similar to literature (Marquez et al., 2006). It is clear that, in each drying system, the constant-rate period was not observed and the drying process took place in the falling rate period. These results indicated that moisture movement mechanism in zerdali and apricot is by diffusion. Same result was found for prickly pear fruit by Lahsasni et al.(2004) and for apricot by Doymaz (2004).

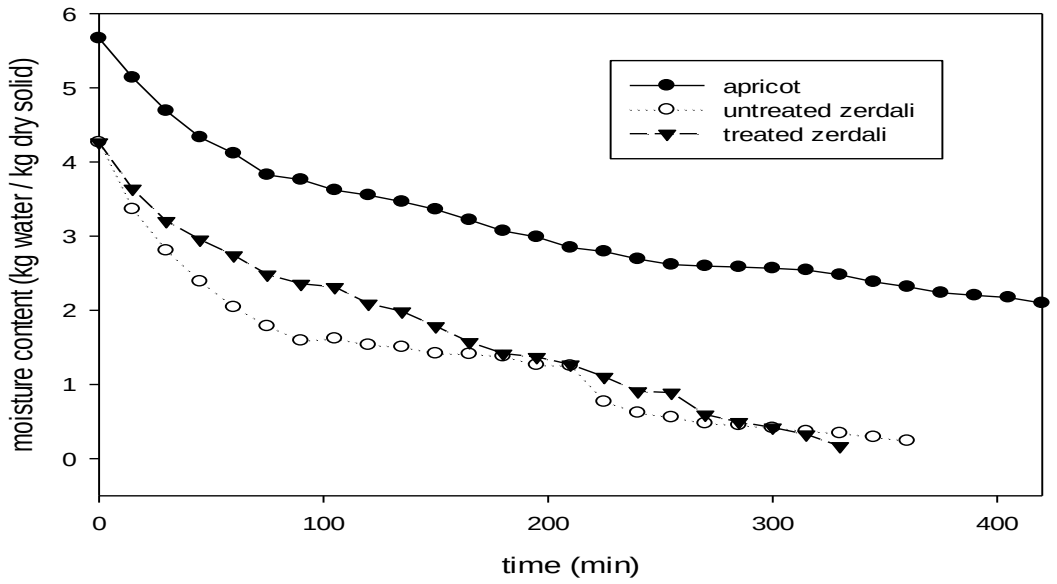

Figure 3.6. Variation of moisture content versus drying time of samples in tray drying

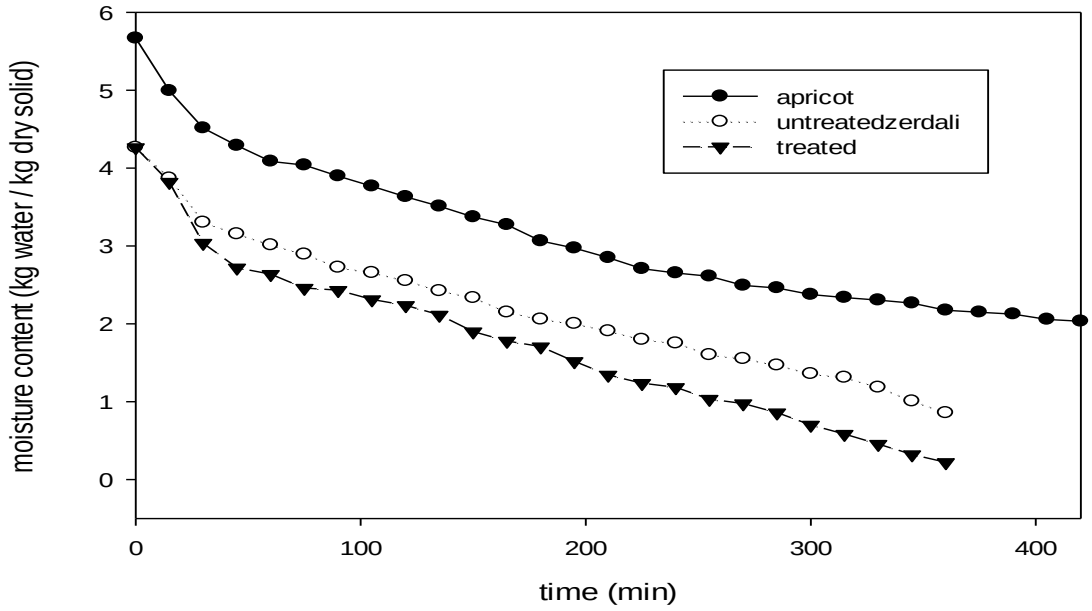

Figure 3.7. Variation of moisture content versus drying time of samples in microwave + tray drying

3.3.2. Drying Rates

The changes in the drying rates of SA treated zerdali, untreated zerdali and apricot versus moisture content are given in Figures 3.8, 3.9 and 3.10, respectively. It was apparent from drying rate graphs that, drying rate decreases with decreasing moisture content or increasing drying time. Initially, moisture content of the samples were high which results in higher drying rates due to higher moisture diffusion. Before drying process, samples were frozen and thawed and this could also be effecting the moisture diffusion due to the possible structural changes of material. In apricot microwave pretreatment did not cause any big changes in drying rate trend. However in zerdali samples drying rate were found higher when using microwave pretreated hot air drying system. Increasing in drying rate by using microwave pretreatment can provide the higher initial sample temperature for hot air drying. Also, SA treatment has effective on drying rate with decrease the drying rate trends differences between tray and microwave pretreated tray drying systems.

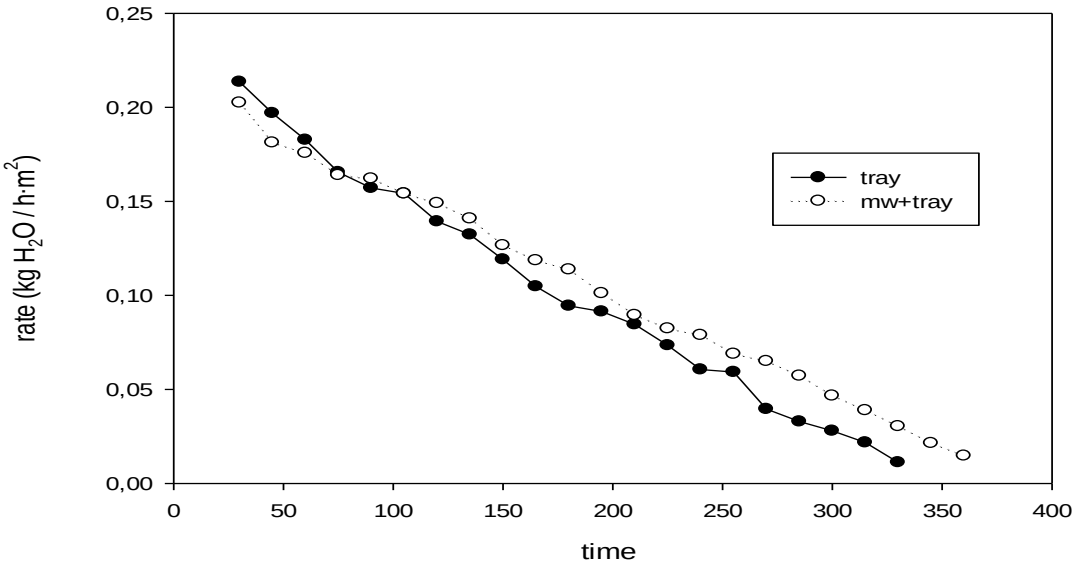

Figure 3.8. Drying rate versus time graph for treated zerdali

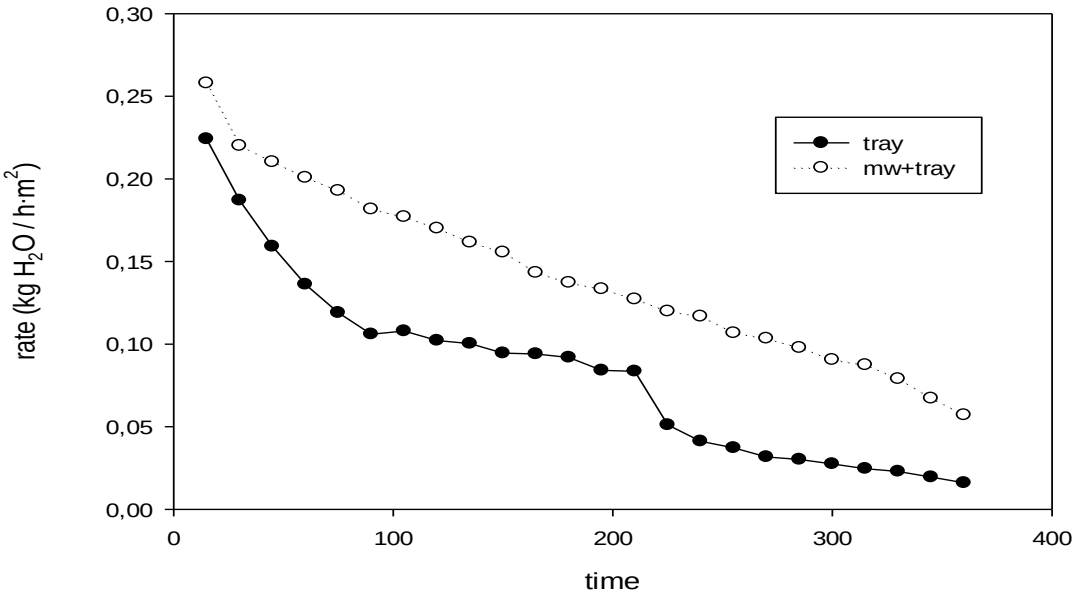

Figure 3.9. Drying rate versus time graph for untreated zerdali

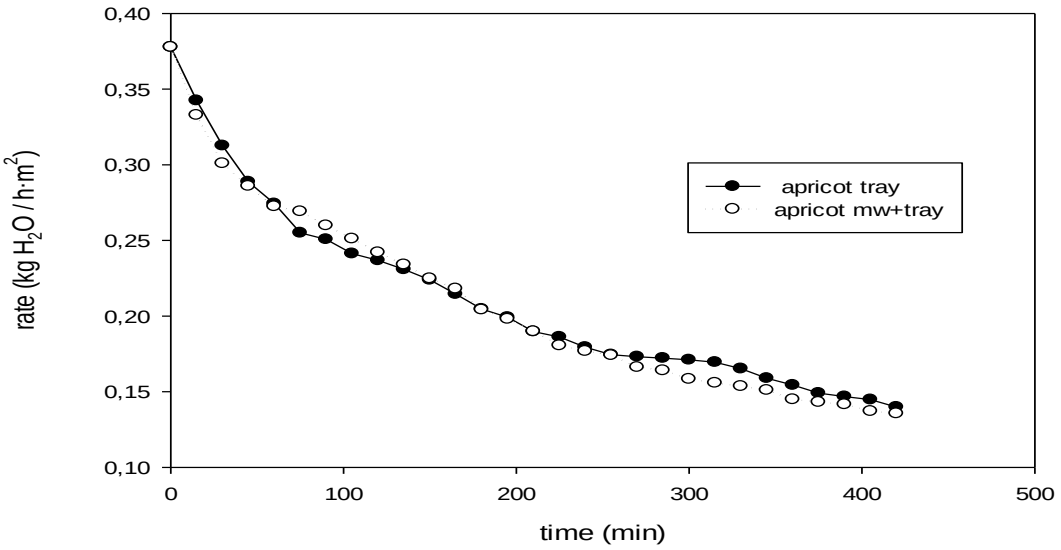

Figure 3.10. Drying rate versus time graph for apricot

3.3.3. Effective Moisture Diffusivity (D_{eff})

Effective moisture diffusivity values of zerdali and apricot samples were determined by using equation (8). Equilibrium moisture content (X^*) of samples was relatively small compared to X or X_0. Therefore moisture ratio can be simplified as MR = $\frac{X}{X_0}$

like for similar studies by Ghatrehsamanı et al (2012); Mırzaee et al (2009) and Chayjan and Alaei (2013).

By plotting natural logarithm of moisture ratio versus time, D_{eff} can be calculated from the slope of linear curve. It was found that there are two linear curves for untreted (Figure 3.11) and treated zerdali (Figure 3.12) proving the presence of two falling rate periods during drying. From each linear part, D_{eff} values were calculated for the first and second falling rate periods. For apricot, only one falling rate period was observed (Figure 3.13). D_{eff} values of untreated zerdali, SA treated zerdali and apricot for tray drying and MW + tray drying, are shown in Table 3.1. D_{eff} values of samples ranged between 2.03×10^{-8} and 1.81×10^{-7} m^2/s. The values of D_{eff} are higher than general range of 10^{-11}- 10^{-9} m^2/s for food materials (Aghbashlo et al., 2008). D_{eff} values of apricot samples were found varied from 1.7×10^{-10} to 1.15×10^{-9} m^2/s by Mırzaee et al (2009) and from 1.755×10^{-10} and 0.767×10^{-10} by Toğrul and İspir (2007). Higher results may be because of the structural change during freezing and thawing operations. Breaking down on the cells may cause higher diffusivity of our zerdali and apricot fruits.

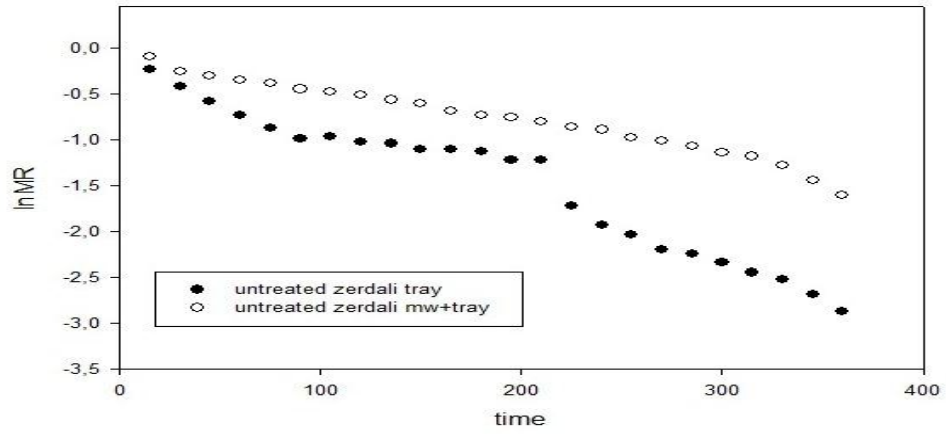

Figure 3.11. Natural logarithm of moisture ratio versus time graph for untreated zerdali

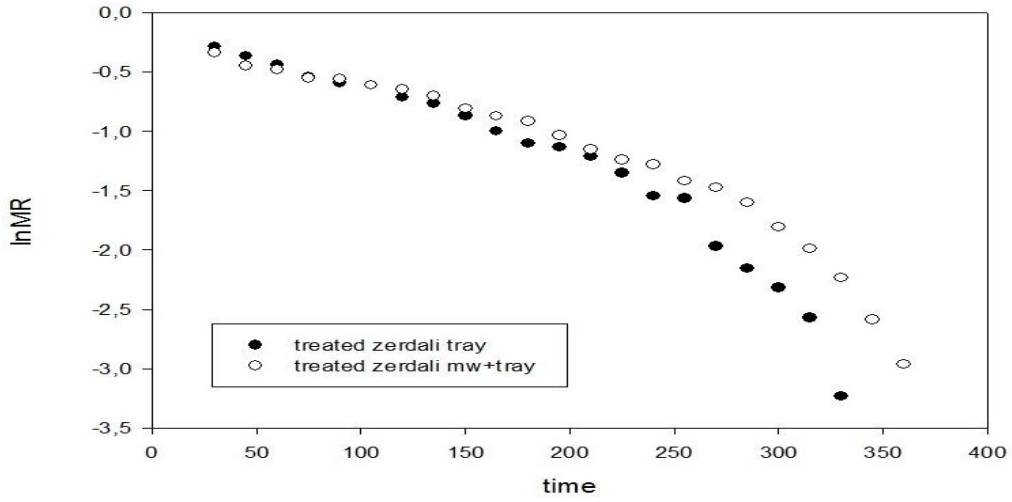

Figure 3.12. Natural logarithm of moisture ratio versus time graph for treated zerdali

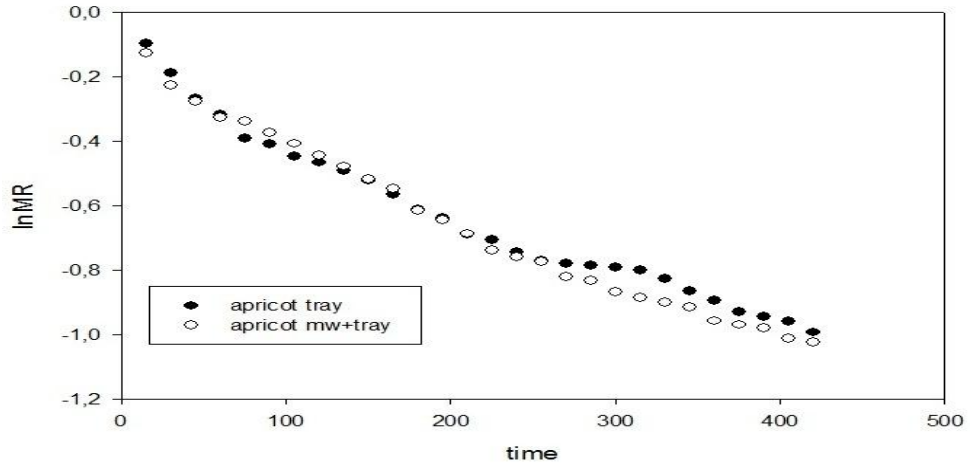

Figure 3.13. Natural logarithm of moisture ratio versus time graph for apricot

Table 3.1. Effective moisture diffusivity and R^2 values of zerdali and apricot

Sample	Operation	D_{eff} 1* 10^{-8} (m^2/s)	R^2	D_{eff} 2 * 10^{-8} (m^2/s)	R^2
Untreated Zerdali	Tray	4.56	0.8606	7.80	0.9819
	Mw + Tray	3.34	0.9926	9.73	0.9898
Treated Zerdali	Tray	5.78	0.9844	13.2	0.9909
	Mw + Tray	4.66	0.976	18.1	0.9769
Apricot	Tray	2.03	0.962	-	-
	Mw + Tray	2.03	0.980	-	-

3.3.4. Modelling of Drying Curves

The moisture content data obtained from experimental drying were converted into moisture ratio (MR). Then drying models listed in Table 1.2 was applied to the

experimental data of zerdali and apricot samples. The statistical values and constants of each model for all samples are shown in Table 3.2.

Table 3.2. Thin Layer Model Fitting for zerdali and apricot samples dried with trayand MW+tray drier

Sample	Model	R^2	RMSE	k	n	a	b	k_0	k_1	c
Treated Zerdali / Tray	Newton	0.9609	0.0413	0.0065						
	Page	0.9610	0.0412	0.0070	0.9843					
	Henderson and Pabis	0.9651	0.0391	0.0061		0.9464				
	Logarithmic	0.9963	0.0127	0.0016		1.8881				-1.0656
	Two Term	0.9651	0.0391			0.5204	0.4261	0.0061	0.0061	
	Wang and Sing	0.9480	0.0476			-0.0051	6.9675 E-006			
Treated Zerdali / MW +Tray	Newton	0.9206	0.0541	0.0059						
	Page	0.9350	0.0489	0.0122	0.8605					
	Henderson and Pabis	0.9543	0.0411	0.0050		0.8679				
	Logarithmic	0.9964	0.0115	0.0003		6.0588				-5.3092
	Two Term	0.9543	0.0411			0.4699	0.3980	0.0050	0.0050	
	Wang and Sing	0.8827	0.0657			-0.0047	6.3586 E-006			
Untreated Zerdali / Tray	Newton	0.8581	0.0725	0.0084						
	Page	0.9477	0.0440	0.0376	0.6995					
	Henderson and Pabis	0.9473	0.0442	0.0064		0.7830				
	Logarithmic	0.9484	0.0437	0.0055		0.8107				-0.0470
	Two Term	0.9598	0.0386			0.4466	0.7045	0.0745	0.0057	
	Wang and Sing	0.7424	0.0976			-0.0063	1.0932 E-005			
Untreated Zerdali / MW +Tray	Newton	0.9449	0.0423	0.0041						
	Page	0.9785	0.0264	0.0125	0.7901					
	Henderson and Pabis	0.9846	0.0224	0.0035		0.8967				
	Logarithmic	0.9864	0.0210	0.0025		1.0806				-0.2052
	Two Term	0.9846	0.0224			0.4054	0.4913	0.0035	0.0035	
	Wang and Sing	0.9322	0.0469			-0.0039	5.2091 E-006			
Apricot / Tray	Newton	0.7634	0.0678	0.0030						
	Page	0.9926	0.0120	0.0278	0.5921					
	Henderson and Pabis	0.9546	0.0297	0.0021		0.8343				
	Logarithmic	0.9893	0.0144	0.0060		0.5739				0.3446
	Two Term	0.9950	0.0098			0.2809	0.7139	0.0215	0.0016	
	Wang and Sing	0.9029	0.0435			-0.0035	5.1481 E-006			
Apricot / MW +Tray	Newton	0.8335	0.0596	0.0030						
	Page	0.9934	0.0119	0.0228	0.6336					
	Henderson and Pabis	0.9818	0.0197	0.0023		0.8462				
	Logarithmic	0.9945	0.0109	0.0044		0.6350				0.2577
	Two Term	0.9945	0.0109			0.6350	0.2577	0.0044	4.1429 E-019	
	Wang and Sing	0.9228	0.0406			-0.0035	4.8732 E-006			

The coefficient of determination (R^2) was one of the primary criterions for selecting the best equation to define the drying curves of apricots and also root mean square error (RMSE) was used to determine the quality of the fit (Delgado et al, 2014).

R-squares were varied between 0.7424 and 0.9963. As some values were nearly 1.0 as desired and these models described well fit with the experimental data. RMSE also presented low values, in the range of 0.0098 and 0.0976, as desired. The results show that Logarithmic model was the most appropriate model both with the highest R-square and lowest RMSE value for tray dried SA treated zerdali, mw+tray dried SA treated zerdali and mw+tray dried untreated zerdali. Two term model was the best fitting model for tray dried untreated zerdali and tray dried apricot. For mw+tray dried apricot best fitting models are Logarithmic and two term. The performance of the best models are illustrated in Figures 3.14 to 3.20. The predicted data generally banded around the straight line which showed the suitability of mathematical model in describing drying behaviour of zerdali and apricots.

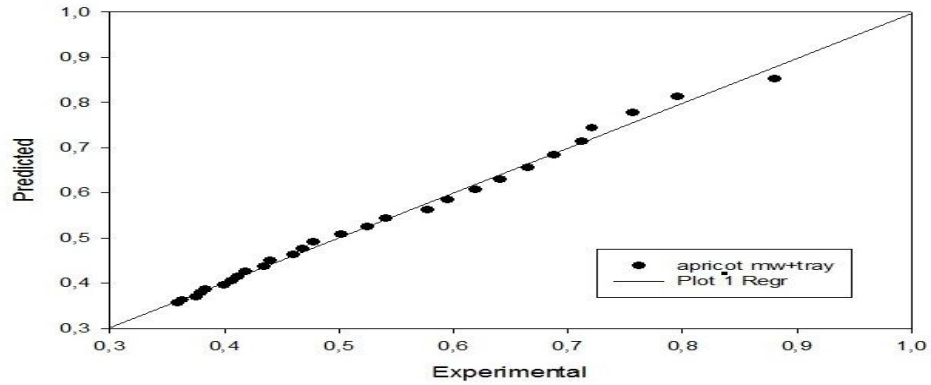

Figure 3.14. The performance of the logarithmic model for MW+tray dried apricot

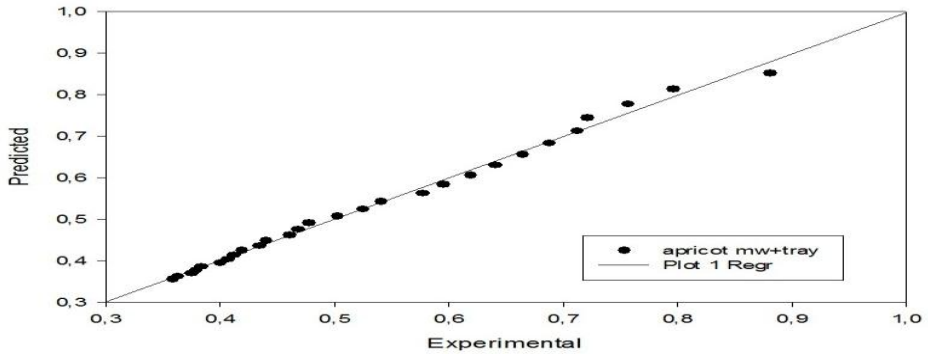

Figure 3.15. The performance of the two term model for MW+tray dried apricot

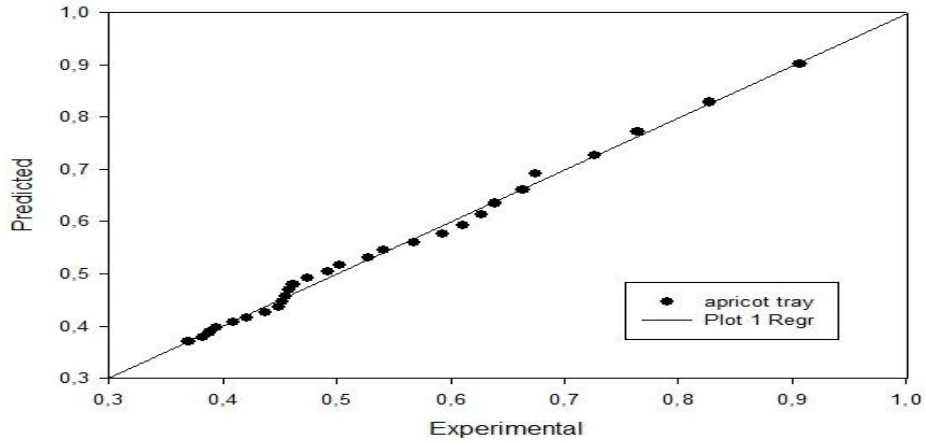

Figure 3.16. The performance of the two term model for tray dried apricot

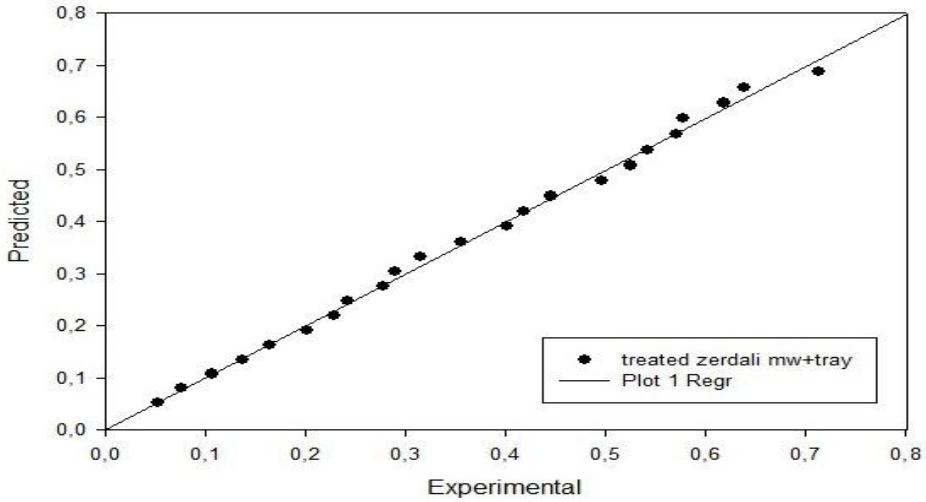

Figure 3.17. The performance of the logarithmic model for MW+tray dried SA treated zerdali

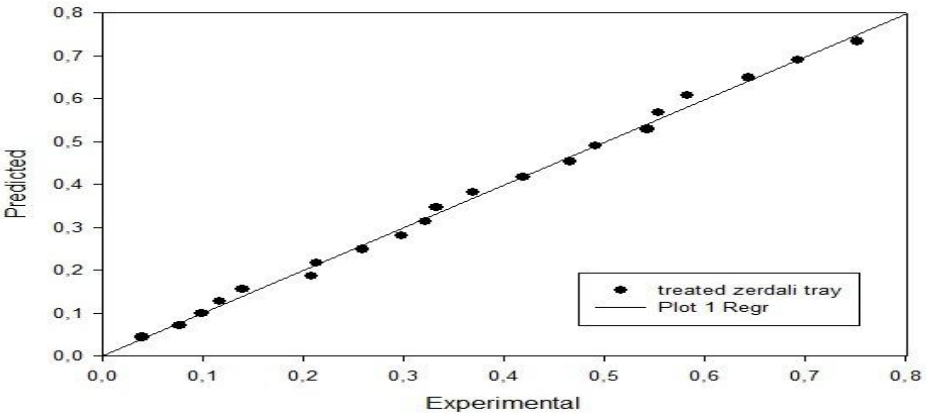

Figure 3.18. The performance of the logarithmic model for tray dried SA treated zerdali

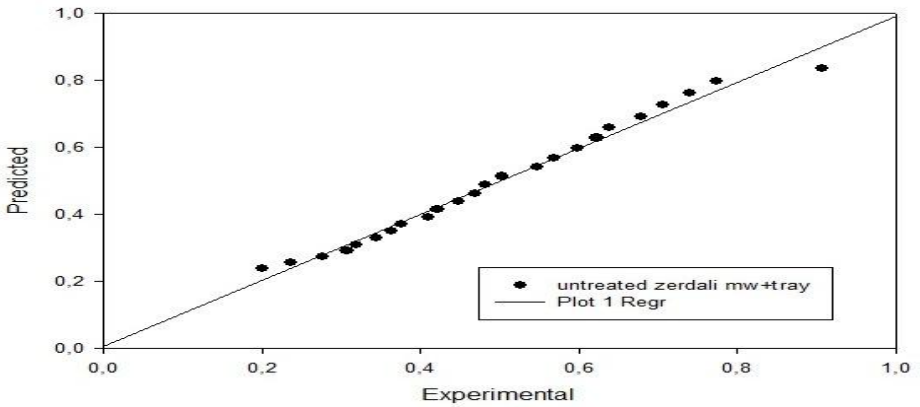

Figure 3.19. The performance of the logarithmic model for MW+tray dried untreated zerdali

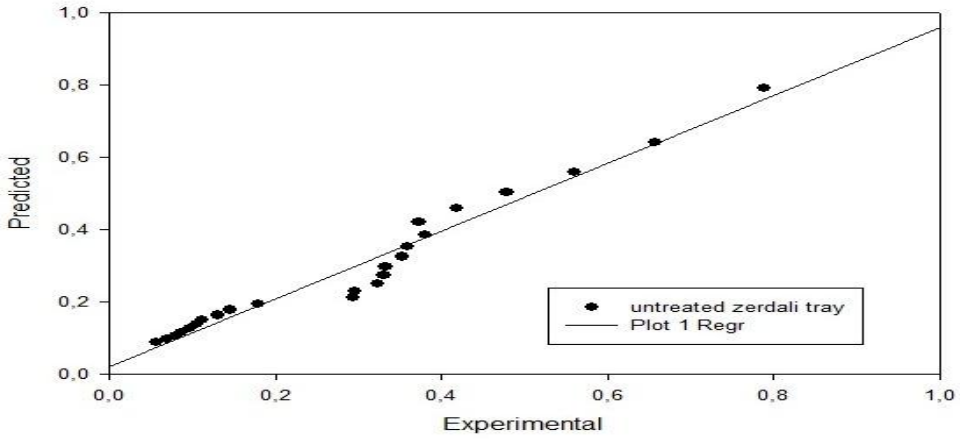

Figure 3.20. The performance of the two term model for tray dried untreated zerdali

Toğrul and Pehlivan (2003) were studied about modeling of drying kinetics of single apricot. They described the logarithmic drying model is best for the drying behavior of single apricot (within 99.9%).

3.4. Effect of Drying on Chemical and Physical Properties

3.4.1.Color

Color is one of the most important factor for consumer preference in food because of the color is interpreted as the indices of freshness, quality, taste, and etc. Color for apricot also gives prediction about carotenoid content which have good role in human health. In general drying processes provides a lot of advantages. However, some undesired chemical or physical changes like color losses or browning occur simultaneously.

Color values were determined before and after drying processes in all samples and the results are given in Table 3.3. All results were statistically analysed for comparing the effect of the sample type (through columns) and also the drying method (through rows).

All color results as L*, a*, b* values and calculated BI value of treated and untreated fresh zerdali and fresh apricot were significantly difference. This difference indicated that sample type had significantly effective ($P<0.05$) on color values.

The effect of SA treatment was found significant in all samples and also after drying process all color values were decreased as predicted. The lightness (L* value) of treated zerdali samples were determined as 36.49±0.16, 26.27±0.06 and 21.77±0.10 for fresh, tray dried and microwave and tray dried respectively. In all samples (treated zerdali, untreated zerdali and apricot) the greater change in color was seen in the combined drying method than only tray drying. This can be due to the rapid increase in temperature during MW treatment which can effect color.

Karabulut et al. (2007) studied the effect of hot air drying and sun drying on color values of apricot. They found all color values (except a*) of the all dried apricots decreased significantly in comparison with the fresh apricots ($P < 0.05$).

ΔE value shows the total color differences and gives general information for color changes. As seen the ΔE values were determined 20.99±0.20 and 19.87±0.16 for untreated and treated zerdali respectively. Salicylic acid treatment in Zerdali samples had positive effect on color protection and this effect seen significantly different. This information give an idea about salicylic acid treatment can be good alternative for protection of apricot color.

Tareen et. al, (2012) studied the effect of salicylic acid on a temperate fruit peach. They indicate that the higher concentration among the studied values of SA (2.0 mmol) proved to be the most effective in keeping peach fruit quality intact along with maintained skin color and delayed fruit surface decay during storage.

ΔE values of apricot samples were higher than Zerdali types meaning that drying causes more color change in apricot than zerdali. This result showed that Zerdali type has more conservative against process conditions than the Apricot as a color.

BI gives information about browning which can occur with the effect of the processes and conditions. All BI values were determined significantly different to each other except tray dried untreated zerdali and tray dried apricot as seen in the Table 3.3. This is also seen fresh fruit values are lower than dried ones because of the less application. More process caused more browning as predicted. Drying of apricot and untreated zerdali with tray and MW+tray caused significant increase in BI values. But it was found that application of MW before tray drying did not couse significant change in BI in salicylic acid treated zerdali.

Table 3.3. Color results for treated, untreated zerdali and apricot samples before and after drying

		Untreated Zerdali	**Treated Zerdali**	**Apricot**
L*	**Fresh**	36.06 ± 0.03^{aA}	36.49 ± 0.16^{aB}	37.86 ± 0.16^{aC}
	Tray	28.92 ± 0.03^{bA}	26.27 ± 0.06^{bB}	24.19 ± 0.05^{bC}
	MW+Tray	25.06 ± 0.03^{cA}	21.77 ± 0.10^{cB}	21.20 ± 0.05^{cC}
a*	**Fresh**	24.16 ± 0.06^{aA}	19.57 ± 0.06^{aB}	23.36 ± 0.04^{aC}
	Tray	17.33 ± 0.08^{bA}	16.96 ± 0.05^{bB}	14.97 ± 0.11^{bC}
	MW+Tray	16.40 ± 0.04^{cA}	15.14 ± 0.12^{cB}	11.38 ± 0.16^{cC}
b*	**Fresh**	39.41 ± 0.23^{aA}	34.99 ± 0.19^{aB}	41.11 ± 0.17^{aC}
	Tray	20.90 ± 0.03^{bA}	18.15 ± 0.13^{bB}	17.38 ± 0.13^{bC}
	MW+Tray	16.44 ± 0.21^{cA}	15.06 ± 0.36^{cB}	13.33 ± 0.24^{cC}
ΔE	**Tray**	20.99 ± 0.20^{aA}	19.87 ± 0.16^{aB}	28.64 ± 0.23^{aC}
	MW+Tray	26.63 ± 0.02^{bA}	25.18 ± 0.40^{bB}	34.54 ± 0.87^{bC}
BI	**Fresh**	288.58 ± 2.99^{aA}	226.01 ± 2.28^{aB}	283.02 ± 2.99^{aC}
	Tray	157.42 ± 0.40^{bA}	152.40 ± 1.53^{bB}	157.57 ± 0.71^{bA}
	MW+Tray	144.73 ± 1.59^{cA}	155.63 ± 4.43^{bB}	131.43 ± 1.85^{cC}

Suna et al. (2014) studied about impact of drying methods on physicochemical and sensory properties of apricot pestil. They indicated that the drying methods considerably influenced the color changes of pestil samples. Chromatic parameters were found higher in microwave oven dried samples than sun dried and vacuum oven dried ones.

3.4.2. pH, Total Soluble Solids, Total Phenolics and Total Carotenoid Content

pH results of all samples are given in Table 3.4. As seen pH of zerdali was lower than that of apricot, which caused to the sour typical taste of Zerdali. pH of untreated zerdali was higher that treated one. Differences between treated and untreated zerdali was as predicted and this difference indicated that salicylic acid had significant effect on pH value. In addition the drying process has significant effect on pH of all the samples.

Total phenolics give us information about health beneficial pigments which shows antioxidant activity. Total phenolic content was found by using calibration curve (Figure 3.21) which obtained from known gallic acid concentrations. Resuts were given as mg of gallic acid equivalents (GAE) per 100g of dry weight. Total phenolic content of zerdali was higher than apricot ($p < 0.05$). This is indicated that the healthy pigment content of Zerdali is more than apricot fruit. There was also significant difference between control and dried samples. The results showed that after the drying experiment total phenolic content determined higher than the control ones.

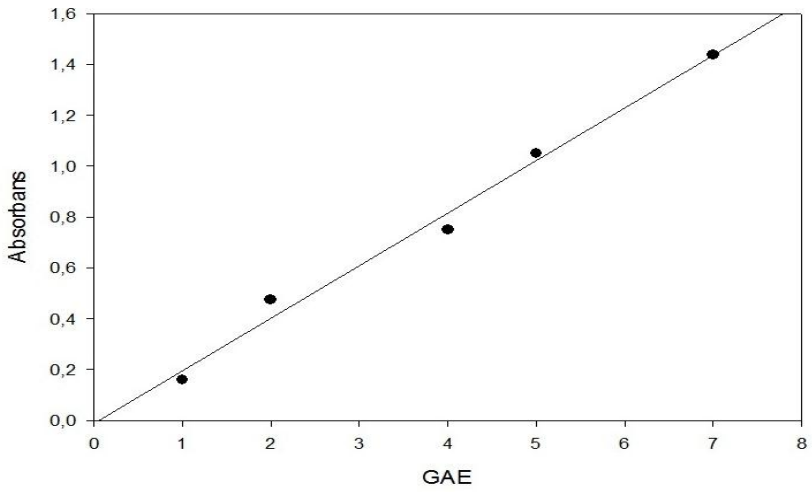

Figure 3.21. Calibration Curve for Total Phenolic Content

Albanese et al (2013) indicated that the AA (antioxidant activity) of both hot air and MW dried apricots were significantly higher than the fresh samples. Similar results were previously obtained by Igual et al (2012). Madrau et al (2009) found antioxidant values four times higher in apricots dried at 75 °C than in fresh apricots. This behaviour could be explained by two factors: (i) oxidation of polyphenols that

leads to the formation of stable intermediates which exhibit strong antioxidant capacity; (ii) formation of Maillard Reaction Products (MRPs) known to exhibit various antioxidant properties (Morales and Perez, 2001).

Total carotenoid content mainly β-carotene of samples is important criteria for apricot type fruit because of the giving color to the sample and also have important role against most of diseases such as cancer, degenerative diseases and etc. Drying like other processing methods can lead to the isomerization and even degradation of β-carotene. Moreover carotenoids are susceptible to oxidation when exposed to light, oxygen and enzymes. Because of their heat-sensitive nature even other antioxidants carotenoids degrade significantly during apricot heating. Total carotenoid content results as a β-carotene equivalent are shown in Table 3.4. Total carotenoid content decreased in all samples with the drying. In addition to that results indicated that both sample type and process had significant effect on total carotenoid content.

In literature similar decrease was reported for β-carotene content of apricots after hot air drying. This can be ascribed to oxidation with air, temperature and time also effective on β-carotene losses. β-carotene loss in nearly 50-60°C is higher than 80-90°C. This higher loss could cause to increase solubility of β-carotene at high temperatures. Time effect on β-carotene loss is depend on the temperature. The losses of β-carotene with increasing time is higher at 50-60°C drying conditions. (Karabulut et al., 2007; Lopez et al., 2013).

The effects of microwave and hot air drying methods on β-carotene content of apricots were evaluated by Albanese et al. (2013). The evolution of β-carotene in fresh apricots (61.2 +/- 5.6 mg / kg dw) during drying highlighted a wider decrease (about 50%). Total carotenoid content of apricot was higher than zerdali as shown in Table 3.4. Drying of all samples with hot air and microwave + hot air drying caused significant decrease in total carotenoid contents but total carotenoid content of apricot was more affected with drying. Microwave and hot air drying caused 92.87% total carotenoid loss in apricot whereas 40% loss in untreated zerdali and 36.13% in treated zerdali was observed. To preserve natural and sensorial quality of fresh apricots, need to careful selection of drying technique and optimization of the drying conditions.

Table 3.4. pH, Brix, Total Phenolics and Total Carotenoids results for treated, untreated zerdali and apricot samples before and after drying

		Untreated Zerdali	Treated Zerdali	Apricot
pH	**Fresh**	$3.30 \pm 0.01^{a\,A}$	$3.22 \pm 0.01^{a\,B}$	$3.88 \pm 0.01^{a\,C}$
	Tray	$3.12 \pm 0.01^{b\,A}$	$3.18 \pm 0.01^{b\,B}$	$3.81 \pm 0.01^{b\,C}$
	MW+Tray	$3.17 \pm 0.01^{c\,A}$	$3.15 \pm 0.01^{c\,B}$	$3.96 \pm 0.07^{c\,C}$
Brix	**Fresh**	$15.40 \pm 0.10^{a\,A}$	$15.40 \pm 0.10^{a\,A}$	$13.20 \pm 0.06^{a\,B}$
	Tray	$68.53 \pm 0.06^{b\,AB}$	$70.40 \pm 0.10^{b\,A}$	$67.10 \pm 0.10^{b\,B}$
	MW+Tray	$69.63 \pm 0.06^{b\,A}$	$63.80 \pm 0.10^{c\,B}$	$38.83 \pm 0.06^{c\,C}$
Total Phenolics (GAE/100g)	**Fresh**	$3302.37 \pm 73^{a\,A}$	$4127.97 \pm 73^{a\,B}$	$1715.69 \pm 116^{a\,C}$
	Tray	$4874.13 \pm 185^{b\,A}$	$6470.62 \pm 108^{b\,B}$	$1468.95 \pm 12^{b\,C}$
	MW+Tray	$5663.43 \pm 101^{c\,A}$	$4845.17 \pm 216^{c\,B}$	$907.53 \pm 19^{c\,C}$
Total Carotenoids (β-carotene eq./100g)	**Fresh**	$3.90 \pm 0.04^{a\,A}$	$2.38 \pm 0.03^{a\,B}$	$18.67 \pm 0.01^{a\,C}$
	Tray	$3.36 \pm 0.01^{b\,A}$	$2.10 \pm 0.01^{b\,B}$	$6.39 \pm 0.13^{b\,C}$
	MW+Tray	$2.34 \pm 0.01^{c\,A}$	$1.52 \pm 0.01^{c\,B}$	$1.33 \pm 0.01^{c\,C}$

CONCLUSION

The study of salicylic acid treatment and drying of zerdali samples revealed the following conclusions:

1. Salicylic acid treatment can be used to increase postharvest quality of zerdali.
2. Hot air drying and microwave + hot air drying were found to be suitable for drying of apricot and zerdali.
3. Drying curves for both zerdali and apricot samples only showed falling rate period. That results indicated that moisture movement mechanism in zerdali and apricot could be by diffusion.
4. Drying rate graphs for treated zerdali, untreated zerdali and apricot showed that, drying rate decreases with decreasing moisture content or increasing drying time.
5. D_{eff} values of samples determined between 2.03 and $8.11*10^{-8} m^2/s$, higher than general range (10^{-11}- 10^{-9} m^2/s) for foods.
6. The fit quality of 6 thin-layer drying models (Newton, Page, Logarithmic, Henderson and Pabis, Two Term and Wang and Sing) to experimental data were evaluated. Good results according to the coefficient of determination (R^2) and root mean square error (RMSE) were obtained with the Logarithmic and Two Term models.
7. After drying all color values in all samples decreased as predicted. Sample type and drying method found significantly effective on decreasing the color values. SA treatment in zerdali prevented the more decrease on color values. Also zerdali found more conservative than apricot on color changes.
8. Total phenolic content of zerdali determined significantly higher than apricot before and after drying.
9. Total carotenoid results was decreased in all samples after both drying processes. Sample type and process effect found significant on carotenoid content changes.

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